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Explanatory Research on the Protection of Carbon-Carbon Composites Against Oxidation at Very High Temperatures (*3000°F) with Engel-Brewer and Other Intermetallic Compounds

George St. Pierre
Department of Metallurgical Engineering and Materials Science

Department of the Navy
Office of Naval Research
Arlington, Virginia 22217

Contract No. N00014-86-K-0130
Final Report

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RF Project 765280/718158

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PROPOSAL FOR CONTINUATION OF ONR CONTRACT NO. N00014-86-K-0310, "EXPLORATORY RESEARCH ON THE PROTECTION OF CARBON/CARBON COMPOSITES AGAINST OXIDATION AT VERY HIGH TEMPERATURES (>3000°F) WITH ENGEL-BREWER COMPOUNDS AND OTHER INTERMETALLIC COMPOUNDS" FOR THE PERIOD FROM NOVEMBER 1, 1988 TO OCTOBER 30, 1989.

Amount Requested: $95,555

Project Officer	Investigators
Dr. John Sendriks	George R. St.Pierre
Materials Division	Robert A. Rapp
Office of Naval Research	John P. Hirth
	The Ohio State University
	Columbus, Ohio 43214

June 29, 1988

PROPOSAL FOR CONTINUATION OF ONR CONTRACT NO. N00014-86-K-0310, "EXPLORATORY RESEARCH ON THE PROTECTION OF CARBON/CARBON COMPOSITES AGAINST OXIDATION AT VERY HIGH TEMPERATURES (>3000°F) WITH ENGEL-BREWER COMPOUNDS AND OTHER INTERMETALLIC COMPOUNDS" FOR THE PERIOD FROM NOVEMBER 1, 1988 TO OCTOBER 30, 1989.

I. INTRODUCTION

Attached to this proposal as Appendix A is a set of manuscripts and reports based on our work for the period from November 1, 1985 to May 30, 1988. We request a fourth year of effort in order to pursue some recently developed concepts for the protection of carbon/carbon composites. A description of the proposed work follows in Section II.

II. Research Plan for the Period November 1, 1988 to October 30, 1989

A. Formation of Ir_3Hf on C/C Composites

The chemical compatibility of Ir_3Hf with Ir, HfC and C has been studied by Ir/HfC diffusion couple experiments. The resuts have shown that the Ir_3Hf layer is thermodynamically stable in contact with Ir, HfC and C. However, many voids were formed along the Ir/Ir_3Hf interface and in the Ir_3Hf layer. These voids made the annealed samples weak along the Ir/Ir_3Hf interface. Therefore when one uses Ir_3Hf layers in the multi-layer protection system for carbon-carbon composites, the diffusional growth of the Ir_3Hf must be controlled. The research for 1988-1989 will be focused on the further study of the properties of Ir_3Hf as follows:

1. Ir/Hf and Ir/IrHf diffusion couple experiments.

The HfC used for the Ir/HfC diffusion couple experiments had about 91% theoretical density. Thus the porosity of HfC might have affected the growth kinetics and void formation for the Ir_3Hf product layer. A comparison of the results for Ir/Hf and Ir/IrHf experiments with those for the Ir/HfC experiments should provide more information on the thermodynamic and kinetic properties of Ir_3Hf.

2. HfC/Ir_3Hf(Ir-rich) diffusion couple experiments.

This study is designed to find a way to avoid the void formation and have a good chemical bond between Ir_3Hf and HfC. The HfC is bonded to the underlying C/C composite structure.

B. Oxidation Studies of Ir Alloys

Iridium-based coatings have been proposed for the protection of carbon/carbon composites against oxidation at temperatures greater than 1600°C. However, Ir exposed to an oxidizing atmosphere at such high temperatures reacts with oxygen to form volatile oxides. Alloying Ir with a reactive element that forms a protective scale has been proposed as a method to prevent the evaporation of Iridium base coatings. Hafnium and Zr were suggested as possible alloying elements. Investigations of the Ir-Hf and the Pt-Zr systems, however, have shown that Hf and Zr are only moderately protective. In both systems the reactive element, Hf and Zr, did not form a highly protective oxide scale.

Aluminum is another possible alloying addition for the prevention of evaporation of the noble metal suboxides. In both the Pt-Al and the Ir-Al systems the formation of alumina (Al_2O_3) scales protects the noble metal substrates. However, in the Ir-Al system the amount of Al necessary to form a continuous protective scale is greater than 50 atomic percent. Such an alloy would be liquid at the desired temperatures. Below 50 atomic percent Al, the oxidation of Ir-Al alloys results in the internal precipitation of Al_2O_3. These results are similar to the well known Fe-Al, Ni-Al and Co-Al systems. It is proposed, similar to the Fe, Ni, and Co-base superalloys, that Ir be alloyed with both Al and Cr. The addition of Cr should greatly reduce the amount of Al needed to produce a continuous Al_2O_3 scale. By reducing the amount of Al, the melting point should increase. The oxidation should proceed similarly to the Fe, Ni, and Co-Cr-Al alumina forming alloys.

The following areas will be investigated:

1. The amount of Cr necessary to form a continuous Cr_2O_3 scale on Ir-Cr alloys at temperatures greater than 1600°C.
2. The amount of Al necessary to form a continuous Al_2O_3 scale on Ir-Cr-Al alloys at temperatures greater than 1600°C.
3. The oxidation kinetics of Ir-Cr-Al alloys at temperatures greater than 1600°C.
4. The effect of rare earth additions on the amount of Al necessary to form a continuous Al_2O_3 scale, the oxidation kinetics of Ir-Cr-Al alloys and the adhesion of the Al_2O_3 scale.

Coatings; oxidation; hafnium;
carbon carbon composites; (KT)

C. Oxidation of C/C Composites Coated with HfC, Ir, and Ir-Al-Cr Alloys

Samples of C/C composite would be coated with HfC and then a layer of Iridium would be applied. It has been demonstrated that we can grow an adherent layer of Ir_3Hf between these coatings. The surface of the Ir would be impregnated with Al and Cr following the guidelines in Part B. The oxidation kinetics of the combined system would be studied. Part of this work would be conducted by John Brimhall and Edward Courtright at Battelle Pacific Northwest Laboratories.

3. Proposed Budget

The budget proposed for the one-year period is $95,555 as shown in Table I. Two graduate students working under the direction of Professors George R. St.Pierre and Robert A. Rapp will be employed in the program. In addition, Professor John P. Hirth will be retained as a consultant. Curriculum vitae of these three individuals are included in Appendix B. Dr. St.Pierre will serve as P.I. In addition some of the coating studies will be done by Dr. John Brimhall and Dr. Edward Courtright at Battelle Pacific Northwest Laboratories. The details of the budget are given in Table I.

4. Personnel

In addition to the C.V.'s of Drs. St.Pierre, Hirth and Rapp given in Appendix B, Denis O'Connell and Jong-Won Kwon, doctoral candidates, will be employed as graduate research associates. Also, Dr. J. Brimhall and Dr. E. Courtright of Battelle Pacific NW Laboratories will be engaged in the program to prepare coated samples and to conduct oxidation tests.

Table I
Proposed Budget to Office of Naval Research
November 1, 1988 through October 31, 1989

		Sponsor	OSU
PERSONNEL			
Dr. G.R.St.Pierre, Principal Investigator			
3% time 8 months		$2,042	$2,042
3% time 4 months		$1,072	$1,072
R.A. Rapp, Co-P.I.			
3% time, 8 months		$2,016	$2,016
3% time, 2 mo. summer		$504	$0
3% time 1 month		$265	$265
Graduate Research Associates (2)			
50% time, 12 months FTE	$21,600	$10,800	$0
50% time, 12 months FTE	$21,600	$10,800	$0
Support Staff			
Electronic Technician			
20% time, 8 months FTE	$25,920	$3,456	$0
20% time, 4 months FTE	$27,216	$1,814	$0
Secretary/typist			
20% time, 8 months FTE	$20,550	$2,740	$0
20% time, 4 months FTE	$21,578	$1,439	$0
SUBTOTAL SALARIES AND WAGES		$36,948	$5,395
FRINGE BENEFITS			
Faculty Retirement @	14.00%	$826	$755
Staff Retirement @	13.71%	$1,295	$0
Insurance $2,232 FTE	46.00%	$1,069	$223
SUBTOTAL FRINGE BENEFITS		$3,190	$978
MATERIALS AND SUPPLIES			
Consumables		$6,500	$0
SUBTOTAL M & S		$6,500	$0
TRAVEL			
3 Scientific meetings		$1,200	$0
SUBTOTAL TRAVEL		$1,200	$0
OTHER DIRECT COSTS			
Long Distance Tolls		$200	$0
Copy Services		$200	$0
Page Charges and Reprints		$300	$0
Reports		$200	$0
Microscope & Computer Services		$2,000	$0
SUBTOTAL OTHER DIRECT COSTS		$2,900	$0
TOTAL DIRECT COSTS		$50,738	$6,373
SUBCONTRACT		$23,000	$0
INDIRECT COSTS			
43% MTDC base	$50,738	$21,817	$2,740
TOTAL REQUESTED FROM SPONSOR		$95,555	$9,113

Appendix A

Reports of work for the period from November 1, 1985 to May 30, 1988.

"Formation of Ir_3Hf Layers at an Ir/HfC Interface between 1900°C and 2200°C": J. Kwon, G.R. St.Pierre, and J.P. Hirth. June, 1988

"Research Summary for the Period October 1, 1987 to March 31, 1988". G.R. St.Pierre, R.A. Rapp, and J.P. Hirth

Letter Report from J. Brimhall: 4/18/88

"Oxidation Behavior of HfO_2 Coated Iridium", J.L. Brimhall. Feb., 1988.

"Summary of Results on Oxidation of Coated and Uncoated Ir_3Hf", J.L. Brimhall. 9/2/87

"Oxidation Protection of c/c composites", J.L. Brimhall. August, 1987

Letter Report from J. Brimhall: 4/21/87

Letter Report from J. Brimhall: 2/9/87

Formation of Ir_3Hf Layers at an Ir/HfC Interface between 1900°C and 2200°C

J. Kwon, G. R. St. Pierre, and J. P. Hirth

ABSTRACT

The chemical compatibility of Ir_3Hf with Ir and HfC was investigated by an Ir/HfC diffusion couple experiment. Ir_3Hf was the only reaction product formed at the Ir/HfC interface, although there exist other binary intermetallic compounds: IrHf, Ir_3Hf_5 and $IrHf_2$. The growth kinetics of the Ir_3Hf layer follow a parabolic rate law. The parabolic rate constants and the activation energy for the growth of the Ir_3Hf layer were estimated. Ir atoms are the dominant diffusing species in Ir_3Hf. Many voids were observed along the Ir/Ir_3Hf interface and in the Ir_3Hf layer. The activities and activity coefficients of Ir at both interfaces are calculated. The average Ir diffusion coefficients in Ir_3Hf, D_{Ir}^{av}, was calculated from the measurments of parabolic rate constants.

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* This document has been prepared for submission to Metallurgical Transactions, June 1988.

I. INTRODUCTION

There has been an increasing demand for new structural materials for the future generation of high performance engine systems. Carbon/carbon composites have been proposed as one of the materials for this application due to their light weight and good high temperature mechanical properties [1]. However, C/C composites must be protected against oxidation by an external coating at high temperatures in oxidizing environments. Silicon carbide coatings applied by pack cementation or chemical vapor deposition have successfully protected C/C composites in high temperature applications, as in the space shuttle application [2]. Since the operating temperatures of the high performance engine systems will be higher than the maximum working temperature of the SiC/SiO_2 protection system, around $1650^{\circ}C$ [3], the development of a new protection system is required.

One of the new multi-layer coating concepts incorporates the use of highly stable intermetallic compounds which consist of noble and reactive transition metal elements, e.g., Ir_3Hf, Ir_3Zr, and Pt_3Hf. Both Engel-Brewer theory [4] and Miedema's model [5] predict an extraordinary stability for these intermetallic compounds, often called the Engel-Brewer compounds.

The lack of thermochemical data for Engel-Brewer compounds has made it very difficult to predict the chemical compatibility of these compounds with the C/C substrates. This investigation is an attempt to determine the chemical compatibility of Ir_3Hf, one of the Engel-Brewer compounds, with C/C composites by Ir/HfC diffusion couple experiments.

II. EXPERIMENTAL PROCEDURE

Ir foils and HfC coupons were used for the diffusion couple experiment. Ir foils of 0.25mm thickness were purchased from Johnson Matthey Inc. Battelle Pacific Northwest Laboratories supplied a HfC rod which was prepared by Los Alamos National Laboratories by hot pressing Cerac HfC powders at 3000°C and under 21 MPa. The powders were annealed prior to pressing to form a homogeneous carbide solid solution. The final density was 11.6 g/cc, representing 91 % theoretical density, and the lattice constant was 0.460 nm, corresponding to a stoichiometric, carbon-saturated, carbide. HfC coupons of 1.5 mm thickness were cut from the rod. Ir/HfC diffusion couples with sizes from 1x1 mm to 3x3 mm were used for the diffusion experiments.

Figure 1 shows the experimental setup used for the diffusion couple experiment. A 23.5 kVA LEPEL RF generator was used to supply the power for induction heating. Diffusion couples were sandwiched between two graphite discs, which were used as susceptors.Since the Ir foils were thin and had high thermal conductivity, the temperature at the Ir/HfC interface was assumed to be the same as that of the graphite susceptor on the Ir foil. A Williamson two color pyrometer was used to read the temperature of the susceptor. Diffusion couples in magnesia crucibles were annealed for 2 to 32 hours at 1900, 2000, 2100 and 2200°C in an Ar flow.

Most of the diffusion couples were sectioned perpendicular to the interfaces for analysis after annealing. Conventional microscopy was used to determine the microstructure of the reaction zone. The samples were polished with 6, 3 and 1 μm diamond polishing compounds. A Scintag PAD V X-ray diffractometer was used for phase identification of the reaction products. A JEOL JXA-35 electron probe microanalyzer with EDAX 9100 system was used to determine the concentration profiles in the reaction zone. Pure Ir and Hf standards were used to calculate the concentrations. An X-ray carbon map was used to determine the distribution of carbon in the reaction zone.

III. EXPERIMENTAL RESULTS

Figure 2 and Figure 3 show the cross sections of Ir/HfC diffusion couples treated at 2200°C and 2100°C, respectively. X-ray diffraction analysis revealed that Ir_3Hf is the only intermediate reaction product, although there are three other intermetallic phases, i.e. IrHf, Ir_3Hf and $IrHf_2$, on the Ir-Hf binary phase diagram shown in Figure 4 [6]. The reaction of Ir_3Hf formation is

$$3Ir + HfC = Ir_3Hf + C \tag{1}$$

Note that there are rather large planar pores along the original interface and smaller pores distributed in the Ir_3Hf layer, some of which often grow in the same direction as the Ir_3Hf layer grows. There are also small bowouts of the Ir_3Hf phase boundary into the Ir phase which indicates that the growth of Ir_3Hf phase proceeds in part by net Hf diffusion. These bowouts are noticeable only at temperatures above 2100°C. Graphite fiber markers, which are stable in contact with Ir and C-saturated HfC, are used to determine the original interface. As shown in Fig. 5, the markers were found at the Ir/Ir_3Hf interface, indicating that Ir is the dominant diffusing species. Concentration profiles of Ir and Hf through the Ir_3Hf layer, measured by Energy Dispersion Spectroscopy(EDS), are shown in Figures 6 and 7. To determine where the dissociated carbon from HfC goes, probably to the voids, carbon dot mapping by Wavelength Dispersion Spectroscopy(WDS) has been performed on the cross section of the reaction zone. Figure 9 shows a carbon pattern on a WDS map that matches with the pores in Ir_3Hf in Figure 8. Loss of carbon by evaporation is discussed in the next section.

The presence of planar voids at the Ir/Ir_3Hf interface made the diffusion couples fragile along that interface. Table 1 shows the results of the X-ray diffraction analysis on the Ir_3Hf side of the broken interface of a diffusion couple that was reacted at $2100^{\circ}C$ for 20 hours. The lattice constant of Ir_3Hf as determined by the Nelson-Riley extrapolation method is 0.3934nm, whereas the value reported by Dwight and Beck is 0.3935 nm [7].

The thicknesses of Ir_3Hf layers are plotted with respect to $\sqrt{t}$ in Figure 10. The growth kinetics of the Ir_3Hf layer follow a parabolic rate law. To calculate the activation energy for Ir diffusion in Ir_3Hf, an Arrhenius plot is drawn in Figure 11, which gives $Q = 325$ kJ/mol.

IV. Discussion

A. Thermodynamics

The Engel-Brewer theory predicts an extraordinary stability of intermetallic compounds between noble and reactive transition metal elements [4]. According to the Engel-Brewer theory, Ir and

Hf atoms are excited to have a maximum number of electrons available for bonding, i.e., $5d^76s^2 \rightarrow 5d^66s6p^2$ for Ir and $5d^26s^2 \rightarrow 5d^26s6p$ for Hf, when they form Ir_3Hf. Thus Ir_3Hf is a highly stable alloy due to the high electron bonding energy.

Miedema's model can[5] be expressed by

$$\Delta H_f \propto [-Pe(\Delta\phi^*)^2 + Q(\Delta n_{ws})^2] \qquad (2)$$

where the first term represents the difference in electronegativity between two types of atoms in an alloy, and the second term the discontinuity in the density of electrons at the boundary between dissimilar atomic cells. The calculated Heat of formation of Ir_3Hf[5] is

$$\Delta H_f(Ir_3Hf) = -271 \text{ kJ/mol} \qquad (3)$$

Though Miedema's model contradicts the Engel-Brewer theory because the charge transfer occurs in the opposite direction, i.e., from hafnium to iridium [5], both predict the high stability of Engel-Brewer intermetallic compounds.

The entropy of formation of Ir_3Hf is not available in the literature. However, the entropies of formation of ordered compounds are small. If the values for Cu_3Au and Ni_3Al, which have the same crystal structures, are assumed to apply to Ir_3Hf as well, the Gibbs free energy of formation of Ir_3Hf is given by

$$\Delta G_f^o(Ir_3Hf) \sim -271300 - 0.535T \text{ J/mol} \qquad (4)$$

where $\Delta S_f^o(Ir_3Hf) = -0.535$ $JK^{-1}mol^{-1}$ is the average of $\Delta S_f^o(Cu_3Au) = 5.04$ $JK^{-1}Mol^{-1}$ and $\Delta S_f^o(Ni_3Al) = -3.97$ $JK^{-1}mol^{-1}$ at 25°C [8].

Several authors have investigated the stability of Engel-Brewer compounds by the heat treatment of powder mixtures of a noble metal and a reactive metal carbide [4,9]. Their studies have confirmed the high stability of E-B compounds. Figure 12 shows an Ir-Hf-C ternary isotherm that is drawn, on the basis of the experimental results of the Ir/HfC diffusion couple experiment shown in the previous section. The dashed line corresponds to the diffusion couple before the reaction. The overall reaction during the heat treatment is

$$3Ir + HfC \rightarrow Ir_3Hf + C(pure) \qquad (1)$$

If one assumes that the Ir_3Hf layer grows by Ir diffusion, there are three phase equilibria locally at the interfaces: Ir, Ir_3Hf and C at the Ir/Ir_3Hf interface, and Ir_3Hf, HfC and C at the Ir_3Hf/HfC interface. These equilibria are shown by the triangles on the ternary diagram.

A calculation of the component activities of various ternary three phase systems that are in equilibrium was made by Brewer and Wengert [4]. Similar calculations can be made for the Hf activity at an HfC/Ir_3Hf interface. The standard Gibbs free energy of HfC formation [10] is given by

$$\Delta G_f^o(HFC) = -229{,}106 + 13.64T \text{ J/mol} \quad (2013\text{-}2300 \text{ K}) \qquad (5)$$

At an Ir_3Hf/HfC interface there exists the following local equilibrium:

$$\underline{Hf} + C = HfC \qquad (6)$$

Then

$$\Delta G_f^o(\mathrm{HfC}) = -RT\ln(1/a_{Hf}) \tag{7}$$

where the pure standard states for solid phases are assumed. At 2200°C, $\Delta G_f^o(\mathrm{HfC}) = -195.4$ kJ/mol. Therefore, the Hf activity at the Ir_3Hf/HfC interface at 2200°C is

$$a_{Hf} = 7.46 \times 10^{-5} \tag{8}$$

As mentioned in the previous section, Ir_3Hf is the only stable product phase during the reaction between Ir and HfC, although there are other compounds, IrHf, Ir_3Hf_5 and $IrHf_2$ on the Ir-Hf binary phase diagram shown in Figure 4 [6]. While these other compounds are not present, the following inequality must hold true:

$$7.46\times10^{-5} < a_{Hf}^{IrHf} \leq a_{Hf}^{Ir_3Hf_5} \leq a_{Hf}^{IrHf_2} \tag{9}$$

The Ir activity at the HfC/Ir_3Hf interface is given by

$$a''_{Ir} = e^{\Delta G_r^o/3RT} \tag{10}$$

where ΔG_r^o refers to the reaction at the HfC/Ir_3Hf interface:

$$\mathrm{HfC} + 3\underline{\mathrm{Ir}} = \mathrm{Ir_3Hf} + \mathrm{C(pure)} \tag{11}$$

Therefore

$$\Delta G_r^o = \Delta G_f^o(\mathrm{Ir_3Hf}) - \Delta G_f^o(\mathrm{HfC}) \tag{12}$$

From Eqs. (4) and (5),

$$\Delta G_r^o = -42194 - 14.175T \text{ J/mol} \tag{13}$$

The mole fractions, activities and activity coefficients of Ir at Ir/Ir_3Hf and HfC/Ir_3Hf interfaces at 2200°C are shown in Table 2.

B. Diffusion

Ir_3Hf intermetallic compounds have a $L1_2$(Cu_3Au-type) ordered crystal structure. Figure 13 shows a closed packed plane and unit cell of the $L1_2$ crystal structure [7,11]. In the unit cell of the Ir_3Hf compound, iridium atoms occupy the face-center sites and hafnium atoms occupy the corner sites. Each iridium atom has two types of nearest neighbors: eight of them are Ir atoms and four of them are Hf atoms, and each hafnium atom has twelve Ir nearest neighbors and six Hf next-nearest neighbors.

The diffusion in intermetallic compounds with an ordered crystal structures is expected to occur by the vacancy-nearest neighbor atom mechanism. The general diffusion coefficient derived by random walk method is given by

$$D = nr^2f/6t \qquad (14)$$

where n/t is the jump frequency of a vacancy to a neighboring site, r is the jump distance, and f is the correlation factor. Kikuchi and Sato introduced an approach of using averaged quantities to describe the diffusion in ordered alloys [12]. Bakker used this approach to describe the diffusion coefficients of ordered alloys with a bcc unit cell [13]. For the diffusion coefficient of A_3B(Cu_3Au-type) alloys with a fcc unit cell, as shown in Figure 13, a similar approach also can be used. First, it is assumed that A and B atoms can jump between α and β sublattices with the degree of order remaining unchanged. The number of A atom jumps per second is given by

$$n_A/t = (N_A^\alpha/N_A)\Gamma_A^\alpha + (N_A^\beta/N_A)\Gamma_A^\beta \tag{15a}$$

$$= (N_A^\alpha/N_A)(\Gamma_A^{\alpha\alpha} + \Gamma_A^{\alpha\beta}) + (N_A^\beta/N_A)\Gamma_A^{\beta\alpha} \tag{15b}$$

where N_A^α is the number of A atoms in the α sublattice, N_A is the total number of A atoms, Γ_A^α is the jump frequency of A atoms on the α sublattice, $\Gamma_A^{\alpha\beta}$ is the jump frequency of A atoms on the α sublattice to any nearest neighbor site on the β sublattice, etc. Since the degree of disorder is not changed by the jumps of A atoms,

$$N_A^\alpha \Gamma_A^{\alpha\beta} = N_A^\beta \Gamma_A^{\beta\alpha} \tag{16}$$

that is, the number of A atom jumps from the α sublattice to the β sublattice must be equal to the number of opposite jumps. The jump frequency of A atoms on the α sublattice is given by

$$\begin{aligned}\Gamma_A^\alpha &= \Gamma_A^{\alpha\alpha} + \Gamma_A^{\alpha\beta} \\ &= 8n_v^\alpha \omega_A^{\alpha\alpha} + 4n_v^\beta \omega_A^{\alpha\beta}\end{aligned} \tag{17}$$

where n_v^α is the vacancy concentration on α sublattice,, $\omega_A^{\alpha\alpha}$ is the probability that an A atom on the α sublattice will jump into a particular vacant site on the α sublattice, etc. In an A_3B

alloy, $r = \frac{\sqrt{2}}{2}a_o$ where a_o is the lattice constant. From Eqs. (10)-(13), the A diffusion coefficent is

$$D_A = \frac{2}{3}(N_A^{\alpha}/N_A)(n_v^{\alpha}\omega_A^{\alpha\alpha} + n_v^{\beta}\omega_A^{\alpha\beta})f_A a_o^2 \qquad (18)$$

Similar equations can be found for D_B, that is,

$$D_B = \frac{2}{3}(N_B^{\alpha}/N_B)(n_v^{\beta}\omega_B^{\alpha\beta} + n_v^{\alpha}\omega_B^{\alpha\alpha})f_B a_o^2 \qquad (19)$$

The Ir diffusion in Ir_3Hf alloys is expected to occur mainly by Ir jumps on the Ir sublattice, because Ir atoms have eight Ir nearest neighbors and this process will not create disorder. The Hf diffusion is expected to occur by a somewhat different nearest neighbor atom-vacancy exchange mechanism. Figure 14 shows a (100) plane for the Cu_3Au-type alloys. If Hf diffusion occurs by normal atom-vacancy exchange and next nearest jumps of Hf atoms are assumed to be negligible, Hf diffusion will produce a large amount of disorder. Thus the normal atom-vacancy exchange mechanism can not describe the Hf diffusion behavior. In order to maintain the degree of disorder for the diffusion in B2(AB) structure, two possible mechanisms are proposed: the divacancy mechanism and multiple vacancy jump mechanism [14,15]. A similar approach can be used to describe the diffusion in $L1_2(A_3B)$ structure. Figure 14(a) shows schematically the divacancy mechanism for Hf diffusion on a (100) plane in $Ir_3Hf(L1_2$ structure). Figure 14(b) shows the multiple vacancy jump mechanism in which a B atom moves by a complete cycle of six vacancy jumps. Six-cycles of vacancy jumps are shown by the numbers from 1 through 6. A similar type of jumps can also occur between two intersecting {100} planes [16]. The strong correlation effect of this process will make the correlation factor for Hf, f_{Hf}, much smaller than f_{Ir}. Therefore, both mechanisms of Hf diffusion predict that Ir diffusion should be faster than Hf diffusion. The calculation of D_A and D_B could be done by computer simulation, but the necessary exact values of f_{Hf} and f_{Ir} are not available as of yet. The results for the Ir/HfC diffusion couple experiment in the previous section confirm that iridium diffusion is faster than hafnium diffusion in Ir_3Hf compounds even when the compounds are Ir-rich. To be more quantitative, the vacancy formation energy, vacancy migration energies for different type of jumps, degree of disorder, and alloy composition should be known.

Ansel et al[17] studied the diffusion of Mn in Pt_3Mn compounds with various compositions. The measured density of a compound with 18 at% Mn was 18.1, whereas the theoretical density of a compound without vacancies was 19.1 and that with 7 % structural Mn vacancies was 17.4. By comparing these values, they deduced that there are 4.6% Mn vacancies and 3.2% antisite defects, i.e., Pt atoms on Mn sites. Since the density measurements cannot provide the information on the formation energy of different type of vacancies and antisite defects, the estimated concentrations of point defects by the density measurements are not reliable values, but the presence of antisite defects can be easily proved.

Foiles and Daw [18,19] used the embedded atom method to calculate phase stability, lattice vibrational frequencies, point defect properties, antiphase boundary energies, and surface energies and relaxations for the Ni_3Al, which has the $L1_2$ ordered crystal structure. The properties of Ni_3Al and Ir_3Hf are compared in Table 3 [7,20,21,22]. According to Foiles and Daw [18], the antisite concentration on the α sublattice in an A_3B ordered alloy is given by

$$n_B^\alpha = \frac{3}{4}\,\frac{e^{-(E_B^\alpha + \mu_A - \mu_B)/T}}{1 + e^{-(E_B^\alpha + \mu_A - \mu_B)/T}} \qquad (20)$$

and the vacancy concentration is given by

$$n_V^\alpha = \frac{3}{4}\,\frac{e^{-(E_V^\alpha + \mu_A)/T}}{1 + \bar{e}^{(E_V^\alpha + \mu_A)/T}} \qquad (21)$$

where n_B^α is the number of α sublattice sites occupied by B atom divided by the total number of lattice sites, n_V^α is the number of vacancies on the α sublattice divided by the total number of lattice sites, E_B^α is the energy difference between the ideal lattice and the lattice with a single B atom substituted for an A atom, and E_V^α is the energy difference between the ideal lattice and the lattice with a vacancy on the α sublattice. Similar expressions for the defects on β lattice can be found by replacing $\frac{3}{4}$ by $\frac{1}{4}$. Foiles and Daw [18,19] showed that the formation energy of antisite defects is less than that for vacancies and so the off-stoichiometries of A_3B alloys are accommodated by the production of antisite defects rather than by the production of structural vacancies. They also showed that the vacancy formation energy and vacancy concentration in Ni_3Al depend on the overall composition, and that the vacancy concentration is much larger on the Ni sublattice than on the Al sublattice. Since the negative heat of formation of Ir_3Hf is larger in magnitude than that of Ni_3Al, as shown in Table 3, Ir_3Hf should be a more ordered alloy than Ni_3Al. This indicates that the antisite concentration is less in Ir_3Hf than in Ni_3Al.

As mentioned earlier, the Hf diffusion in Ir_3Hf mainly occurs by the divacancy or the complex atomic jump procedure, whereas the Ir diffusion occurs by the vacancy-nearest neighbor exchange mechanism. The decrease in antisite concentration should reduce the possibility of direct exchange between Hf vacancies and Hf nearest neighbors on the Ir sublattice. Therefore the six jump-cycle mechanism becomes more dominant for Hf diffusion in Ir_3Hf. In conclusion, Ir diffusion is expected theoretically to be faster than Hf diffusion in Ir_3Hf, as proved by the experimental results shown in the previous section.

The solubility of carbon in the Ir_3Hf phase is negligible [4,23] and the activity of carbon is equal to unity across the Ir_3Hf layer. Thus, the dissociated carbon from the reaction in

Eq(4) should precipitate in the Ir_3Hf layer and/or evaporate as C, C_2 and C_3 vapor species. The vapor pressure data of C are given in Table 4 [24]. Since these data correspond to an equilibrium, the vaporization coefficients of C, C_2 and C_3 must be taken into account to calculate the effective vapor pressure and the recession rate when a solid carbon continuously evaporates. The vaporization coefficients of carbon are: $\alpha_1 = 0.37$, $\alpha_2 = 0.34$, and $\alpha_3 = 0.08$ [25]. The effective vapor pressures, $P_{C_i}^{eff} = \alpha_i P_{C_i}$, are given in Table 5. The recession rate derived from the Hertz-Langmuir equation is given by

$$R_C = 1x10^4 \frac{J_{C_i}}{\rho_C}$$

$$= 1.6x10^9 \frac{P_{C_i} M_{C_i}^{1/2}}{\rho_C T^{1/2}} \qquad (22)$$

where R_C is expressed in μm/h, P_{C_i} is the vapor pressure of C, expressed in atm, M_{C_i} is the molecular weight of C_i, ρ_C is the density of C, expressed in g/cm^3. In Table 6, the calculated recession rates of carbon at different temperatures are given.

The diffusional growth of Ir_3Hf product layers is modeled as shown in Figure 15. At the early stage of Ir_3Hf formation, there are net fluxes of Ir and Hf away from the original interface in the opposite direction to each other. The counter-fluxes of vacancies toward the original interface will condense at the original interface to form planar voids along the interface. At a later stage, the Ir vacancy flux form smaller voids in the Ir_3Hf Layer, some of which grow toward the Ir_3Hf/HfC interface by receiving the Ir vacancy flux. Since the Ir vacancy concentration in Ir_3Hf will decrease with increasing Ir concentration, analogous to changes in the Ni vacancy concentration in Ni_3Al [18,19], the flux of Ir vacancies will become lower toward the Ir/Ir_3Hf interface. Therefore void formation is easier near the Ir/Ir_3Hf interface, because the vacancies will be locally supersaturated if the vacancy annihilation processes are slow. Also void formation within the Ir_3Hf layer would require accomodating diffusion of the slower diffusing Hf species, while voids formed at the interface can be accomodated by diffusion in the Ir phase, another factor favoring nucleation at the Interface location. This type of voids can be seen in Figures 2 and 3.

The growth of voids at the metal/oxide interface during the scale growth and the migration of pores in an oxides placed between environments with two different oxygen potentials have been investigated by several authors [26,27]. A Similar interpretation can be done for the voids in Ir_3Hf. Since the Ir vapor flux through the voids at the Ir/Ir_3Hf interface is smaller than the Ir diffusion flux in the early stages of Ir_3Hf layer growth, the following local reactions can exist:

1. $3V_{Ir}(\rightarrow) + Ir_3Hf = 3Ir(\leftarrow) + Hf(g)(\rightarrow)$ at the Ir_3Hf surfaces in the voids
2. $Hf(g)(\rightarrow) + V_{Ir}(\leftarrow) = \underline{Hf}(\text{in Ir})(\rightarrow)$ at the Ir surface in the voids

These reactions will widen the planar voids formed along the Ir/Ir_3Hf interface at the early stage. For the small voids within the Ir_3Hf layer, the first reaction above can also occur at the void surface nearer the HfC/Ir_3Hf interface and the other reaction taking place at the opposite void surface can be

$$Hf(g)(\rightarrow) + 3\underline{Ir}_{Ir}(\leftarrow) = Ir_3Hf + V_{Ir}(\rightarrow)$$

By these local reactions, as well as growing, the voids in Ir_3Hf will translate in the same direction as does the Ir_3Hf layer.

The vapor pressure [28], recession rate, and mass flux of Ir vapor species through the planar voids at Ir/Ir_3Hf interfaces at different temperatures are shown in Table 7. The Hertz-Langmuir equation can be used to calculate the mass flux of Ir vapor species, J_{Ir}, which is given by

$$J_{Ir} = 1.6\text{x}10^5 P_{Ir}(M_{Ir}/T)^{1/2} \qquad (23)$$

where J_{Ir} is expressed in g/cm^2h, P_{Ir} is the vapor pressure of Ir, expressed in atm, and M_{Ir} is the molecular weight of Ir vapor species. If this vapor flux is larger than the flux by solid diffusion, the presence of voids at the Ir/Ir_3Hf interface will not affect the parabolic growth of Ir_3Hf product layer. The growth rate of Ir_3Hf layer by the quasi-steady state flux, J_{Ir}, is given by

$$\frac{d\xi}{dt} = \frac{1}{3} J_{Ir} \Omega_{Ir_3Hf} \tag{24}$$

Where Ω_{Ir_3Hf} is the molar volume. Thus J_{Ir} is given by

$$J_{Ir} = \frac{3}{\Omega_{Ir_3Hf}} \frac{d\xi}{dt} \tag{25}$$

$$= \frac{3}{\Omega_{Ir_3Hf}} \frac{k_p}{\xi} \tag{26}$$

The calculated Ir diffusion fluxes are given in Table 7, which shows that the Ir vapor flux through the pores at Ir/Ir_3Hf interface is smaller than the Ir diffusion flux at early stages of reaction. Only when the Ir_3Hf layer grows to an appreciable thickness, does the Ir vapor flux become larger than the Ir diffusion flux. The difference between the two fluxes increases as the temperature decreases. If the vapor flux is smaller than the diffusion flux, the voids will become markers. This may explain why the graphite fiber markers stay in the planar voids, which are also markers, along the Ir/Ir_3Hf interfaces, as shown in Figure 5.

Wagner [29] and others derived the equations for the calculation of the average interdiffusion coefficients of the intermetallic phases growing at the interfaces of a diffusion couple from kinetic data and concentration measurments. The average interdiffusion coefficient is defined as

$$\tilde{D}_{av}^{(i)} = \frac{1}{X_2^{(i)''} - X_2^{(i)'}} \int_{X_2^{(i)'}}^{X^{(i)''}} \tilde{D}(X_2) dX_2 \qquad (27)$$

However, since Ir_3Hf has two different Ir and Hf sublattices, the Ir diffusion and the Hf diffusion are independent to first order (with negelect of motion of antisite defects). Moreover, as mentioned earlier, the growth of the Ir_3Hf layer proceeds mainly by Ir diffusion. Hence, in this case the parabolic rate constant, k_p, can be related simply to the average component diffusion coefficient of Ir, D_{Ir}^{av}. The component diffusion coefficient is related to the tracer diffusion coefficient by

$$D_{Ir} = \frac{D_{Ir}^{*}}{f_{Ir}} \qquad (28)$$

where f_{Ir} is the correlation factor for Ir diffusion.

The quasi-steady state flux of Ir through the Ir_3Hf layer is given by

$$J_{Ir} = - \frac{D_{Ir}^{av} C_{Ir}}{RT} \frac{\Delta\mu_{Ir}}{\xi} \qquad (29)$$

where J_{Ir} is the Ir flux, expressed in mol/m^2s, C_{Ir} the Ir concentration, expressed in mol/m^3, $\Delta\mu_{Ir}$ the chemical potential difference across ξ, expressed in m, and D_{Ir}^{av} the average tracer diffusion coefficient of Ir, expressed in m^2/s. From equations (24) and (29),

$$\xi\frac{d\xi}{dt} = -\frac{D_{Ir}^{av}C_{Ir}\Omega_{Ir_3Hf}\Delta\mu_{Ir}}{3RT} \qquad (30)$$

Here

$$C_{Ir}\Omega_{Ir_3Hf} = 3 \qquad (31)$$

and $\Delta\mu_{Ir}$ can be expressed as

$$\Delta\mu_{Ir} = \frac{1}{3}[\Delta G_f^o(Ir_3Hf) - \Delta G_f^o(HfC)] \qquad (32)$$

from the local equilibrium reaction at the HfC/Ir_3Hf interface:

$$HfC + 3\underline{Ir} = Ir_3Hf + C \qquad (11)$$

The integral of Eq(29) becomes

$$\xi^2 = -2\frac{D_{Ir}^{av}[\Delta G_f^o(Ir_3Hf) - \Delta G_f^o(HfC)]}{3RT}t \qquad (33)$$

The parabolic rate law is given by

$$\xi^2 = 2k_pt \qquad (34)$$

Finally, a comparison of (32) and (33) shows that

$$D_{Ir}^{av} = -\frac{3RTk_p}{\Delta G_f^o(Ir_3Hf) - \Delta G_f^o(HfC)} \qquad (35)$$

The measured parabolic rate constants and the calculated D_{Ir}^{av} values are given in Table 9. From the Arrhenius equation for the temperature-dependence of D_{Ir}^{av}, drawn in Figure 16, the frequency factor, $D_{o,Ir}$, and the activation energy, Q_{Ir}, are calcualated:

$D_{o,Ir} = 0.01\ cm^2/s$

$Q_{Ir} = 331$ kJ/mol

In view of the relative stabilities of the compounds, these values compare favorably with the values of $D_o^* = 1\ cm^2/s$ and $Q^* =$

303 kJ/mol for the tracer diffusion coefficient of Ni in Ni_3Al [16].

The values of D_{Ir}^{av} calculated from Eq.(34) may be somewhat uncertain because of the entropic approximation in $\Delta G_f^o(Ir_3Hf)$ and because of a factor associated with the areal blocking of diffusion by voids, somewhat ameliorated by vapor flow at the highest temperatures. In any case the values of k_p and D_{Ir}^{av} phenomenologically explain the layer growth.

V. CONCLUSIONS

Ir_3Hf is the only product phase produced from the reaction of Ir and HfC, although there exist other binary intermetallic compounds, IrHf, Ir_3Hf_5 and $IrHf_2$. The growth of the Ir_3Hf layer follows a parabolic rate law. Ir atoms are the the dominant diffusing species in Ir_3Hf, and this can be explained by a random walk treatment and atomistic models for Ir and Hf diffusion in Ir_3Hf. Many voids are observed along the Ir/Ir_3Hf interface and in the Ir_3Hf layer. A model for the void formation is proposed. From the assumption of local equilibria at the Ir/Ir_3Hf and the HfC/Ir_3Hf interfaces, the activities and activity coefficients of Ir and at the interfaces are calculated. An expression for D_{Ir}^{av}

in Ir_3Hf is derived and the values of D_{Ir}^{av} are calculated for temperatures between 1900°C and 2200°C.

REFERENCES

1. E. Fitzer: Carbon, 1987, vol. 25, p. 163.
2. Vought Corp., ELITE Program Review, vol. 1, Jan.-Apr., 1985.
3. R. A. Rapp and G. R. ST.Pierre: "Options for Oxidation Protection pf Carbon-Carbon Composites at 3500°F", reported to Vought Corp., Dallas, TX., Aug., 1980.
4. L. Brewer and P. R. Wengert: Metall. Trans., 1973, vol. 4, p. 83
5. A. R. Miedema: J. Less-Common Met., 1975, vol. 41, p. 117
6. M. I. Copeland and D. Goodrich: J. Less-Common Metals, 1969, vol. 18, p. 347.
7. A. E. Dwight and P. A. Beck: AIME Trans., 1959, vol. 215, p. 83.
8. Smithells Metals Reference Book(Ed. E. A. Brandes), Sixth Edition, Butterworths, London, 1983, p. 8-15.
9. J. M. Criscione, R. A. Mercuri, E. P. Schram, A. W. Smith, and H. F. Volk: Technical Documentary Report No. ML-TDR-^$-173, Part II, Union Carbide Corporation, Carbon Product Division, Parma, Ohio. p. 81
10. R. G. Coltters: Mater. Sci. Eng., 1985, vol. 76, p. 1.
11. H. J. Beattie, Jr: in "Intermetallic Compounds"(Ed. J. H. Westbrook), John Wiley & Sons, New York, 1967, p. 144

12. R. Kikuchi and H. Sato: J. Chem. Phys., 1969, vol. 51, p. 161
13. H. Bakker: in "Diffusion in Crystalline Solids"(Ed. G. E. Murch and A. S. Nowick), Academic Press, New York, 1984, p. 189
14. E. W. Elcock and C. W. McCombie: Phys. Rev., 1958, vol. 109, P. 605
15. G. Frohberg and H. Wever: in "Point Defects and Defect Interactions in Metals",(Eds. J. I. Takamura, M. Doyoma, and M. Kiritani), Univ. of Tokyo Press, Tokyo, 1982, p. 614
16. G. F. Hancock: Phys. Stat. Sol. (a), 1971, vol. 7, p. 535.
17. D. Ansel, J. Barre, C. Meziere, and J. Debuigne: J. Less-Common Met., 1979, vol. 65, P1
18. S. M. Foiles and M. S. Daw: J. Mater. Res., 1987, vol. 2(1), P. 5
19. S. M. Foiles: in "High-Temperature Ordered Alloys II"(Eds. N. S. Stoloff, C. C. Koch, C. T. Liu, and O. Izumi), Mat. Res. Soc. Proceedings, 1986, p. 51.
20. W. B. Pearson: "Handbook of Lattice Spacings and Structures of Metals and Alloys", Pergamon Press, New York, 1958, p. 377
21. M. Hansen: "Constitution of Binary Alloys", 1958, McGraw-Hill, New York.
22. W. W. Wood: J. Chem. Phys., 1970, vol. 52, p. 729.

23. L. Brewer: in " Phase Stability in Metals and Alloys"(Eds. R. Rudman, J. Stringer, and R. I. Jaffee), 1967, McGraw-Hill, New York, p. 39
24. R. Hultgren, P. Desai, D. Hawkings, M. Gleiser, and K. K. Kelly: " Selected Values of the Thermodynamic Properties of the Elements and Binary Alloys", American Society for Metals, Metals Park, OH, 1973.
25. R. Thorn and G. Winslow: J. Chem. Phys., 1957, vol. 26, p. 186.
26. R. A. Rapp: Metall. Trans., 1984, vol. 15B, p. 195.
27. H. Schmalzried: "Solid State Reactions", Verlag Chemie, Weinheim, 1981, p. 236.
28. R. E. Honig and D. A. Kramer: in "Techniques in Metals Research", vol. IV, Part 1(Ed. R. A. Rapp), John Wiley & Sons, New York, 1970, p. 516.
29. C. Wagner: Acta Met., 1969, vol. 17, p. 99.

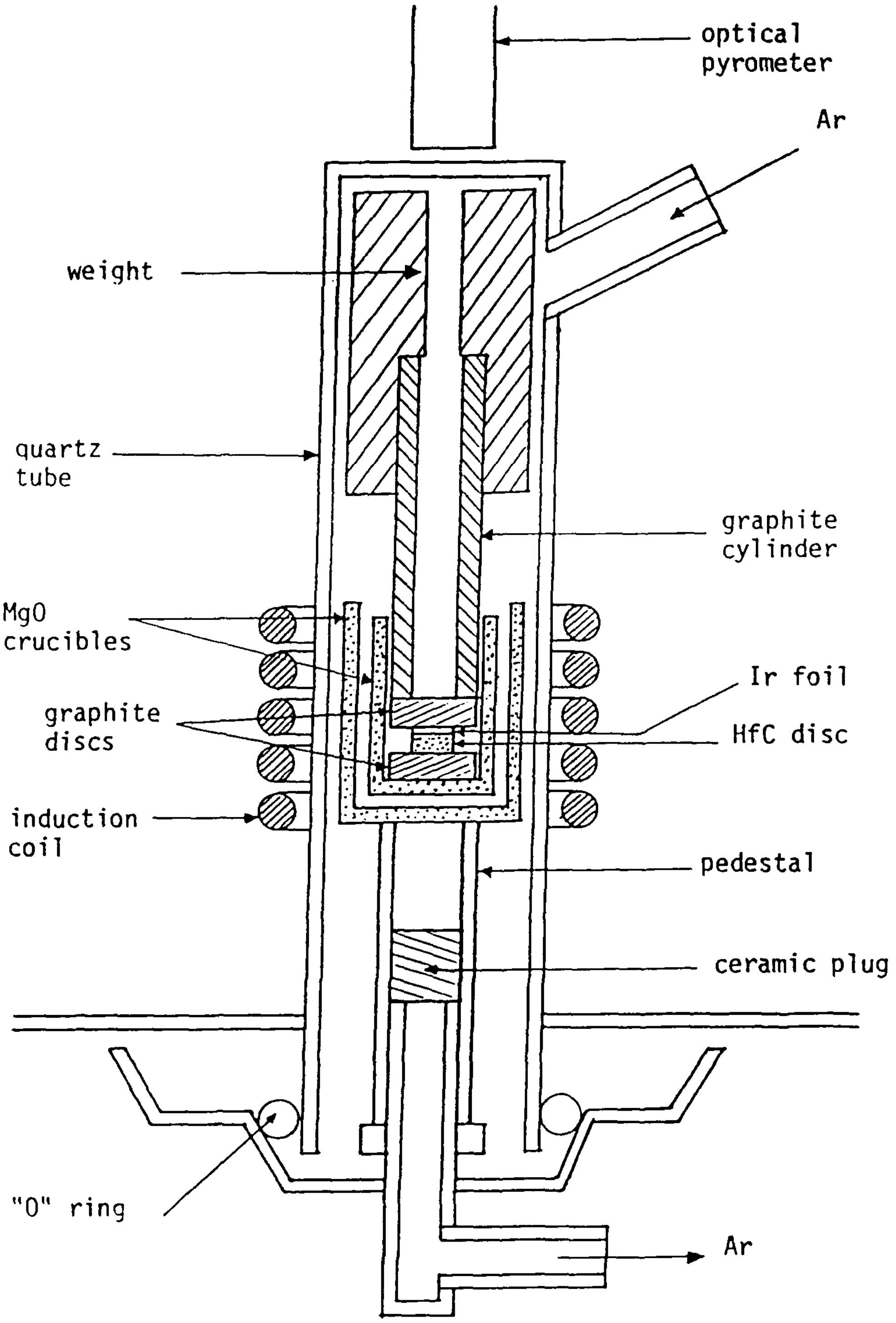


Figure 1. Schematic representation of the experimental setup.

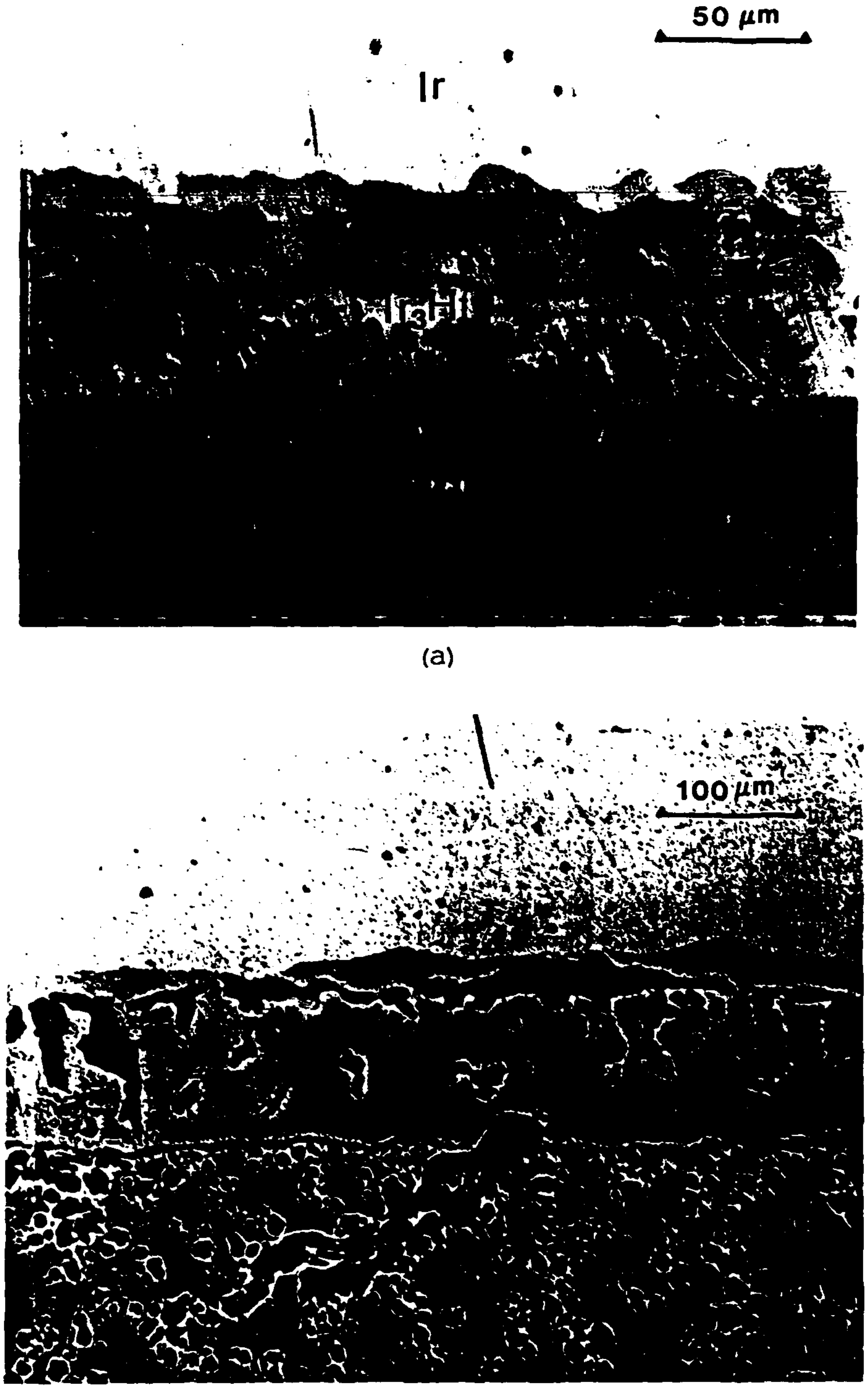


Figure 2. Light micrographs of the reaction zone produced by reaction of Ir with HfC at 2200°C.

(a) for 4 hours
(b) for 16 hours

Figure 3. Light micrograph of the reaction zone produced by reaction of Ir with HfC at 2100°C for 16 hours.

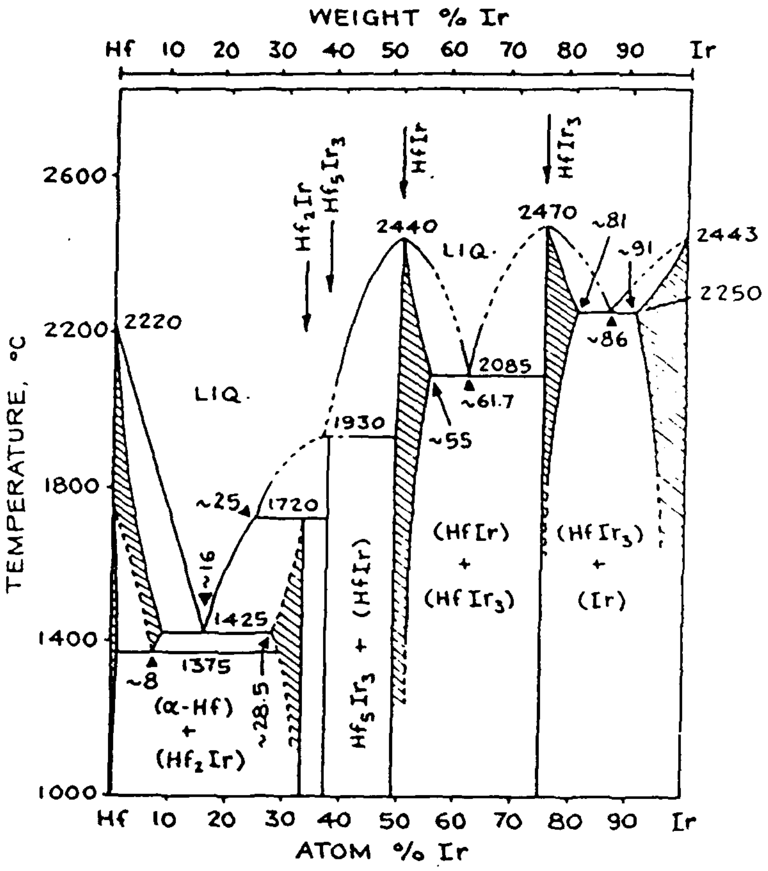


Figure 4. The Ir-Hf binary phase diagram.

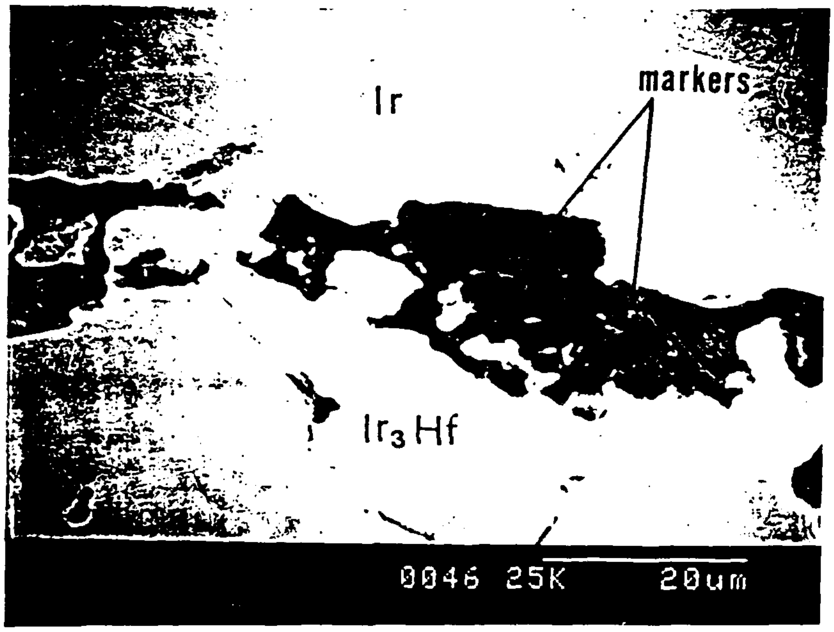


Figure 5. Secondary electron image of graphite fiber markers inside the pores along the Ir/Ir_3Hf interface. (2100°C, 16H)

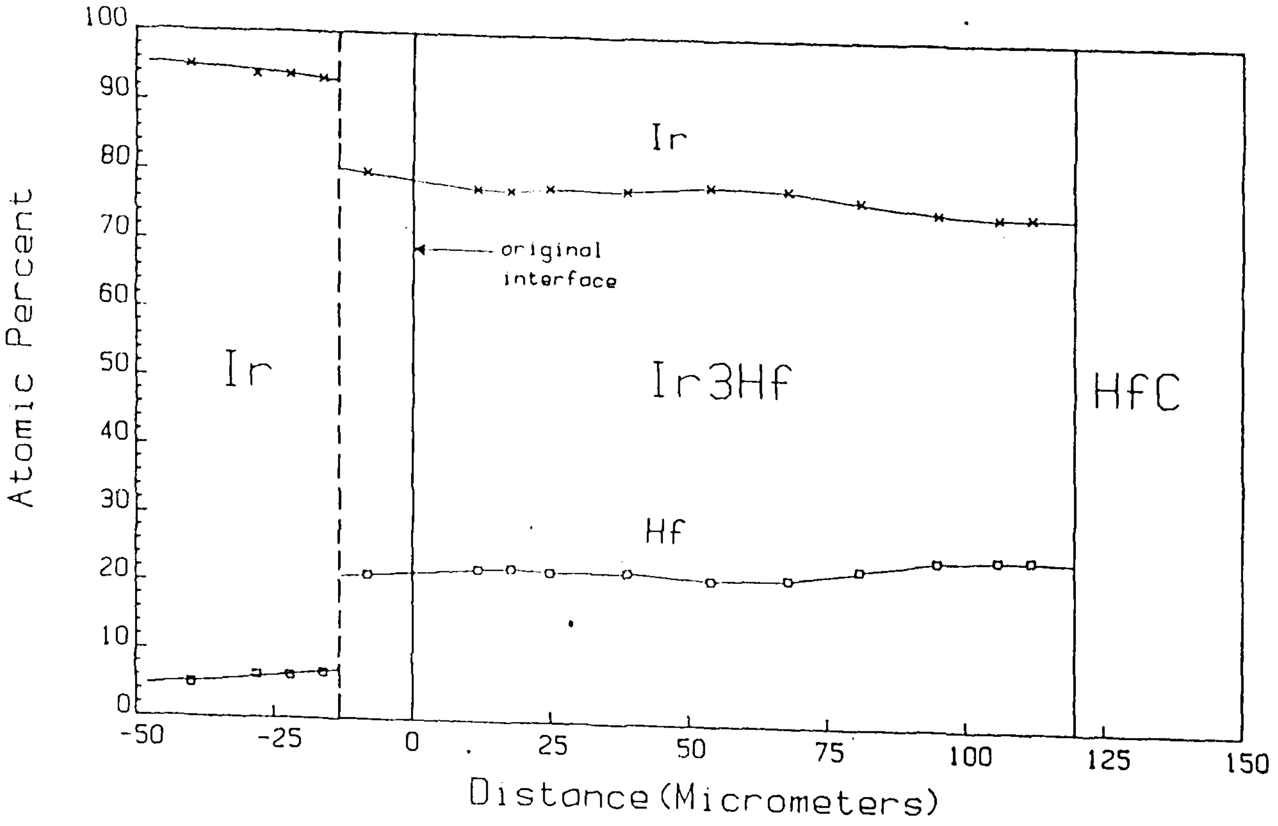


Figure 6. Electron microprobe analysis across reaction zone in figure 2(b)

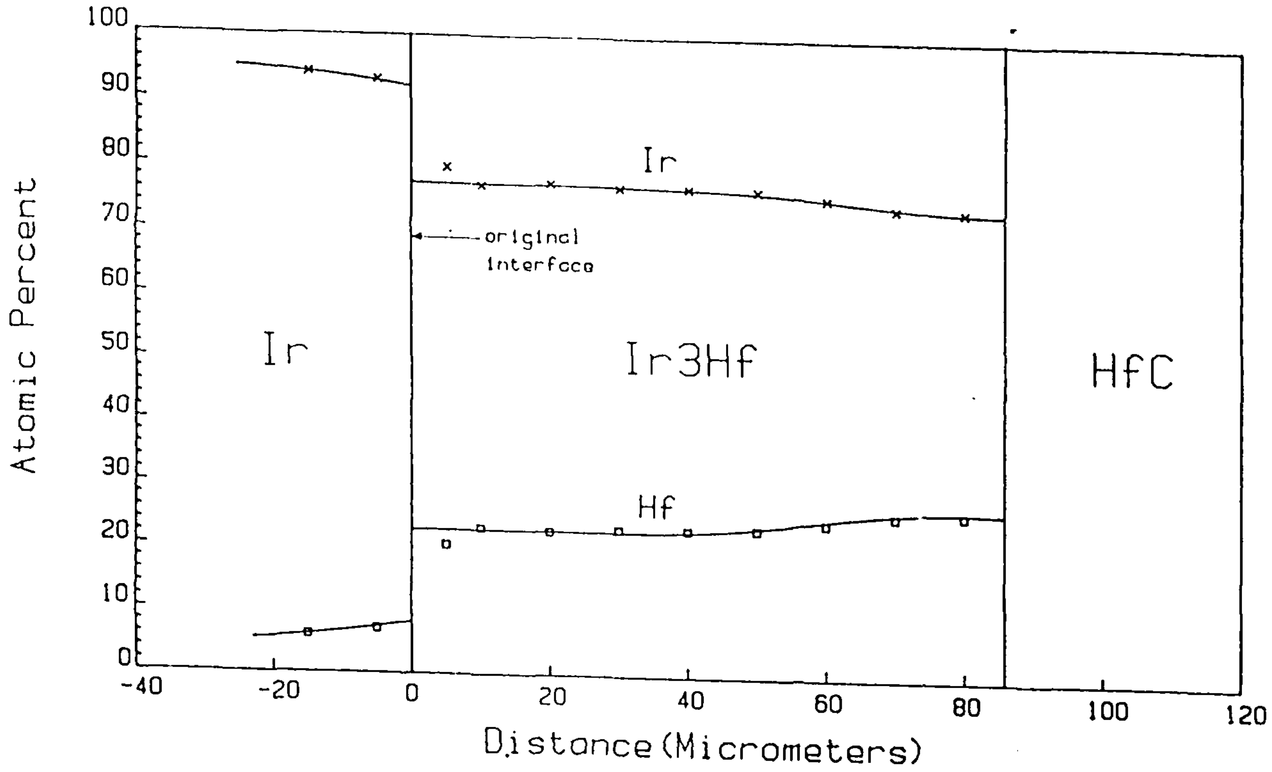


Figure 7. Electron microprobe analysis across reaction zone in figure 3.

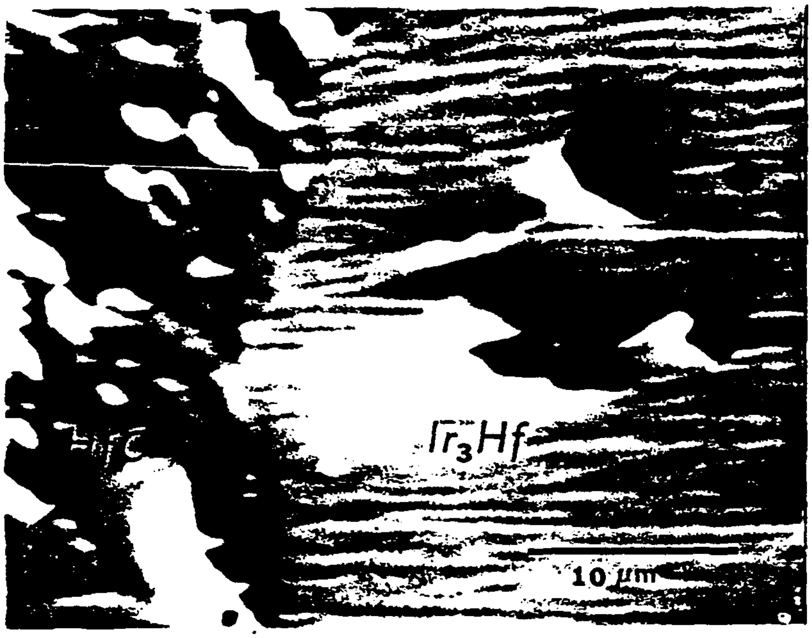


Figure 8. Secondary electron image of sample treated at 2200°C for 8 hours.

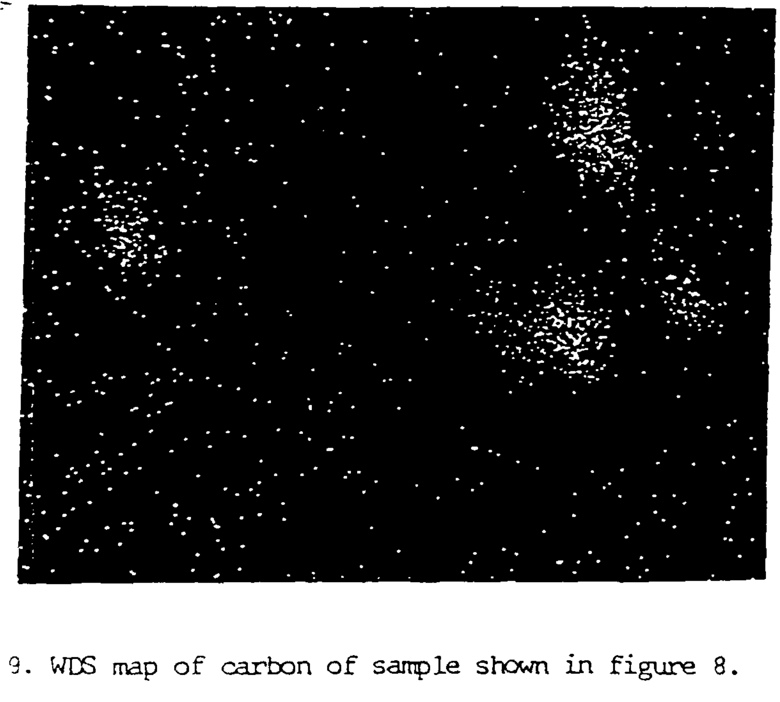


Figure 9. WDS map of carbon of sample shown in figure 8.

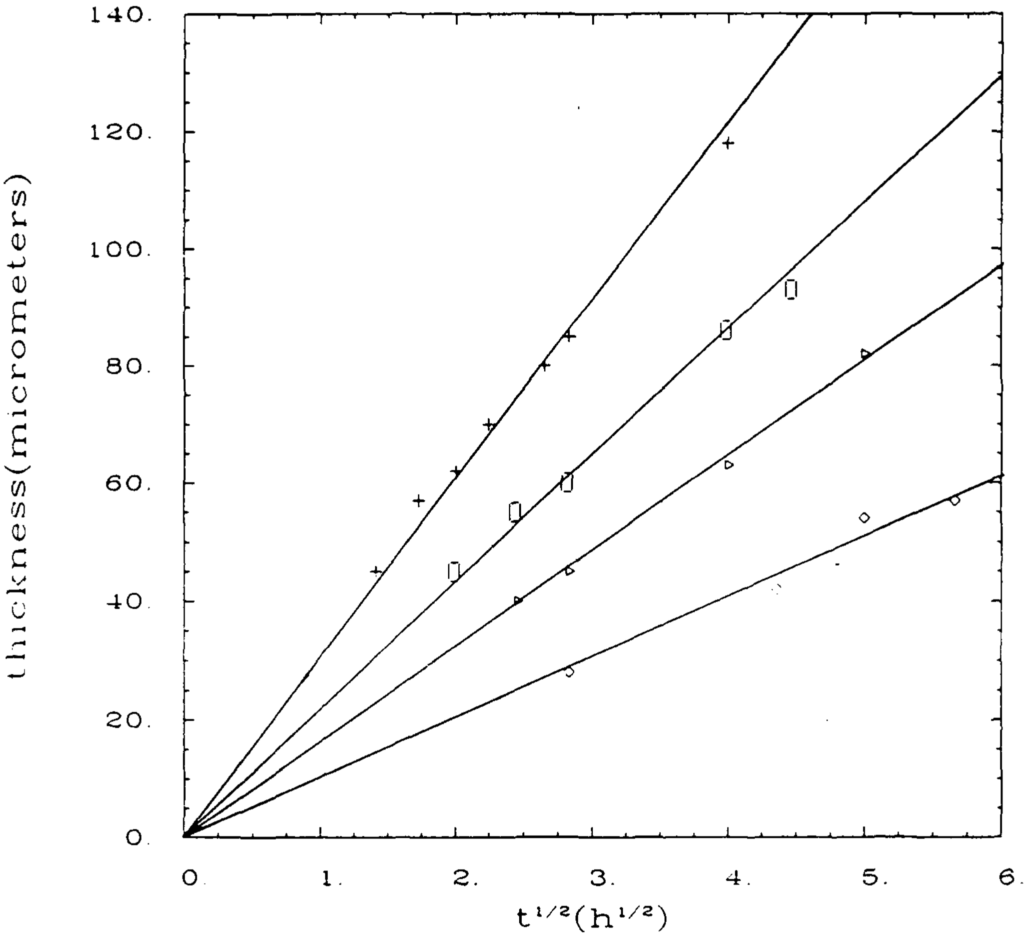


Figure 10. Thickness of Ir_3Hf vs. $t^{1/2}(h^{1/2})$.

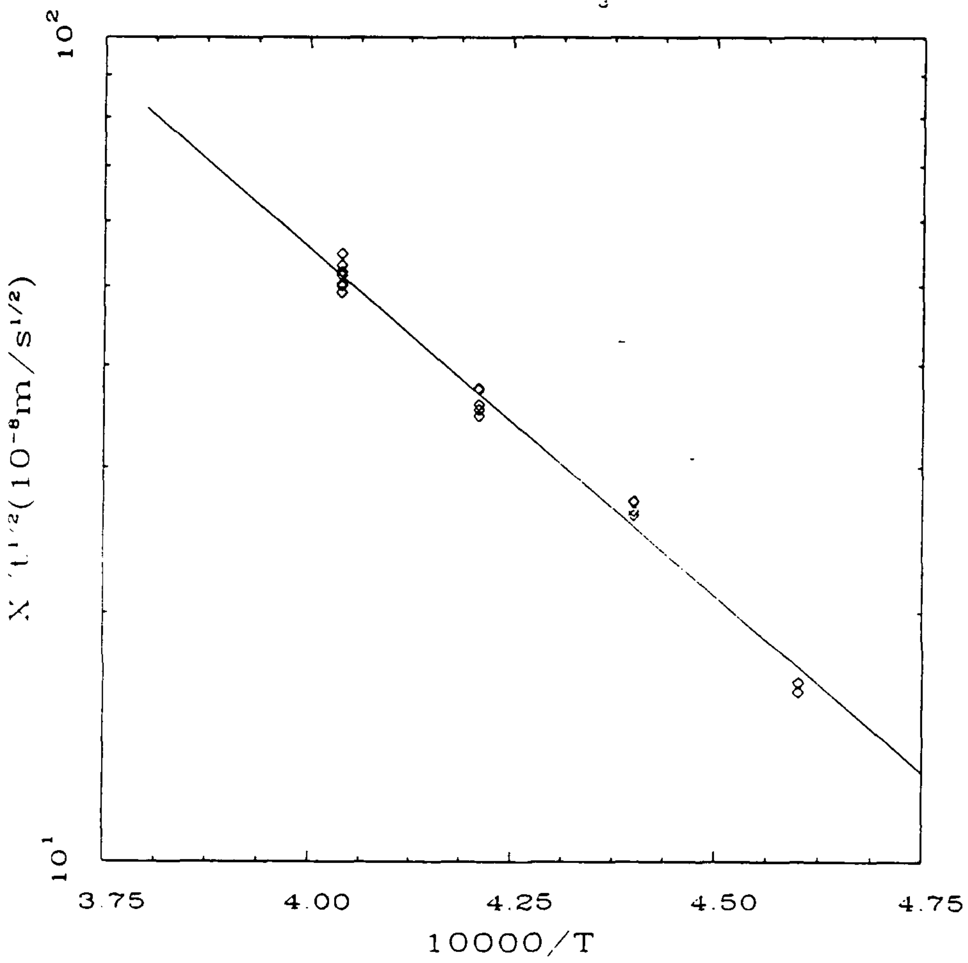


Figure 11. Arrhenius plot for the growth of Ir_3Hf layer.

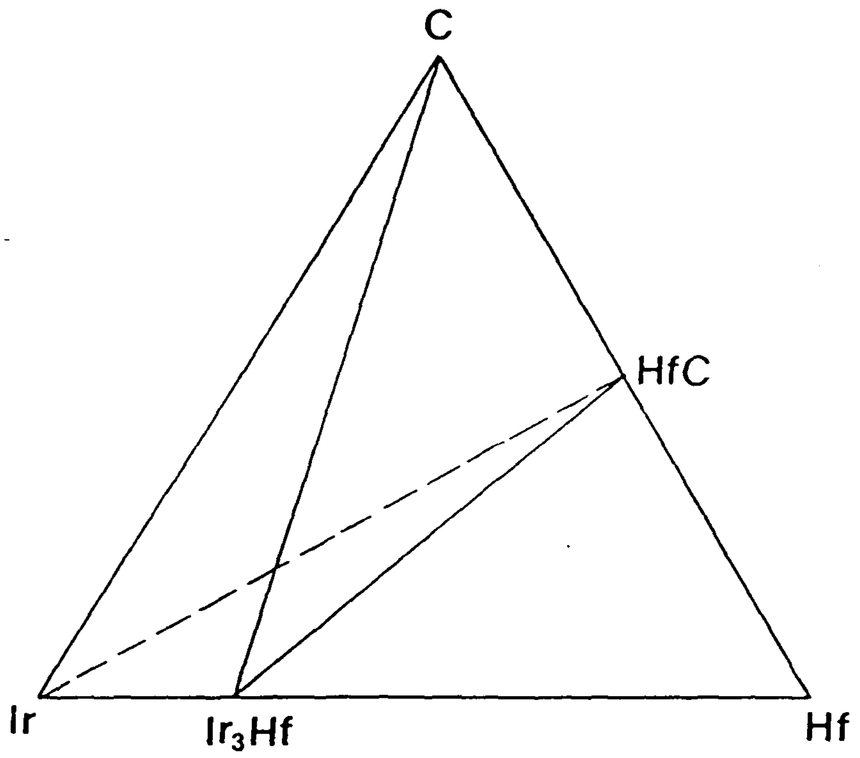


Figure 12. An Ir-Hf-C ternary isotherm, drawn on the basis of the experimental results.

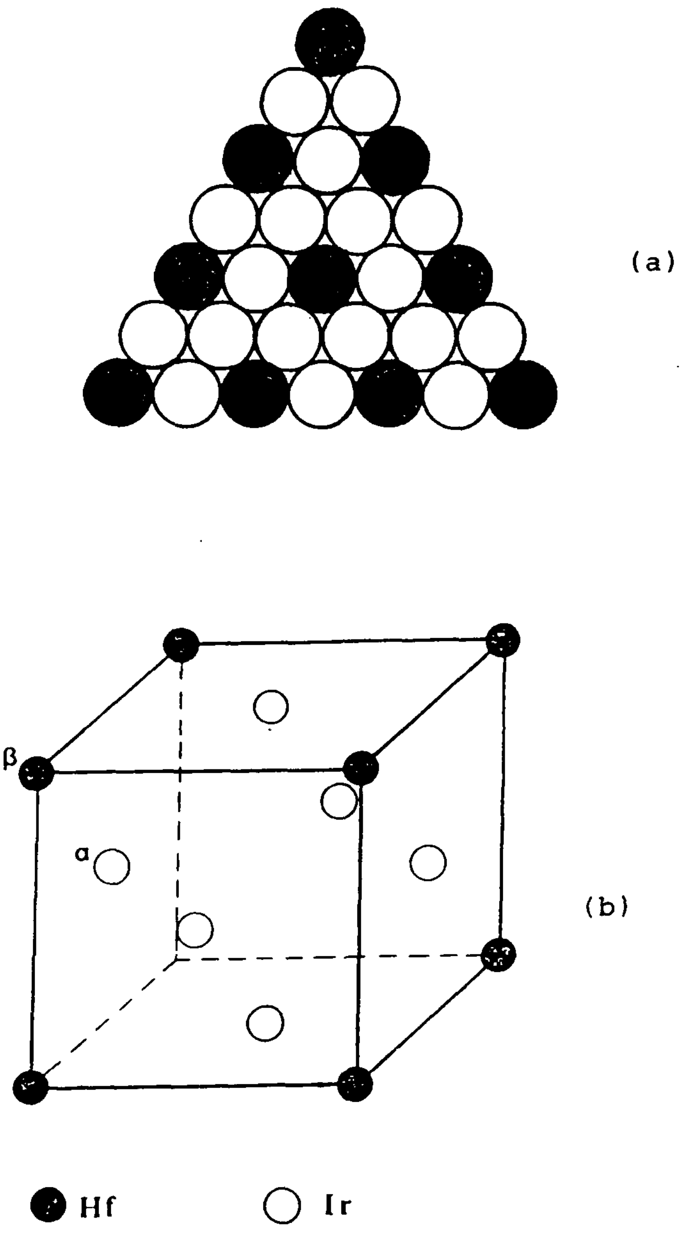


Figure 1·3. $L1_2$(Cu_3Au-type) structure [7,11].

(a) (111) closed-packed plane

(b) unit cell

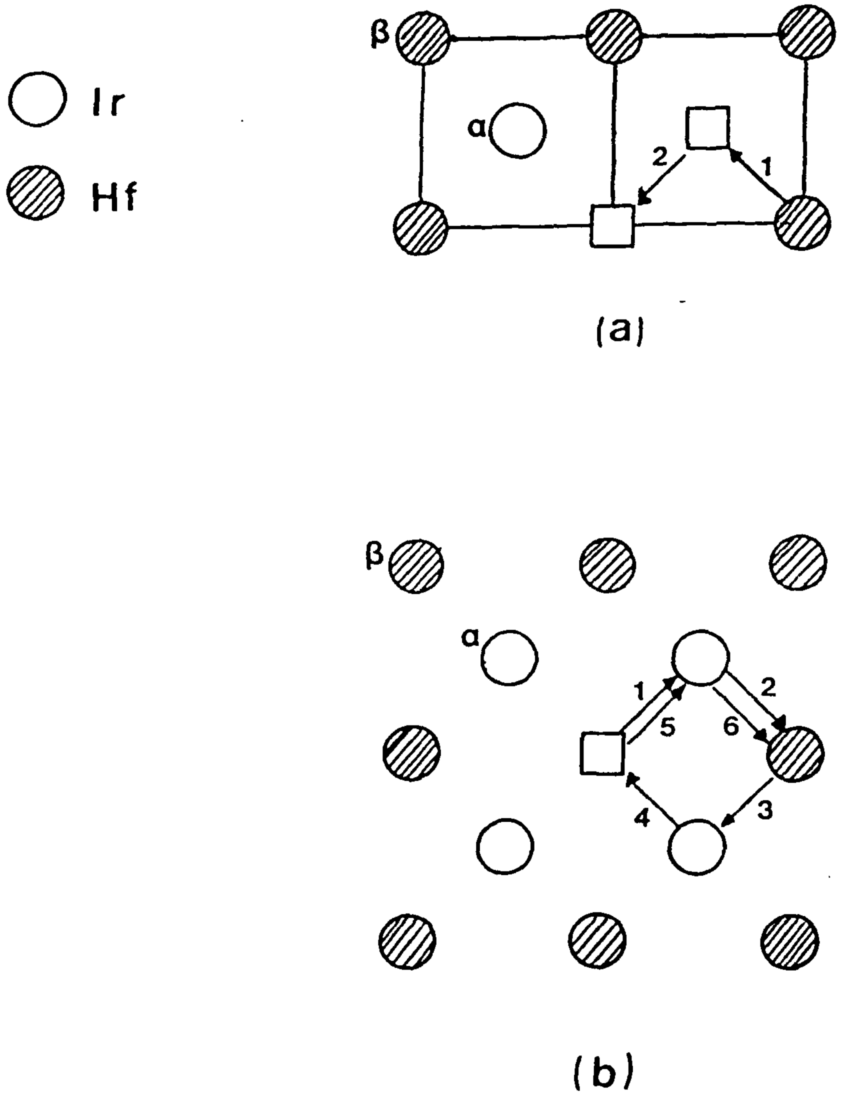


Figure 14. Atomic jump mechanisms of Hf in Ir_3Hf.

(a) divacany mechanism
(b) six jump-cycle mechanism

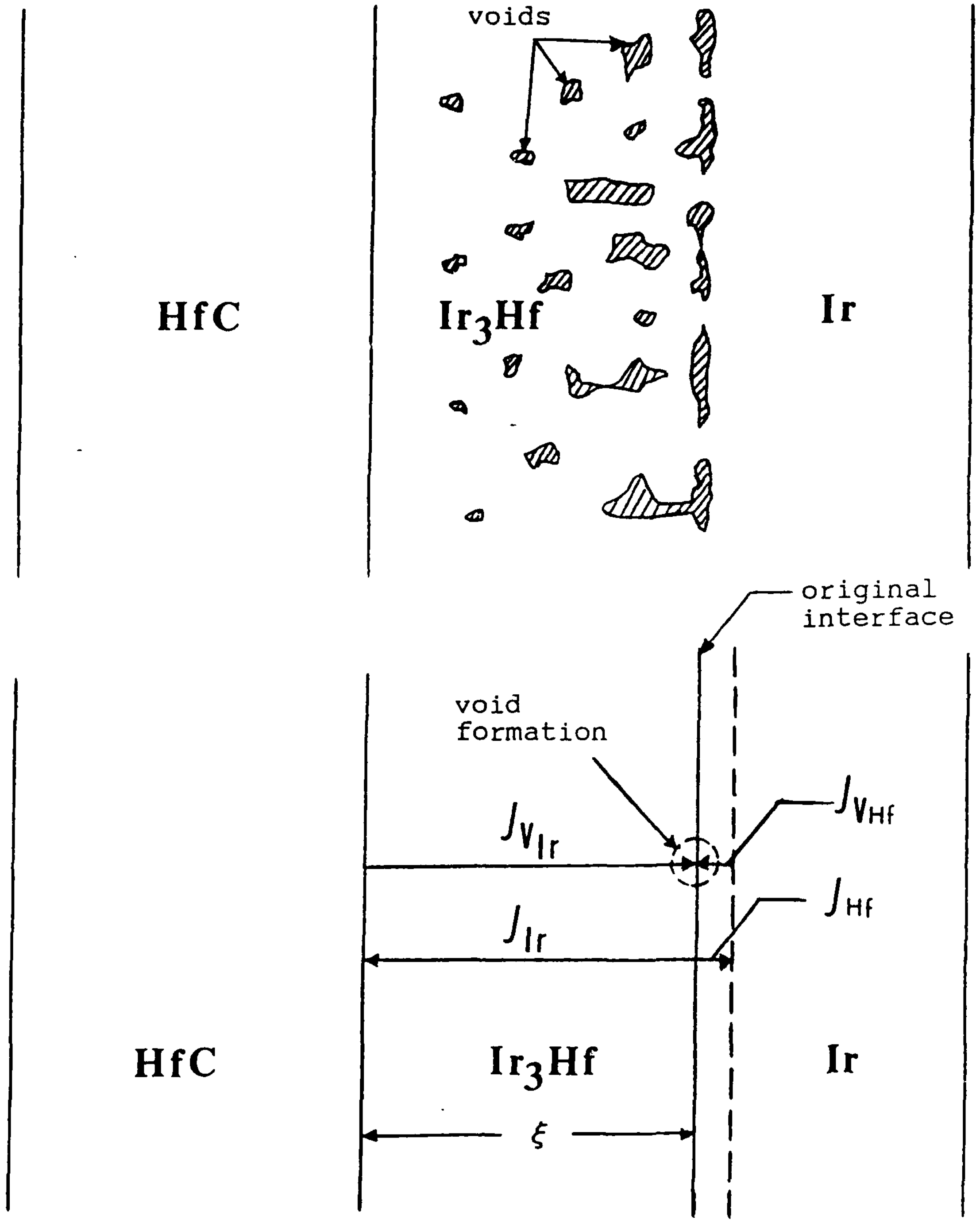


Figure 15. Void formation at the original interface and in the Ir_3Hf layer.

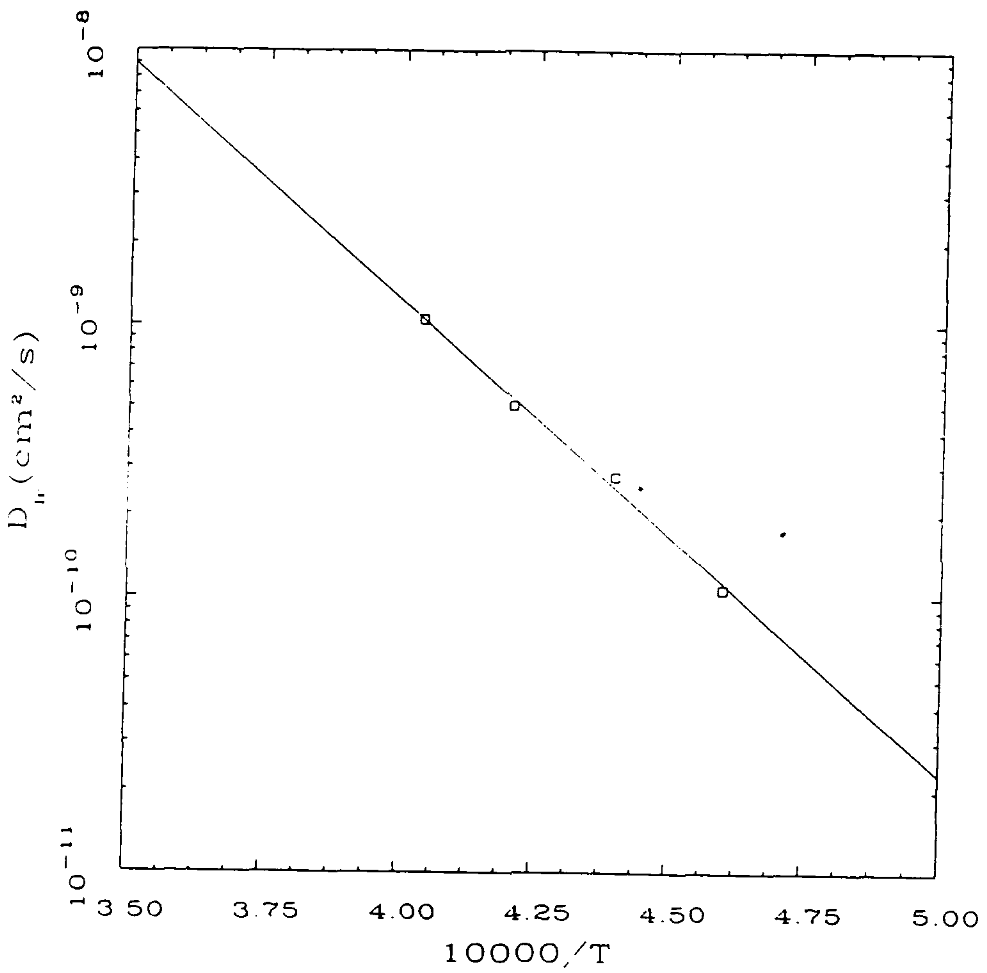


Figure 16. Temperature dependence of Ir diffusion in Ir_3Hf.

Table 1. X-ray data and lattice constant calculated by the Nelson-Riley extrapolation method for Ir_3Hf.

d(nm)	Bragg angles	hkl planes
0.2275	19.791	111
0.1969	23.030	200
0.1392	33.599	220
0.1188	40.421	311
0.1135	42.741	222
0.0983	51.593	400
0.0903	58.544	331

a_o = 0.3934 nm

Table 2. Mole fractions, activities, activity coefficients of Ir at the Ir/Ir_3Hf and HfC/Ir_3Hf interfaces.

	Ir/Ir_3Hf Interface			HfC/Ir_3Hf interface		
	X^*_{Ir}	a^{**}_{Ir}	γ_{Ir}	X^*_{Ir}	a_{Ir}	γ_{Ir}
2200°C	0.7789	1	1.284	0.7491	0.286	0.382
2100°C	0.7736	1	1.293	0.7426	0.278	0.374
2000°C	0.7640	1	1.301	0.7454	0.269	0.361
1900°C	0.7567	1	1.322	0.7439	0.260	0.350

* measured by electron microprobe analysis.

** assumed to be equal to unity at the Ir/Ir_3Hf interface.

Table 3. Atomic radii of A and B atoms, lattice constants and entropies of formation for A_3B alloys(Cu_3Au-type)

	r_B/r_A	a_o(nm)	ΔH(kJ/mol)
Ni_3Al	1.149[a]	0.3570[c]	-37.5[d]
Ir_3Hf	1.170[b]	0.3934	-271.3

a. reference 20
b. reference 7
c. reference 21
d. reference 22

Table 4. Equilibrium vapor pressures(atm) of carbon [24].

Temperature	P_C	P_{C_2}	P_{C_3}	P_{total}
2100 K	$2.3x10^{-10}$	$3.7x10^{-11}$	$2.4x10^{-10}$	$5.2x10^{-10}$
2200 K	$1.51x10^{-9}$	$3.0x10^{-10}$	$1.83x10^{-9}$	$3.76x10^{-9}$
2300 K	$8.26x10^{-9}$	$2.21x10^{-9}$	$1.16x10^{-8}$	$2.30x10^{-8}$
2400 K	$3.92x10^{-8}$	$1.25x10^{-8}$	$6.30x10^{-8}$	$1.22x10^{-7}$
2500 K	$1.64x10^{-7}$	$6.34x10^{-8}$	$2.96x10^{-7}$	$5.60x10^{-7}$

Table 5. Effective vapor pressures(atm), $\alpha_i P_{C_i}$, of carbon.

Temperature	P_C^{eff}	$P_{C_2}^{eff}$	$P_{C_3}^{eff}$	P_{total}^{eff}
2100 K	$8.51\text{x}10^{-11}$	$1.26\text{x}10^{-11}$	$1.92\text{x}10^{-11}$	$1.17\text{x}10^{-10}$
2200 K	$5.56\text{x}10^{-10}$	$1.02\text{x}10^{-10}$	$1.46\text{x}10^{-10}$	$8.04\text{x}10^{-10}$
2300 K	$3.06\text{x}10^{-9}$	$7.21\text{x}10^{-10}$	$9.28\text{x}10^{-10}$	$4.71\text{x}10^{-9}$
2400 K	$1.45\text{x}10^{-8}$	$4.25\text{x}10^{-9}$	$5.01\text{x}10^{-9}$	$2.38\text{x}10^{-8}$
2500 K	$6.07\text{x}10^{-8}$	$2.16\text{x}10^{-8}$	$2.37\text{x}10^{-8}$	$1.06\text{x}10^{-7}$

Table 6. Recession rates of carbon (µm/hour)

Temperature	R(C)	R(C_2)	R(C_3)	R(total)
2100 K	$3.90\text{x}10^{-3}$	$8.24\text{x}10^{-4}$	$1.53\text{x}10^{-3}$	$6.26\text{x}10^{-3}$
2200 K	$2.49\text{x}10^{-2}$	$6.52\text{x}10^{-3}$	$1.14\text{x}10^{-2}$	$4.28\text{x}10^{-2}$
2300 K	$1.34\text{x}10^{-1}$	$4.51\text{x}10^{-2}$	$7.08\text{x}10^{-2}$	$2.50\text{x}10^{-1}$
2400 K	$6.22\text{x}10^{-1}$	$2.60\text{x}10^{-1}$	$3.74\text{x}10^{-1}$	1.26
2500 K	3.57	1.30	1.73	6.60

Table 7. Vapor pressures [28], vapor fluxes and recession rates of Ir.

Temperature	P_{Ir}(atm)	J_{Ir}(g/cm^{2}h)	R_{Ir}(μm/h)
2200°C	5.8×10^{-7}	2.8×10^{-2}	11.50
2100°C	1.6×10^{-7}	7.5×10^{-3}	3.20
2000°C	3.6×10^{-8}	1.6×10^{-3}	0.74
1900°C	7.2×10^{-9}	3.4×10^{-4}	0.15

Table 8. Diffusion flux of Ir as a function of the Ir_3Hf layer thickness, ξ, which is expressed in μm.

Temperature	J_{Ir}^{diff}(g/cm^{2}h)
2200°C	2.91/ξ
2100°C	1.42/ξ
2000°C	0.806/ξ
1900°C	0.316/ξ

Table 9. Parabolic rate constants and average tracer diffusivities of Ir for Ir_3Hf layer.

	k_p(cm^2/sec)	D_{Ir}^{av}(cm^2/sec)
2200°C	1.31×10^{-9}	1.05×10^{-9}
2100°C	6.43×10^{-10}	5.02×10^{-10}
2000°C	3.60×10^{-10}	2.74×10^{-10}
1900°C	1.43×10^{-10}	1.06×10^{-10}

To: Dr. John Sedriks, Office of Naval Research
From: Professors George R. St.Pierre, Robert A. Rapp, and John P. Hirth; Graduate Research Associates Jong-Won Kwon and Denis O'Connell

Subject: Research Summary for the Period 1 October 1987 to 31 March 1988, Contract No. N00014-86-K-0130 "Exploratory Research on the Protection of Carbon-Carbon Composites against Oxidation at Very High Temperatures (>3000°F) with Engel-Brewer and Other Intermetallic Compounds"

This serves as the summary of research for the period 1 October 1987 to 31 March 1988. The research performed for this period is divided into two areas:

1. Ir/HfC diffusion couple experiments
2. Oxidation study of Pt-Zr alloys

Pure iridium foils and carbon-saturated HfC discs with 91% theoretical density were polished and reacted under pressure at temperatures in the range from 1900°C to 2200°C for 2 to 32 hours. Figure 1 shows a cross section of a diffusion couple treated at 2200°C for 4 hours. Ir_3Hf is the only intermediate reaction product, although there are three other intermetallic phases, IrHf, Ir_3Hf_5 and $IrHf_2$, on the Ir-Hf binary phase diagram. The reaction of Ir_3Hf formation is

$$3Ir + HfC = Ir_3Hf + C \qquad (1)$$

There are large planar pores along the Ir/Ir_3Hf interface, and smaller pores distributed in the product layer which often extend in the same direction as the Ir_3Hf layer grows, i.e. toward the HfC, as shown in Figures 2 and 3. There are also small intrusions of the Ir_3Hf phase into Ir phase; these are noticeable only at temperatures above 2100°C. Graphite fiber markers which are stable in contact with iridium and C-saturated HfC were used to determine the original interface. From the result shown in Figure 4, Ir is the dominant diffusing species. Concentration profiles of Ir and Hf through the Ir_3Hf layer measured by EDS are shown in Figures 5 and 6. Figure 7 shows a possible mechanism of pore formation at the original interface. Some small pores also grew in the direction of Ir flux by condensing the Ir vacancy flux in the opposite direction. Carbon produced by the reaction (1) is expected to segregate in the pores. Figure 9 shows a carbon pattern on a WDS map that matches with the pores in Ir_3Hf in Figure 8. Further analysis should be done to determine the carbon movement and distribution. Diffusion kinetics are shown in Figures 10 and 11.

For the oxidation study, a Pt-9.64wt%Zr-2.73wt%W alloy was heated in the air at temperatures from 1000°C to 1400°C. During the preparation by the arc melting process, the alloy was contaminated with tungsten from the tungsten cathode rod. The oxidation kinetics of TGA experiment are plotted in Figure 12. The oxidation of the alloys does not obey a parabolic relation. Figure 13 shows a distribution of fine internal oxide particles which are associated with a second phase resulting from the W contamination, and no external scale formation. The oxidation kinetics are orders of magnitude faster than those calculated for rate control by oxygen diffusion in Pt.

Future Work

1. Some other diffusion couples such as Ir/Hf, Hf/C-C, etc. will be used to determine the chemical compatibility of potential protection systems with Carbon-Carbon composites.

2. Another Pt-dilute Zr alloy will be prepared, with attention to avoid W contamination, and its oxidation kinetics will be studied. Thereafter, Ir-Al-Cr alloys are expected to form steady-state alumina external scales in the oxidizing atmosphere. These alloys will be studied in the future.

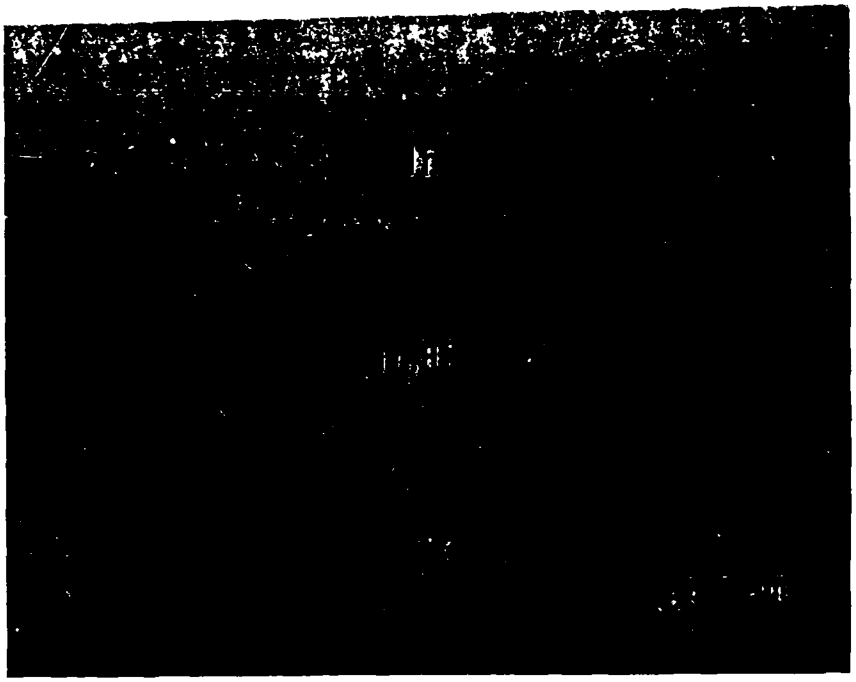


Figure 1. Light micrograph of the reaction zone produced by reaction of Ir with HfC at 2200°C for 4 hours.

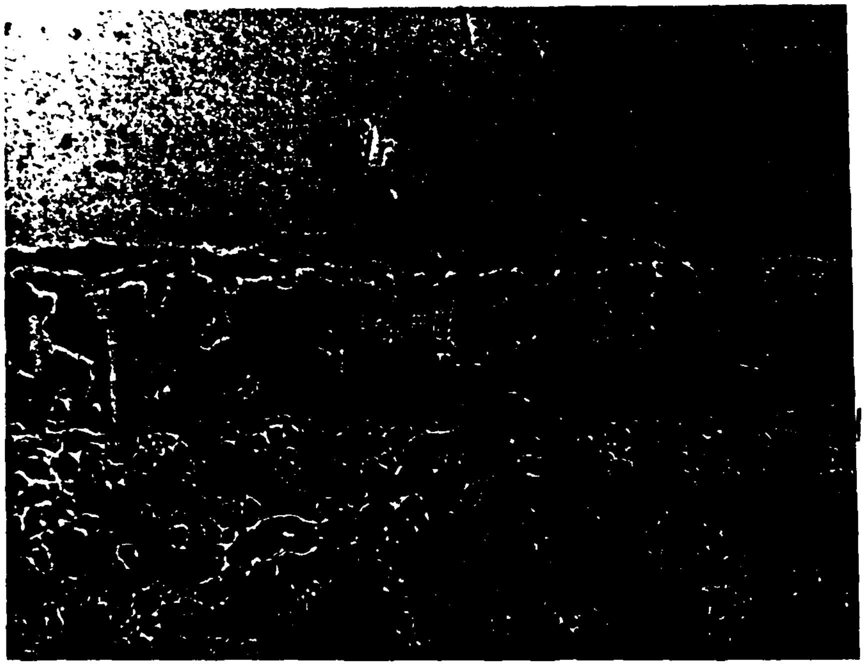


Figure 2. Light micrograph of the reaction zone produced by reaction of Ir with HfC at 2200°C for 16 hours.

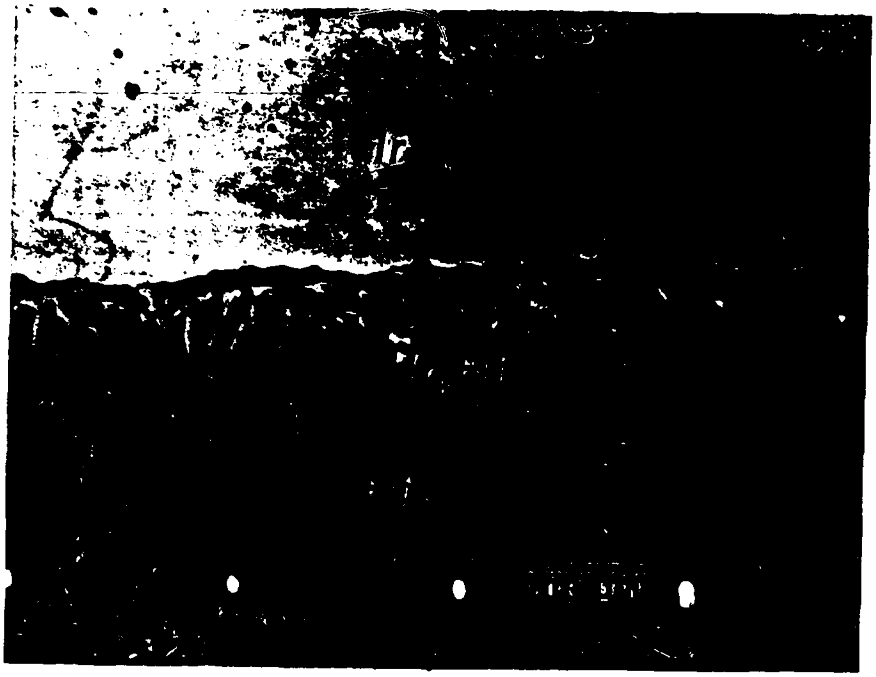


Figure 3. Light micrograph of the reaction zone produced by reaction of Ir with HfC at 2100°C for 16 hours.

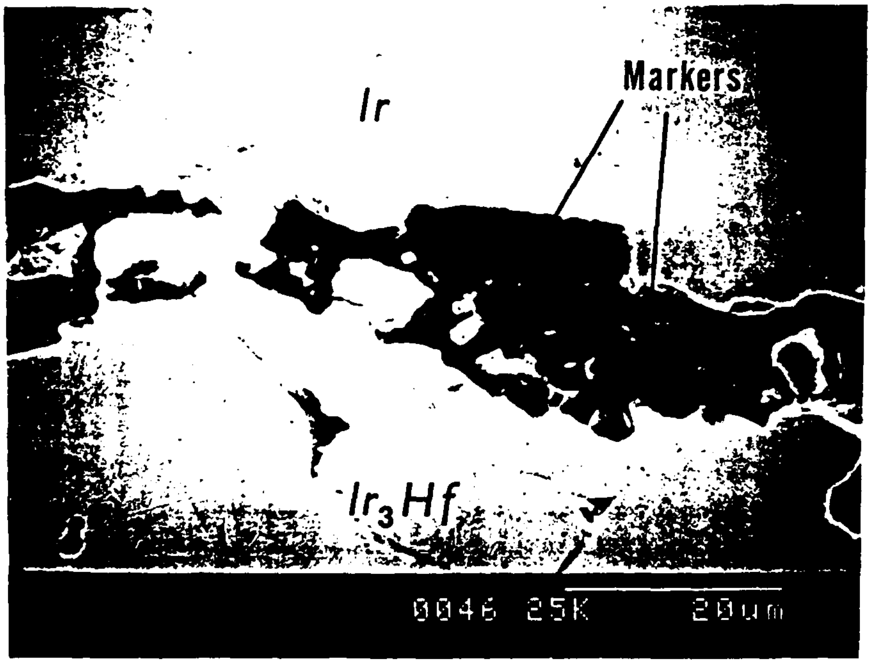


Figure 4. Secondary electron image of graphite fiber markers inside the pores along the original interface.

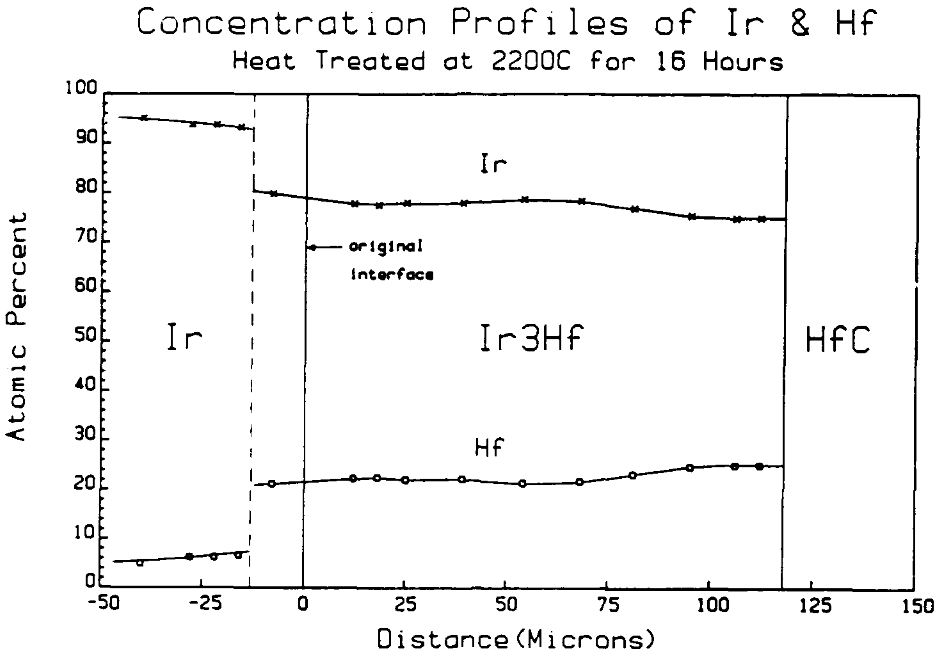


Figure 5. Electron microprobe analysis across reaction zone in figure 2.

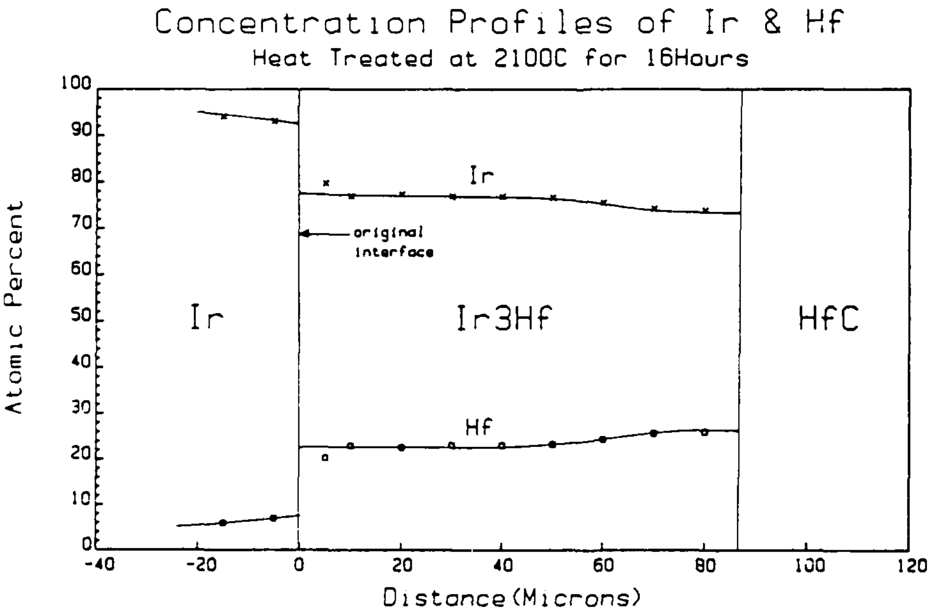


Figure 6. Electron microprobe analysis across reaction zone in figure 3.

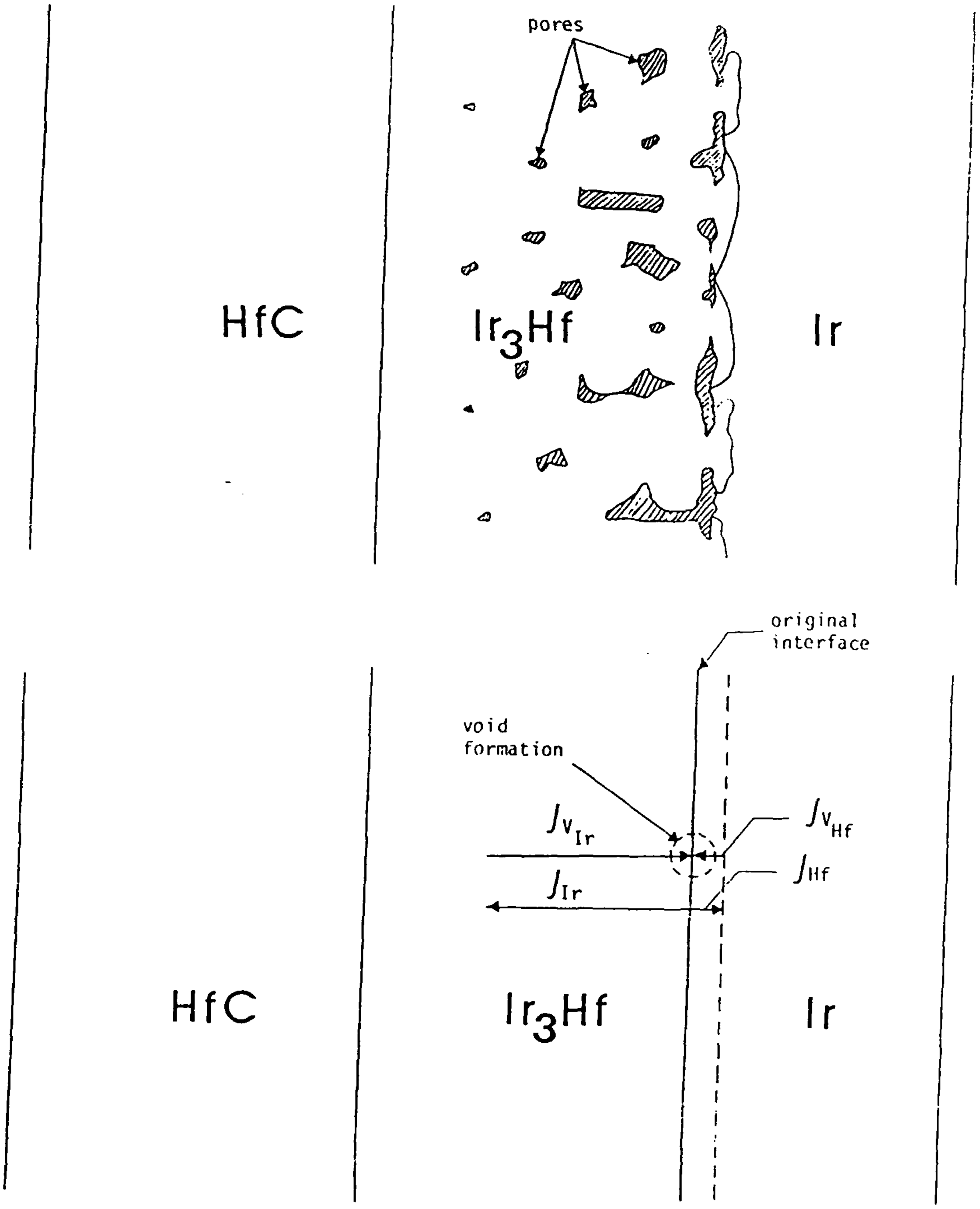


Figure 7. Pore formation at original interface and in the reaction zone.

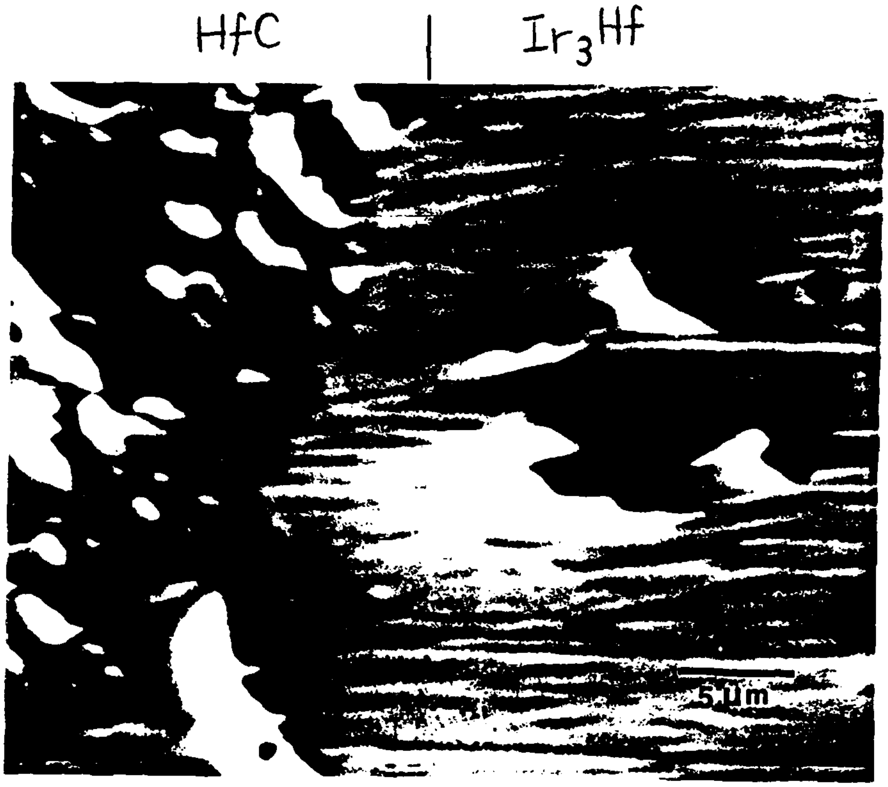


Figure 8. Secondary electron image of sample treated at 2200°C for 8 hours.

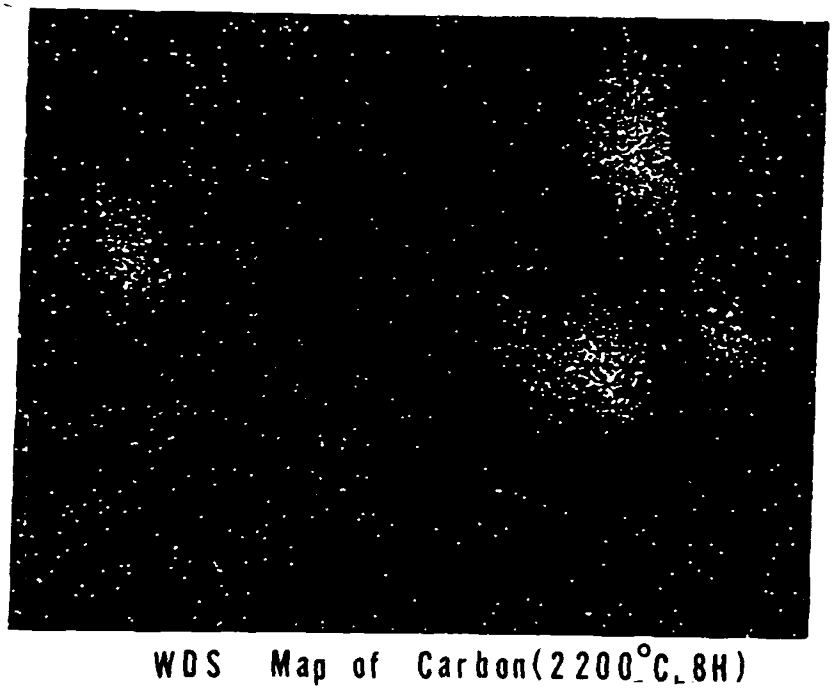


Figure 9. WDS map of carbon of sample shown in figure 8.

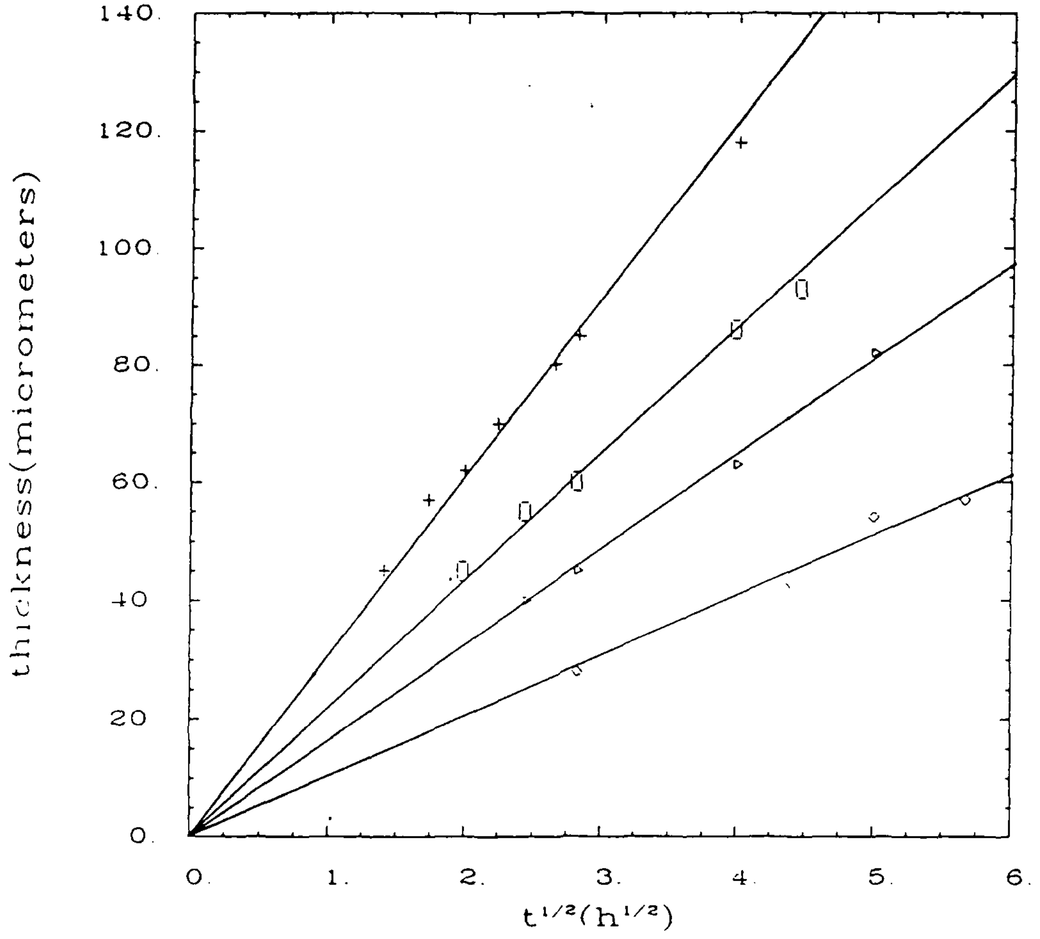


Figure 10. Thickness of Ir_3Hf vs. $t^{1/2}(h^{1/2})$.

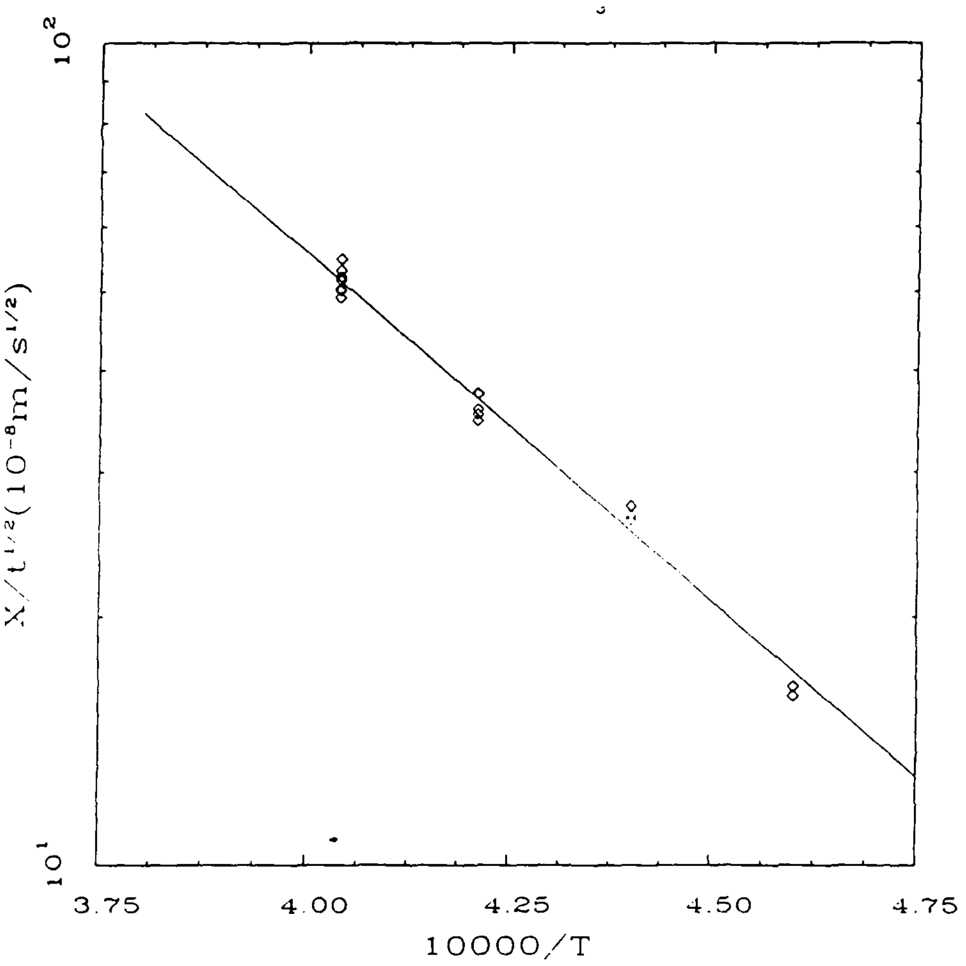


Figure 11. Arrhenius plot for the growth of Ir_3Hf layer.

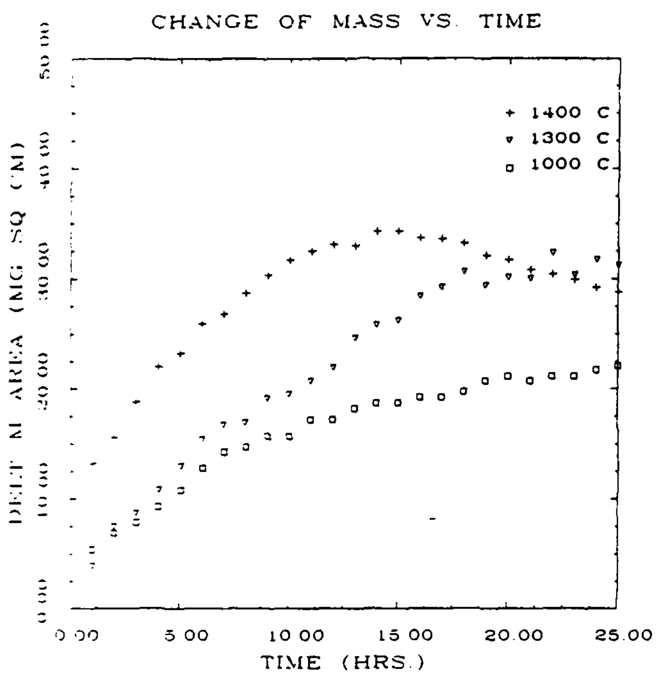


Figure 12. TGA analysis of oxidation of Pt-9.74wt%Zr-2.63wt%W.

Figure 13. Microstructure of oxidized sample at 1000°C for 25 hours.

The Formation of Intermetallic (Engel-Brewer) Phases at Metal/Metal Carbide Interfaces

George R. St.Pierre, Professor and Chairman
Department of Metallurgical Engineering
The Ohio State University

The Office of Naval Research is funding a four-year program on the use of Engel-Brewer and other high melting point intermetallic compounds in the protection of carbon/carbon composites against high temperature oxidation. In connection with that study, J. Kwon, graduate student, and Dr. G.R. St.Pierre have studied the growth of Ir_3Hf at Ir/HfC interfaces in diffusion couples at temperatures between 1900°C and 2200°C. Figure 1 shows a phase diagram for the Ir-Hf system, in which the Ir_3Hf phase has a melting point of 2470°C. Also shown in Fig. 1b is a schematic diagram of the Ir-C-Hf system in which the Ir_3Hf-C pair is markedly more stable than the Ir-HfC pair. The reaction isotherm is illustrated in Equation 1 for which ΔG^0 is strongly negative

$$3Ir + HfC = Ir_3Hf + C \tag{1}$$

Figure 2 shows the microstructure of an Ir-HfC diffusion couple after four hours at 2200°C. The concentration profiles of Ir and Hf through the system are presented in Figure 2b. The porosity of the initial HfC is estimated to be 6-8 percent. Figure 3 shows that the carbon from the solid state reaction accumulates in the pores of the Ir_3Hf product layer. Figure 4 shows that growth is approximately represented by $x=kt^{1/2}$ where x is the thickness and t is time. The dependence of the growth rate constant, k, on temperature is shown in Figure 4b. These data are currently being analyzed to determine interdiffusion coefficients of Ir and Hf in HfC, Ir_3Hf and Ir. The crystal structure and microhardness of Ir_3Hf are under investigation. Comparison studies with other metal/metal carbide couples, e.g. Pt/ZrC, are continuing. Dr. R.A. Rapp and Dr. J.P. Hirth are also associated with the work of this project under the sponsorship of Dr. John Sedriks of the ONR.

March 1988

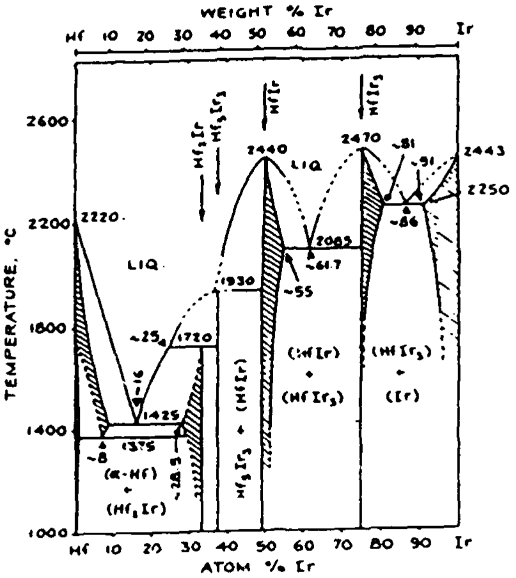


Fig. 1a The Ir-Hf Phase Diagram (Moffatt, GE Compilation). Pairs of electrons available in each Iridium atom d^6sp^2 donate to the three vacant d orbitals in d^2sp *Hafnium*. ($3Ir^{+1} + Hf^{-3} = Ir_3Hf$).

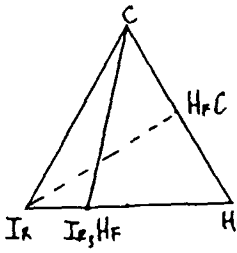


Fig. 1b A Schematic Diagram The Ir-Hf-C System. L. Brewer and P.R. Wengert: Met. Trans., 1973, Vol. 4, p. 83.

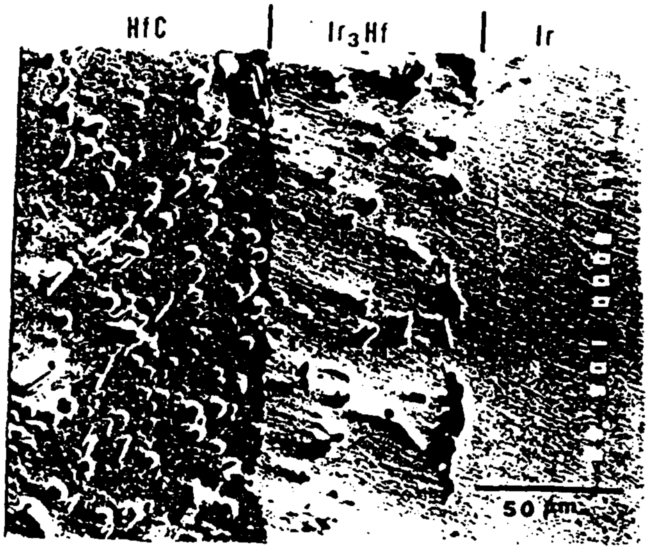


Fig. 2a Formation of Ir_3Hf Layer at the Interface of Ir/HfC Diffusion Couple Heated at 2200°C for 4 Hours. (SEM)

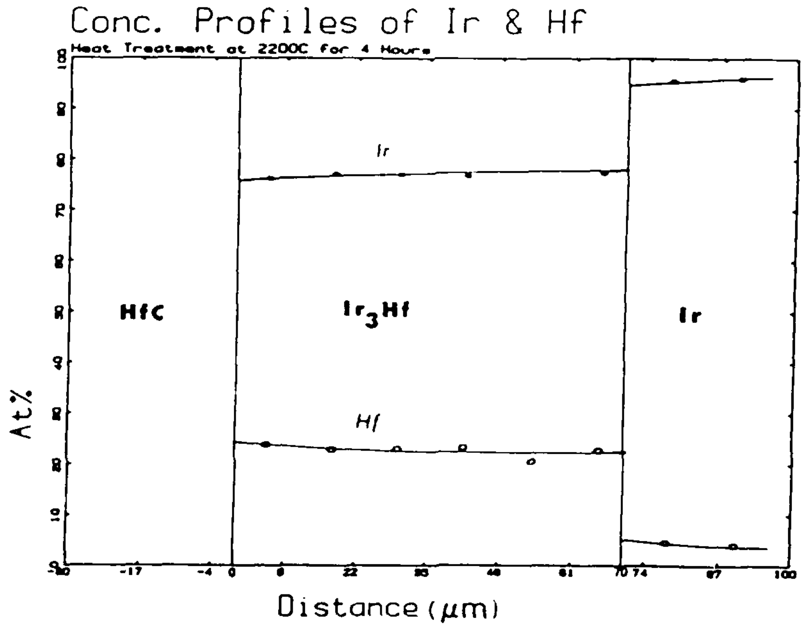


Fig. 2b Composition Profile of Ir-HfC Couple at 2200°C (Kwon and St.Pierre)

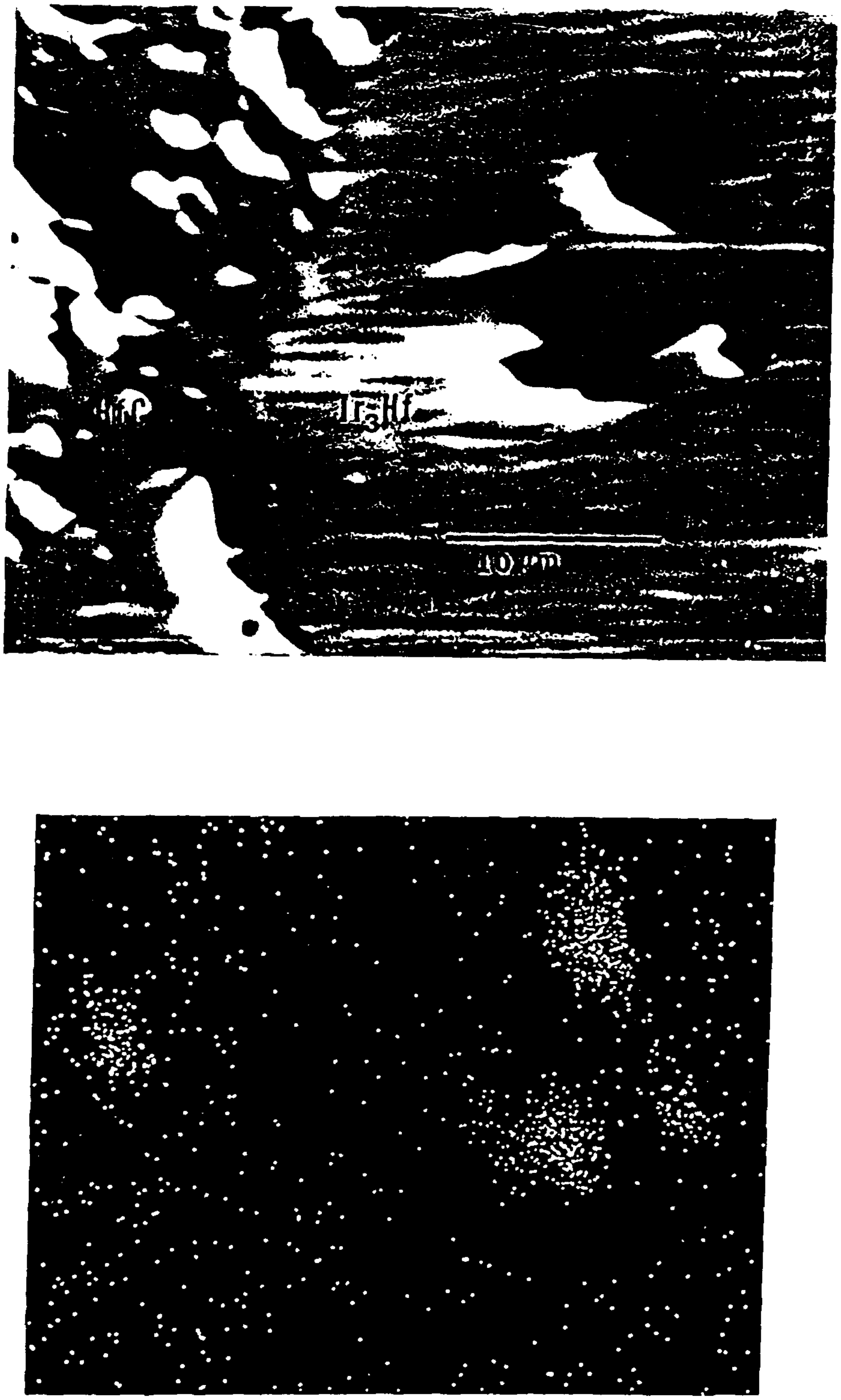


Fig. 3 Carbon Mapping Near the HfC - I$_3$HF Interface

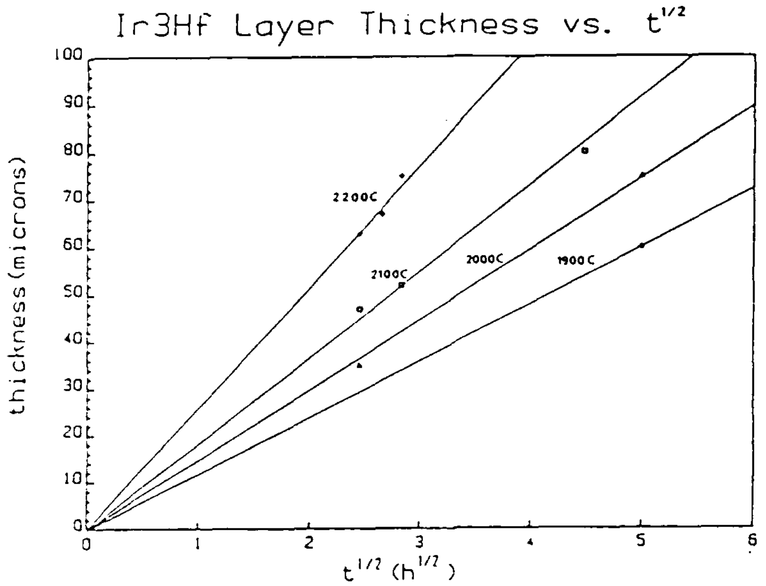


Fig. 4a Growth Kinetics of the Intermetallic Phase

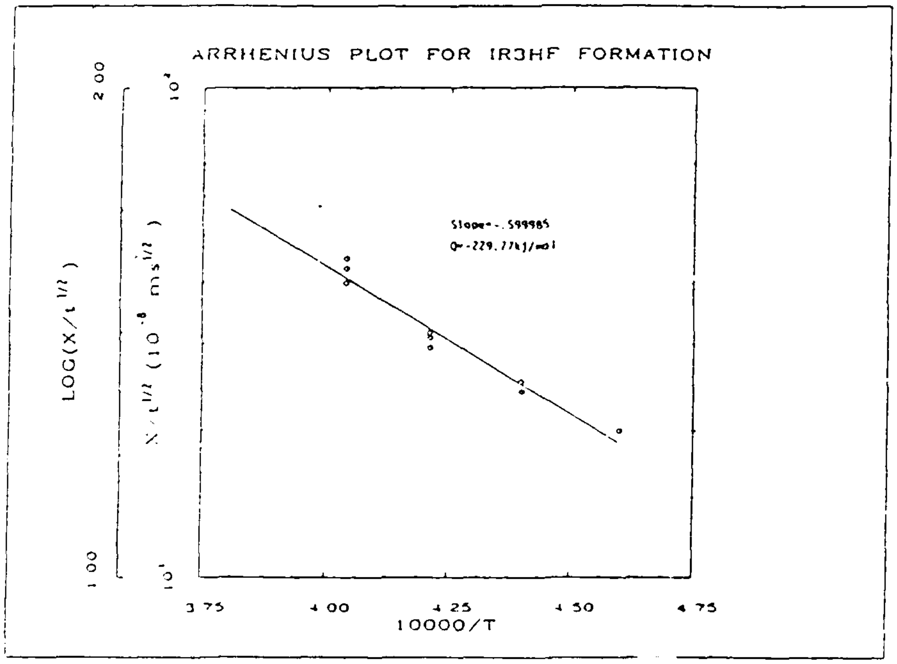
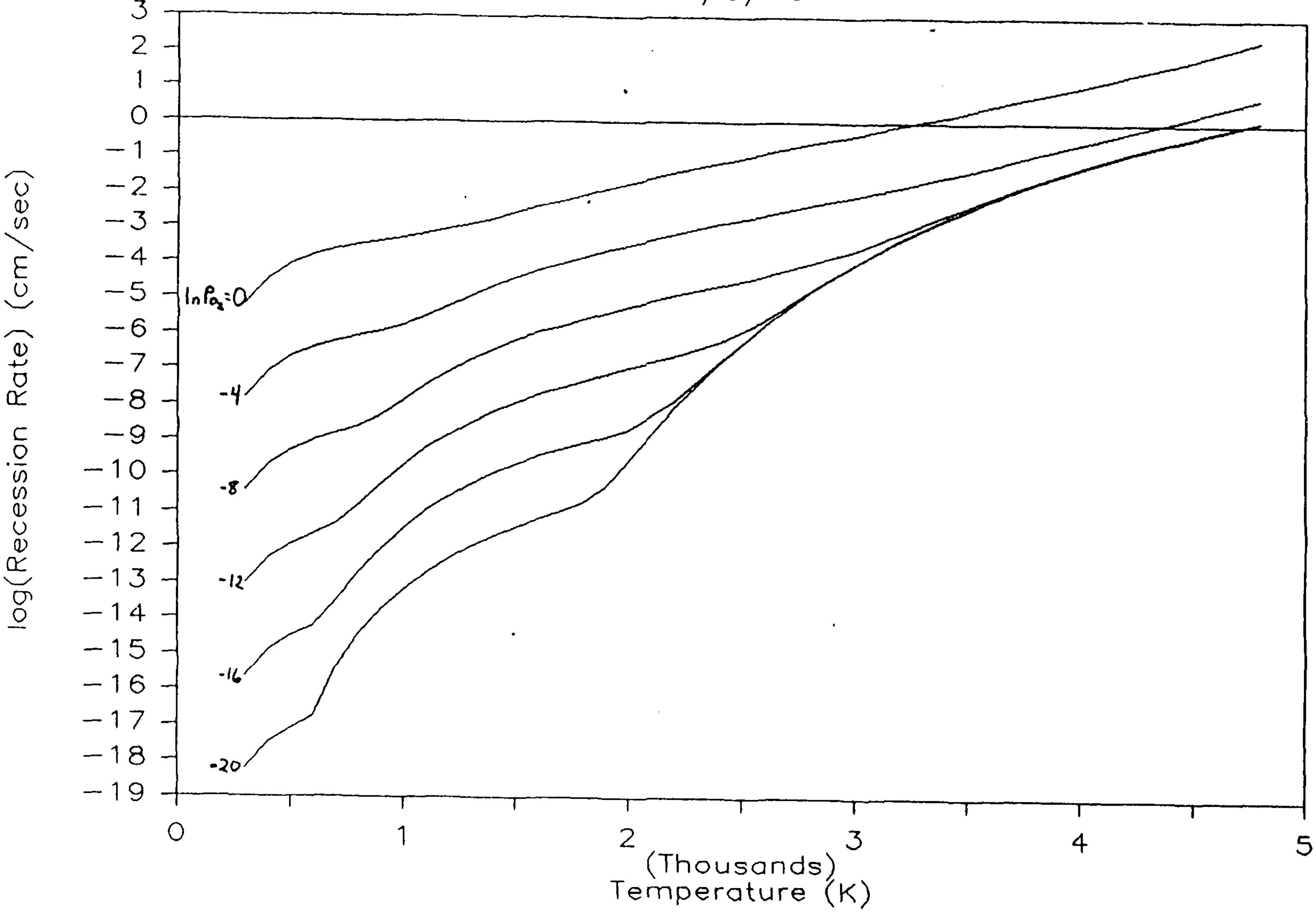


Fig. 4b Temperature Dependence of Growth Rate Constant

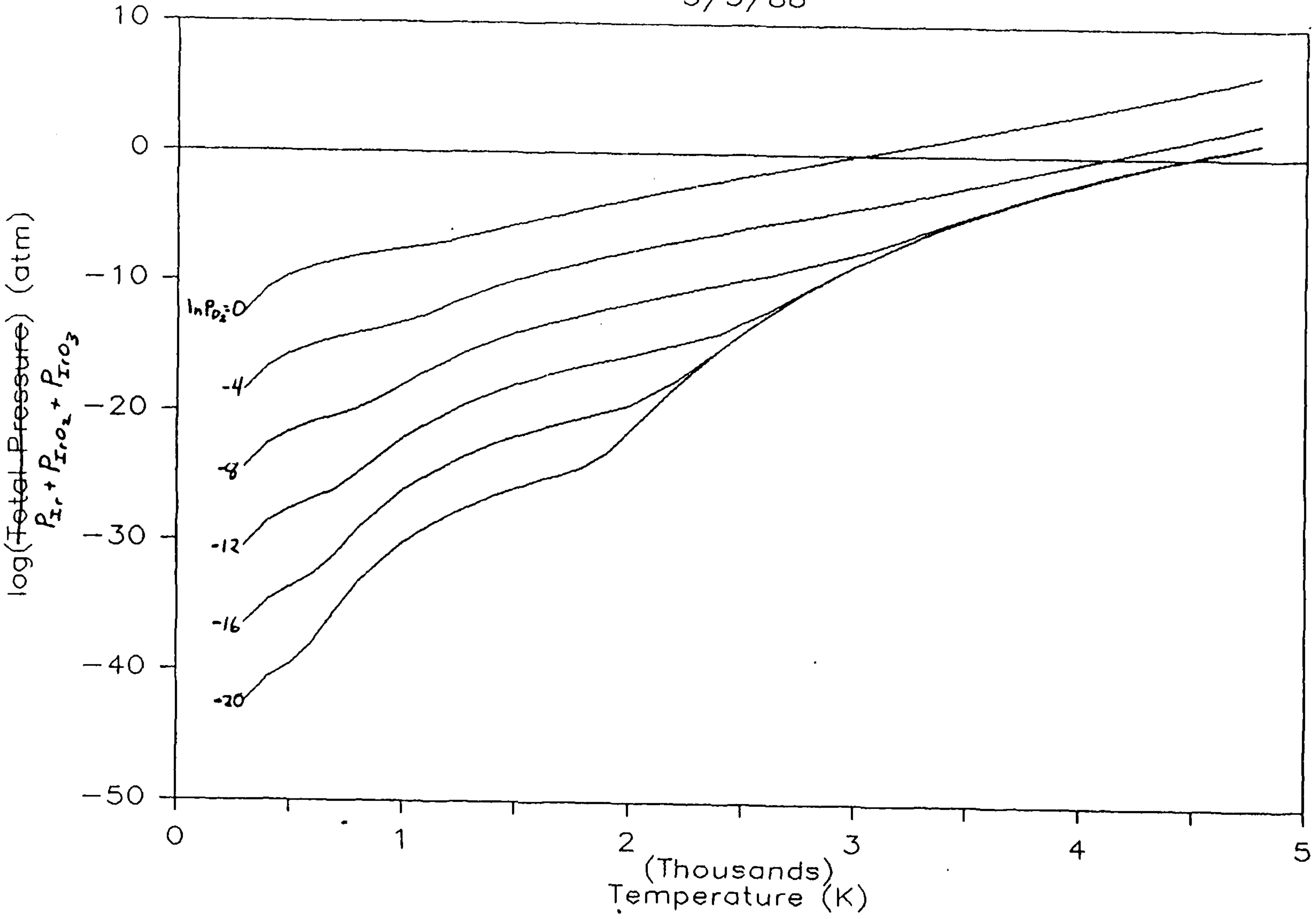
Iridium Recession Rates

5/5/88



Total Pressure Over Iridium

5/5/88



						lnPO2:	0	-4	-8	-12	-16	-20	0	-4	-8	-12	-16	-20
T	dGIr	dGIrO3	dGIrO2	lnPIr	ln PIrO3 -1.5* lnPO2	ln PIrO2 -1* lnPO2	lnPt	lnPt	lnPt	lnPt	lnPt	lnPt	logR	logR	logR	logR	logR	logR
k	cal/m	cal/m	cal/m	atm	atm	atm	atm	atm	atm	atm	atm	atm	cm/s	cm/s	cm/s	cm/s	cm/s	cm/s
298	147748	7368	23357	-249	-12	-39	-12.4	-18.4	-24.4	-30.4	-36.4	-42.4	-5.20	-7.81	-10.41	-13.02	-15.63	-18.23
300	147672	7390	23347	-248	-12	-39	-12.4	-18.4	-24.4	-30.4	-36.4	-42.4	-5.18	-7.79	-10.40	-13.00	-15.61	-18.21
400	143913	8470	22873	-181	-11	-29	-10.7	-16.7	-22.7	-28.7	-34.7	-40.7	-4.49	-7.10	-9.70	-12.31	-14.91	-17.52
500	140183	9550	22425	-141	-10	-23	-9.6	-15.6	-21.6	-27.6	-33.6	-39.6	-4.09	-6.69	-9.30	-11.90	-14.51	-17.09
600	136477	10630	21995	-114	-9	-18	-8.9	-14.9	-20.9	-26.9	-32.7	-38.0	-3.82	-6.43	-9.03	-11.63	-14.16	-16.44
700	132792	11710	21574	-95	-8	-16	-8.4	-14.4	-20.4	-26.1	-31.2	-35.5	-3.64	-6.24	-8.83	-11.33	-13.52	-15.38
800	129125	12790	21156	-81	-8	-13	-8.0	-14.0	-19.8	-24.9	-29.2	-33.3	-3.51	-6.10	-8.61	-10.83	-12.71	-14.48
900	125475	13870	20733	-70	-8	-12	-7.7	-13.6	-19.0	-23.5	-27.6	-31.6	-3.40	-5.95	-8.28	-10.24	-12.02	-13.76
000	121839	14950	20296	-61	-8	-10	-7.5	-13.1	-18.0	-22.2	-26.2	-30.2	-3.30	-5.76	-7.87	-9.69	-11.44	-13.18
100	118216	16030	19838	-54	-7	-9	-7.2	-12.5	-17.0	-21.1	-25.1	-29.1	-3.20	-5.51	-7.46	-9.23	-10.97	-12.71
200	114605	17110	19352	-48	-7	-8	-6.8	-11.8	-16.1	-20.1	-24.1	-28.1	-3.07	-5.23	-7.08	-8.83	-10.57	-12.31
300	111006	18190	18629	-43	-7	-7	-6.5	-11.1	-15.3	-19.3	-23.3	-27.3	-2.93	-4.95	-6.75	-8.49	-10.23	-11.97
400	107417	19270	18261	-39	-7	-7	-6.0	-10.5	-14.6	-18.6	-22.6	-26.6	-2.76	-4.68	-6.45	-8.20	-9.93	-11.67
500	103837	20350	17642	-35	-7	-6	-5.6	-9.9	-13.9	-17.9	-21.9	-25.9	-2.57	-4.43	-6.19	-7.93	-9.67	-11.41
600	100267	21430	16962	-32	-7	-5	-5.1	-9.3	-13.3	-17.3	-21.3	-25.3	-2.39	-4.20	-5.95	-7.69	-9.43	-11.17
700	96706	22510	16584	-29	-7	-5	-4.7	-8.9	-12.9	-16.9	-20.9	-24.9	-2.24	-4.04	-5.78	-7.52	-9.26	-10.98
800	93152	23590	15861	-26	-7	-4	-4.3	-8.4	-12.4	-16.4	-20.4	-24.3	-2.07	-3.85	-5.59	-7.33	-9.06	-10.72
900	89606	24670	15075	-24	-7	-4	-3.9	-8.0	-12.0	-16.0	-20.0	-23.2	-1.90	-3.67	-5.41	-7.15	-8.87	-10.26
00	86068	25750	14221	-22	-6	-4	-3.5	-7.6	-11.6	-15.6	-19.5	-21.5	-1.74	-3.50	-5.24	-6.98	-8.66	-9.56
00	79012	27910	12286	-18	-6	-3	-2.8	-6.8	-10.8	-14.8	-17.7	-18.1	-1.44	-3.19	-4.93	-6.65	-7.91	-8.08
00	71982	30070	10008	-15	-6	-2	-2.1	-6.1	-10.1	-13.8	-15.0	-15.1	-1.16	-2.90	-4.63	-6.24	-6.79	-6.81
00	64976	32230	7341	-13	-6	-1	-1.4	-5.4	-9.4	-12.2	-12.6	-12.6	-0.88	-2.62	-4.34	-5.58	-5.73	-5.73
00	57992	34390	4238	-10	-6	-1	-0.8	-4.8	-8.6	-10.3	-10.4	-10.4	-0.61	-2.35	-4.02	-4.77	-4.81	-4.81
00	51029	36550	652	-9	-6	0	-0.1	-4.1	-7.6	-8.5	-8.6	-8.6	-0.35	-2.08	-3.61	-4.01	-4.02	-4.02
00	44086	38710	-3462	-7	-6	1	0.5	-3.4	-6.5	-6.9	-6.9	-6.9	-0.08	-1.80	-3.12	-3.32	-3.33	-3.33
00	37162	40870	-8152	-6	-6	1	1.2	-2.7	-5.3	-5.5	-5.5	-5.5	0.20	-1.51	-2.61	-2.71	-2.72	-2.72
00	30255	43030	-13465	-4	-6	2	1.9	-2.0	-4.1	-4.2	-4.2	-4.2	0.48	-1.21	-2.12	-2.18	-2.18	-2.18
00	23366	45190	-19447	-3	-6	3	2.6	-1.3	-3.0	-3.1	-3.1	-3.1	0.77	-0.90	-1.66	-1.69	-1.70	-1.70
00	16492	47350	-26144	-2	-6	3	3.3	-0.5	-2.0	-2.1	-2.1	-2.1	1.07	-0.57	-1.23	-1.26	-1.26	-1.26
00	9634	49510	-33603	-1	-6	4	4.0	0.3	-1.1	-1.2	-1.2	-1.2	1.38	-0.25	-0.85	-0.87	-0.87	-0.87
00	2791	51670	-41872	0	-6	5	4.8	1.1	-0.3	-0.3	-0.3	-0.3	1.70	0.08	-0.50	-0.52	-0.52	-0.52
00	-4037	53830	-50996	0	-6	6	5.6	1.9	0.5	0.4	0.4	0.4	2.03	0.41	-0.18	-0.20	-0.20	-0.20
00	-10852	55990	-61022	1	-6	6	6.4	2.6	1.2	1.1	1.1	1.1	2.38	0.75	0.12	0.09	0.09	0.09

$$P_{torr} = 17.14 \left(\frac{T}{M}\right)^{1/2} G$$ where G is in grams/cm² sec

$$\therefore R\,(\text{cm/sec}) = \frac{760\, P_{Atm}}{17.14\, \rho_{Ir}} \left(\frac{M_{Ir}}{T}\right)^{1/2}$$

ferences

r(g) : Pankratz 298-2000 K (direct ΔG data)

rO_2(g): Brewer (IrO_2), Pankratz$^{298\text{-}2000K}$ (Ir(s)), Hildenbrand$^{298\text{-}3000K}$ (O_2) ($-(G-H_{298})/RT$ data

rO_3(g): Kubaschewski and Alcock (direct ΔG data) (1473-1673K)

Unpublished Thermodynamic Stabilities from. L. Brewer

$Ir_{(s)} + O_{2(g)} \rightarrow IrO_{2\,(g)}$ $\Delta H^\circ_{298} = -25000$ cal/mole

$$-(G - H_{298})/RT = 29.820 + 4.928 \cdot 10^{-3} T + 0.262 \cdot 10^{-6} T^2 - 0.391 \cdot 10^{-9} T^3 + 0.0590 \cdot 10^{-12} T^4$$

Battelle
Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington U.S.A. 99352
Telephone (509)
Telex 15-2874

April 18, 1988

Professor George St. Pierre
Department of Metallurgical Engineering
Ohio State University
116 West 19th Avenue
Columbus, OH 43210

Dear George:

This letter is to provide you with some suggestions for follow-on work on the ONR project. Further development of the mechanism of oxidation in the Engel Brewer compounds definitely appears warranted. A mechanism based on rapid diffusion through the oxide phase should be explored. The conventional model of external scale formation assumes that the oxide that forms e.g. Al_2O_3 is an effective oxygen barrier. Diffusion through the oxide is orders of magnitude less than through the metal matrix. However, if diffusion of oxygen through the oxide is as rapid as through the matrix, the model no longer applies. There is little data on diffusion in these materials but oxygen has been shown to be a relatively slow diffuser in pure platinum. The ratio of the atomic sizes of Hf in Ir is the same as Al in Ni and aluminum diffuses readily in nickel. The oxygen solubility in Ir compounds is not known but is apparently very low in pure Ir. All these factors actually suggest that external scales should be possible in these alloys. The apparent easy internal oxidation may be due mainly to oxygen diffusing through the oxide network that develops. In this case the weight gain would still be parabolic as it is controlled by diffusion. This would be balanced by a linear weight loss from iridium oxidation. The weight gain would be higher initially due to the high rate constant for an element like Hf but eventually would be balanced by the weight loss from iridium oxide formation. In fact, for an infinitely thick sample, a steady state should be reached where there is no gain or loss. The data of Worrell for Ir-Hf could be interpreted in this manner.

It would be fruitful to look at other compounds which form different oxides that would be more of an oxygen barrier. Two such systems are the Ir-Ti and Ir-Y systems. Ir-Ti is similar to Ir-Hf although Ti appears more soluble in Ir. Ti is a smaller atom than Hf and may diffuse faster in the compound. This would tend to promote scale formation. It is not certain which oxide of titanium would form but hopefully it would be more of an oxygen barrier than the metal matrix. Relatively low temperature experiments would be necessary with these compounds. Ir-Y would form Y_2O_3, an hexagonal structure which should be a better oxygen barrier than HfO_2 or ZrO_2. Unfortunately, there is no Ir-Y phase diagram but if it is similar to Ir-La, richer iridium phases such as Ir_5Y and Ir_7Y_2 can be expected. The solubility of yttrium in iridium would also be negligible. If one started with a compound such as Ir_3Y, the oxidation behavior could be rather complex if the richer iridium phases formed as the yttrium was oxidized. Unless the relative diffusion rates in the compound are vastly different however it should be possible to form an external scale in this material. The mechanism should be similar to that in the aluminides. A wide temperature range should be studied because the relative diffusion rates will change with temperature and hence the mechanism will change as has been demonstrated in the Ni-Al system.

The influence of an externally applied oxide coating on the oxidation mechanism of these compounds is another area to explore. For an oxygen permeable coating such as HfO_2, little change is expected in the basic oxidation behavior of the active element in the compound except some change in absolute numbers. A more significant effect could be the influence on residual iridium oxidation. As the active element is oxidized, nearly pure iridium remains which will subsequently oxidize and drift away if exposed to air. For a dense, adherent coating, this would not occur. The possibility exists that a continuous iridium film would eventually form which in itself is an oxygen barrier. Whether this could happen before the coating spalled off due to swelling from the active oxide formers would have to be determined. Coating of the Ir-Y compounds may be a good choice in this case also as less volume expansion is expected from Y_2O_3 formation than from the other oxides. In any event, if the iridium is not removed by oxidation and volatilization, it will alter the overall oxidation mechanism of the underlying compound.

We would see our role in several ways. We could assist in the evaluation of the oxidation mechanism in the different compounds. We could also determine how the mechanisms are altered by the presence of an externally applied coating. The coating could be sputter deposited but bulk compounds should be used for ease in evaluating the various reactions and interactions that may occur.

Let me know what you think. We can put these in a more formal proposal as required.

Sincerely,

John

Dr. John L. Brimhall
Senior Research Scientist
Advanced Materials Section
RTL Building, Room 447
MSIN: K3-59
(509) 375-2545

JLB:vbs

Oxidation Behavior of HfO_2 Coated Iridium

J. L. Brimhall

February 1988

Pacific Northwest Laboratory
Richland, WA 99352

Introduction

Pure iridium is known to be an effective oxygen barrier at high temperatures(1). Iridium however does form volatile oxides so the surface will be continually eroded away when heated in air. The oxidation of the Ir may be reduced by providing a protective oxide either by oxidizing an Ir compound or applying a dense coating by some vapor deposition process. It was the purpose of this work to study the influence of a vapor deposited oxide coating on the oxidation behavior of pure iridium. Weight loss measurements and metallography of iridium and iridium coated with HfO_2 were evaluated over the temperature range of 1000-1500°C. The results could be interpreted in terms of different mechanisms controlling the oxidation process in the two materials.

Experimental Procedures

The iridium specimens were in the form of flakes, formed by sputter deposition, approximately 1 cm^2 in area and 15 μm thick. Some of the flakes were subsequently coated with HfO_2 on both sides using RF sputter deposition. The coating was ~ 5-10 μm thick and appeared to be dense on an optical microscopy scale, fig. 1. The coating has debonded on one side, believed to be a result of the mounting procedure for metallography. While the coating remained intact, it does point out that there is not strong bonding across the interface.

The weight loss was measured both continuously by a thermogravimetric method and by intermittent weight measurements. The continuous measurements were done at 1000°C. At higher temperatures, the sample was removed from the furnace periodically and measured. The flakes were irregular in shape and the area was estimated from the external dimensions as accurately as possible. The area used to calculate a weight loss per unit area is actually a projected area. The true area would be larger due to the surface topography. This can be a factor when comparing the absolute values with data from other sources. Cross-sectional metallography was performed on selected samples after oxidation.

Results

The rate of weight loss in pure Ir is essentially linear as shown by the weight loss vs. time curves in fig. 2. Similar behavior was shown when the weight loss was determined continuously by thermogravimetry, fig. 3. Data at short times in fig. 2 is not included as it can be unduly influenced by experimental factors such as furnace heat up time. The data at 1500°C represents several different samples and had the most scatter. Duplicate samples run at 1200°C show some differences in absolute values but the slope of the curve was similar for the two samples. Due to the thinness of the samples, it was not possible to get long time data at 1500°C as there was danger of the specimen disappearing completely.

Preferential edge attack during Ir oxidation has been reported(1) but did not appear to be too severe in our experiments. This is based on the fact that the area of the specimen did not show a measurable decrease after oxidation. There was some decrease in area after the longest time at 1500°C. Whereas preferential edge attack occurs it was considered to be a minor contribution to the overall weight loss.

The rate of weight loss in the HfO_2 coated Ir also shows linear behavior but at a significantly lower rate than in the uncoated Ir, fig. 4. The data appears to be well behaved even at 1500°C. Duplicate samples run at 1200°C and 1500°C showed different absolute values but the slopes of the curves were very similar.

The temperature dependence of the oxidation reaction for both pure Ir and HfO_2 coated Ir is shown in fig. 5. The temperature dependence is relatively weak, equivalent to about 16 Kcal/mol. The slopes are similar for both materials with the uncoated Ir showing an oxidation rate 3-4 times greater than the coated material. The temperature dependence is also similar to that found by other investigators (shown on fig. 5) although the absolute magnitudes vary (2-4). Only experiments done in static or lightly flowing air are compared. There are many experimental variables to be considered, e.g., sample geometry, air flow, surface topography, etc. in comparing data so a wide range of values could be expected.

The rather well behaved data seems surprising after observing the microstructure. The oxidation in the coated material was very non-uniform, occurring preferentially at cracks or defects in the coating. Examples are shown in fig. 6 where in places the Ir has completely oxidized through the thickness. The Ir at the edges of the samples was also generally eaten away as this was a weak point in the coating. It cannot be determined whether the cracks formed during heating as a result of differences in thermal expansion or were already present and just enlarged during oxidation.

The oxidation appears to penetrate preferentially through the iridium at a crack as pointed out by the X in fig. 6B. This is analogous to pitting or crevice corrosion. The oxidation then spreads preferentially along the Ir-coating interface, eventually consuming the entire iridium thickness.

The structures shown in fig. 6, however, only represent a small fraction of the entire length of the sample cross section. There were extensive regions in which there were no cracks and hence no oxidation was evident. An example is the high magnification micrograph in fig. 6C. There was no evidence of oxygen diffusing through the coating causing uniform oxidation of the iridium. The interface region appeared to be identical to an unoxidized sample.

Discussion

Although the temperature dependence of the oxidation indicates similar behavior or mechanisms in both coated and uncoated iridium, an analysis of the data and microstructure suggests different behavior in the coated material. Analysis by Wimber, et. al.(5,6) of the oxidation of pure Ir in air shows the reaction to be controlled by diffusion of the volatile oxides, IrO_x, through a gaseous boundary layer. As the partial pressure of oxygen is reduced, the diffusion layer is reduced until the reaction kinetics becomes controlled by a surface reaction mechanism. At very low pressures, the rate is determined by the evaporation of Ir atoms. The process is shown schematically in fig. 7. The data of Wimber follows closely such a pressure dependence.

The oxidation kinetics will also change from diffusion controlled to surface reaction controlled with increasing the gas velocity. Rexer(7) found the loss rate to increase with velocity up to a velocity ~ 20,000 ft/min (6×10^3 cm/sec) at which point it remained constant. The data of Rexer for an oxygen partial pressure of 152 torr (= to air) is shown in fig. 8 plotted as a recession rate. The data reported here is recalculated as a recession rate and plotted on the same graph. The absolute rates are considerably greater for gas at high velocity and the temperature dependence is somewhat greater.

The observations suggest that the oxidation of the coated iridium in the region of defects is controlled more by surface reaction behavior than diffusion through a gaseous boundary layer. The rate controlling behavior is related to the mean free path of the oxygen molecules at the surface. The oxidation rate becomes surface reaction controlled when the sample size becomes smaller than this mean free path as there would be a low probability of the Ir oxide molecule being reflected back to the surface. Oxidation rates are observed to be much higher for fine filaments(8). The small surface area exposed at a crack could be considered analogous to a fine filament. There is undoubtedly interaction and reflection of the oxide molecules at the walls of the crack but the net direction is out of the crack. The higher kinetics of surface reaction controlled behavior is manifest by oxidation completely through the foil at the cracks. Complete oxidation was not observed in the uncoated material for similar times and temperatures.

It is actually difficult to conceive of a gaseous boundary layer for the configuration of a crack in a coating. The boundary layers are of the order of 0.1 to 1 cm, much larger than the sample and crack dimension under consideration. The conditions in a crack or cavity may be more representative of turbulent flow behavior for which higher oxidation rates would be expected.

If IrO_x diffusion thru a boundary layer were controlling in the coated material then the rates of oxidation should be much less than actually observed. It was estimated that ~ 2% of the area along the cross section shown in fig. 6 was oxidized. If it were oxidizing with the same kinetics as uncoated then the weight loss should only be about 2% of the uncoated rate. It was much greater than this however the rate for the surface reaction controlled process at 1000°C is about an order of magnitude more than boundary layer controlled. This is deduced by comparing the high velocity data of Rexer to our data, fig. 8. A similar result is found if the curve for surface reaction kinetics in fig. 7 is extrapolated to the partial pressure of oxygen in air. Therefore if the localized rate is about a factor of 10 higher in the coated material but only about 2% of the area is affected, then the apparent rate would be 20% of that of the uncoated material. This is consistent with a reduction by a factor of 3-4 in the oxidation rate for the coated material compared to bare material.

The smooth weight loss curves shown for the coated iridium indicates that the defect structure of the coating doesn't change significantly with time. Although, it could also be that increased oxidation due to additional cracking is compensated by a slowing of the absolute rate as the oxidized region becomes greater. The fact that the results from two different tests and samples were reasonably consistent shows that the coating microstructure, in terms of defect formation, is not too different from sample to sample at least when averaged over a square centimeter of area.

Because of the dependence of the oxidation on the coating defect structure, the close similarity in the temperature dependence of coated and uncoated material is mostly coincidental. However, even for the data of Rexer the temperature dependence is not greatly different from that reported here. For iridium oxidation, the temperature dependence may not be a good way to distinguish between mechanisms. The experimental parameters would have to be very closely controlled.

Conclusions

An HfO_2 coating can prevent iridium oxidation when no defects are present in the coating. Cracks in the coating allow oxygen ingress and accelerated localized oxidation of the underlying iridium. The higher localized rates are believed due to surface reaction controlled behavior as opposed to diffusion controlled behavior in uncoated material. The localized rates in this case are about a factor of 10 higher than the rates in the uncoated material. The overall loss rate however is still lower than the uncoated because only a small fraction of the total area is being oxidized.

Acknowledgment

The support of the Office of Naval Research through the Ohio State University is gratefully acknowledged.

References

1. J.M. Criscione, H.F. Volk, J.W. Niess, R.A. Mercuri, S. Sarean and F.W. Meszaros, "High Temperature Protective Coatings for Graphite", ML-TDR-64-173, 1965.

2. H. Jehn, J. Less Common Metals, 100 (1984) p. 321-339.

3. C.A. Krier and R.I. Jaffee, J. Less Common Metals, 5, (1963) p. 411-431.

4. W.L. Phillips, Jr., Trans A.I.M.E., 57 (1964) p. 33-37.

5. R.T. Wimber and H.G. Kraus, Met. Trans., 5 (1974) p. 1565-1572.

6. R.T. Wimber, et al., Met. Trans., 8A, (1977) p. 193-199.

7. J. Rexer in "Refractory Metals and Alloys IV Research and Development", ed. by R.I. Jaffee, G.M. Ault, J. Moltz and M. Semchysen, Gordon and Breach, New York, 1965, p. 1055-1068.

8. G.C. Fryburg, Trans. AIME., 223 (1965) p. 1986-1989.

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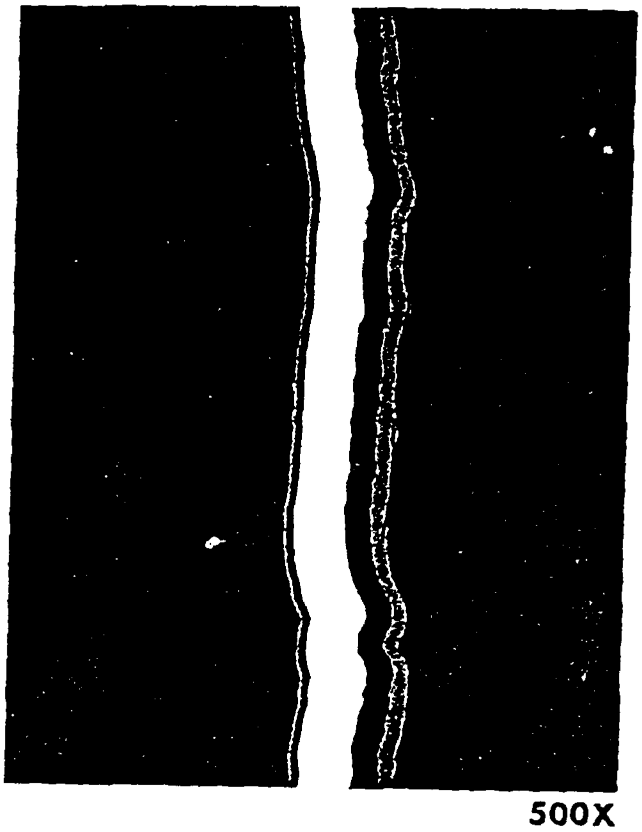
Fig. 8 Recession rate of iridium as a function of temperature. Data of Rexer (7) is for a gas flow of 12000 ft/min (~ 6 X 10^3 cm/sec).



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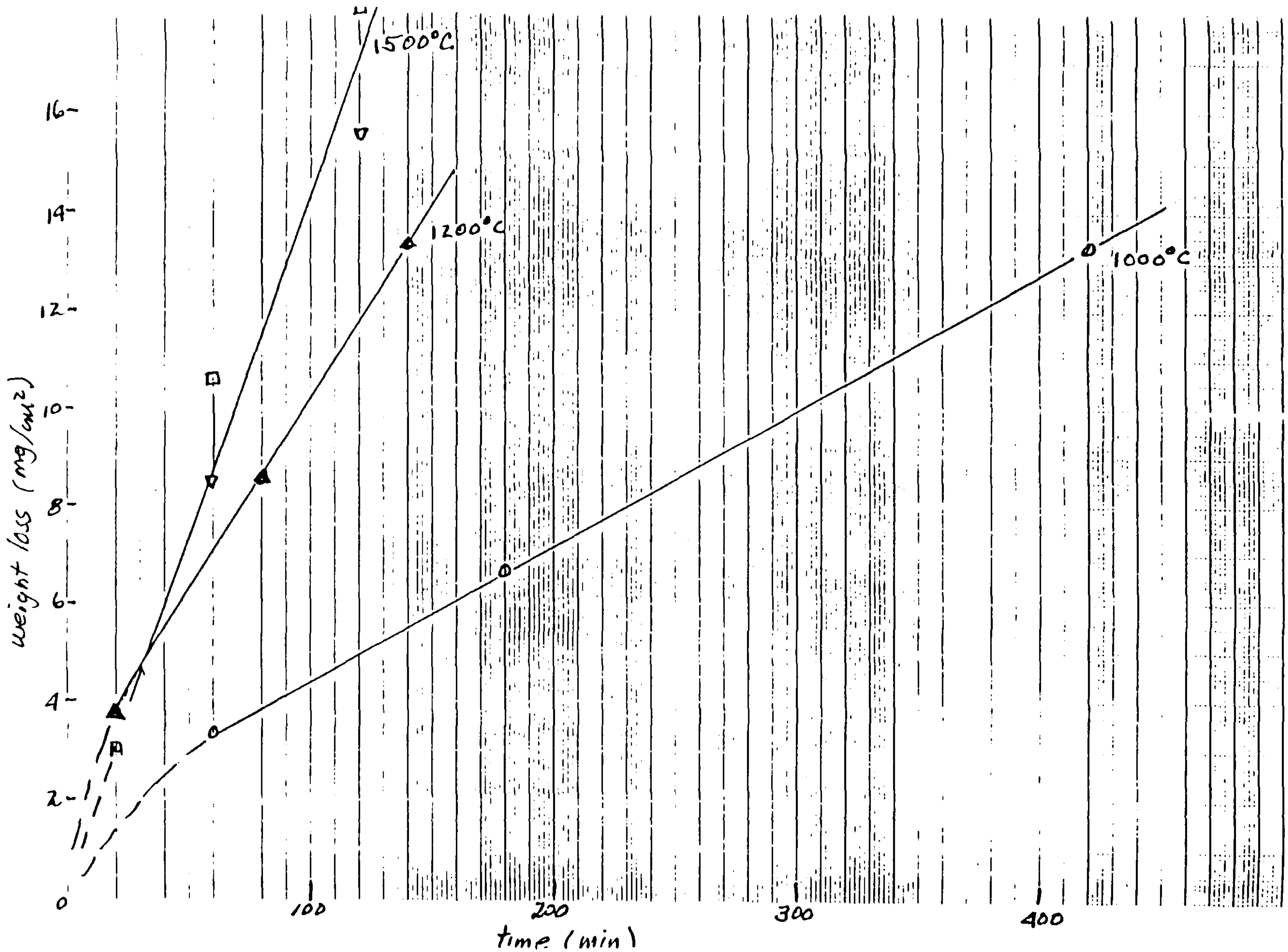

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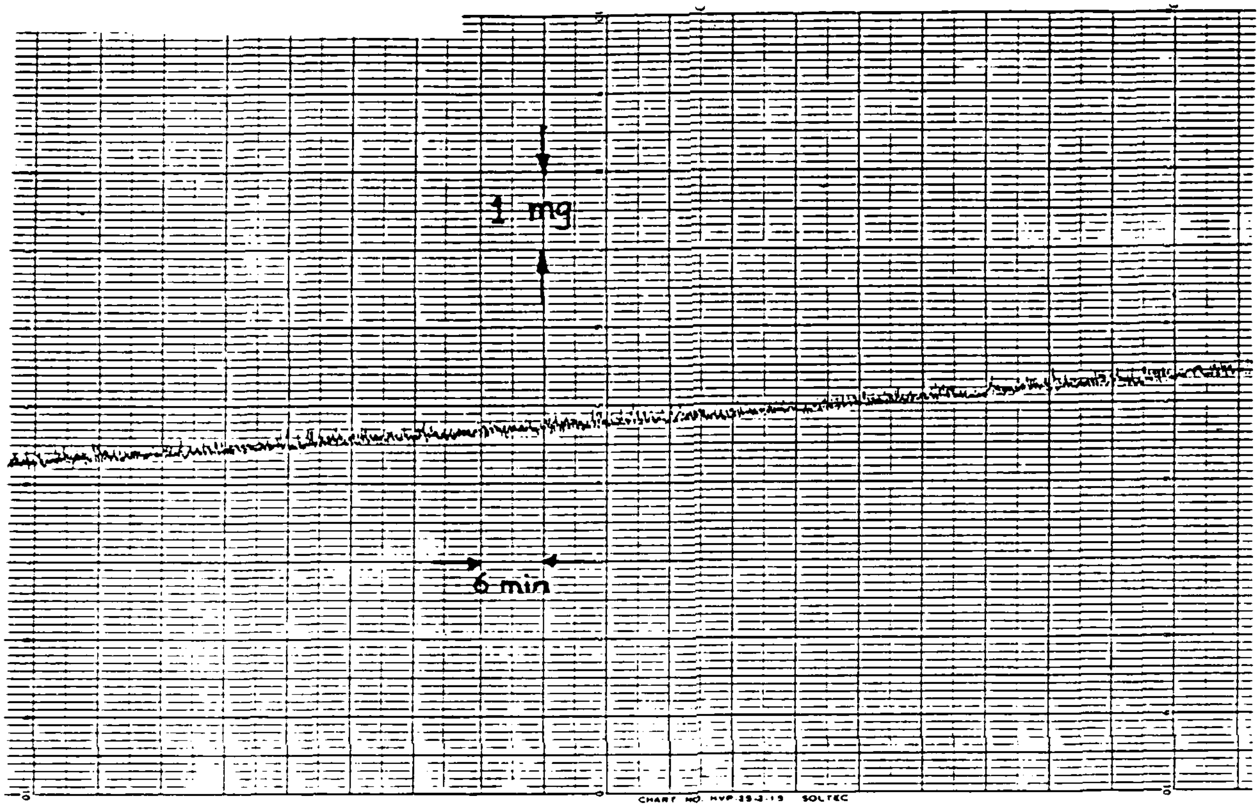

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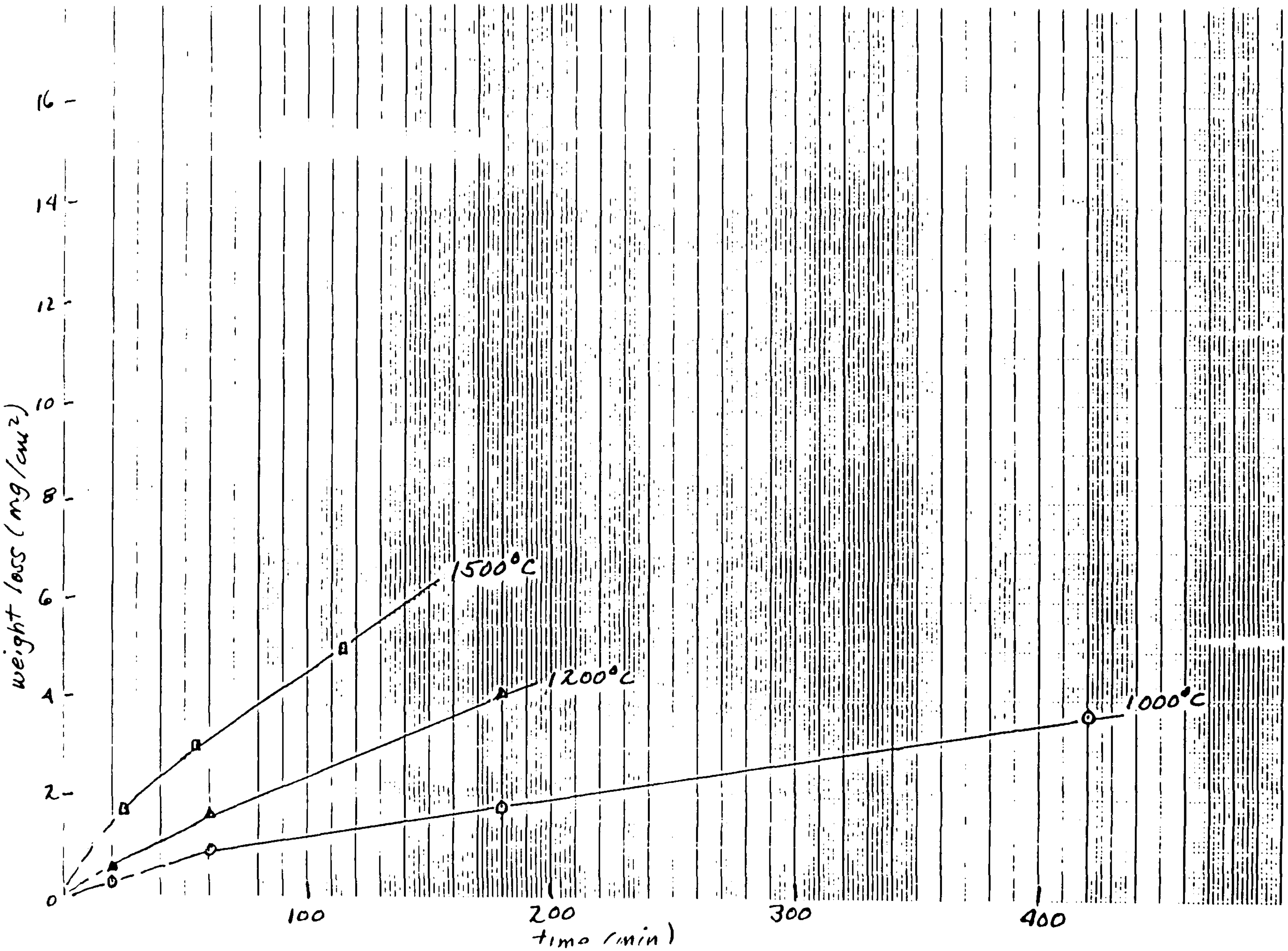

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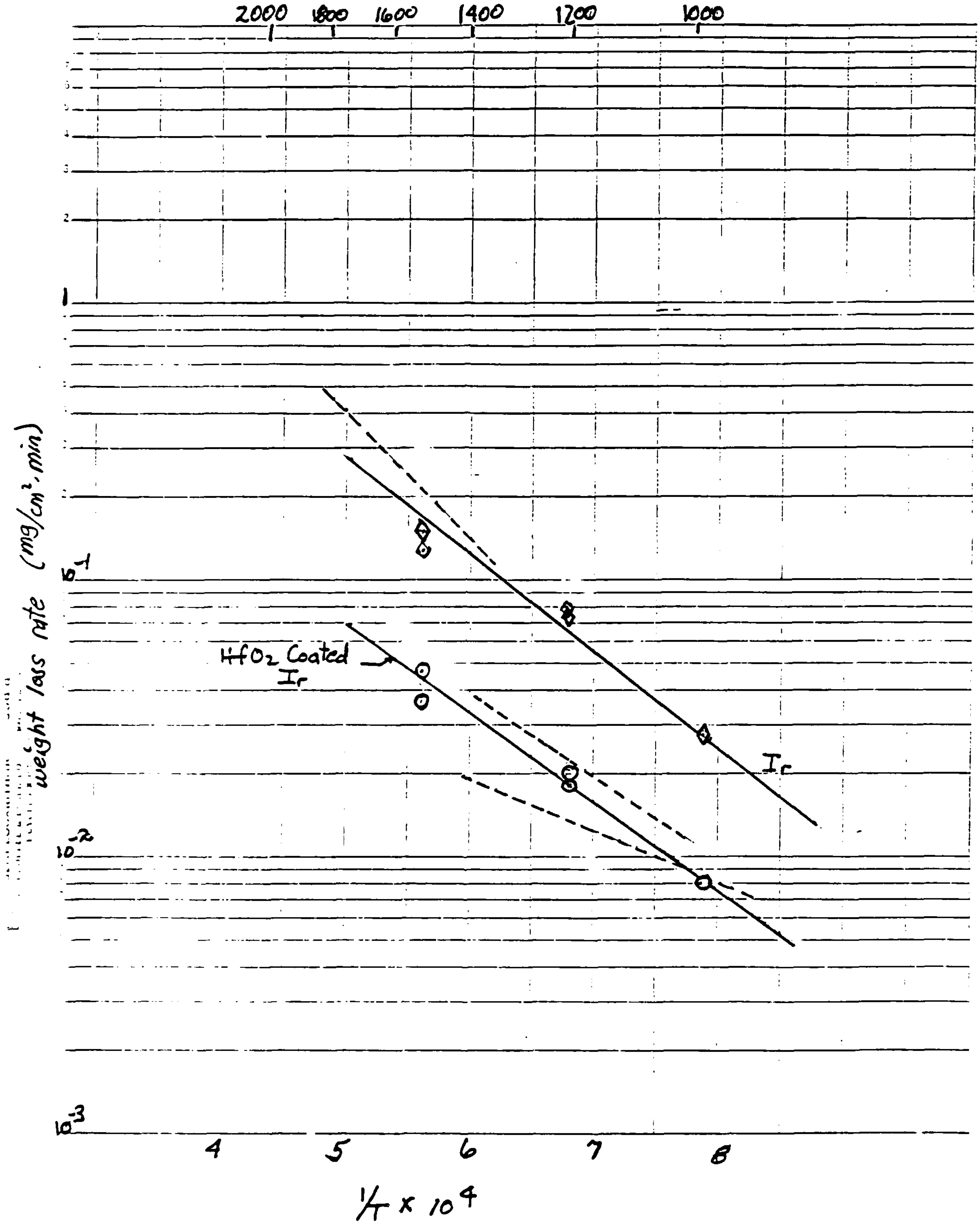

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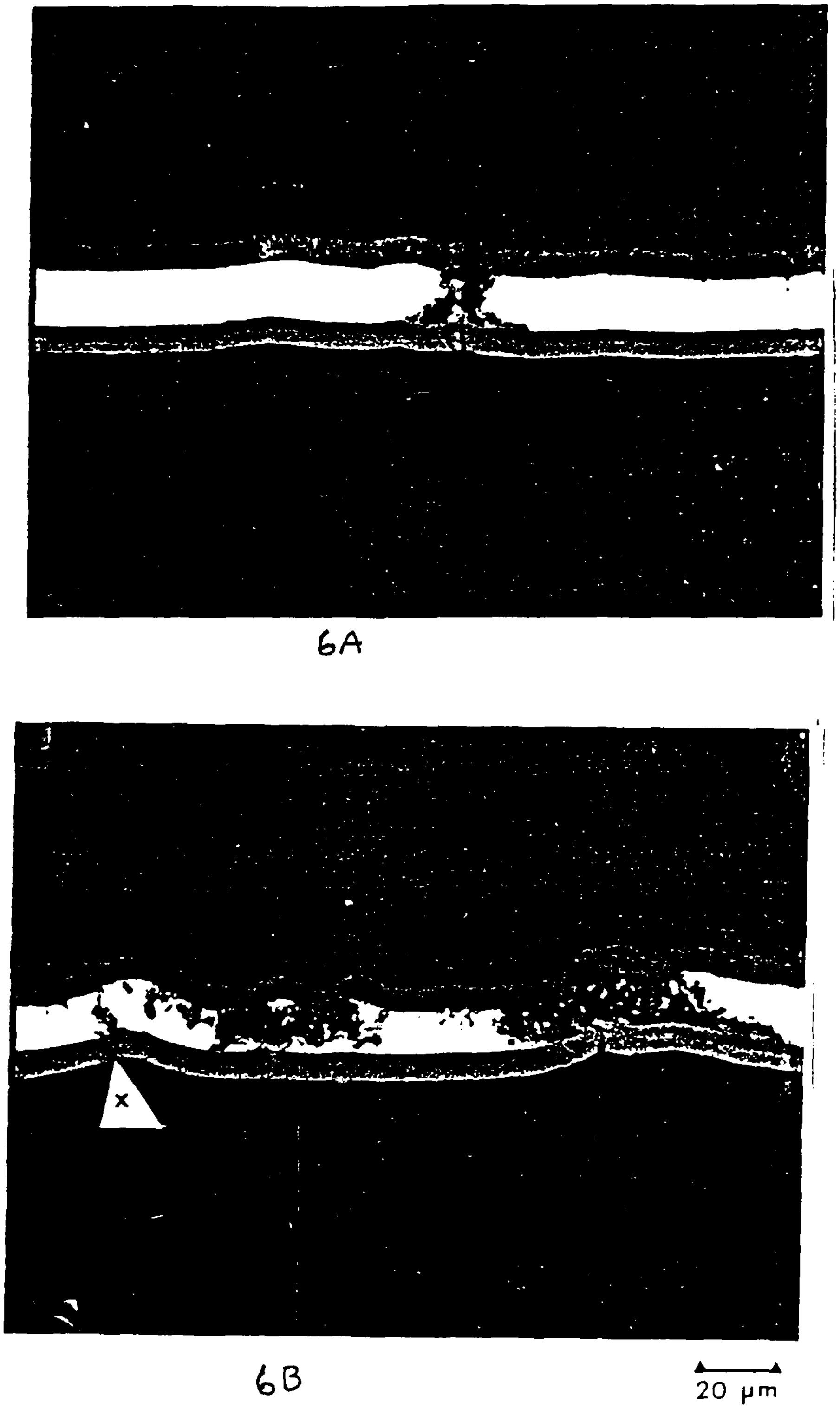

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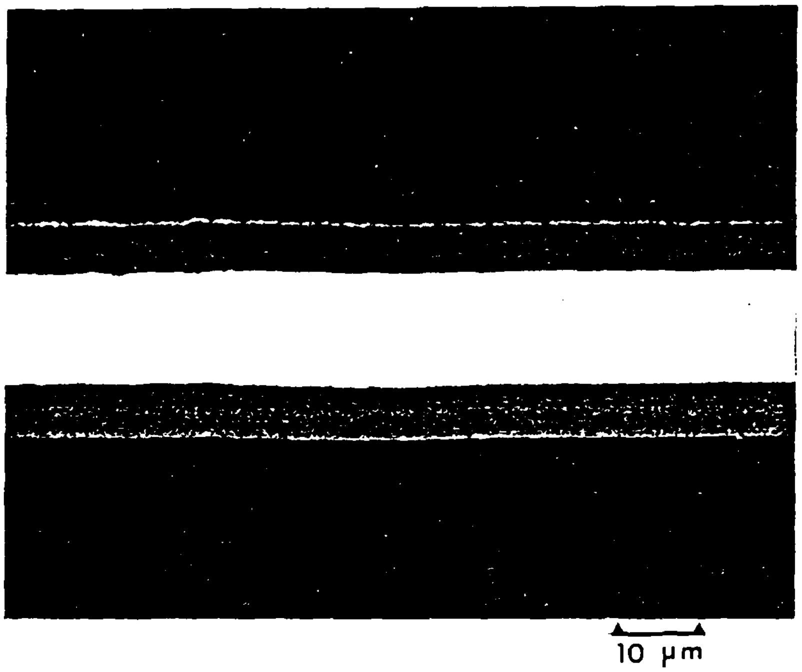

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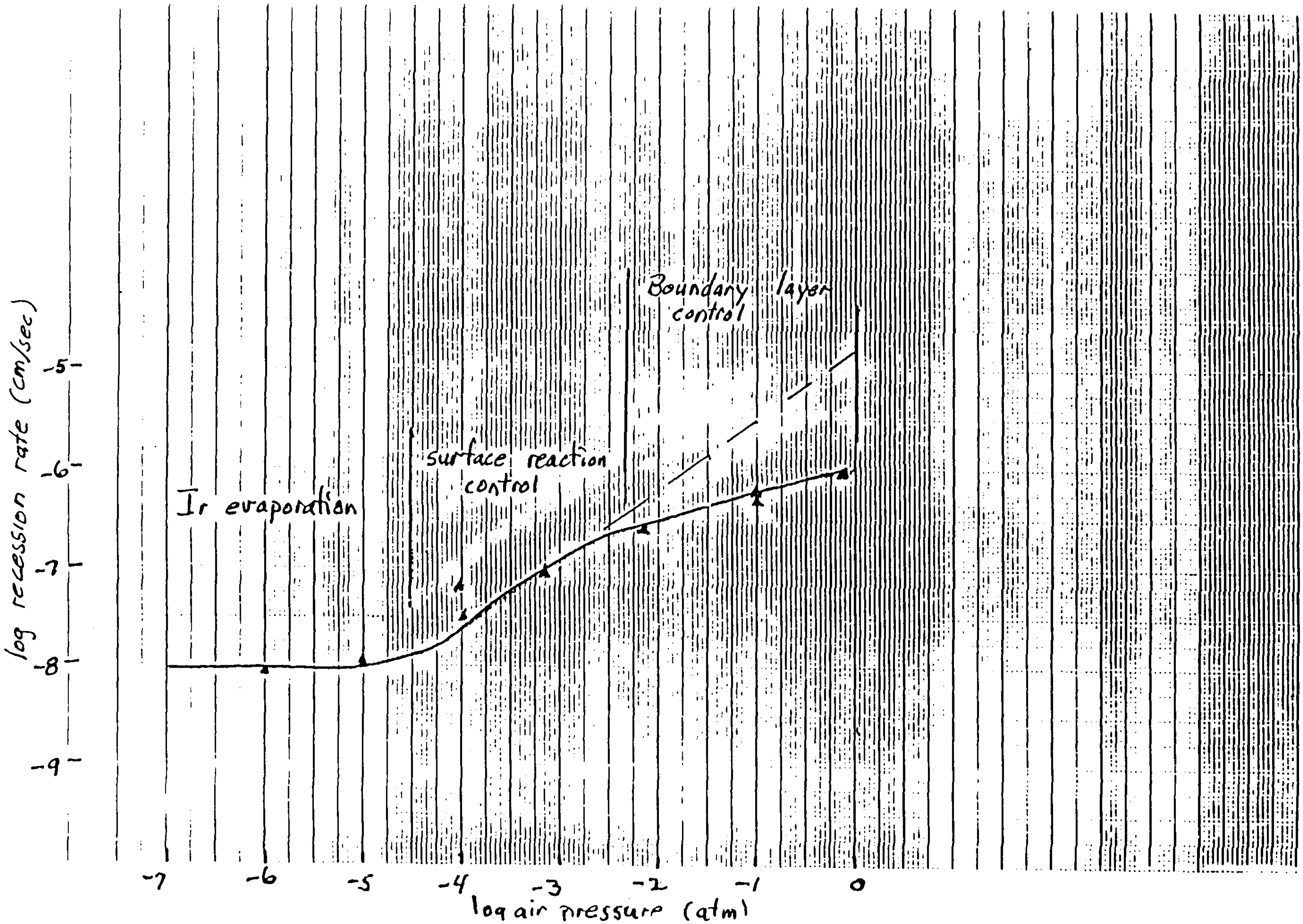

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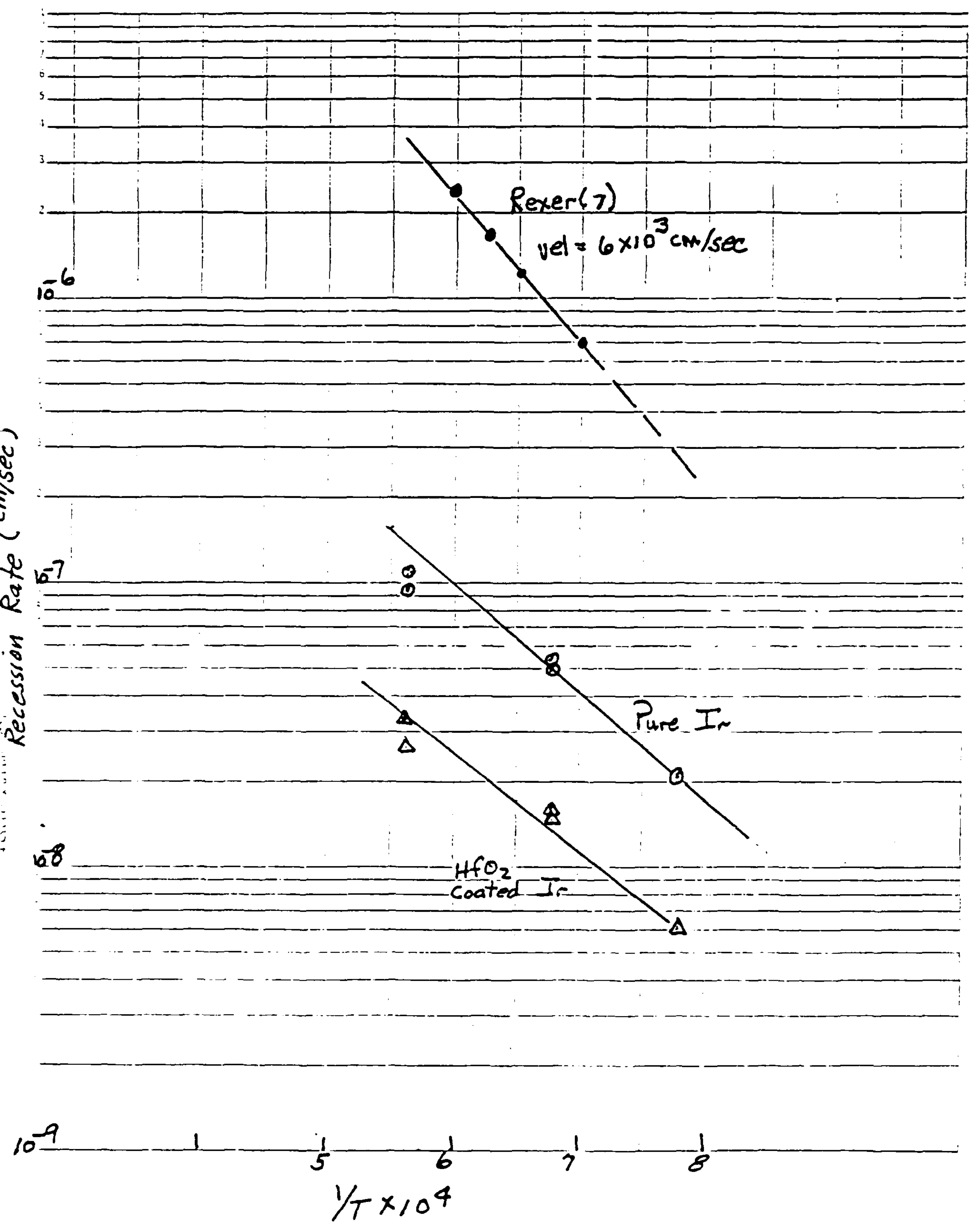

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RECEIVED

GRS

Battelle
Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington U.S.A. 99352
Telephone (509) 375-2545

Telex 15-2874

September 2, 1987

Professor George St. Pierre
Ohio State University
116 West 19th Avenue
Columbus, OH 43210

Dear Professor St. Pierre:

Enclosed is a report which summarizes our studies on the research project on oxidation protection of carbon-carbon composites. We believe we have demonstrated that iridium oxidation can be retarded by a surface coating, even if the coating is permeable to oxygen. The Ir_3Hf did not appear to behave as hoped but altering the stoichiometry or alloying may improve its oxidation behavior. This is something that could be considered for next year. Please let me know if you have any questions.

Sincerely,

John Brimhall

John L. Brimhall

JLB:cr

Enclosure

Summary of Results on Oxidation of Coated and Uncoated Ir_3Hf

J.L. Brimhall

Abstract

Sputter deposited Ir_3Hf and Ir_3Hf coated with HfO_2 were oxidized in air at temperatures up to 1000°C. Oxidation was complete at 1000°C causing the thin flakes to break into small particles. No continuous, protective oxide formed. The coated compounds oxidized in a similar manner. Preferential oxidation of the Hf in the compound was extensive presumably causing swelling and cracking which contributed to further oxidation.

Experimental Procedure

The compound Ir_3Hf was sputter deposited onto a substrate of pure rhenium. Total thickness of the deposit varied from 25 to 50 μm. Some of the compound was removed from the rhenium by etching in dilute HNO_3. Pieces of the Ir_3Hf varying in size from 0.3 to 1 cm^2 in area, were subsequently coated on both sides with HfO_2 by RF sputter deposition. Oxidation tests were performed in still air. Evaluation was by weight change and metallography.

Results and Discussion

X-ray analysis showed the deposit to be mostly Ir_3Hf compound with some fcc Ir also present, fig. 1. Estimate of the x-ray peaks indicated about 92% Ir_3Hf and 8% Ir. Microstructural analysis in the TEM showed an extremely fine grained microstructure, fig. 2. In the coated material, the HfO_2 did not fully cover the Ir_3Hf as shown in the cross-sectional micrograph in fig. 3. The particles, believed to be undissolved substrate, caused a shadowing effect resulting in poor coverage in some areas.

Oxidation of the Ir_3Hf did not result in formation of an oxide scale or at least one that would be considered continuous and protective. For times longer than ~ 20 minutes at 1000°C, the sample was completely oxidized. X-ray analysis showed HfO_2, IrO_2 and some pure Ir, fig. 4. There was no remaining Ir_3Hf. The samples were mostly converted to an ash-like deposit after oxidation. Figure 5 shows the microstructure after a short time oxidizing treatment. Severe cracking and degradation is evident even after only 5 minutes oxidation. Preoxidation treatments up to 1200°C in vacuum to cause grain growth were performed but there was no effect in subsequent oxidation behavior. Different rates of heating to high temperature were tried but also had no effect on the oxidation behavior.

It is obvious that the Hf is preferentially oxidized in the compound but the HfO_2 does not form any sort of continuous barrier to further oxidation. The measured weight loss rate of 0.9 Mg/cm^2 min was much greater than for pure Ir oxidized at the same temperature, 0.26 Mg/cm^2 min. The strong preferential oxidation of Hf is probably causing much internal cracking and constantly exposing new surfaces to the oxygen environment. This would account for the apparent increased Ir oxidation and weight loss. Lee and Worrell found that even an alloy of Ir + 60% Hf did not form a protective oxide film.

Precoating of the Ir_3Hf material with HfO_2 did not have much affect on the oxidation behavior. The alloys still oxidized essentially completely. Observation of the particles after oxidation showed flakes of HfO_2 which probably had spalled off during the oxidation treatment. Oxidation would originate at weak and defected regions of the oxide coating. As oxidation proceeded throughout the sample, the subsequent swelling of the Ir_3Hf could easily cause the coating to spall off. Preheating in a vacuum did not cause the oxide to spall so the CTE match was fairly good.

The results show that oxidation of the Ir_3Hf can be catastrophic. Coating with HfO_2 does not help as any defects in the coating that allow ingress of oxygen will still cause oxidation and swelling which will eventually destroy the coating. The precise mechanism of oxidation was not evaluated. Whether a protective oxide would eventually form if the sample were thick enough could not be answered. At least for coatings in the 25-50 μm thickness range, the Ir_3Hf is not stable against oxidation.

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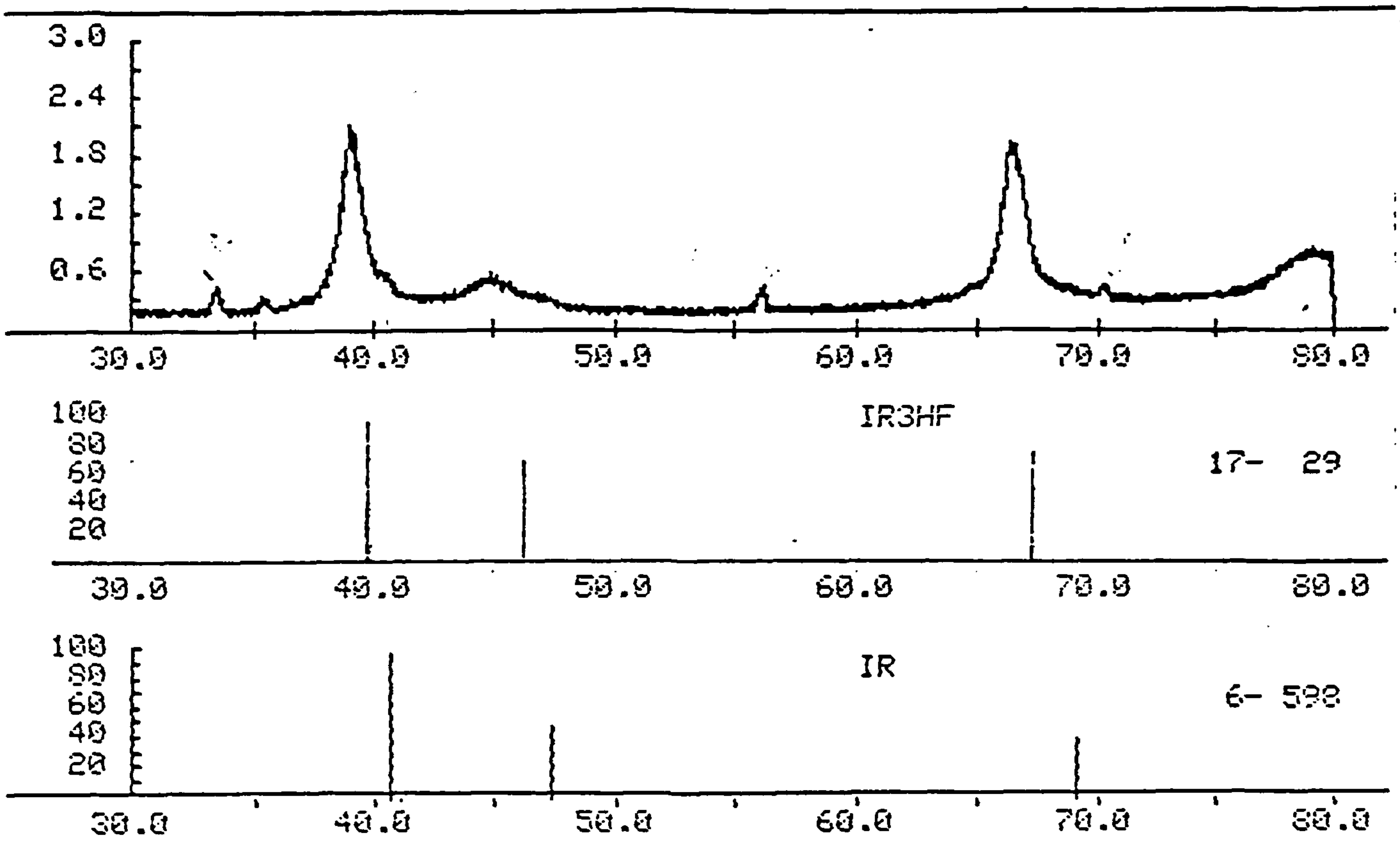
Fig. 4. X-ray diffraction spectra of Ir_3Hf after oxidizing in air at 1000°C for 20 minutes. The standardized peak positions for the various phases are shown below the spectra.

Fig. 5. Optical micrograph of Ir_3Hf after oxidizing.



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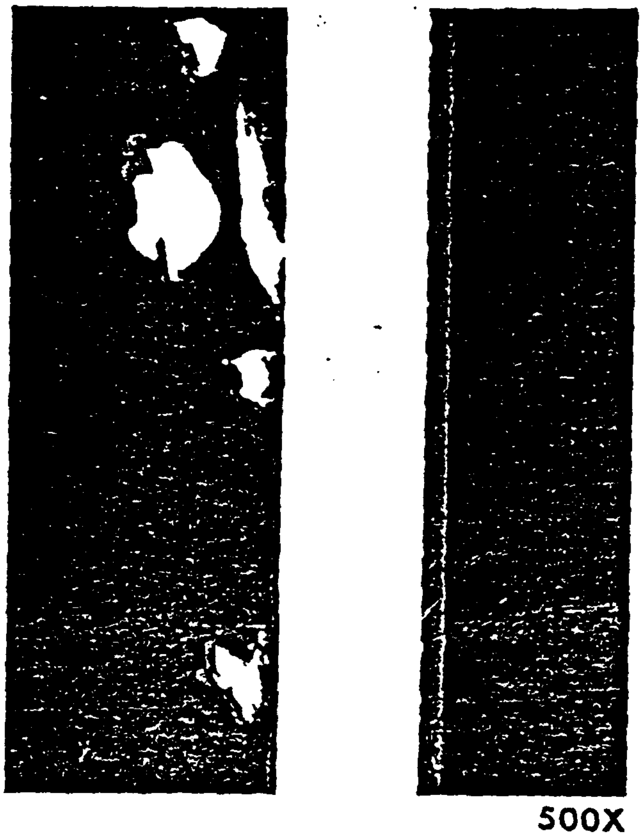

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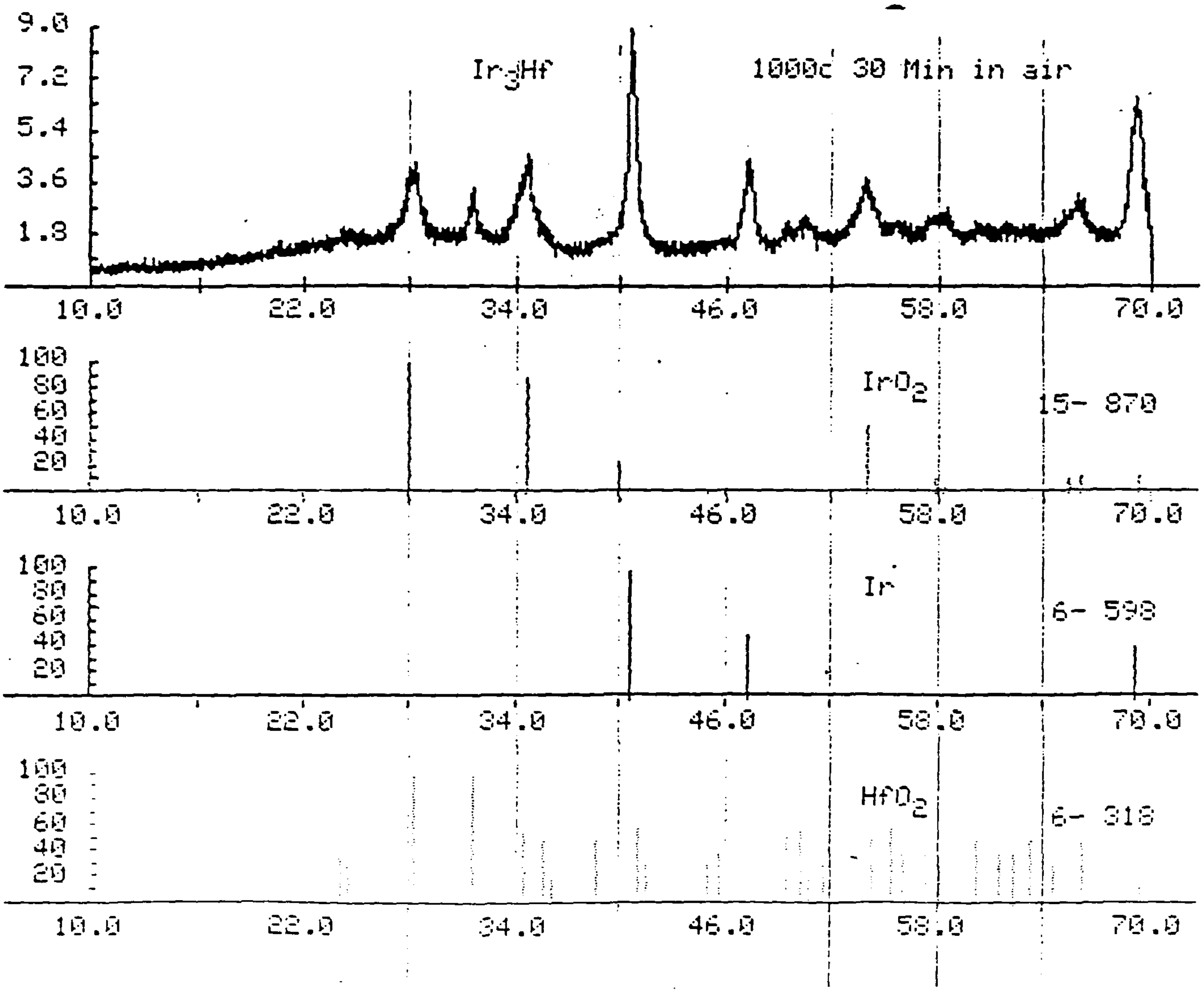

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350 X

Fig. 5. Optical micrograph of Ir_3Hf after oxidizing, 5 min. at 1000°C.

Report to OSU on PNL Contribution to "Exploratory Research on the Use of Engel-Brewer and Other Intermetallics for Oxidation Protection of Carbon-Carbon Composites"

J.L. Brimhall
Battelle-Northwest
Richland, WA 99352

August 1987

Introduction

There is a need to develop very high temperature, oxidation protection for carbon materials. The noble metals, particularly, Ir, show a very slow permeability to oxygen. Thus, Ir and Ir compounds should be good candidates as oxygen barrier coatings. Unfortunately, Ir forms a volatile oxide at high temperature and as the oxide is swept away, the Ir coating eventually disappears. However, if a stable oxide covers the Ir, the volatile iridium oxide should not migrate and the Ir would remain as a diffusion barrier.

This study investigated the influence of a stable oxide coating on the oxidation behavior of Ir. The purpose of the coating was not to serve as a complete oxygen barrier but to restrain the volatile IrO_2 from migrating off the surface. The Engel-Brewer compound Ir_3Hf was also studied. It was surmised that the Hf would react preferentially and form a stable, adherent HfO_2 film on the compound [1]. Stable oxide films were also coated on the Ir_3Hf compound.

Procedure

The iridium was in the form of sputter deposited foil pieces 15-20 μm thick. These iridium foils were either coated on one side with yttria stabilized zirconia ZrO_2 (YS) or coated on both sides with yttria stabilized hafnia, HfO_2 (YS). The HfO_2 was the preferred coating due to its higher melting point. Both types of coatings were applied by sputter deposition and were 5-8 μm thick.

Ir_3Hf compound was made by sputter deposition upon a rhenium substrate. Rhenium was used because of a good match in the thermal expansion and it could be dissolved in nitric acid. The maximum thickness of the Ir_3Hf was ~ 50 μm. Some of the Ir_3Hf material was subsequently coated on both sides with HfO_2 (YS).

The oxidation of the iridium was determined by measuring the weight loss continuously by thermogravimetry and by precision weighing of the test sample before and after heating. The sample material was heated in flowing air at temperatures up to 1200°C. Oxidation times ran from .5 to 8 hr., the flow rate was ~ 500 ccm unless otherwise specified. The area of the sample was measured before the test and estimated to be accurate to ± 10% due to some irregularity in the shape of the foil pieces. Both uncoated and coated samples were oxidized in the same test run to provide a basis for comparison. Selected metallography was performed on the test samples.

Results and Discussion

A. Pure Iridium

The rate of weight loss of pure iridium during heating in air was linear in time. Fig. 1 shows a portion of the trace of the sample weight during heating in flowing air (300 ccm) at 1000°C. A summary of the test results on weight loss is presented in Table 1. The absolute magnitude of the rate at 1000°C was generally in the range of 1.7 mg/cm^2/hr when a high flow rate was used (300-500 ccm). This is significantly greater than the value of 0.65 mg/cm^2/hr found in some earlier studies by Krier and Jaffee [2] and Philip [3]. One reason for the discrepancy is the rough surface of the samples used in our experiments. A completely flat surface was tacitly assumed in calculating the area whereas the actual surface area exposed to oxygen was undoubtedly greater. This would lead to an apparent higher oxidation rate when making the calculation. Other factors such as fine grain size in the sputtered iridium may also be a factor. The temperature dependence of the rate of weight loss was similar to that found by Krier and Jaffee however.

The air flow rate had a significant effect on the oxidation rate. Reducing the air flow by a factor of four reduced the rate by more than a factor of two. As the air flow is reduced, the rate at which the volatile IrO_2 is swept away is also reduced. The IrO_2 must be removed to expose fresh surface to the air allowing for more formation of oxide. Some of the observed variation in rates may be due to some restrictions of the air flow around the sample. An attempt was made to always keep the sample on edge to allow good air flow but this was not always assured.

The HfO_2 (YS) coating on the Ir appeared to be uniform and dense. However, there was not good bonding as demonstrated by the micrograph in fig. 2. The oxide separated cleanly along the interface as opposed to periodic cracking of the oxide. This suggests a weak attachment of the HfO_2 to the iridium. There should be a good match of the thermal expansion between HfO_2 and Ir. This would minimize the stress that would be generated during thermal cycling. The debonding shown in the micrograph could have happened during the metallographic preparation.

Despite poor bonding, coating of the sample with a stable oxide such as ZrO_2 or HfO_2 significantly reduced the rate of weight loss of the iridium, Table I. If the ZrO_2, which was only coated on one face, were completely protective the rate should be half that of the uncoated material. In fact, the rate was about 70% of the uncoated material indicating incomplete protection. The HfO_2 which was deposited on both sides was also not completely protective as a small but finite rate of weight loss occurred. The effect of the HfO_2 in reducing weight loss was greater however at higher temperatures. In the uncoated iridium the rate of weight loss was a factor of two higher at 1200°C than at 1000°C. For the samples coated with HfO_2, the rate was little changed at 1200°C compared to 1000°C, Table 1.

The microstructure after oxidation shows that the coating remained relatively intact with only localized degradation, fig. 3-5. Where the coating was intact and not debonded from the Ir, there was no indication of any loss of iridium. There are places where the coating has cracked and allowed air ingress and IrO_2 outflow. Loss of Ir at these locations was significant. This was particularly true in the region of the foil shown in fig. 4. In fig. 5, a small crack can be seen at the location where some of the iridium has eroded away. Loss of Ir at the edge of the foil where the oxide protection would be poor is undoubtedly a contributing factor to the weight loss.

Thus, an intact oxide coating does appear to reduce Ir volatilization. However, it is apparently very important that the coating be free of defects such as gross cracks. The volatile IrO_2 readily escapes through cracks or gross defects in the coating based on the appearance of the section in fig. 4. The increase pressure as a result of IrO_2 formation could provide the driving force for dispersal of the volatile oxide.

B. Ir_3Hf

The Ir_3Hf was sputter deposited on a cold rhenium foil substrate using a composite Ir-Hf target. X-ray analysis revealed primarily Ir_3Hf with a small amount of Ir. Based on the areas of the diffraction peaks, there is ~ 9% Ir phase and 91% Ir_3Hf phase. This gives an overall Ir composition of 77%. In the as-deposited condition, the lattice parameters were also larger than reported for reference standard.

Some of the foil was heat treated in vacuum to 1000°C for 3 hr and re-examined. The peaks were much sharper but otherwise there was no phase change. The lattice parameters had decreased and were closer to standard values. There was also an unidentified peak in both as-deposited and annealed condition. This is possibly a super lattice line from an ordered phase.

The grain size of the sputtered material was extremely small as shown by the electron micrograph in fig. 6. There was no evidence of amorphous phase formation.

Heating of the Ir_3Hf in air resulted in disintegration of the foil into small chunks. X-ray analysis after heating at 1000°C for 30 min showed Ir, IrO_2 and HfO_2 to be present, there was no evidence of Ir_3Hf compound or the unidentified peak. An estimation of the rate of weight loss was ~ 5.7 $mg/cm^2/hr$ which is much higher than pure Ir. The small amount of weight gain due to oxidation of the Hf was taken into account in the calculation of the weight loss. There was also some entrapped IrO_2 which was not accounted for so the actual oxidation rate or weight loss is greater than calculated.

After several attempts at oxidation of the Ir_3Hf, it was evident that the Hf in the compound does not form a protective oxide film. It is surmised that the Hf oxidizes preferentially leaving pure Ir to form IrO_2. No metallography of the oxidized material was performed due to lack of integrity in the remaining material. The lack of a uniform oxide film on the Ir_3Hf is somewhat surprising in that a uniform TiO_2 film formed on Pt_3Ti during oxidation at high temperature [4]; Pt_3Ti and Ir_3Hf have similar structures. Studies in Pt_3Ti used single crystal whereas the Ir_3Hf was very fine grained material which could account for the differences.

Coating of the Ir_3Hf with HfO_2 did not provide additional protection. The coated samples disintegrated in a similar manner to the uncoated material. The coating did not completely cover the Ir_3Hf surface. The micrograph in fig. 7 shows some coated particles adhering to the as-deposited Ir_3Hf foil and the Ir_3Hf is not coated in the region surrounding these particles. The particles are believed to be undissolved bits of rhenium substrate and during subsequent coating of the Ir_3Hf they served as a shadowing barrier preventing good coating deposition in that region. The uncoated regions would oxidize rapidly during subsequent heating in air. Once the formation of HfO_2 started within the Ir_3Hf, the coating probably cracked extensively allowing more oxygen ingress and accelerated the deterioration. No micrographs were attempted on the oxidized material.

TABLE 1 - Oxidation Rate for Bare Ir and Ir Coated with ZrO_2 and HfO_2

Sample	Avg. wt. loss @ 1000°C (mg/cm^2/hr)	Avg. wt. loss @ 1200°C (mg/cm^2/hr)
Bare Ir	1.7 ± .2	3.0 ± .5
Bare Ir (low flow rate)	.75	not tested
Ir + ZrO_2 (YS) (one side)	1.15 ± .1	not tested
Ir + HfO_2 (YS)	.6 ± .2	.55 ± .2
Bare Ir_3Hf	~ 5.7 (sample in pieces)	
Ir_3Hf + HfO_2 (YS)	Not measured (sample disintegrated)*	

* Integrity of HfO_2 (YS) coating questionable

Conclusions

1) Ir shows a linear rate of weight loss during oxidation due to formation of a volatile oxide. The rate of weight loss is greater for higher flow rates of air across the material.

2) Stable, relatively adherent oxide coatings of ZrO_2 or HfO_2 on Ir greatly reduce the weight loss, presumably by preventing the migration and escape of the volatile oxide.

3) Significant oxidation of the iridium occurred in regions where the coating had cracked.

4) Ir_3Hf did not form a stable oxide film during oxidation as the Hf completely oxidized. Coating of the Ir_3Hf did not provide protection mostly as a result of defects in the coating.

List of Figures

1. Trace of the weight change as a function of time for iridium foil heated in flowing air at 1000°C.

2. HfO_2 coating on iridium foil. Coating has debonded on one side.

3. HfO_2 coating on iridium foil after heating in flowing air for 2.6 hours at 1000°C.

4. End section of same specimen shown in fig. 3 showing loss of iridium at region of degraded coating.

5. Different section of specimen shown in fig. 3. A crack in the coating is present at region where reaction occurred.

6. Electron micrograph of as-deposited Ir_3Hf compound.

7. HfO_2 coating on Ir_3Hf. The particles which shadowed the Ir_3Hf during deposition of the HfO_2 are believed to be undissolved Re.

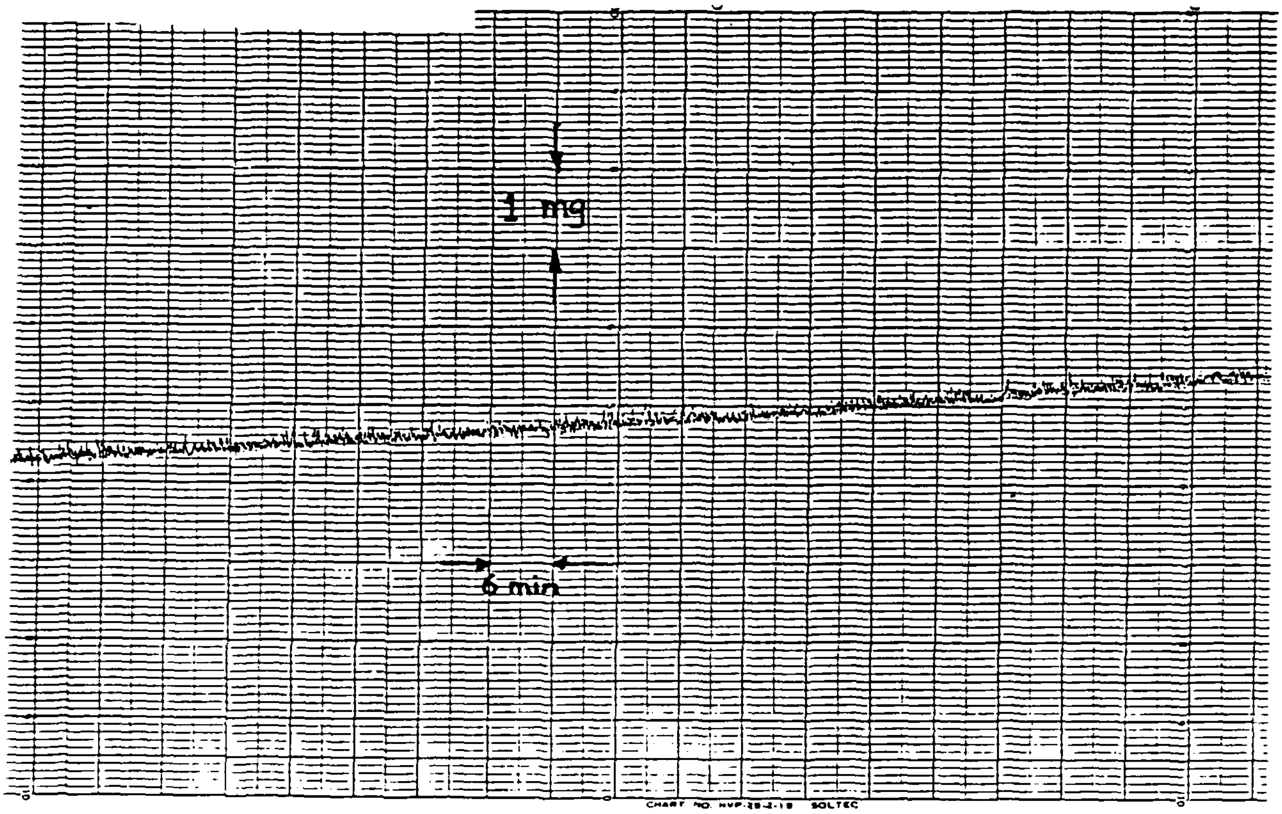
References

1. R.A. Rapp and G.R. St. Pierre, "New Options for Oxidation Protection of Carbon-Carbon Composites at 3500°F".

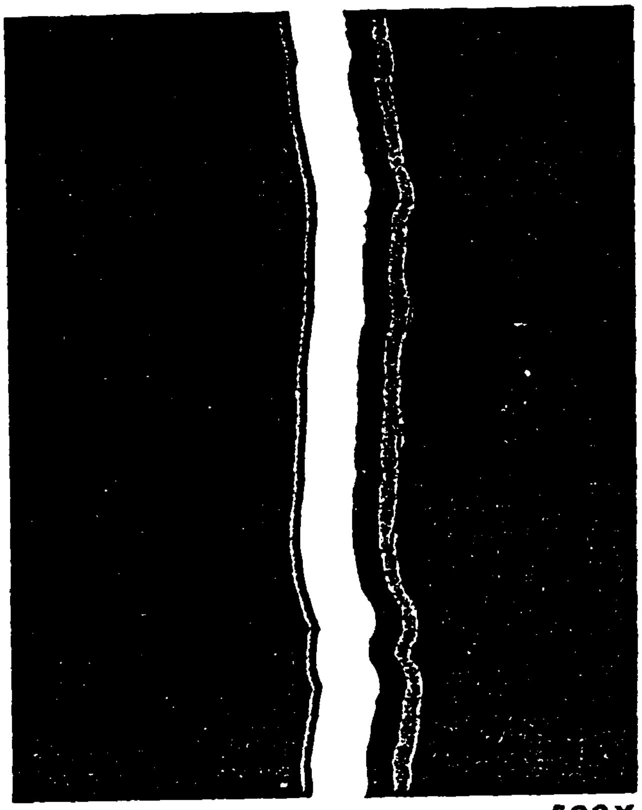
2. C.A. Krier and R.I. Jaffee, J. of the Less Common Metals, 5, 411 (1963).

3. W.L. Philips, Trans. ASM, 57, 33 (1964).

4. V. Bardi and P.N. Ross, J. Vac. Sci. Tech., A2, 1461 (1984).



1. Trace of the weight change as a function of time for iridium foil heated in flowing air at 1000°C.



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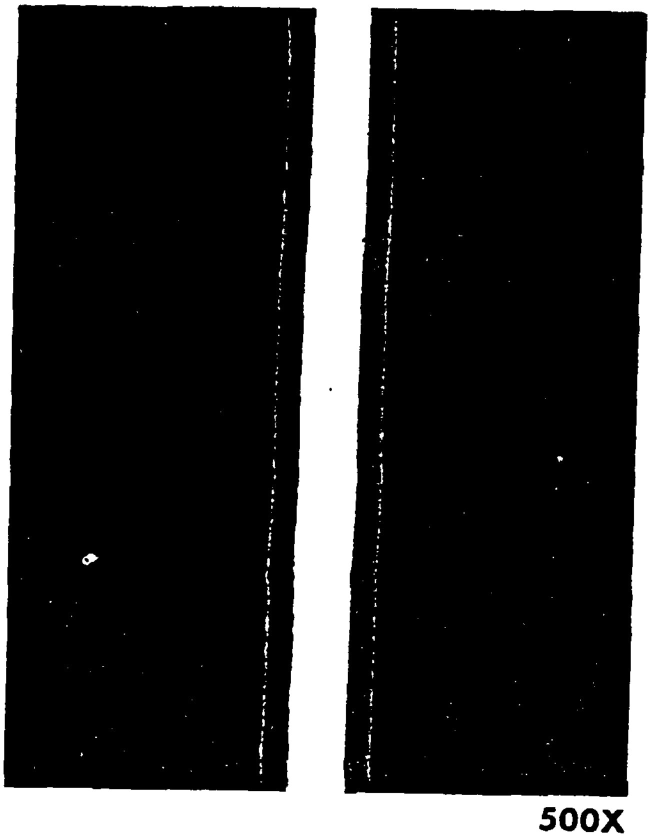
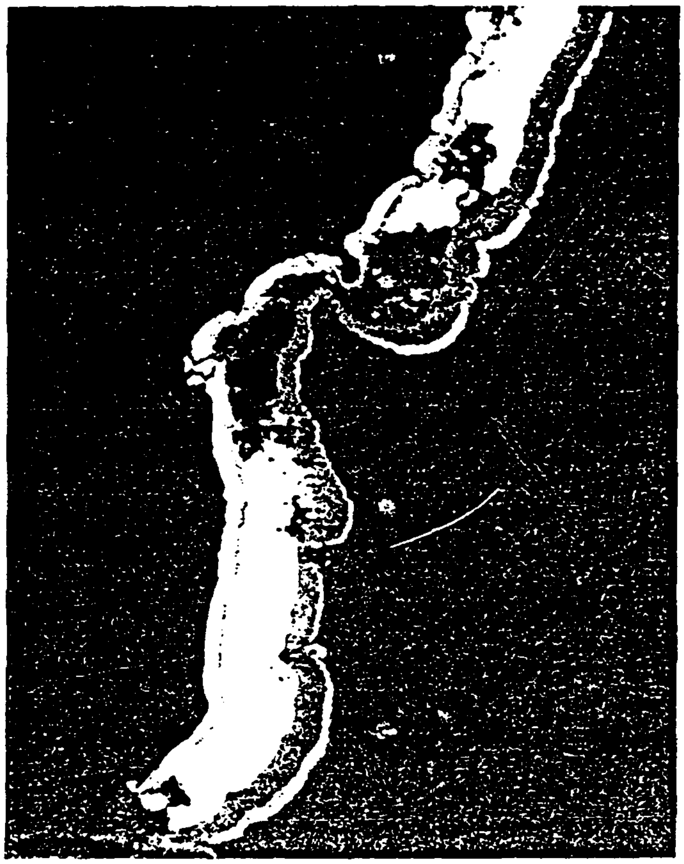
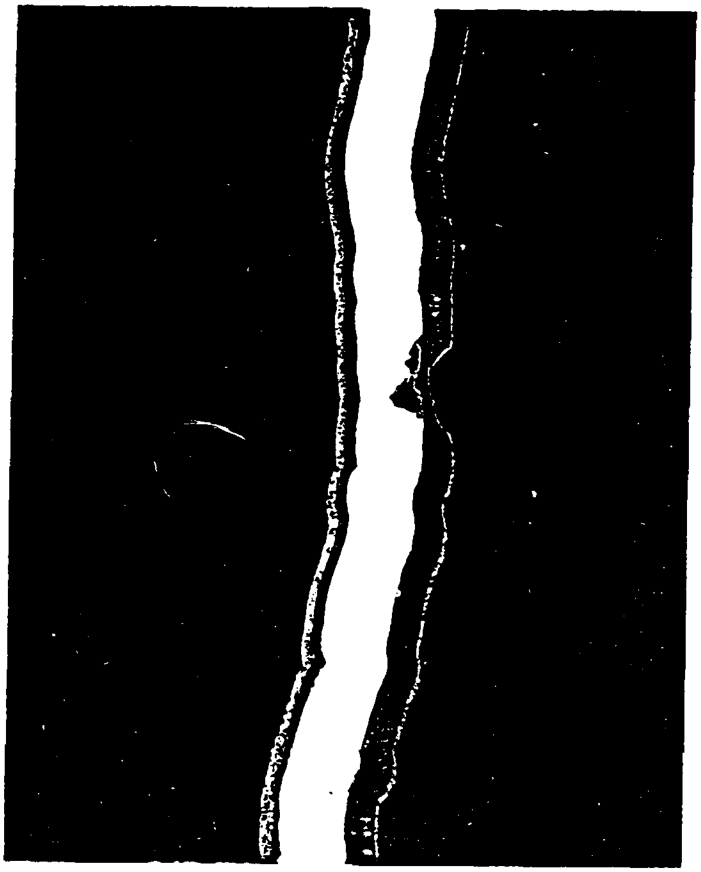


3. HfO_2 coating on iridium foil after heating in flowing air for 2.6 hours at 1000°C.



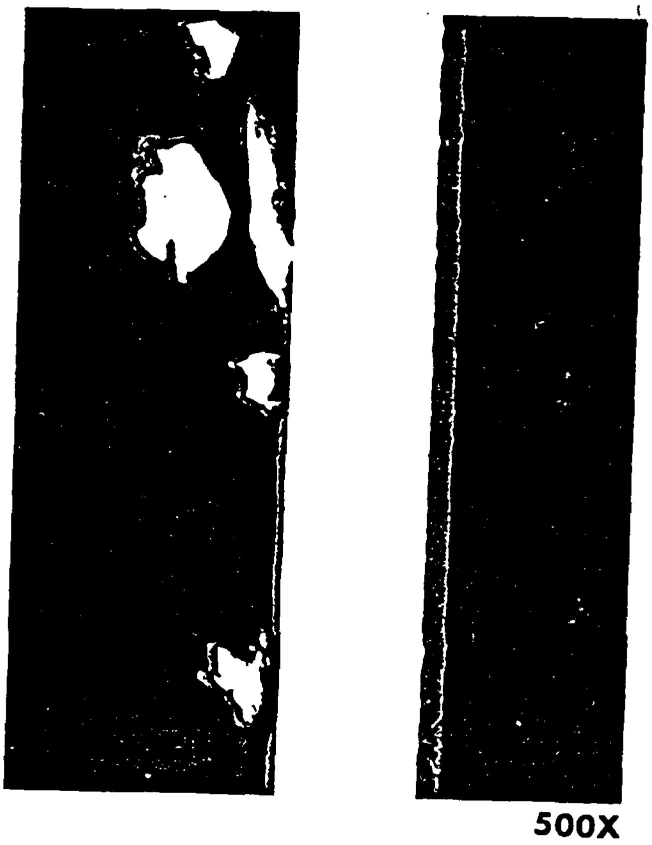
4. End section of same specimen shown in fig. 3 showing loss of iridium at region of degraded coating.



500 x

5. Different section of specimen shown in fig. 3. A crack in the coating is present at region where reaction occurred.

6. Electron micrograph of as-deposited Ir_3Hf compound.



7. HfO_2 coating on Ir_3Hf. The particles which shadowed the Ir_3Hf during deposition of the HfO_2 are believed to be undissolved Re.

Battelle
Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington U.S.A. 99352
Telephone (509)

Telex 15-2874

April 21, 1987

Professor George St. Pierre
Department of Metallurgical Engineering
Ohio State University
116 West 19th Avenue
Columbus, OH 43210

Dear Professor St. Pierre:

This letter updates the progress on our work on the ONR Project "Exploratory Research on the Protection of Carbon-Carbon Composites Against Oxidation at Very High Temperatures with Engel-Brewer and Other Intermetallic Compounds".

We have coated both pure Ir and the Ir_3Hf compound with HfO_2. Two different sputtering runs were used and the pieces were turned over between runs. The HfO_2 greatly reduced the weight loss from the Ir after testing at both 1000° and 1200°C as shown in the table.

Test #	Weight Loss		Conditions
	Ir (mg/cm^2 hr)	Ir+HfO_2 (mg/cm^2 hr)	
8	1.85	--	2.6 hr @ 1000°C
9	--	0.8	2.6 hr @ 1000°C
11	1.72	0.4	2.6 hr @ 1000°C
12	2.5	0.37	.5 hr @ 1200°C (1.6 hr > 1200°C)
13	3.6	0.7	2 hr @ 1200°C (3.1 hr > 1000°C)

The difference in loss rates between coated and uncoated is about a factor of 3-4 @ 1000°C and a factor of ~ 7 at 1200°C. The coating is apparently not impervious to oxygen diffusion but does prevent the rapid deterioration of the Ir by inhibiting IrO_2 migration. Tests on the Ir_3Hf have not been successful. Ir_3Hf oxidized readily in air and the HfO_2 coating seems to offer no protection. Even at temperatures down to 800°C, the materials break up into small chunks during oxidation.

Metallographic examination showed no obvious degradation in the HfO_2 coatings on the pure Ir. In the as-deposited micrographs, fig. 9A, the coating appears to have separated from the Ir. This could have happened during sample preparation for metallography. After oxidation, the coating is still intact fig. 9B, however, there appears to be a gap or poor adherence of the coating on one side. It is not entirely obvious how IrO_2 would be lost through such a coating, but it may be migrating along the gap and leaking out the ends. There is little evidence for cracking of the coating or any interaction/diffusion between the Ir and the coating.

Metallography of the coatings on the Ir_3Hf indicated degradation of the as-deposited material. In fig. 9C some of the Ir_3Hf material with coating attached has broken off from the original structure. The Ir_3Hf is extremely brittle. The underlying Ir_3Hf would then be unprotected during subsequent high temperature oxidation as was observed. We have not been successful in getting a good specimen for metallography after testing in air as it mostly ends up as powder.

For our future plans, we plan to do some metallography on specimens tested at 1200°C. We will also test a specimen of carbon-carbon composite which has been coated by iridium and then coated with HfO_2.

Sincerely,

John Brimhall

Dr. John L. Brimhall
Senior Research Scientist
Advanced Materials
RTL Building, Room 117
(509) 375-2545

JLB:vbs

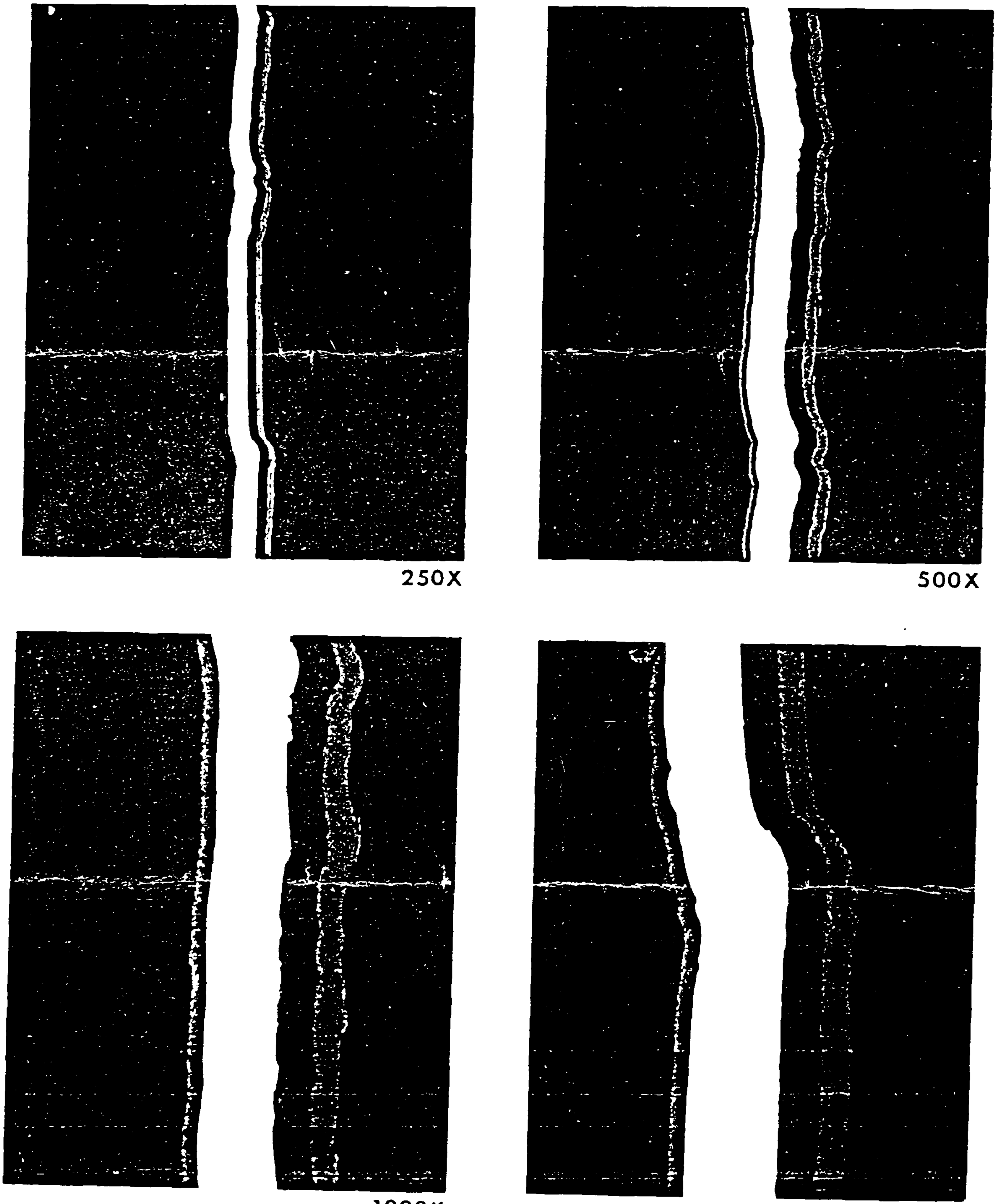
cc: Denis O'Connell (OSU)
Ed Courtright

Figures

Fig. 9A: HfO_2 coating on pure Ir. As-deposited condition

Fig. 9B: HfO_2 coating on pure Ir. Tested for 2.6 hours in flowing air at 1000°C

Fig. 9C. HfO_2 coating on Ir_3Hf. As-deposited condition



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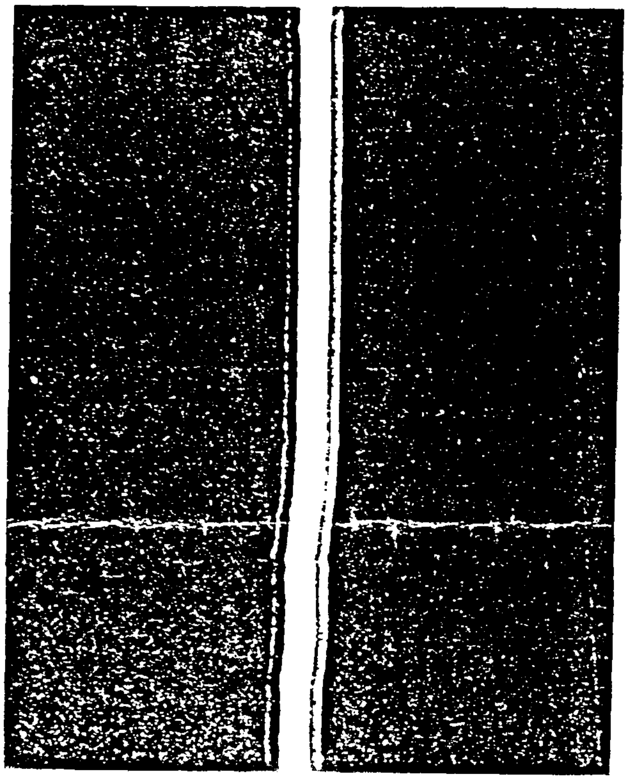

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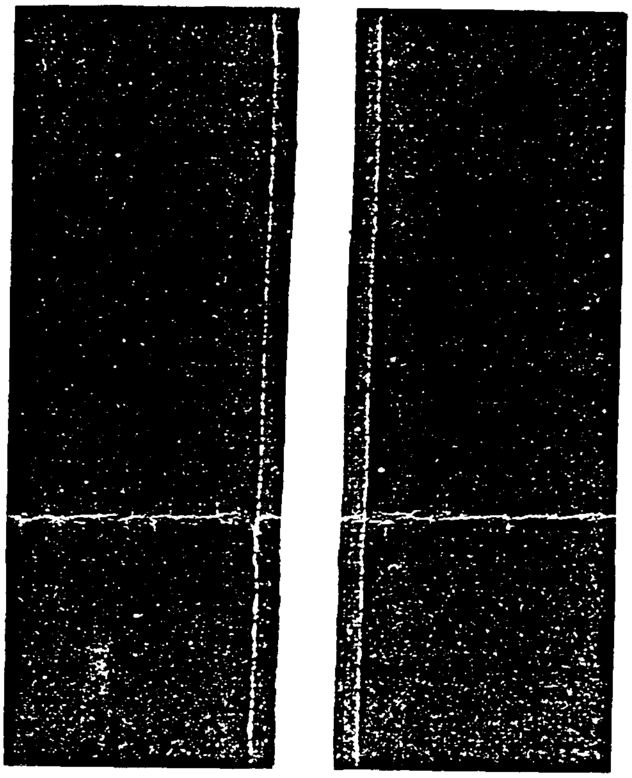

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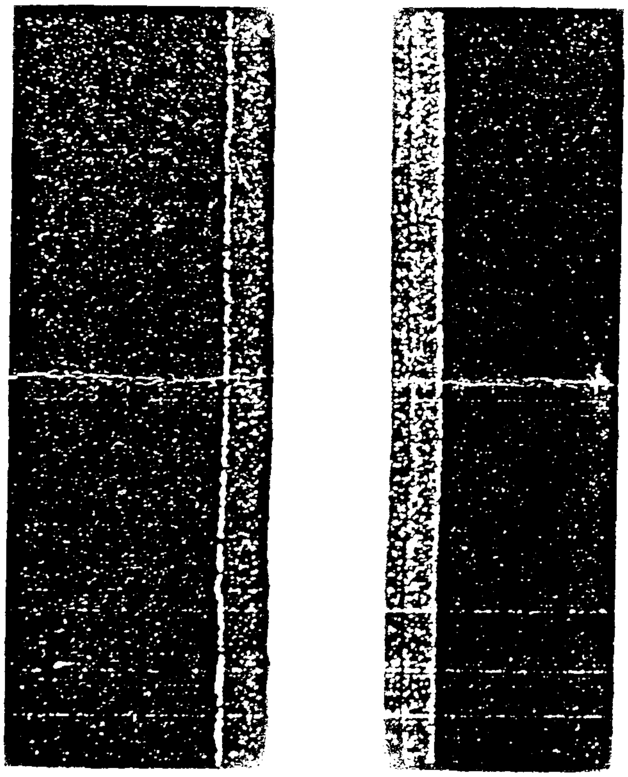

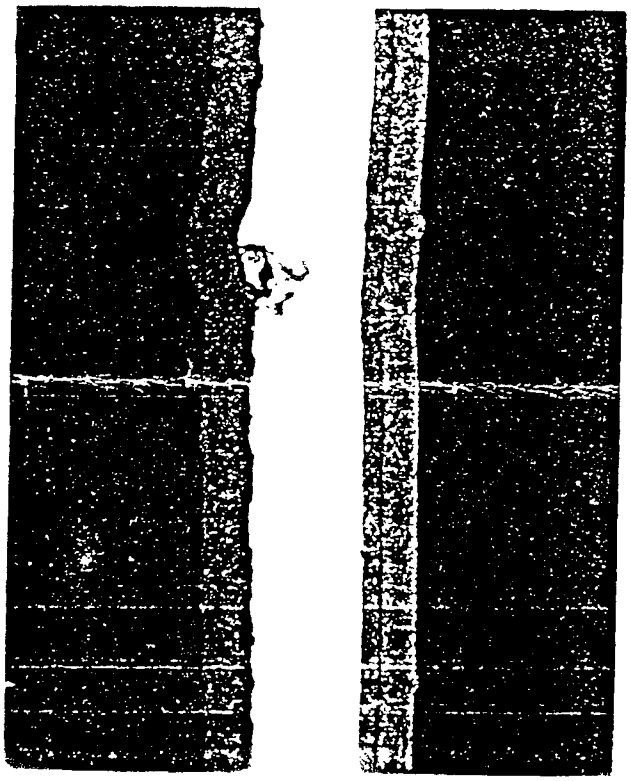

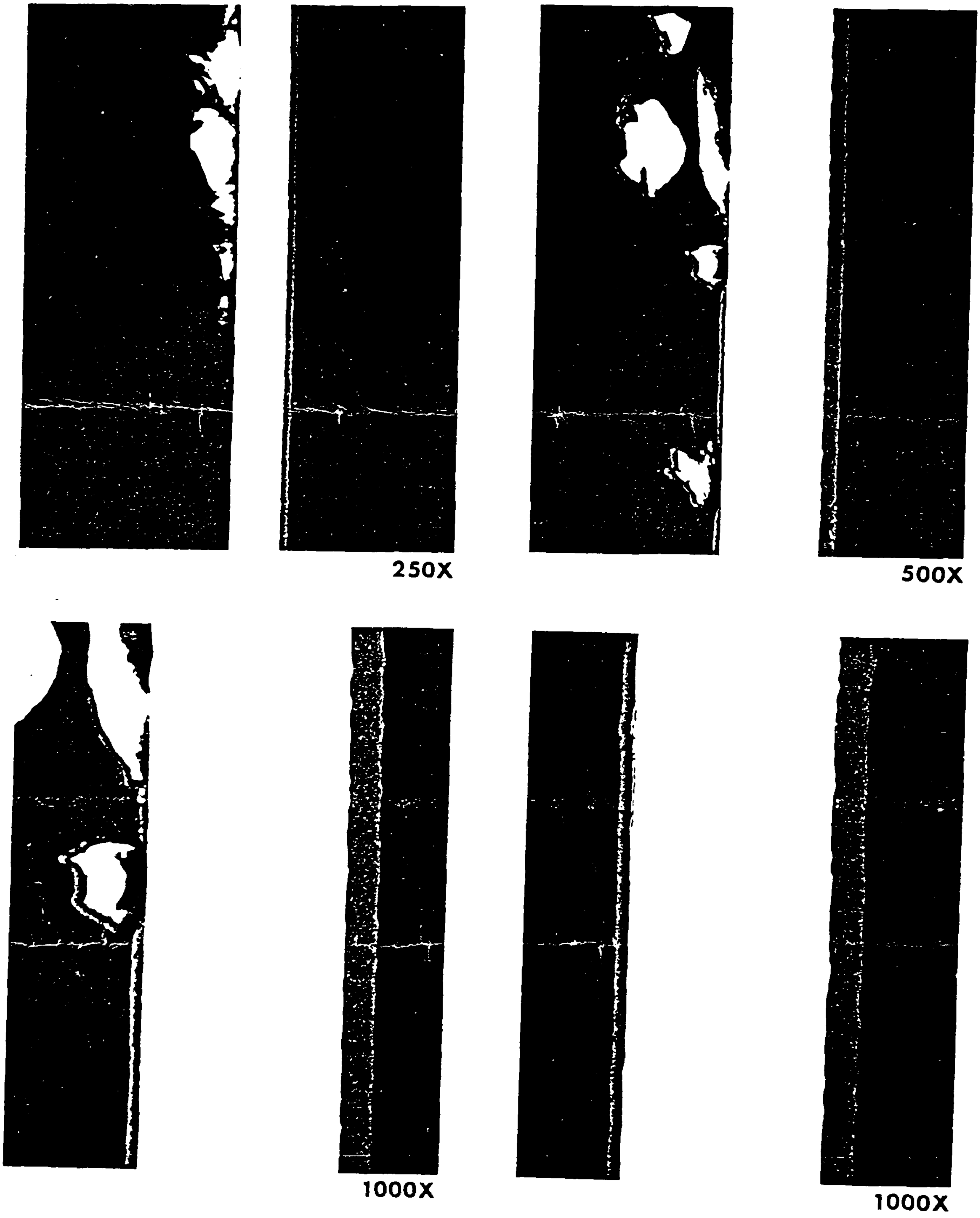

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Battelle
Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington U.S.A. 99352
Telephone (509)
Telex 15-2874

February 9, 1987

Mr. Denis O'Connel
Dept. of Metallurgical Eng.
141A Fontana Laboratories
116 West 19th Avenue
Columbus, OH 43210

Dear Mr. O'Connel:

During discussion with Professor St. Pierre, he indicated that you could make use of some Ir_3Hf coated material in your oxidation studies for the ONR program. The material is being sent in a separate package. The Ir_3Hf was sputter deposited on a rhenium substrate and is 1-2 mils thick. Rhenium has nearly the same thermal expansion coefficient as Ir_3Hf so the coating can be heated without removing it from the substrate. The rhenium will dissolve (slowly in HNO_3 so you can remove it if you wish. The concave or painted side is the rhenium substrate. There is an extremely thin coating of Ir_3Hr on this side which can also be removed by light sanding with emery paper. The curling apparently resulted from the stresses induced by the coating.

The coating is an extremely fine grained Ir_3Hf compound as verified by both x-ray and TEM analysis. Some pure Ir is also present in the x-ray pattern (see attached). The material used for the x-ray analysis were chips that flaked off some HfC substrates that were also in the sputtering chamber so some HfC appeared in the pattern. This was not seen in the Ir_3Hf material that was removed from the rhenium substrate and observed in the TEM.

We did a simple test and oxidized the material for 30 min @ 1000°C in air. The resulting x-ray pattern shows IrO_2, Ir and HfO_2. There was no evidence of the Ir_3Hf compound. I did not do any metallography, so can only speculate as to what is happening. I hope this will be of value. If you have any questions, give me a call.

Sincerely,

John Brimhall

Dr. John L. Brimhall
Advanced Materials
RTL Building, Room 117
(509) 375-2545

JLB:vbs

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MAR

Battelle
Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington U.S.A. 99352
Telephone (509)
Telex 15-2874

February 25, 1987

Professor George St. Pierre
Department of Metallurgical Engineering
Ohio State University
116 West 19th Avenue
Columbus, OH 43210

Dear Professor St. Pierre:

This letter will give you a progress report on our work on the ONR Project "Exploratory Research on the Protection of Carbon-Carbon Composites Against Oxidation at Very High Temperatures with Engel-Brewer and Other Intermetallic Compounds".

We have located some Ir flakes and have been oxidizing them in flowing air to determine a rate of removal of the volatile iridium oxide. The Ir flakes as well as Ir_3Hf will subsequently be sputter coated with HfO_2 and the experiments repeated.

Thermogravimetric analysis was carried out in a vertical tube with air flowing either from the top or bottom. A linear loss rate was clearly evident at 1000°C for times up to 4 hours. A lower loss rate occurred when the air flow entered from the top, perhaps a result of the air flow running counter to the natural convective currents. Straight forward before and after weight change tests were also done in a horizontal furnace in flowing air. Several of the Ir flakes were coated with ZrO_2 on one face only. (We managed to ride piggy back in someone else's sputtering experiment). Assuming a linear rate, a weight loss rate was calculated and the results are summarized in the table.

TABLE

Weight loss during oxidation in flowing air (~ 500 CCM) at 1000°C

A. Thermogravimetric Experiments

Test #	Ir (mg/cm^2/hr)	
1	1.1	air from bottom
2	0.81	air from top

B. Before/After Weight Change Experiments

Test #	Ir (mg/cm^2/hr)	Ir+ZrO_2 (mg/cm^2/hr)
3	0.7	0.45
4	1.78	1.14
5	1.80	1.17
6	1.69	0.6

The units were chosen to compare with some very early data of Jaffe, et al., in which a loss rate of 0.65 mg/cm^2/hr at 1000°C was reported for Ir. Except for test # 3, our values are considerably higher than those of Jaffee, et al. At the present time, the only explanation seems to be that there are differences in the air flow behavior around the specimens in the different tests. The data always show a lower loss rate for the ZrO_2 coated Ir. If the ZrO_2 were perfectly protective of the one face, the rate should be about one-half of that of the uncoated material. The exceptionally low value for the coated specimen in test # 6 may indicate a particularly good coating for that specimen.

When we have coated the Ir and Ir_3Hf we will be testing up to 1300°C. Metallographic analysis of the interface region after oxidation is also planned. If you have any questions, give me a call.

Sincerely,

John Brimhall

Dr. John L. Brimhall
Senior Research Scientist
Advanced Materials Section
RTL Building, Room 117
(509) 375-2545

JLB:vbs

cc: Denis O'Connell - OSU
Ed Courtright - PNL

Appendix B

Dr. George R. St.Pierre

Dr. Robert A. Rapp

Dr. John P. Hirth

6/17/88
Revised

DR. GEORGE R. ST.PIERRE
PRESIDENTIAL PROFESSOR AND CHAIRMAN
DEPARTMENT OF METALLURGICAL ENGINEERING
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO 43210

Summary of Professional Information

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Section 1

RESUME and BIOGRAPHICAL INFORMATION

DR. GEORGE R. ST.PIERRE

Present Position and Address:

Presidential Professor and Chairman
Department of Metallurgical Engineering
The Ohio State University
141 Fontana Laboratory
116 W. 19th Avenue Columbus, Ohio 43210-1179
Phone: (614) 422-2491

Home Address:

3595 Olentangy Boulevard
Columbus, Ohio 43214
Phone: (614) 262-8755

Personal Data:

Birth:	June 2, 1930 Cambridge, Massachusetts
Family:	Married: Mary Elizabeth Adams, Librarian M.A., Univ. of North Carolina, Chapel Hill Four Children: Ages 24-31
Health:	Excellent
Height:	6'
Weight:	190 lbs.
Hobbies:	Handball, golf, bridge, gardening

Education:

Sc.D.:	June, 1954; Metallurgy; Massachusetts Institute of Technology
S.B.:	June 1951; Metallurgy; Massachusetts Institute of Technology
H.S. Diploma	June, 1947; Milton High School, Milton, MA

BIOGRAPHICAL INFORMATION

Dr.St.Pierre, born June 2, 1930, received his doctorate in June, 1954, from the Massachusetts Institute of Technology. His dissertation, completed under the direction of Professor John Chipman, included the determination of the dissociation energies of sulfur monoxide and diatomic sulfur and the determination of the sulfide and sulfate absorption capacities of oxide melts. After a tour of duty at the Air Force Materials Laboratory and Industrial Research at the Inland Steel Company, he joined the faculty at the Ohio State University where he has been full professor since 1964 and Chairman since January 1, 1984.

Other recent associations include serving as Visiting Professor at the University of Newcastle, Australia, in 1975 and as I.P.A. Fellow, U.S.E.P.A., during the summer of 1976. He was elected a Fellow of the Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers in 1976, and a Fellow of the American Society for Metals in 1982. He has received several awards for his research and teaching including the ASM Bradley Stoughton Outstanding Young Teacher Award in 1961, the Mars Fontana (1967, 71, 75, 84) and Charles MacQuigg (1971) Teaching Awards at OSU, the 1978 Alumni Association Distinguished Teacher Award, the College Boyer Award in 1985, the 1987 Mineral Industry Education Award of AIME, and the Gold Medal of ASM International in 1987 for his applications of materials science. In 1988, he received the Outstanding Scholar Award at The Ohio State University. During the past thirty years, he has served on many University councils, professional society committees, government advisory panels, and industrial consulting groups. He served as Associate Dean of the OSU Graduate School during the period form 1964 to 1966. His teaching and research activities have been concentrated in the areas of extractive and process metallurgy; thermodynamics, kinetics, and statistical mechanics; and high-temperature science and technology of metallic, ceramic, and composite systems including coatings for carbon/carbon structural composites. He has published over one hundred papers as well as many technical reports for government and industry in connection with contract research, consulting, and committee assignments including reports for the Office of Technology Assessment, U.S. Congress and several National Studies. In addition to his duties as Chairman of Metallurgical Engineering, he is Director of the Ohio Mineral Research Institute and he serves on the Technical Steering Committees of the NSF Engineering Research Center (OSU) on "Net Shape Manufacturing" and the Edison Materials Technology Center (EMTEC,Dayton). He is a member of the Board of Directors of The Metallurgical and Materials Society of AIME.

Dr. St.Pierre has had a variety of teaching, industrial, research, administrative, military, and consulting experiences since receiving his doctorate in 1954. His teaching assignments have covered a range of topics from mineral benefication for mining students to materials science for advanced engineering students; however, major emphasis has been on the application of physical chemistry in metallurgical and materials processes. He has received a number of awards for his teaching and research efforts including the Alumni Distinguished Teaching Award in 1978 and the Distinguished Scholar Award in 1988. In 1988, he was appointed Presidential Professor.

His industrial and consulting experiences include work on the importance of sulfur content in oil on steelmaking operations, the design of pulverized coal-oxygen burners, the design and supervision of a pilot plant for direct reduction of iron ores, L-D Oxygen steelmaking, refining of high-silicon iron and specialty alloys, annealing systems for electrical steels, evaluation of Krupp and Lurgi direct reduction processes in Germany, heat exchanger failures, induction melting, transporting of molten iron, sponge iron production in Arizona and New Zealand, floruspar and manganese substitutes for the steel industry, gas content in cobalt alloys, development of zinc and lead alloys, air and water treatment systems for steel plants, ferroalloy production in submerged arc furnaces, oxidation of alloys, limestone quality, coking, and a variety of other problems in high-temperature materials and processes. Recently, he has been active in the development of protective coatings for carbon/carbon composites,the properties of intermetallic compounds, thin film coatings on glass products, and the application of statistical mechanics to the behavior of interstitial solutes in alloys and compounds. He has maintained an active research program at Ohio State University with major grants from industrial firms and government agencies. This research has led to advanced degrees for more than sixty graduate students and more than one hundred reviewed publications. His work was recognized in 1976 by election to the grade of Fellow of the Metallurgical Society by the American Institute of Mining, Metallurgical, and Petroleum Engineering and Fellow of the American Society for Metals in 1982. He received the American Society for Metals Gold Medal in 1987. His administrative experiences include a two-year term (1964-1966) as Associate Dean of the Graduate School during which time he was responsible for the U.S.A.F. Wright Field Graduate Program and all fellowship and grant activities, and numerous chairmanships of major committees within the university and national professional societies. Dr. St.Pierre has been Chairman of the Department of Metallurgical Engineering since January 1, 1984. He is Director of the Ohio Mineral Research Institute and he serves on the boards of the NSF Center for "Net Shape Manufacturing" and the Edison Materials Technology Center in Dayton. He has participated in many international activities and worked overseas on several occasions. Most recently, he was a member of the NSF Workshop on Ferrous Metallurgy in Ranchi, India in 1986. He was a Visiting Professor at four universities in the Peoples' Republic of China in September 1987. He was guest lecturer at a NATO workshop in Kiel University in Germany, July 1987. In 1985, he was Special Lecturer at the Japan Institute of Metals. In the Summer of 1988 he will be a member of an NSF Workshop in Dusseldorff on "Advances in Ferrous Metallurgy". He is Co-Chairman for a NATO Meeting to be held in France/Italy in the Summer of 1989 on the Subject of "Thermodynamics of Advanced Materials."

Honors and Awards

DR. GEORGE R. ST.PIERRE

Appointed Presidential Professor, OSU, 1988

Distinguished Scholar Award, OSU, 1988

Inaugral Tutorial Lecturer, TMS-AIME, 1988

Gold Medal of ASM INTERNATIONAL, 1987

Mineral Industry Education Award of AIME, 1987

Boyer Award, Dean College of Engineering, OSU, 1985

FEF Honorary Scholar, 1984

Fellow of American Society for Materials, 1982

Alumni Distinguished Teaching Award, OSU, 1978

I.P.A. Fellow, USEPA., 1976

Fellow of The Metallurgical Society of AIME, 1976

Visiting Professor, University of Newcastle, N.S.W. Australia, 1975

Armco Professor, 1972-75

Charles E. MacQuigg Teaching Award (OSU), 1971

Fellow of American Institute of Chemists, 1969

Mars G. Fontana Teaching Award (OSU), 1984, 1975, 1971, 1967

Bradley Stoughton Outstanding Young Teacher Award of American Society for Metals, 1961

Union Carbide and Republic Corp. Fellowship, 1951-54

Distinguished Air Force Military Student, 1951

James C. Melvin Memorial and FEF Scholarships, 1947-51

Milton High School Science Prize and MIT Scholarship, 1947

Dr St.Pierre is a Silver Life Master of the American Contract Bridge League and is included in several biographical volumes including Who's Who

Section 3

Recent Professional Activities Including Professional Societies

DR. GEORGE R. ST.PIERRE

Panelist, NSF Committee to Select MRG, June, 1988

Member, Technical Steering Committee, Edison Materials Technology Center, Dayton, 1986-present

Director, Ohio Mining and Mineral Resources Research Institute, 1985-present

Director, Pyrometallurgy Center (OSU), 1984-present

Member of Technical Steering Committee of the NSF Net Shape Manufacturing Center (OSU), 1986-present

Member of Advisory Board of the Welding Research Center (OSU), 1984-1985

Member of the Advisory Board for Joint Industry/Government Ferrous Metallurgy Program at Argonne National Labs., 1986

TMS-AIME Fellows and Educator Award Selection Committee, 1979-1982, Chairman 1982; 1987-1990

Met. Trans. A. Board of Review 1977-1980, Chairman 1980, 1981- present

Solid State Sciences Committee Forum, 1987-present

Founder Member of American Society of Composites, 1986-present

TMS-AIME Leadership and Application to Practice Awards Committee, 1986-88 Chairman, 1988

Joint Commission on Metallurgical Transactions of The American Society for Metals and The Metallurgical Society, 1979-1982, Chairman 1982, 1986-present

ASM Henry Marion Howe Medal and Marcus A. Grossmann Young Author Awards Committee, 1986-88, Chairman, 1988

TMS-AIME Officers Nominating Committee, 1986-1989

University Materials Council (Depth Committee), 1984-present

Steering Committee. Process Technology Division, Iron and Steel Society, AIME, 1986-present

ASM Thermodynamics Committee, 1979-present

TMS-AIME Membership Director, 1988-1991

Member, Board of Directors, The Materials Society of AIME, 1988-1991

NSF Advisory Board for Chemical and Process Engineering, 1984

UNIDO Expert, 1984

Advanced Seminar Lecturer for A.F.S., 1967, 1972, 1973

NATO Lecturer, 1964

Member NSF India-USA Exchange, 1985-1986

Visiting Professor, University of Newcastle, N.S.W., Australia, 1975

I.P.A. Fellow, U.S.E.P.A., Research Triangle Park, North Carolina, 1976

Armco Professor, 1972-1975

Japan-US Cooperative Research Program on Phys. Chem. of Composites, 1985

NMAB, Member of Panels on Manganese, Fluorspar and other Stategic Materials, 1970-1975

NSF/AISI Organizer of major workshops on coking, sensor development, direct reduction, coal gasification, electromagnetic casting, 1970-1986

Advanced Seminar Lecturer of American Foundryman's Society, 1967-1973

Member of Alpha Sigma Mu, American Society for Composites, American Society for Engineering Education, American Society for Metals, Iron and Steel Society of AIME, Materials Research Society, Sigma Xi, Society of Mining Engineers of AIME, The Metallurgical and Materials Society of AIME.

Section 4

Recent Teaching Assignments
Excluding 693, 694, 795 (Sem./Colloq.) and 999

DR. GEORGE R. ST.PIERRE

Year	Quarter	Course	Cred. Hrs.	Approx. No. Studts.	Activity
1988	Spring	MetE 526-Chem.Met.(U.G.)	3	34	3 lect./wk.
1988	Spring	MetE 720-Met.Processing(w/Sahai)	3	15	about 9 lects.
1988	Winter	MetE 731-Adv.Chem.Met.II (w/Rapp)	4	18	2 lect./wk.
1987	Autumn	MetE 730-Adv.Chem.Met.I (w/Rapp)	4	20	2 lect./wk.
1987	Spring	MetE 401-Met.Thermodynamics(w/Mobley)	4	140	about 10 lects.
1987	Spring	MetE 720-Met.Processing (w/Sahai)	3	15	about 10 lects.
1987	Winter	MetE 832-Met.Processing II	2	7	2 lect./wk.
1986	Autumn	MetE 730-Adv.Chem.Met.I (w/Johnson)	4	21	2 lect./wk.
1986	Autumn	MetE 310-Cast Met.Tech.(w/Rapp/Mobley	4	45	about 12 lects.
1986	Spring	MetE 330-Met.Thermodynamics(w/Mobley)	4	150	about 15 lects.
1986	Spring	MetE 720-Met.Processing (w/Sahai)	3	15	about 12 lects.
1986	Winter	MetE 731-Adv.Chem.Met.II (w/Hirth)	4	19	2 lect./wk.
985	Autumn	MetE 730-Adv.Chem.Met.I (w/Johnson)	4	27	2 lect./wk.
1985	Spring	MetE 720-Met.Processing (w/Sahai)	3	17	about 12 lects.
1985	Spring	MetE 330-Met.Thermodynamics(w/Mobley)	4	150	about 12 lects.
985	Winter	MetE 832-Met.Processing II	2	7	2 lect./wk.
984	Autumn	MetE 730-Adv.Chem.Met.I (w/Johnson)	4	26	2 lect./wk.
1984	Spring	MetE 720-Met.Processing (w/Sahai)	3	20	about 15 lects.
1984	Winter	MetE 330-Met.Thermodynamics	4	41	4 lect./wk.
983	Autumn	MetE 730-Adv.Chem.Met.I (w/Johnson)	4	33	2 lect./wk.

Section 5

GRADUATE AND POSTDOCTORAL STUDENTS OF GEORGE R. ST.PIERRE

NAME	B.S.(YEAR)	M.S.(YEAR)	Ph.D.(YEAR)	POST-DOC(YEAR)
David L. Douglass			1958	
David Wyeth Hoffman		1959		
David Pezdirtz				
William T. Ebihara		1960		
Gerald Wayne Worth			1963	
Antoine Jean Wilhelem		1960		
Gopi Krishnamurti	1962			
James E. Battles		1961	1964	
Ahindra Ghosh				1963-64
Kazuhiro S. Goto			1962	
James Sheridan Foster		1962	1964	
Thomas Barnes				
Lee M. Adlesberg			1964	
James Russell Myers			1964	
John William Patterson		1962	1966	
Jerris C. Moeller		1965		
Daniel Edward Ries	1975			
Richard Bruce Reese		1963	1965	
Stephen Warner Gilby			1966	
William Thomas Black		1969		
Edward Robert Duffy		1967		
Craig Forsythe Landefeld		1966	1970	
Robert Dale Blackburn		1968		
Timothy K. Leonard				
Thomas Ritson Ferguson		1968		
Sigurd Wagner				1969-1970
Clarence Warren Weidner		1967	1971	
Donald James Shade		1970		
James Michael McCormick			1971	
Randall Michael German		1971		
Minoru Arita			1974	
Yuan Kai Tang		1973	1976	
John P. Bachlet		1972		
Quentin Robert Skrabec		1973		
Arturo Bronson			1977	
Thomas Tefelske				
June Bok Lee		1976	1978	
Rein Roman Mutso			1979	
Mukund Muralidhar Desai		1976	1979	
Stephen Agyei-Damoa		1976	1978	
Mohamad Karamiezhaad Ranjbar		1977	1983	
Viswanathan Krishnamoorthi		1977		
Ajibola Olutoyin Ibidunni		1979	1982	
Rhonda L. Ericson Mckimpson		1979		
Chanvootti Tangchitvittaya			1980	

NAME	B.S.(YEAR)	M.S.(YEAR)	Ph.D.(YEAR)	POST-DOC(YEAR)
Jose Fabio Velez		1979		
Adil Khan		1981		
Ho Jin Choi			1981	
Samuel K. Somuah		1980	1982	
Yu-Su Won (Huang)		1980		
T.A. Parthasarathy		1982	1983	
Richard T. Gass		1982		
Mark E. Watkins		1984	1987	
Chia-Ho Chao				
Thomas A. Bamford		1984		
Mahmoud Abbas				1984-1985
Gordon R. Holcomb		1985		
Susana F. Protasio		1986		
Lisa Jo DuVernay		1986		
Daniel Ray Wallem		1986		
Mohamed El Zeky				1985-86
Moonyong Lee			1986	
Moustafa Ismail				1986-1987
Huang, Zhen-Qi				1987-88

Current Students
Jong-Won Kwon
Gordon Holcomb
Ileese Glatter
Karthick Gourishankar
Tsengyou Syau

Current Post-Doc
Iguchi, Visiting Professor

Section 6

DR. GEORGE R. ST.PIERRE
Recent Theses & Dissertations

RECENT M.S. THESIS TITLES

Ibidunni, Bola - "High Temperature Reactions of Ni-Cr and Fe-Cr Alloys in $H_2/H_2O/H_2S$ Gases at 850 and 950 Degrees C" - G.R. St.Pierre, Advisor

McKimpson, Rhonda - "A Study of Water-Formed Calcium Carbonate Scale Deposits on Metallic Surfaces" - G.R. St.Pierre, Advisor

Khan, Adil Hamid - "The Effect of Operating and Metallurgical Variables on Nucleation and Growth Characteristic of Water-Formed Calcium Carbonate Scales in Heat Exchangers" - G.R. St.Pierre, Advisor

Gass, Richard T. - "Experiments on Reduction of Iron Ore Pellets in Coal" - G.R. St.Pierre, Advisor

Malhotra, Manoj Kumar - "An Experimental Evaluation of the Thermodynamic Properties of Concentrated Aqueous Potassium Hydroxide Solutions" - W.B. Johnson and G.R. St.Pierre, Co- Advisors

Protasio, Susana Fonseca - "Studies on the Influence of Inclusion Morphology on Hydrogen Related Problems in Low Alloy Steels" - G.R. St.Pierre, Advisor

Wallem, Daniel Ray - "The Hydrodynamics of Slag-Refractory Interactions" - Y. Sahai and G.R. St.Pierre, Co-Advisors

RECENT PH.D. DISSERTATION TITLES

Desai, Mukund - "The Influence of Na_2O and K_2O on the Dissolution Kinetics of Mullite and Alumina Refractories in Coal Ash Slags" - G.R. St. Pierre, Advisor

Mutso, Rein R. - "The Catastrophic Swelling of Iron Oxides During Chemical Reduction" - G.R. St.Pierre, Advisor

Ibidunni, Ajibola O. - "Carbon Deposition by the Decomposition of Carbon Monoxide on Iron Oxide (Hematite)" - G.R. St.Pierre, Advisor

Watkins, Mark E. - "Calcium Modification of Surface Oxides Formed on Levitated Iron and Steel Droplets and Related Surface Tension Phenomena" - G.R. St.PIerre, Advisor

Section 7
GEORGE R. ST.PIERRE

MAJOR COMMITTEES AT OSU

Approximate Dates	Committee Assignment
1987-88	Co-Chairman of University United Way Campaign
1986-87	Member of Selection Committee for Presidential Professors
1986	Member of Committee with Professor Harvey Friedman and Dean William Kern to present proposal for a "Center for Foundational Studies"
1984 - Present	Currently on College of Engineering Administrative and Policy Committee, Engineering Dean's Council, Engineering Research Center Steering Committee, Steering Committee of the Ohio Mineral Institute (Chair).
1980 to 1984 1974 to 1977	The OSU representative to the Faculty Advisory Committee of the Chancellor for Higher Education in Ohio. Elected by Senate.
1979 - 1981	Selection Committee for Alumni Distinguished Teachers, Ch. 1980/81.
1960 - Present	Served on several University Advisory Committees for selection of graduate fellows, postdoctoral fellows, visiting professors, tenure and promotion matters, and publications.
1970	Member of University "Committee of Five" (Elected by Faculty Council to Represent the Faculty during the Crisis of 1970) with Herbert Parnes (Economics), Louis Nemzer (Political Science) Jack Calvert (Chemistry) and Richard Day (Law).
1968	The Faculty Hearing Committee on the David Green Dismissal. Elected as special faculty member with Robert Fisher (Math) and Albert Kuhn (English).
1966 to 1969	Elected Member of Advisory Committee to the President and Board of Trustees; Chairman 1968/69.
1966 to 1972	University Faculty Council
1970 to 1972	University Senate
1968 to 1969	University Centennial Commission
1966 to 1968	University Committee on Rights and Responsibilities

Section 8

CURRENT AND RECENT SPONSORED CONTRACT RESEARCH AWARDS

DR. GEORGE R. ST.PIERRE

A. National Science Foundation Indo/USA Cooperative Project with Dr. B.D. Tripathi, RDCIS-Ranchi and T.K. Namboodiri, BHU-Varanasi on "Hydrogen-Induced Cracking and Sulfide Stress Corrosion Cracking of High Strength Steel".

Amount of Award	Grant Period	% Time Ac. Year Sum
$28,000 (plus $6,000 travel)	11/86 - 10/89	2% - 12 mos.

B. Office of Naval Research (OSURF 718158) with J.P. Hirth and R.A. Rapp

"Exploratory Research on the protection of Carbon-Carbon Composites against Oxidation at Very High Temperatures (above 3000 Degrees F) with Engel-Brewer and Other Intermetallic Compounds".

Amount of Award	Grant Period	% Time Ac. Year Sum
$320,000	11/85 - 9/88	5% - 12mos.

C. The Office of Research and Graduate Studies (OSU) with P.G. Shewmon, W.A.T. Clark and other departments.

"Electronic Materials/ Structure and Properties".

Amount of Award	Grant Period	% Time Ac. Year Sum
$200,000	7/85 - 9/87	2% - 12 mos.

D. National Science Foundation (OSURF 716097) with S. Smialowska

"A Study of the Influence of Sulfur Content and Ladle Refining Practices on the Susceptibility of Low Alloy Steels to Hydrogen Flaking".

Amount of Award	Grant Period	% Time Ac. Year Sum
$178,150	3/84 - 2/87	5% - 12 mos

E. U.S. Bureau of Mines (OSURF 716638) with R.A. Rapp, and Y. Sahai

"Electrochemical Factors in The Carbothermic Reduction of Oxides".

Amount of Award	Grant Period	% Time Ac. Year Sum
$347,389	10/84 -9/88	5% - 12 mos

F. U.S. Bureau of Mines (OSURF 716855) with Y. Sahai and R. Rapp.

"Reaction Kinetics in Fused Salt/Slag/Ceramic Systems".

Amount of Award	Grant Period	% Time Ac. Year Sum
$226,644	10/84 - 9/87	%5 - 12 mos

G. U.S. Bureau of Mines (OSURF 719723) with other departments

"Mining and Mineral Resources Research Institute Annual Allotment".

Amount of Award	Grant Period	% Time Ac. Year Sum
$427,000	7/85 - 6/88	5% - 12 mos

H. Battelle Northwest Pacific Labs (OSURF 718855) with R.A. Rapp

"Modification of Hafnium Carbide for Enhanced Oxidation Resistance Through Addition of Prasedoymium and Tantalum".

Amount of Award	Grant Period	% Time Ac. Year Sum
$39,950	9/86 - 8/87	3% - 12 mos

I. Garrett Turbine Engine Company (OSURF 719490) with R.A. Rapp

"Corrosion Resistant Ceramic Coatings for Superalloys".

Amount of Award	Grant Period	% Time Ac. Year Sum
$37,120	2/87 - 1/88	2% - 12 mos

J. United States Air Force (OSURF 740002) with J. Cawley

"Thermodynamic and Diffusivity Measurements in Potential Ultra-High Temperature Composite Materials".

Amount of Award	Grant Period	% Time Ac. Year Sum
$151,697	10/87 - 9/89	2% - 2 yrs.

All research done at OSU in Columbus

Section 9

Selected Publications

DR. GEORGE R. ST.PIERRE

G.R. St.Pierre and J. Chipman, "Thermal Dissociation of SO2 and the Dissociation Energies of SO and S2", J. Am. Chem. Soc., 1954, Vol. 76, pp. 4784-91.

G.R. St.Pierre, "Sulfur Distribution Between Flame and Slag in the Open Hearth Furnace", Proceedings of the Chicago Technical Meeting of the American Iron and Steel Institute, 1954, pp. 227- 34, Republished in Industrial Heating, November, 1955, pp. 2306- 14.

G.R. St.Pierre and J. Chipman, "Sulfur Equilibria Between Gases and Slags Containing FeO", Trans. AIME, 1956, Vol. 206, pp. 1474- 83.

G.R. St.Pierre, "Gas Utilization in the Reduction of Iron Oxides," Proceedings of the International Conference on the Physical Chemistry of Steelmaking (J.F. Elliott, Editor), 1958, Wiley and Technology Press, pp. 159-64.

R. Speiser and G.R. St.Pierre, "Determination of Activities in Multi-Component Metallic Solutions", J. Electrochem. Soc., 1959, Vol. 106, pp. 629-31.

G.R. St.Pierre, "The International Symposium on the Physical Chemistry of Process Metallurgy", J. of Metals, July, 1959, pp. 454-55.

D.L. Douglass, G.R. St.Pierre, and R. Speiser, "The Kinetics and Mechanism of the Conversion of Titanium Oxide to Titanium Nitride", Proceedings of the International Symposium on the Physical Chemistry of Process Metallurgy, (G.R. St.Pierre, Editor) Interscience Press, 1961, pp. 705-20.

A.J. Wilhelm and G.R. St.Pierre, "The Kinetics of the Iron Oxide Reduction Steps", Trans. AIME, 1961, Vol. 221, pp. 1267-69.

Editor of Volumes 7 and 8, Metallurgical Society of AIME Conferences, The Physical Chemistry of Process Metallurgy, Interscience Press, 1961.

A.T. Chapman, G.R. ST.Pierre, W.R. Foster, and T.S. Shevlin, "Concerning the Stable Phase of Silicon Monoxide", J. Am. Ceramic Soc., 1960.

G.R. St.Pierre, W.T. Ebihara, M.J. Pool, and R. Speiser, "The Tungsten-Oxygen System", Trans. AIME, 1962, Vol. 334, pp. 259-64.

K. Goto and G.R. St.Pierre, "Activities of Pb and Sn in Lead-Tin Alloys", Tetsu to Hagane, 1963, Vol. 49, pp. 1873-79.

K. Goto and G.R. St.Pierre, "Direct Measurements of Oxygen Pressure in High Temperature Gases", Tetsu to Hagane, 1963, Vol. 49, pp. 1760-65.

J.J. Simmons, S.R. Blanich, and G.R. St.Pierre, "Krupp-Renn Rotary Kiln Reduction Process Applied to Non-Magnetic Lean Iron Ores of the Cuyuna and Mesabi Ranges", State of Minnesota Iron Range Resources and Rehabilitation Commission, March 1, 1963.

R. Speiser and G.R. St.Pierre, "Fundamentals of Refractory Metal-Gaseous Environment Interaction", The Science and Technology of Refractory Metals (N.E. Promisel, Editor) Pergamon Press, New York, 1964, pp. 289-330.

R. Speiser and G.R. St.Pierre, "Methods for Studying High Temperature Oxidation Reactions", Proceedings of the AIME Symposium on the Oxidation of Refractory Metals, Technical Documentary Report No. ML-TDR-64-162, 1965, pp. 3-23.

G.R. St.Pierre and R. Speiser, "The Reactions of Gaseous Systems with Tongsten at Elevated Temperatures", AIME Symposium on the Oxidation of Refractory Metals, Technical Documentary Report No. ML-TDR-64-162, 1965, pp. 109-24.

G.R. St.Pierre, "Inequality Statements for Some Metallurgical Systems", Proceedings of AIME Symposium on Process Simulation and Control in Iron and Steelmaking, (J.M. Uys and H.L. Bishop, Editors), Gordon and Breach, 1966, pp. 63-68.

L.M. Adelsberg, G.R. St.Pierre, and R. Speiser, "On the Origin and Identity of the Oxide Platelets Observed in Tantalum After Oxidation", Trans. AIME, 1966, Vol. 236, pp. 1363-66.

G.R. St.Pierre, "The Use of Free Energy Balances in Process Analysis", Applications of Fundamental Thermodynais of Metallurgical Processes, G.R. Fitterer, Editor, Gordon and Breach Publ., 1967, pp. 235-47.

J.E. Battles, R. Speiser, and G.R. St.Pierre, "The Reactions of Water Vapor With Tungsten", Metallurgie, 1967, Vol. VII-2, pp. 69-77.

L.M. Adelsberg, G.R. St.Pierre, and R. Speiser, "Kinetics of the Oxidation of Tantalum by Water Vapor", Trans. AIME, 1967, Vol. 239, pp. 490-96.

M.J. Pool, R. Speiser, and G.R. St.Pierre, "Activities of Cr and Ti in Cr-Ti Alloys", Trans. AIME, 1967, Vol. 239, pp. 1180-1186.

G.R. St.Pierre and R.D. Blackburn, "The Relationship Between First-Order Interaction Parameters and Oxide Solubilities in Liquid Iron", Trans. AIME, 1968, Vol. 242, pp. 2-5.

R. Reese, R.A. Rapp, and G.R. St.Pierre, "The Activities of Iron and Chromium in Fe-Cr Alloys", Trans. AIME, 1968, Vol. 242, pp. 1719-26.

A.J. Stone, H.W. Lownie, and G.R. St.Pierre, "Blast Furnace Limitations and Alternative Processes", Chapter XIX, Blast Furnace - Theory and Practice, Gordon and Breach, 1969, pp. 987- 1040.

G.R. St.Pierre, "Theory and Fundamentals of Ironmaking", Iron Ores and Ironmaking in the World, Battelle Memorial Institute, 1968, pp. IX-1-20.

S.W. Gilby and G.R. St.Pierre, "Equilibrium Vapor Compositions and Activities of Components for Fe-Cr-Ni Alloys at 1600 Degrees C", Trans. TMS-AIME. 1969, Vol. 245, pp. 1749-58.

A. Ghosh and G.R. St.Pierre, "Ternary Phase Diagrams for the Si- C-O System", Trans. TMS-AIME, 1969, Vol. 245, pp. 2106-8.

G.R. St.Pierre, "Kinetics of Gas Evolution From Molten Alloys", Electric Furnace Proceedings, 1969, Vol. 27, pp. 2-13.

J.P. Hirth, G.M. Pound, and G.R. St.Pierre, "Thermodynamics of Bubble Nucleation", Met. Trans., 1970, Vol. 1, pp. 939-45 and Met Trans., 1971, Vol. 2, pp. 616-17.

G.R. St.Pierre, "Method and Apparatus for Sulphur Dioxide Emission Control in Combustion Systems", United States Patent No. 3,690,808, Sept. 12, 1972. See News in Engineering (OSU), Nov. 1970, pp. 8-9 and Chemical Engineering, Jan. 11, 1970, p. 30.

S. Wagner and G.R. St.Pierre, "Thermodynamic Activities in the Ternary System Cr-Fe-Ni at 1600 Degree C by Mass Spectrometry", Advances in Mass Spectrometry, Vol 5, Institute of Petroleum, 1970, pp. 388-93. (Triennial Conf. on Mass Spectrometry- Brussells).

G.R. St.Pierre and C.W. Weidner, "Kinetics of Evolution of Compound Gases From Steels", Proceedings ICSTIS (Tokyo), Trans.Iron and Steel Inst., Japan, 1970, pp. 555-59.

G.R. St.Pierre, "Application of Thermodynamics to the Development of Collection Systems for the Control of Sulphur Dioxide Emissions-The Liquid Copper Scrubbing Process", Proceedings of the Western Resources Conference, (J.P. Mather, 1971), Colorado School of Mines, pp. 242-62.

S. Wagner, D.J. Shade, and G.R. St.Pierre, "Activities in Dilute Solutions of Chromium and Iron in Nickel at 1600 Decree C by Mass Spectrometry", Met. Trans., 1972, Vol. 3, pp. 47-50.

R.M. German and G.R. St.Pierre, "The High Temperature Thermodynamic Properties of Ni-Ti Alloys", Met Trans., 1972, Vol. 3, pp. 2819-23.

S. Wagner and G.R. St.Pierre, "Thermodynamics of the Liquid Binary Iron-Tin by Mass Spectrometry", Met. Trans., 1972, Vol. 3, pp. 2873-77.

S. Wagner and G.R. St.Pierre, "Thermodynamics of the Liquid Binary Iron-Titanium by Mass Spectrometry", Met Trans., 1974, Vol 5, pp. 887-9.

G.R. St.Pierre, "Thermodynamics of Solutions", Applications of Thermodynamics to Metallurgical Processes, AIME, 1975.

C.W. Weidner and G.R. St.Pierre, "The Thermodynamic Properties of the Liquid Cu-Al Binary."

J.M. McCormack and G.R. St.Pierre, "Thermodynamic Properties of Ni-Co Alloys."

G.R. St.Pierre, "Solubility Minima of Complex Compounds in Molten Alloys", Symposium on "Metal-Slag-Gas Reactions and Processes", The Electrochemical Society, 1975, pp. 81-6.

M. Arita and G.R. St.Pierre, "Vapor Compositions and Activities of Fe-Mn-Si Alloys", Met Trans., 1976.

G.R. St. Pierre, "The Solubility of Oxides in Molten Alloys", Met Trans., 1977, Vol. 8B, pp. 215-7.

A.B. Weaver, D.L. Johnson, and G.R. St.Pierre, "Thermodynamic Computation of Phase Equilibria in the Na-O-C System", Met Trans. A., 1977, Vol 8A, pp. 603-7.

M. Arita and G.R. St.Pierre, "Surface Dehomogenization of Binary Alloys During Evaporation and Ion Sputtering", Trans. Japan Inst. of Metals, 1977, Vol. 18, pp. 545-51.

M. Arita and G.R. St.Pierre, "Methods to Calculate Thermodynamic Partial Molar Quantities From Know Quantity of One Component in a Multicomponet Alloy", Trans. Japan Inst. of Metals, 1977, Vol. 18, No. 7, pp. 552-4.

M. Arita and G.R. St.Pierre, "Thermodynamic Activities in Fe-Mn Alloys at 1833K", Tetsu-tō-Hagane, 1978, Vol. 64, No. 2, pp. 206- 14.

G.R. St.Pierre, "Recommendations for Research and Development Programs on Water Treatment and Recycling Systems in Integrated Steel Plants", U.S.E.P.A., R.T.P., Oct. 1976.

G.R. St.Pierre, "A Necessary Surface Condition for Stability- Positive Divisibility", Scripta Met., 1978, Vol. 12, No. 4, pp. 383-8.

M. Arita and G.R. St.Pierre, "Activity Measurements in Liquid Fe- Mn-si Alloys at 1833 Degree K", Trans. J.I.S.I., 1979, Vol. 19, pp. 374-6.

A. Bronson and G.R. St.Pierre, "Determination of Sulphide Capacities in CaO-SiO_2 Slags Containing CaF_2 and B_2O_3 by an Encapsulation Method", Met Trans., 1979, pp. 375-80.

G.R. St.Pierre, C.E. Mobley, C.B. Shumaker, and D.W. Gusching, "Impacts of New Technologies and Energy/Raw Material Changes on the Steel Industry", Office of Technology Assessment, July, 1979.

G.R. St.Pierre, "Iron Metallurgy", Encyclopedia of Science and Technology, McGraw-Hill, 1982, pp. 375-8.

N. Kolesnik and G.R. St.Pierre, "Carbon Deposition on Reduced Iron Oxide", Met Trans., 1980, Vol. 11B, pp. 285-9.

G.R. St.Pierre and A. Bronson, "Steelmaking Slags", Electric Furnace Steelmaking, I.S.S.-AIME, 1982.

A. Bronson and G.R. St.Pierre, "The Sulphide Capacities of CaO- SiO2 Melts Containing MgO, FeO, TiO2, and Al2O3", Met Trans., 1981, Vol. 12B, pp. 729-31.

G.R St.Pierre and R.L. McKimpson, "Formation and Structure of Water-Formed Scales", Symposium on Iron and Steel Pollution Abatement Technology, Chicago, Oct., 1979.

G.R St. Pierre, "Iron and Steel", World Book Encyclopedia, 1982, pp. 346-62.

G.R. St.Pierre, "Iron Units for Steelmaking", Electric Furnace Conference, AIME, 1980-82 (Pittsburgh, Toronto, Chicago).

G.R. St.Pierre and C.B. Shumaker, "Strong Solute Activity Interactions in Liquid Alloys-A Statistical Mechanical Approach", Carl Wagner Comm. Symposium, AIME, 1981, pp. 137-52.

G.R. St.Pierre and C.B. Shumaker, "Solvation Shells for Interstitial Solutes in Alloys", Scripta Met., 1981, Vol. 15, pp. 571-6.

G.R. St.Pierre, "New Technologies for the Steel Industry", Chapter VI in Technology and Steel Industry Competitiveness, J.S. Hirschhorn, Office of Technology Assessment, June, 1980.

N.J. Kolesnik and G.R. St. Pierre, "Morphology of Carbon Deposits", U.S.S.R., 1981.

G.R. St.Pierre and E.J. Ray, "The Impact of Possible Legislation on Energy Use, Capital Investment and Employment in the U.S. Steel Industry", O.T.A., U.S. Congress, March 29, 1982.

G.R. St.Pierre, R.G. Hoagland, G. Meyrick, W.A.T. Clark, and P. Barron, "Use of Manganese in Steelmaking and Steel Products and Trends in the Use of Manganese as an Alloying Element in Steels", O.T.A., U.S. Congress, Sept. 29, 1982.

G.R. St.Pierre, "Kinetics of Limestone Calcination," Proceedings Extractive Metallurgy Laboratory Exercises, AIME, 1982, pp. 23- 33.

G.R. St.Pierre, "Desulphurization of Molten Iron by Slags", Proceedings of the Ext. Met. Lab. Exerc., AIME, 1982, pp. 101-5.

G.R. St.Pierre and A.H. Khan, "Control of Scale Formation in Water Recycle Systems", Symposium on Iron and Steel Pollution Abatement, Philadelphia, U.S.E.P.A. 1981, Dec. 1982, pp. 362-72.

G.R. St.Pierre, "Suitability of Blast Furnaces for Destruction of Hazardous Waste", Symposium Iron and Steel Pollution Abatement, Philadelphia, U.S.E.P.A., 1981, Dec. 1982, p. 280.

G.R. St.Pierre, "Iron Production", Encyclopedia of Materials Science and Engineering, Pergamon Press, 1983, pp. 2438-2443.

C.B. Shumaker and G.R. St.Pierre, "A Statistical Mechanics Description of Interstitial Solutes in Molten Alloys", in process.

G.R. St.Pierre, C.E. Mobley, C.B. Shumaker, L.T. Winkler, and J.D. Goins: "Improved Method for Refining Precious Metals", U.S. Patent No. 4,397,686, 1983.

A. Bronson and G.R. St.Pierre, "Electric Furnace Slags", Electric Furnace Steelmaking, C.R. Taylor, Editor, The Iron and Steel Society of AIME, 1985, pp 321-35.

G.R. St.Pierre and S.F. Protasio: "The Use of Metals and Metal Oxides for Sulfur Capture in Combustion Systems", Proceedings at the First International Conference on Processing and Utilization of High Sulfur Coals, Columbus, Ohio, Oct. 13-17, 1985, Edited by Y.A. Attia, pp. 467-84.

G.R. St.Pierre, M.I. Abbas, and C.E. Mobley: "Porosity in Binary and Ternary Aluminum Alloys", Trans. AFS, 1986, Vol. 86-11, pp. 47-56.

G.R. St.Pierre: "Review of Solute Enrichment at Interfaces Estimated by Statistical Thermodynamics", Proceedings at the Fall Meeting of the Japan Institute of Metals, Niigata City, Japan, October 4-6, 1985.

R.A. Rapp and G.R. St.Pierre: "New Options for the Protection of Carbon-Carbon Composites", High Temperature Composites Symposium, Dayton, Ohio, October 22, 1985.

G.R. St.Pierre: "The Influence of Sulfur and Inclusions on the Susceptibility of Low Alloy Steels to Hydrogen Cracking", Proceedings at the First Indo-US Workshop on Co-Operative Research on Iron and Steel Technology, January 6-9, 1987, Ranchi, India.

S. Protasio, L. DuVernay, and G.R. St.Pierre, "Effect of Sulfur Content and Inclusion Morphology on Hydrogen Flaking and Hydrogen Induced Cracking", Proceedings at the Fifth International Iron and Steel Congress, Washington, D.C., April 6-9, 1986, pp. 301-5.

K.H. Han, K.S. Goto, G.R. St.Pierre, H. Ono and K. Nagata, "Rate of Oxidation of Carbon Fiber/Carbon Matrix Composites with anti-Oxidation Treatments at High Temperature", Proceedings at the International Symposium on High Temperature Corrosion in Marseille, France, July 7-11, 1986.

K.S. Goto, K.H. Han, and G.R. St.Pierre, "A Review on Oxidation Kinetics of Carbon Fiber/Carbon Matrix Composites at High Temperature", Trans. of ISI-Japan, 1986, Vol. 26, No. 7, pp. 597-603.

G.R. St.Pierre: "Partial Pressures of Gas Species Generated at Metal Carbide - Metal Oxide and Metal Nitride - Metal Oxide Interfaces", Proceedings at the Gas-Solid Reactions in Pyrometallurgy Conference, Purdue University, West Lafayette, Indiana, April 24-25, 1986, edited by D.G.C. Robertson and H.Y. Sohn, pp. 321-336.

M.E. Watkins and G.R. St.Pierre, "Studies of Oxide Film Formation and Surface Tension Phenomena in Levitated Steel Droplets", Proceedings of The Reinhardt Schuhmann International Symposium, Colorado Springs, Colorado, November 9-12, 1986, pp. 691-708. (Edited by D.R. Gaskell et al.)

K.H. Han, H. Ono, K.S. Goto, and G.R. St.Pierre, "Rate of Oxidation of Carbon-Fiber-Carbon Matrix Composites with Antioxidation Treatment at High Temperature", Journal Electrochemical Society, 1987, Vol. 134, no. 4, pp 1003-9.

R.J. Fruehan, J.F. Elliott, and G.R. St.Pierre, Proceedings of New Steelmaking Technologies and The Role of NSF, Steelcon (Ed J.J. Bosley), June 5, (1987).

Section 10

Recent Presentations

DR. GEORGE R. ST.PIERRE

G.R. St.Pierre: "Review of Solute Enrichment at Interfaces Estimated by Statistical Thermodynamics". Presented at the Fall Meeting of the Japan Institute of Metals, Niigata City, Japan, October 4-6, 1985.

G.R. St.Pierre and S.F. Protasio: "The Use of Metals and Metal Oxides for Sulfur Capture in Combustion Systems". Presented at the First International Conference on Processing and Utilization of High Sulfur Coals, Columbus, Ohio October 13-17, 1985.

R.A. Rapp and G.R. St.Pierre: "New Options for the Protection of Carbon-Carbon Composites". Presented at the High Temperature Composites Symposium, Dayton, Ohio, October 22, 1985.

G.R. St.Pierre: "The Influence of Sulfur and Inclusions on the Susceptibility of Low Alloy Steels to Hydrogen Cracking". Presented at the First Indo-US Workshop on Co-Operative Research on Iron and Steel Technology, January 6-9, 1986, Rachi, India.

S. Protasio and G.R. St.Pierre: "The Influence of Inclusion Morphology in Hydrogen Related Problems in Low Sulfur Clean Steel". Presented at the Annual TMS-AIME Meeting, New Orleans, LA, March 2-6, 1986.

L. DuVernay and G.R. St.Pierre: "Effect of Sulfur Content on Hydrogen Embrittlement in Low Alloy Steel". Presented at the Annual TMS-AIME Meeting, New Orleans, LA, March 2-6, 1986.

M.E. Watkins and G.R. St.Pierre: "Thermodynamic Activities and Phase Equilibria in the CaO-TiO2 Binary Systems". Presented at the Annual TMS-AIME Meeting, New Orleans, LA, March 2-6, 1986.

G. Holcomb and G.R. St.Pierre: "Statistical Mechanics of Fused Salt Systems". Presented at the Annual TMS-AIME Meeting, New Orleans, LA, March 2-6, 1986.

S. Protasio, L. DuVernay, and G.R. St.Pierre: "Effect of Sulfur Content and Inclusion Morphology on Hydrogen Flaking and Hydrogen Induced Cracking". Presented at the Fifth International Iron and Steel Congress, Washington, D.C., April 6-9, 1986.

G.R. St.Pierre: "The Protection of Carbon-Carbon Composites Against High Temperature Oxidation". Amax Foundation Lectures in Chemical and Metallurgical Engineering. Presented in the Department of Chemical and Metallurgical Engineering, MacKay School of Mines, University of Nevada Reno, Reno, Nevada, April 18, 1986.

G.R. St.Pierre: "Partial Pressures of Gas Species Generated at Metal Carbide-Metal Oxide and Metal Nitride - Metal Interfaces". Presented at the Gas-Solid Reactions in Pyrometallurgy Conference, Purdue University, West Lafayette, Indiana, April 24- 25, 1986.

K.H. Han, K.S. Goto, G.R. St.Pierre, H. Ono and K. Nagata, "Rate of Oxidation of Carbon Fiber/Carbon Matrix Composites with Anti Oxidation Treatments at High Temperature". Presented at the International Symposium on High Temperature Corrosion in Marseille, France July 7-11, 1986.

K.S. Goto, K.H. Han, and G.R. St.Pierre: "A Review On Oxidation Kinetics of Carbon Fiber/Carbon Matrix Composites at High Temperature". Presented at the International Symposium on High Temperature Corrosion in Marseille, France July 7-11, 1986.

G.R. St.Pierre: "Failure Limiting Conditions for Coated Carbon/Carbon Composites in High Temperature". Presented at the Annual Meeting of TMS-AIME and ASM, Orlando, Florida, October 4- 9, 1986.

G.R. St.Pierre: "Partial Pressures of Gas Species Generated at Metal Carbide - Metal Oxide and Metal Nitride - Metal Oxide Interfaces," Proceedings of the Gas-Solid Reactions in Pyrometallurgy Conference, Purdue University, West Lafayette, Indiana, April 24-25, 1986, edited by D.G.C. Robertson and H.Y. Sohn, pp. 321-336.

M.E. Watkins and G.R. St.Pierre, "Studies of Oxide Film Formation and Surface Tension Phenomena in Levitated Steel Droplets," Presented at The Reinhardt Schuhmann International Symposium, Colorado Springs, Colorado, November 9-12, 1986, pp. 691-708. (Edited by D.R. Gaskett et al.) Dr. George R. St.Pierre

G.R. St.Pierre: "Net Shape Casting of Steels". Presented at NSF Workshop, Washington, D.C., April 14, 1987.

G.R. St.Pierre, G. Holcomb, J. Kwon, D. O'Connell, "Technical Presentation, No.8, Conversion Coatings", Presented at the AF Workshop on Oxidation-Resistant Carbon-Carbon Composites on Wednesday, October 21, 1987 in Dayton, Ohio.

G.R. St.Pierre: "Oxidation of Metal Carbides", Presented at the 117th TMS Annual Meeting and Joint TMS/SME Exhibit in Phoenix, Arizona, January 26, 1988.

G.R. St.Pierre: "Solute Interactions in Molten Alloys", Presented at the 117th TMS Annual Meeting and Joint TMS/SME Exhibit in Phoenix, Arizona, January 26, 1988.

G.R. St.Pierre: "Thermodynamics of Materials", Tutorial Lecture Series initiated by TMS at the 117th TMS Annual Meeting and Joint TMS/SME Exhibit in Phoenix, Arizona, January 27, 1988.

G.R. St.Pierre: "Sulfide Capacities in Oxide Melts", ISS-AIME International Meeting, Toronto, April, 1988.

Section 11

Recent Consulting Activities

DR. GEORGE R. ST.PIERRE

1987-Present	Libbey-Owens-Ford Toledo, Ohio	Development of thin films on glass applied by C.V.D.
1982-Present	Vought-LTV (Dallas)	Protection of carbon/carbon composites for aerospace and engine applications
1986-Present	U.S. Air Force	High-Temperature Materials
1986-Present	Universal Technologies	High-Temperature Materials
1986-87	Steelcon	Advanced Research in Steel Processing
1985-86	Airco Carbon	High-Temperature Intermetallic Compounds
1986-87	SOHIO	Non-Ferrous Metal Production Processes
1986-Present	Battelle	Electrolytic Protection of Carbon/Carbon Composites Against Oxidation
1985	Cummins Engines	Development of Bimetallic Elements

Other activities included helping companies select materials and processes for special applications.

Section 12

Principal Work Experience

DR. GEORGE R. ST.PIERRE

1988-Present	Presidential Professor and Chairman, OSU
1984-Present	The Ohio State University, Columbus, Ohio, Professor and Chairman Department of Metallurgical Engineering
1976(Summer)	U.S. Environmental Protection Agency, RTP,NC, I.P.A. Fellow
1975(6 mos.)	University of Newcastle, NSW, Australia, Visiting Professor
1972-75	The Ohio State University, Columbus, Ohio, Armco Professor
1964-Present	The Ohio State University, Columbus, Ohio, Professor
1964-66	The Ohio State University, Columbus, Ohio, Associate Dean, Graduate School (1/3 time)
1960-64	The Ohio State University, Columbus, Ohio, Associate Professor
1958(Summer)	U.S. Steel Corp., Monroeville, PA, Research Scientist
1957-60	The Ohio State University, Columbus, Ohio, Assistant Professor, Department of Metallurgical Engineering
1956-57	U.S. Air Force, Dayton, Ohio, Officer at Wright-Patterson AFB
1954-56	Inland Steel Company, E.Chicago, Indiana, Supervisor Research Metallurgist
1954-56	Purdue University, Hammond, Indiana, Part-time Instructor in Mathematics, Metallurgy
1951-54	Massachusetts Institute of Technology, Cambridge, MA, Graduate Fellow
1950(Summer)	U.S. Atomic Energy Commission, Cambridge, MA, Research Aide
1949(Summer)	Cushman Bakery Co., Boston, MA, Substitute Route Delivery and Sales
1948(Summer)	Cushman Bakery Co., Boston, MA, Substitute Route Delivery and Sales
1947(Summer)	YMCA, Manchester, NH, Senior Counselor, Half Moon Lake
1946(Summer)	Boston Boys' Clubs, Counselor, Bald Peak Caddy Camp, NH
1945(Summer)	Boston Boys' Clubs, Caddy, Bald Peak Caddy Camp, NH
1944(Summer)	Boston Boys' Clubs, Caddy, Bald Peak Caddy Camp, NH
1943(Summer)	Boston Boys' Clubs, Caddy, Oyster Harbors Caddy Camp, MA

RECENT BIOGRAPHICAL SUMMARY
(Special Form, 3 pages)

George R. St.Pierre
Presidential Professor and Chairman
Department of Metallurgical Engineering
The Ohio State University

George R. St.Pierre, born June 2, 1930, received his doctorate in June, 1954, from the Massachusetts Institute of Technology. His dissertation, completed under the direction of Professor John Chipman, included the determination of the sulfide and sulfate absorption capacities of oxide melts and the dissociation energies of diatomic sulfur and sulfur-monoxide. After a tour of duty at the Air Force Materials Laboratory and industrial research at the Inland Steel Company, he joined the faculty at The Ohio State University where he has been professor since 1964 and Chairman since January 1, 1984. Other recent associations include, serving as Visiting Professor at the University of Newcastle, Australia, in 1975 and as I.P.A. Fellow, U.S.E.P.A., during the summer of 1976. He was elected a Fellow of The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers in 1976, and a Fellow of the American Society for Metals in 1982. He has received several awards for his research and teaching, including the ASM Bradley Stoughton Outstanding Young Teacher Award in 1961, the Fontana (1967, 71, 75, 84) and MacQuigg (1971) Awards at OSU, the 1978 Alumni Association Distinguished Teacher Award, the Boyer Award in 1985, and the 1987 Mineral Industry Education Award of the AIME. He received the Gold Medal of ASM International in 1987. He was named Distinguished Scholar and Presidential Professor at OSU in 1988.

During the past thirty years, he has served on many University councils, professional society committees, government advisory panels and industrial consulting groups. He served as Associate Dean of the Graduate School during the period from 1964 to 1966. His teaching and research activities have been concentrated in the areas of extractive and process metallurgy; thermodynamics, kinetics, and statistical mechanics; and high-temperature science and technology of metallic, ceramic, and composite systems including coatings for carbon/carbon structural composites.

He has published over 125 papers as well as many technical reports for government and industry in connection with contract research, consulting, and committee assignments including reports for the Office of Technology Assessment, U.S. Congress and other government agencies.

In addition to his duties as Chairman of Metallurgical Engineering, he is Director of the Ohio Mineral Research Institute and he serves on the Technical Steering Committees of the NSF Engineering Research Center (OSU) on "Net Shape Manufacturing" and the Edison Materials Technology and Engineering Center (EMTEC, Dayton). He is a member of the Board of Directors of The Metallurgical and Materials Society and he chairs the Leadership and Practice Awards Committee and is a member of the Fellows Selection Committee. He is a member of the Joint Publications Commission for Metallurgical Transactions, the ASM Howe and Grossman Medal Selection Committee, and the University Materials Council.

Education: Sc.D., Metallurgy, Massachusetts Institution of Technology, 1954
S.B., Metallurgy, Massachusetts Institution of Technology, 1951

Areas of Professional Specialization: High-Temperature Materials and Processes, Oxidation of Carbon/Carbon Composites and Coatings, Physical Chemistry of Liquid Alloys, Intermetallic Compounds.

Recent Professional Appointments:

1988 - 1991	Director, The Metallurgical and Materials Society of AIME
1986 - present	Technical Steering Committee, Edison Materials Technology Center
1984 - present	Advisory Board for Materials Research Laboratory
1985 - present	Director, Ohio Mineral Research Institute
1986 - present	Technical Advisory Committee, OSU-ERC for Net Shape Manufacturing

Consultant: Vought-LTV (Dallas), U.S. Air Force, Universal Technologies, Libby-Owens-Ford, Steelcon, Airco Carbon, SOHIO, Battelle, Cummins Engines.

Professional Affiliations: Fellow, ASM International; Fellow, The Metallurgical and Materials Society of AIME; American Society for Composites; Materials Research Society; Alpha Sigma Mu; Sigma Xi; American Society for Engineering Education; Iron and Steel Society of AIME; Society of Mining Engineers of AIME; University Materials Council; Solid State Science Committee Forum, etc.

Honors Received: 1988 Distinguished Scholar Award, OSU; 1987 Gold Medal of ASM International; 1987 Mineral Industry Educator Award of AIME; Fellow ASM, 1982; Alumni Distinguished Teaching Award OSU, 1978; Fellow of the Metallurgical and Materials Society of AIME, (limited to 100 members) 1976; M.G. Fontana Teaching Award (OSU), 1984, 1975, 1971, 1967; MacQuigg Teaching Award (OSU), 1971; Boyer Award (OSU), 1985; Bradley Stoughton Outstanding Young Teacher Award of American Society for Metals, 1961; Fellow, American Institute of Chemists, 1969.

Scholarly Activities: Author of over 125 papers; presented more than 100 papers and invited lectures at technical meetings, conferences, and international symposia; supervised more than 30 Ph.D. Dissertations, and 30 M.S. Theses.

Employers	Work Performed	Rank or Title	Dates
Ohio State University Department of Metallurgical Eng.	Teaching/Research	Asst. Prof.	1957-60
		Assoc. Prof.	1960-64
		Professor	1964-88
		Assoc. Dean	1964-66
		Chairman	1984-88
U.S. Environmental Protection Agency	Research	I.P.A. Fellow	1976
Univ. of Newcastle, Australia	Teaching/Research	Visiting Prof.	1975
U.S.Air Force Materials Laboratory	Research and Development	Project Officer	1956-58
Inland Steel Co.	Research & Development	Supervisor	1954-56
Massachusetts Institute of Tech.	Research	Graduate Fellow	1951-54

Selected Recent Publications:

1. K.S. Goto, K.H. Han, and G.R. St.Pierre: "A Review of Oxidation Kinetics of Carbon Fiber/Carbon Matrix Composites at High-Temperatures", Trans ISI-Japan, 1986, Vol. 26, No. 7, pp. 597-603.

2. K.H. Han, K.S. Goto, G.R. St.Pierre, H. Ono, "Rate of Oxidation of Carbon Fiber/Carbon Matrix Composites with Anti-Oxidation Treatments at High Temperatures". J. Electrochem. Soc., 1987, Vol. 134, No. 4, pp. 1003-9.

3. G.R. St.Pierre, "Partial Pressures of Gas Species Generated at Metal Carbide - Metal Oxide and Metal Nitride - Metal Oxide Interfaces", Proceedings of Gas-Solid Reactions at the Pyrometallurgy Conference, Purdue University, West Lafayette, April, 1986, (edited by D.G.C. Robertson and H.Y. Sohn), pp. 321-336.

4. M.E. Watkins and G.R. St.Pierre, "Studies of Oxide Film Formation and Surface Tension Phenomena in Levitated Droplets", Proceedings of The Reinhardt Schuhmann International Symposium, Colorado Springs, November, 1986, (edited by D.R. Gaskell), pp. 691-708.

5. R.A. Rapp and G.R. St.Pierre, "New Options for the Protection of Carbon-Carbon Composites", High Temperature Composites Symposium, Dayton, October, 1985.

6. S. Protasio, L. DuVernay, and G.R. St.Pierre, "Effect of Sulfur Content and Inclusion Morphology on Hydrogen Flaking and Hydrogen Induced Cracking", Proceedings of the Fifth International Iron and Steel Congress, Washington, D.C., April, 1986, pp. 301-305.

7. N. Kolesnik and G.R. St.Pierre, "Carbon Deposition on Reduced Iron Oxide", Met. Trans., 1980, Vol. 11B, pp. 285-9.

8. G.R. St.Pierre and C.B. Shumaker, "Solvation Shells for Interstitial Solutes in Alloys", Scripta Met., 1981, Vol. 15, pp. 571-6.

9. A. Bronson and G.R. St.Pierre, "Electric Furnace Slags", Electric Furnace Steelmaking, C.R. Taylor, Editor, The Iron and Steel Society of AIME, 1985, pp. 321-35.

10. A. Bronson and G.R. St.Pierre, "Sulfide Capacities of $CaO-SiO_2$ Melts Containing MgO, FeO, TiO_2, and Al_2O_3", Met. Trans., 1981, Vol. 12B, pp. 729-31.

11. G.R. St.Pierre, M.I. Abbas, and C.E. Mobley, "Porosity in Binary and Ternary Aluminum Alloys", Trans. AFS, 1986, Vol. 86-11, pp. 47-56.

12. G.R. St.Pierre and S.F. Protasio, "The Use of Metals and Metal Oxides for Sulfur Capture in Combustion Systems", Proceedings of the First International Conference on Processing and Utilization of High Sulfur Coals, Columbus, October, 1985, (Edited by Y.A. Attia), pp. 467-84.

6/17/88

RECENT BIOGRAPHICAL SUMMARY
(Special Form, 2 pages)

George R. St.Pierre
Presidential Professor and Chairman
Department of Metallurgical Engineering
The Ohio State University

George R. St.Pierre, born June 2, 1930, received his doctorate in June, 1954, from the Massachusetts Institute of Technology. His dissertation, completed under the direction of Professor John Chipman, included the determination of the sulfide and sulfate absorption capacities of oxide melts and the dissociation energies of diatomic sulfur and sulfur-monoxide. After a tour of duty at the Air Force Materials Laboratory and industrial research at the Inland Steel Company, he joined the faculty at The Ohio State University where he has been Professor since 1964 and Chairman since January 1, 1984. Other recent associations include serving as Visiting Professor at the University of Newcastle, Australia, in 1975 and as I.P.A. Fellow, U.S.E.P.A., during the summer of 1976. He was elected a Fellow of The Metallurgical and Materials Society of the AIME in 1976, and a Fellow of the American Society for Materials in 1982. He has received several awards for his research and teaching including the ASM Bradley Stoughton Outstanding Young Teacher Award in 1961, the Fontana (1967, 71, 75, 84) and MacQuigg (1971) Awards at OSU, the 1978 Alumni Association Distinguished Teacher Award, the Boyer Award in 1985, and the 1987 Mineral Industry Education Award of the AIME. He received the Gold Medal of ASM International in 1987 and the OSU Distinguished Scholar Award in 1988. In 1988, he was appointed Presidential Professor.

He has served on many University councils, professional society committees, government advisory panels, and industrial consulting groups. He served as Associate Dean of the Graduate School during the period from 1964 to 1966. His teaching and research activities have been concentrated in the areas of chemical and process metallurgy; thermodynamics, kinetics, and statistical mechanics; and high-temperature science and technology of metallic, ceramic, and composite systems including coatings for carbon/carbon structural composites. He has published over 125 papers as well as many technical reports for government and industry in connection with contract research, consulting, and committee assignments including several reports for the Office of Technology Assessment, U.S. Congress. In addition to his duties as Chairman of Metallurgical Engineering, he is Director of the Ohio Mineral Research Institute and he serves on the Technical Steering Committees of the NSF Engineering Research Center (OSU) on "Net Shape Manufacturing" and the Edison Materials Technology and Engineering Center (EMTEC, Dayton). He is a member of the Board of Directors of The Metallurgical and Materials Society, he chairs the Leadership and Practice Awards Committee and is a member of the Fellows Selection Committee. He is a member of the Joint Publications Commission for Metallurgical Transactions, the ASM Howe and Grossman Medal Selection Committee, and the University Materials Council.

Recent Professional Appointments:

1988 - 1991	Director, The Metallurgical and Materials Society AIME
1986 - present	Technical Steering Committee, Edison Materials Technology Center
1985 - present	Director, Ohio Mineral Research Institute
1986 - present	Technical Advisory Committee, OSU-ERC for Net Shape Manufacturing
1984 - present	Advisory Board for Materials Research Laboratory

DR. GEORGE R. ST.PIERRE

Professional Affiliations: Fellow, ASM International; Fellow, The Metallurgical and Materials Society of AIME; American Soc. for Composites, Materials Research Society, Alpha Sigma Mu, Sigma Xi, American Soc. for Engineering Education, Iron and Steel Soc. of AIME, Soc. of Mining Engineers of AIME, University Materials Council, Solid State Science Forum.

Honors Received: 1988 Distinguished Scholar Award (OSU); 1987 Gold Medal of ASM International; 1987 Mineral Industry Educator Award of AIME; Fellow ASM, 1982; Alumni Distinguished Teaching Award OSU, 1978; Fellow of the Metallurgical and Materials Society of AIME, (limited to 100 members) 1976; M.G. Fontana Teaching Award (OSU), 1984, 1975, 1971, 1967; MacQuigg Teaching Award (OSU), 1971; Boyer Award (OSU), 1985; Bradley Stoughton Outstanding Young Teacher Award of American Society for Metals, 1961; Fellow, American Institute of Chemists, 1969.

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2. K.H. Han, K.S. Goto, G.R. St.Pierre, H. Ono, "Rate of Oxidation of Carbon Fiber/Carbon Matrix Composites with Anti-Oxidation Treatments at High Temperature". J. Electrochem. Soc., 1987, Vol. 134, No. 4, pp. 1003-9.

3. G.R. St.Pierre, "Partial Pressures of Gas Species Generated at Metal Carbide - Metal Oxide and Metal Nitride - Metal Oxide Interfaces", Proceedings of Gas-Solid Reactions in Pyrometallurgy Conference, Purdue University, West Lafayette, April, 1986, (edited by D.G.C. Robertson and H.Y. Sohn), pp. 321-336.

4. M.E. Watkins and G.R. St.Pierre, "Studies of Oxide Film Formation and Surface Tension Phenomena in Levitated Droplets", Proceedings of The Reinhardt Schuhmann International Symposium, Colorado Springs, November, 1986, (edited by D.R. Gaskell), pp. 691-708.

5. R.A. Rapp and G.R. St.Pierre, "New Options for the Protection of Carbon-Carbon Composites", High Temperature Composites Symposium, Dayton, October, 1985.

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7. N. Kolesnik and G.R. St.Pierre, "Carbon Deposition on Reduced Iron Oxide", Met. Trans., 1980, Vol. 118, pp. 285-9.

8. G.R. St.Pierre and C.B. Shumaker, "Solvation Shells for Interstitial Solutes in Alloys", Scripta Met., 1981, Vol. 15, pp. 571-6.

9. A. Bronson and G.R. St.Pierre, "Sulfide Capacities of Silicate Melts Containing Several Oxides", Met Trans., 1981, Vol. 12B, pp. 729-31.

10. G.R. St.Pierre, M.I. Abbas, and C.E. Mobley, "Porosity in Binary and Ternary Aluminum Alloys", Trans. AFS, 1986, Vol. 86-11, pp. 47-56.

NARRATIVE PROFESSIONAL RESUME OF ROBERT A. RAPP

Robert A. Rapp received his B.S. degree with honors in Metallurgical Engineering from Purdue University in 1956. He was the first recipient of the John Bray Award to the outstanding senior in Metall. Eng. During the summer of 1956 he worked on the brazing of stainless steels as a metallurgist with Westinghouse Corporation in Pittsburgh. In the fall of 1956 he entered graduate school as the Thompson Products (now TRW) Fellow in Metall. Eng. at Carnegie Institute of Technology (now CMU). During the summer of 1957 he worked as a metallurgist for Thompson Products Corp. in Cleveland. Rapp received the M.S. degree in Metall. Eng. in January 1958, and upon the submission of his thesis, "The Condensation of Ag, Cd, and Zn from the Vapor Phase", he completed his Ph.D. studies (August 1959). He was awarded a Fulbright Post-Doctoral Scholarship to study in Germany.

From September 1959 to August 1960, Dr. Rapp conducted post-doctoral research under Professor Carl Wagner at the Max Planck Institut fur Physikalische Chemie in Gottingen, West Germany. Upon returning to USA., he served on active military duty as First Lieutenant and Research Metallurgist in the Aerospace Research Laboratory at Wright-Patterson Air Force Base, Ohio. There he conducted research involving the high-temperature oxidation of metals and high-temperature electrochemical studies.

In September 1963, he joined the Dept. of Metallurgical Engineering at The Ohio State University as an Assistant Professor. His teaching is mostly concerned with the chemical, extractive, and high-temperature processes of metals. In 1966, he was promoted to Associate Professor and in 1969 to Professor. In 1967, Dr. Rapp received the Bradley Stoughton Young Teacher Award from the American Society for Metals. In 1969 and 1985 he was selected by the Ohio State students to receive the Mars G. Fontana Outstanding Teacher Award. In 1977, he received the Charles E. MacQuigg Teaching Award of the College of Engineering at OSU. He teaches the subject "High Temperature Corrosion" regularly for the AIChE Today Series and has authored a taped audio-lecture course (10 hrs) for the Amer. Chem. Soc. In 1987, he was named the Mars G. Fontana Professor of Metall. Eng. at OSU.

Besides numerous committee assignments in the AIME, ASM and ECS, Professor Rapp served for 3 years (1968-71) on an NASA Advisory Panel for Materials in Aircraft Engines. He served on three committees of the Materials Advisory Board of the National Academies of Science and Engineering: High-Temperature Corrosion of Superalloys in 1968-69, MAB Committee on Materials for Shipboard Waste Incinerators in 1977-78, and an MAB Committee on Secondary Batteries in 1978-80. He has served as Chairman for four conferences and reviews of the Department of Energy. From 1986-88, he is Chairman of the Corrosion Division of the Electrochemical Society and Director of Honors and Awards for the Metallurgical Society of AIME. He serves on the Editorial Boards for the journals Corrosion and Oxidation of Metals. In 1977, he was Chairman of the Gordon Conference on Corrosion. In 1981, he was Chairman of an NACE International Conference on High-Temperature Corrosion and edited the proceedings for publication.

In the academic year 1972-73, Professor Rapp was supported by a Guggenheim Fellowship to study and teach at the Ecole Nationale Superieure d'Electrochimie in Grenoble, France. In 1985-86, he received a Fulbright Grant to study and teach at the Ecole National Superieure de Chimie in Toulouse, France and at the Universite de Paris-Sud in Orsay, France. He is reasonably fluent in German and French. He translated from German into English the NACE text "Metallic Corrosion" by Kaesche. He has presented five plenary lectures at international meetings abroad. He was a member of two US-Japan seminar teams. In 1980 and 1982, he was a Visiting Lecturer at a dozen laboratories in People's Republic of China.

Professor Rapp has authored about 140 papers, mostly on the topics of high-temperature reactions of metals and high-temperature electrochemistry and corrosion. He had edited Vol. IV, parts 1 and 2 of Techniques of Metals Research. Dr. Rapp has authored three patents at OSU and a number of other patents in role of a consultant to industry.

Professor Rapp is presently serving as a consultant to a number of laboratories: GE, LTV, IGT, Air Products Corp., Lanxide, and Rasor Associates. He has coauthored several patents with industrial laboratories. Dr. Rapp is a professional engineer of the State of Ohio. His research has been principally sponsored by the National Science Foundation, Department of Energy, and Electric Power Research Institute.

In October 1974, Dr. Rapp (along with A. Ezis and G. Yurek) received the 1974 Henry Marion Howe Medal from The American Society for Metals for the paper entitled, "Displacement Reactions in the Solid State," which was chosen as the paper of highest merit published in Metallurgical Transactions in 1973. In 1980, he was selected as a Fellow in the American Society for Metals. In 1982, he was named a Fellow of the Metallurgical Society of the AIME. In 1982, he was named a Distinguished Senior Research Scholar by The Ohio State University, and in 1984, he received the research award of the College of Engineering at OSU. He presented the 1983 ASM Edward DeMille Campbell Memorial Lecture. In 1986, he received the Willis Rodney Whitney Award of the Nat. Assoc. Corr. Eng'rs.

In September 1988, Dr. Rapp served as Visiting Professor to the Department of Chemical Engineering and Industrial Chemistry, University of New South Wales, Kensington, N.S.W., Australia. In April 1988, Professor Rapp received a Distinguished Engineering Alumnus Award from Purdue University. In September 1988, he will be inducted into the National Academy for Engineering. In September 1987, Dr. Rapp was named the Mars G. Fontana Professor of Metallurgical Engineering.

BIOGRAPHICAL INFORMATION

ROBERT A. RAPP

EDUCATION

Ph.D. Met. Eng., Carnegie Institute of Technology, June 1960.
M.S. Met. Eng., Carnegie Institute of Technology, January 1959.
B.S. Met. Eng., Purdue University, June 1956.

EMPLOYMENT HISTORY

1987 -	Mars G. Fontana Professor of Metall. Eng., The Ohio State Univ. Visiting Professor, Univ. New South Wales, Australia
1969 - 87	Professor, Dept. Metall. Eng., The Ohio State Univ.
1985 - 86	Visiting Professor, Ecole Nat. Sup. de Chimie, Toulouse, FR Visiting Professor, Univ. Paris-Sud, Orsay, France
1972 - 73	Visiting Professor, Ecole Nat. Sup. d'Electrochimie, Grenoble, France.
1966 - 69	Assoc. Prof., Dept. Metall. Eng., The Ohio State Univ.
1963 - 66	Assist. Prof., Dept. Metall. Eng., The Ohio State Univ.
1960 - 63	Wright-Patterson Air Force Base, U.S.A.F., Res. Metall.
1959 - 60	Max Planck Inst. fur Physik. Chem., Goettingen, Germany, Fulbright Scholar.

INDUSTRIAL EXPERIENCE:

Westinghouse Electric Company, Summer 1956, Metallurgist.
Thompson Products Company, Summer 1957, Metallurgist.
Lawrence Livermore Laboratory, Summer 1974, Research Metallurgist

CONSULTING ACTIVITIES:

Currently consultant to Vought Corporation, IGT, General Electric Co., Razor Assoc., Air Products Corp., and Lanxide.

RESEARCH INTERESTS:

High temperature materials, corrosion, extractive metallurgy, electrochemistry, thermodynamics and kinetics.

SOCIETAL ACTIVITIES:

American Society for Metals, American Inst. Metall. Engrs., Electrochemical Society, Nat. Assoc. Corrosion Engrs., active in local chapter and national activities.

COMMITTEE SERVICE:

Amer. Inst. Metall. Engrs.

Physical Chemistry of Extractive Metallurgy Committee of AIME, (1964-66, Chairman 1966).

Iron and Steel Division Publications Committee, TMS-AIME, (1965-67, Chairman 1967).

Chairman, Papers and Programs Committee of Extractive Metallurgy Division of AIME (1969-70).

TMS-AIME Honors and Awards Committee (1981-), Chairman (1986-)

TMS-AIME Board of Directors (1986-)

American Society for Metals

ASM Bradley Stoughton Young Teachers Award Committee, (1973-75, Chairman, 1975).

ASM Materials Science Division, Executive Committee, (1978-80).

ASM Fellows Selection Committee (1982-84).

ASM Campbell Memorial Lecture Committee (1986-).

Electrochemical Society

ECS Summer Fellowship Award Committee (1970-72).

ECS Honors and Awards Committee, (1978-83) Chairman, Carl Wagner Award Subcommittee.

Executive Committee, Corrosion Division, Electrochemical Society 1978-. Sec.-Treas. 1980-82; Vice-Chairman 1982-86; Chairman 1986-.

Nominations Committee 1984.

National Materials Advisory Board

NMAB Committee on the High-Temperature Corrosion of Superalloys (1968-69).

NMAB Committee on Materials for Shipboard Waste Incinerators (1977-78).

NMAB Committee on Secondary Batteries (1978-80).

Other

NASA Advisory Panel on Materials for Aircraft Engines (1968-71).

Ohio State University College of Engineering, Committee on Engineering Instruction (1965-68). Honors and Awards Committee (1981-85).

OSU Department of Metallurgical Engineering, Graduate Studies Committee Chairman (1980-84).

EDITORIAL SERVICE:

International Editorial Advisory Board of the journal Oxidation of Metals.

Member, Board of Review, Metallurgical Transactions 1964 - 77.

Member, Board of Review, Corrosion-NACE, 1984 -

Editor, Journal Electrochemical Society, High Temperature Materials Div., 1978 - 1984.

Reviewer for many other journals.

MEETINGS:

Chairman, Gordon Conference on Corrosion, 1977.

Chairman, NACE Internat. Conf. on High-Temperature Corrosion, 1981.

Advisory Comm., Internat. Conf. on Solid-State Electro- chemistry, Tokyo, 1980.

Advisory Comm., JIM Internat. Conf. on High-Temperature Corrosion, Tokyo 1982.

Member, U.S.-Japan Seminar on Chemical Kinetics in Pyrometallurgy, MIT, 1976.

Member, U.S.-Japan Seminar on Defects and Diffusion in Solids, Tokyo, 1976, and Honolulu, 1979.

Advisory Comm., Internat. Sympos. High Temperature Corrosion, Marseille, 1986.

Member, DECHEMA Internat. Conf. High Temperature Corrosion, Bonn, 1985.

Co-Chairman, NATO Advanced Study Institute, Thermochemistry of Alloys, Keil. W. Germany 1987

OTHER:

Visiting Lecturer, People's Republic of China, 1980 and 1982.

Plenary Lecturer, 30th Meeting Internat. Soc. Electrochemistry, Trondheim, 1979.

Plenary Lecturer, Internat. Conf. Solid-State Electrochemistry, Tokyo, 1980.

Plenary Lecturer, JIM Internat. Conf. High-Temperature Corrosion, Tokyo, 1982.

Plenary Lecturer, 10th International Symposium on the Reactivity of Solids, Dijon, 1984.

Plenary Lecturer, International Symposium on High Temperature Corrosion, Marseille, 1986.

Plenary Lecturer, NATO Advanced Study Institute on Thermochemistry of Alloys, Kiel, W. Germany 1987.

Plenary Lecturer, Terkel Rosenqvist Symposium, Trondheim, Norway, 1988.

Plenary Lecturer, Materials Research Society International Meeting on Advanced Materials, Tokyo, Japan, 1988.

AWARDS:

John Bray Award, Purdue University 1956

Post-doctorate Fulbright Scholarship 1959, Max Planck Inst. Physical Chemistry, Goettingen, Germany

Tau Beta Pi, Sigma Xi

ASM Bradley Stoughton Young Teacher Award, 1967

Mars G. Fontana Outstanding Teacher of the Year Award, 1968-69, 1984-85

Guggenheim Fellowship, Ecole Nat. Sup. d'Electrochimie, Grenoble, France 1972-73

Henry Marion Howe Medal, Amer. Soc. Metals, (Best paper in Metall. Trans.) 1973

MacQuigg Teaching Award, College of Engineering, OSU, 1977

Fellow, Amer. Soc. Metals, 1980

Fellow, Met. Soc., Amer. Inst. Metall. Eng'rs, 1982

Edward DeMille Campbell Memorial Lecturer, ASM, 1983

Distinguished Research Award (Senior Research Scholar), The Ohio State University, 1982

Outstanding Research Award, College of Engineering, The Ohio State University, 1984

Fulbright Travel Grant, Ecole Nat. Sup. de Chimie, Toulouse, France, 1985-86.

Willis Rodney Whitney Award of Nat. Assoc. Corr. Eng'rs., 1986.

Citation Classic for paper by J. W. Patterson, E. C. Bogren and R. A. Rapp, J. Electrochem. Soc., 114, (1967) 752.

Mars G. Fontana Professor, September 1987.

Distinguished Engineering Alumnus, Purdue University, 1988.

National Academy of Engineering, 1988.

LANGUAGES:

Fluent in French and German.
Translation of textbook, "Korrosion der Metallen" by Kaesche for NACE.

PUBLICATIONS AND PATENTS:

Over 140 publications and 8 patents. Editor of two books. Author of corrosion courses for AIChE and ACS. List attached.

PATENTS:

R.A. Rapp and D.F. Frank, U.S. Patent No. 3,379,579 - April 23, 1968, "Process of Forming Passivating Internal In_2O_3 Band in Ag-In Alloy."

R.A. Rapp, U.S. Patent 3,699,032 - October 17, 1972, "Devices for the Control of Agents in Fluids."

R.A. Rapp, with W.M. Boorstein, K.E. Oberg and L. Friedman, U.S. Patent 3,878,073 - April 15, 1975, "Oxygen Exchange with Liquid Metals."

R.A. Rapp, with C.Y. Yang, U.S. Patent No. 4,392,928 - July 12, 1983, "Method of Doping a Semiconductor," Brookhaven Lab.

R.A. Rapp, with S.P. Ray, U.S. Patent No. 4,455,211 - June 19, 1984, "Composition Suitable for Inert Electrode," ALCOA.

R.A. Rapp, with S.C. Byrne and P. Ray, U.S. Patent 4,468,299 - August 28, 1984, "Friction Welded Nonconsumable Electrode and Use Thereof for Electrolytic Production of Metals and Silicon," ALCOA.

R.A. Rapp, with S.P. Ray, U.S. Patent No. 4,584,172 - April 22, 1986, "Method of Making Composition Suitable for Use as Inert Electrode Having Good Electrical Conductivity and Mechanical Properties," ALCOA.

R.A. Rapp and C.E. Mobley, U.S. Patent No. 4,657,067 - April 14, 1987, "Hypereutectic Direct-Contact thermal Storage Material and Method of Production Thereof."

CURRENT RESEARCH PROJECTS OF ROBERT A. RAPP:

U.S. Bureau of Mines, "Electrochemical Factors in Fused Salt Enhanced Carbothermic Reduction," (Co-Principal Investigator with G. R. St. Pierre, Y. Sahai and W. B. Johnson) 10/1/87 - 9/30/88, $60,063.

U.S. Forest Service, "High Temperature Wear Mechanisms of Tool Materials in Wood Machining", 10/1/86 - 9/30/88, $105,000.00.

U.S. Office of Naval Research. "Exploratory Research on the Protection of Carbon-Carbon Composites Against Oxidation at Very High Temperatures ($\geq 3000^{o}$F) with Engel-Brewer and Other Intermetallic Compounds." (Co-Principal Investigator with G.R. St.Pierre and J.P. Hirth) 11/1/86 - 10/31/87, $100,000.

U.S. Office of Naval Research, "Pack Cementation Coating of Ni-Base and Co-Base Alloys to Combat Low Temperature Hot Corrosion", 10/1/86 - 9/30/89, $296,618.

National Science Foundation, "Chemistry and Electrochemistry of Hot Corrosion of Metals", 8/1/87 - 7/31/88, $117,400.

Edison Materials Technology Center (EMTEC), "Fabrication of Superconductor Materials", 1/4/88 - 1/4/89, $40,000.

Martin Marietta Corp. (Department of Energy (ORNL), "Pack Cementation Coating of Iron-Base Alloys", 11/1/87 - 11/30/88, $119,466.

PUBLICATIONS - R.A. Rapp

1. R.W. Armstrong and R.A. Rapp, "Simple Etching Cutter", Rev. Sci. Inst. 29 (1958), 433.
2. R.A. Rapp, "New Techniques in the Attainment of High Vacua", Rev. Sci. Inst. 30, (1959) 839.
3. R.A. Rapp, J.P. Hirth, and G.M. Pound, "On the Condensation Coefficient in the Growth of Silver from the Vapor Phase", Can.J. Phys. 38, (1960) 709.
4. R.A. Rapp, J.P. Hirth, and G.M. Pound, "Condensation in the Growth of Cadmium and Zinc from the Vapor", J. Chem. Phys. 34, (1961) 184.
5. R.A. Rapp, "The Transition from Internal to External Oxidation and the Formation of Interruption Bands in Silver-Indium Alloys", Acta Metallurgica 9, (1961) 730.
6. R.A. Rapp and F. Maak, "Thermodynamic Properties of Solid Copper-Nickel Alloys", Acta Metallurgica 10, (1962) 63.
7. J.W. Armitage and R.A. Rapp, "A Mathematical Derivation of a Temperature-Time Program for the Passivation of Silver Alloys", Review, Society of Industrial and Applied Mathematics 5, (1953) 67.
8. R.A. Rapp, "Free Energy of Formation of Molybdenum Dioxide", Trans. Met. Soc. AIME, 227, (1963) 371.
9. R.A. Rapp, D.F. Frank, and J.V. Armitage, "The Formation of Passivating Internal In_2O_3 Bands in Silver-Indium Alloys", Acta Metallurgica 12, (1964) 505.
10. J. Verfurth and R.A. Rapp, "The Diffusivity and Solubility of Oxygen in Silver and Copper", Trans. Met. Soc. AIME 230, (1964) 1310.
11. R.A. Rapp, "Kinetics, Microstructures, and Mechanism of Internal Oxidation - Its Effect and Prevention in High Temperature Alloy Oxidation", Corrosion 21, (1965) 382.
12. M.K. Lasker and R.A. Rapp, "Mixed Conduction in ThO_2-Y_2O_3 Solid Solutions", Zeitschrift fur Physikalische Chemie 49, (1966) 198.
13. R.A. Rapp and H.D. Colson, "The Kinetics of Simultaneous Internal Oxidation and External Scale Formation for Binary Alloys, Trans. Met. Soc. AIME, 236, (1966) 1616.
14. R.A. Rapp and G.N. Goldberg, "The Oxidation of Cb-Zr and Cb-Zr-Re Alloys in Oxygen at 1000°C, Trans. Met. Soc. AIME, 236, (1966) 1619.
15. R.A. Rapp, "The Oxidation of Metals Containing Dispersed Oxide Particles", Proceedings of Second Bolton Landing Conference on Oxide Dispersion Strengthening, AIME Publ. Vol. 17, (1968) 539.

16. J.W. Patterson, E.C. Bogren and R.A. Rapp, "Mixed Conduction in $Zr_{0.85}Ca_{0.15}O_{1.85}$ and $Th_{0.85}Y_{0.15}O_{1.925}$ Solid Electrolytes", J. Electrochem. Soc. 114, (1967) 752; Citation "classic".

17. J.A. Roberson and R.A. Rapp "The Observation of Markers during the Oxidation of Columbium", Trans. Met. Soc. AIME 239, (1967) 1527.

18. R.A. Rapp, "Mixed Conduction in Solid Oxide Electrolytes", Thermodynamics of Nuclear Materials, Vienna Intern. Atomic Energy Agency, (1967) 599.

19. R.A. Rapp, Associate Editor, Techniques in Metals Research Vol. IV: Physical-Chemical Measurements in Metals Research, parts 1 and 2, Wiley Publ. New York, (1970).

20. R.A. Rapp and D.A. Shores, "Solid Electrolyte Galvanic Cells", Techniques of Metals Research, Vol. IV, part 2, Ed. R.A. Rapp, Wiley Publ. (1970).

21. R. Reese, R.A. Rapp and G.R. St.Pierre, "Chemical Activities of Iron and Chromium in Binary Fe-Cr Alloys", Trans. Met. Soc. AIME 242, (1968) 1719.

22. J.A. Roberson and R.A. Rapp, "Electrical Properties of NbO and NbO_2", J. Phys. Chem. Solids 30, (1969) 1119.

23. Y.D. Tretyakov and R.A. Rapp, "Nonstoichiometry and Defect Structures in Pure Nickel Oxide and Lithium Ferrite", Trans. Met. Soc. AIME 245, (1969) 1235.

24. R.L. Pastorek and R.A. Rapp, "The Solubility and Diffusivity of Oxygen in Copper", Trans. Met. Soc. AIME 245, (1969) 1711.

25. C.E. Polson, D.G. Kesterke, T.R. Kato, J.H. Trapp, and R.A. Rapp, "A Conceptual Cell for Electrowinning Liquid Uranium", Electrometallurgy, AIME, (1968), 122.

26. R.A. Rapp, "The Reaction of Metals and Alloys with Gases at Elevated Temperatures", Proceedings of 34th Meeting of AGARD Propulsion and Energetics Panel, (1969).

27. D.A. Shores and R.A. Rapp, "Solid Bielectrolyte Cells for Thermodynamic Measurements", J. Electrochem. Soc. 118, (1971) 1107.

28. G.H. Meier and R.A. Rapp, "Electrical Conductivities and Defect Structures of Pure NiO and Chromium-Doped NiO", Zeitschrift fur Physikalische Chemie 54, (1971) 168.

29. D.A. Shores and R.A. Rapp, "Hydrogen Ion (Proton) Conduction in Thoria-Base Solid Electrolytes", J. Electrochem. Soc. 119, (1972) 300.

30. G.E. Wasielewski and R.A. Rapp, "The High-Temperature Oxidation of Superalloys", Ch. 10 in Superalloys, Eds. C.T. Sims and W.C. Hagel, Wiley Publ. (1972), 287.

31. K.E. Oberg, L.M. Friedman, R. Szwarc, W.M. Boorstein and R.A. Rapp, "Diffusivity of Oxygen in Liquid Iron from Electrochemical Measurements", J. Iron and Steel Inst., May, (1972) 359.

32. R. Szwarc, K.E. Oberg and R.A. Rapp, "The Diffusivity and Solubility of Oxygen in Liquid Lead from Electrochemical Measurements", High Temp. Sci. 4, (1972) 347.

33. R.A. Ramanarayanan and R.A. Rapp, "The Diffusivity and Solubility of Oxygen in Liquid Tin and Solid Silver and the Diffusivity of Oxygen in Solid Nickel", Metall. Trans. 3, (1972) 3239.

34. R.A. Rapp, "Vaporization Losses from Cr_2O_3 Protective Scales", AGARD (NATO) Conference on High-Temperature Corrosion of Structural Materials", Copenhagen (1972).

35. D.W. Short, R.A. Rapp and J.P. Hirth, "Influence of Surface Charge and Surface Structure on the Sublimation of Ionic Crystals", J. Chem. Phys. 57, (1972) 1381.

36. L. Friedman, K. Oberg, W.M. Boorstein and R.A. Rapp, "Electronic Conductivities of Commercial ZrO_2 + 3 wt Pct CaO Electrolytes", Metall. Trans. 4, (1973) 69.

37. K. Oberg, L. Friedman, W.M. Boorstein and R.A. Rapp, "The Diffusivity and Solubility of Oxygen in Liquid Copper and Liquid Silver from Electrochemical Measurements", Metall. Trans. 4, (1973) 61.

38. K.E. Oberg, L.M. Friedman, W.M. Boorstein and R.A. Rapp, "Electrochemical Deoxidation of Induction-Stirred Copper Melts", Metall. Trans., 4 (1975), 75.

39. R. Perkins and R.A. Rapp, "The Concentration-Dependent Diffusion of Chromium in Nickel Oxide", Metall. Trans. 4, (1973) 193.

40. R.A. Rapp, A. Ezis and G.J. Yurek, "Displacement Reactions in the Solid-State", Metall. Trans. 4, (1973) 1283, (ASM Howe Award for Best Paper).

41. G. Yurek, R.A. Rapp and J.P. Hirth, "Kinetics of Displacement Reaction Between Iron and Cu_2O", Metall. Trans. 4, (1973) 1293.

42. Y. Agrawal, D.W. Short, R. Gruenke and R.A. Rapp, "The Control of Oxygen Activities in Argon-Oxygen Mixtures by Coulometric Titration", J. Electrochem. Soc. 121, (1974) 354.

43. G. Yurek, R.A. Rapp and J.P. Hirth, "The Formation of Two-Phase, Layered Scales on Pure Metals", Oxid. Metals, 8, (1974), 265.

44. G.J. Yurek, R.A. Rapp and J.P. Hirth, "Kinetics of the Displacement Reaction Between Fe and Cu_2O at Temperatures Between 800-1500°C, Met. Trans. 10A, (1974) 1473.

45. S. Espevik, P.L. Daniel, R.A. Rapp, and J.P. Hirth, "The Oxidation of Ni-Cr-W Ternary Alloys", Oxid. Metals, 14, (1980), 85.

46. P.L. Daniel and R.A. Rapp, "The Halogenation of Metals and Alloys", Advances in Corrosion Science and Technology, Eds. R.W. Staehle and M.G. Fontana, Pergamon Press, N.Y. (1974).

47. R.A. Rapp, "High-Temperature Gaseous Corrosion of Metals in Mixed Environments:", NSF Workshop on Materials Problems in Coal Conversion, April, 1974, Columbus, Ohio.

48. R.R. Odle and R.A. Rapp, "Electrochemical Studies and Processes Involving Oxygen in Liquid Metals", Metal-Slag-Gas Reactions and Processes, Eds. Electrochem. Soc., (1975), 851.

49. J.E. McVicker, R.A. Rapp and J.P. Hirth, "The Sublimation of Basal Surfaces of Zinc Oxide", J. Chem. Phys. 63, (1975) 2646.

50. R.A. Rapp and R.W. Staehle, "Fundamentals of Corrosion", Short Course in Today Series of Amer. Inst. Chem. Engrs. (1969).

51. R.A. Rapp, "High-Temperature Corrosion", Audio-Lecture Course of American Chemical Society, (1981).

52. R.R. Odle and R.A. Rapp, "Further Study of the Electrochemical Deoxidation of Induction-Stirred Copper Melts", Metall. Trans. 8B, (1977) 581.

53. S.R. Shatynski, J.P. Hirth, and R.A. Rapp, "A Theory of Multiphase Binary Diffusion", Acta Met. 24 (1976), 1071.

54. J.P. Hirth and R.A. Rapp, "The Diffusional Growth of a Scale with Variable Composition, Diffusivity, and Molar Volume", Oxid. Metals 11, (1977) 57.

55. R.A. Rapp, "General Kinetic Aspects in the High-Temperature Oxidation of Metals", High-Temperature Alloys, Eds. Z.A. Foroulis and F.S. Pettit, Electrochem. Soc., (1976), 77.

56. G. Garnaud and R.A. Rapp, "The Growth of Two-Phase, Layered Scales in the Oxidation of Iron," Oxid. Metals, 11, (1977) 193.

57. W.C. Fang and R.A. Rapp, "Electrical Conductivity of Pure α-PbF$_2$," J. Electrochem. Soc. 125, (1978) 683.

58. S.N. Reddy and R.A. Rapp, "Electronic Conductivity of CaF$_2$, Metal-Halide Reactions, D. Cubicciotti, Ed., Electrochem. Soc., (1977), 401.

59. S.F. Chou and R.A. Rapp, "Dual Ionic Conductivity in Solid Electrolytes CaF$_2$ and CaO-Stabilized ZrO$_2$", Metal-Halide Reactions, D. Cubicciotti, Ed., Electrochem. Soc., (1977),392.

60. W.C. Fang and R.A. Rapp, "The Electrical Conductivity of α-PbF$_2$", Metal-Halide Reactions, D. Cubicciotti, Ed., Electrochem. Soc., (1977), 413.

61. W.P. Stroud and R.A. Rapp, "The Solubilities of Cr_2O_3 and α-Al_2O_3 in Fused Na_2SO_4 at 1200 K", Metal-Halide Reactions, D. Cubicciotti, Ed., Electrochem. Soc. (1977) 574.

62. R.A. Rapp, "Materials Selection and Problems for Molten Carbonate Fuel Cells", DOE-EPRI Workshop on High-Temperature Fuel Cells, Oct. 30 - Nov. 1, (1978).

63. S.N.S. Reddy and R.A. Rapp, "The Solubility and Diffusivity of Fluorine in Solid Copper from Electrochemical Measurements", Metall. Trans. 9B, (1978) 559.

64. R.A. Rapp and K.S. Goto, "The Hot Corrosion of Metals by Molten Salts," Molten Salts II, R. Selman and J. Braunstein, Eds., Electrochem. Soc., (1979).

65. G.W. Watt, R.E. Andresen and R.A. Rapp, "A Comparison of Reference Electrodes in Molten Sodium Sulfate", Molten Salts II, R. Selman and J. Braunstein, Eds., Electrochem. Soc., Princeton (1979).

66. S.N.S. Reddy and R.A. Rapp, "The Diffusivity and Solubility of Fluorine in Solid Nickel from Electrochemical Measurements", Metall. Trans. 11B, (1980) 99.

67. S.N.S. Reddy and R.A. Rapp, "Electronic Conduction in the BaF_2 Solid Electrolyte", J. Electrochem. Soc. 126, (1979) 2023.

68. R.A. Rapp, "Professor Carl Wagner-In Memorial", Corrosion 34, (1978), 219.

69. R.A. Rapp, "The Maturing of High Temperature Corrosion Research", Corrosion, 34, Aug. (1978).

70. S.R. Shatynski, J.P. Hirth and R.A. Rapp, "Solid-State Displacement Reactions Between Selected Metals and Sulfides", Metall. Trans. 10A, (1979) 591.

71. M. Kawakami, K.S. Goto, R.A. Rapp and F. Kajiyama, "Mechanism of Accelerated Oxidation of Heat-Resistant Superalloys Induced by Molten Salt Deposition", J. Iron and Steel Inst. Japan 65, (1979) 811.

72. R.A. Rapp, "The Hot Corrosion of Metals: Theory and Experiment", Proceedings of Fourth Navy Conference on Gas Turbine Materials in the Marine Environments, Annapolis, MD, June (1979).

73. S.N.S. Reddy and R.A. Rapp, "Internal Fluoridation of Ni-5.6% Cr Alloy", Met. Trans. 11B, (1980) 534.

74. D.S. Williams, R.A. Rapp and J.P. Hirth, "Multilayer Diffusional Growth in Silver-Zinc Alloys", Met. Trans. 12A, (1981) 639.

75. D.K. Gupta and R.A. Rapp, "The Solubilities of NiO, Co_3O_4, and Ternary Oxides in Fused Na_2SO_4 at 1200K", J. Electrochem. Soc. 127, (1980) 2194; ibid 2656.

76. J.A. Colwell and R.A. Rapp, "Reactions of Fe-Cr and Ni-Cr Alloys in CO/CO_2 Gases at 850 and 950°C", Metall. Trans. 17A, (1986) 1065.

77. S.N.S. Reddy and R.A. Rapp, "Dissolution and Diffusion of Fluorine in Metals", Proceedings of International Conference on High Temperature Corrosion, Ed. R.A. Rapp, NACE (1980).

78. R.A. Rapp, Editor, Proceedings of International Conference on High Temperature Corrosion, NACE (1981).

79. S.K. Verma, G.M. Raynaud and R.A. Rapp, "Hot-Stage SEM for High-Temperature In-Situ Oxidation Studies", Oxid. Metals 15, (1981) 471.

80. S.K. Verma, G.M Raynaud and R.A. Rapp, "In-Situ Oxidation Studies of Pure Copper, Nickel and Iron", Proceedings of Carl Wagner Symposium, N.A. Gokcen, Ed., AIME, (1981).

81. M. Kawakami, K.S. Goto and R.A. Rapp, "Accelerated Hot Corrosion of Alloys by Molten-Salts", Trans. Iron and Steel Inst. Japan 20, (1980) 646.

82. R.A. Rapp, J.H. Devan, D.L. Douglass, P.C. Nordine, F.S. Pettit and D.P. Whittle, "High-Temperature Corrosion in Energy Systems", Materials Science and Engineering, 50, (1981).

83. C. Tangchitvittaya, J.P. Hirth and R.A. Rapp, "Solid-State Displacement Reaction Between Iron and Nickel Oxide at 1000°C, Metall. Trans. 13A, (1982) 585.

84. Y.K. Li and R.A. Rapp, "Oxidation-Sulfidation Behavior of Iron-Chromium Alloys Beneath a Porous Inert Solid Deposit", High-Temperature Materials Chemistry, Eds., D. Cubicciotti, D.L. Hildenbrand and K. Nateson, Electrochem. Soc., (1981).

85. W.C. Fang, B.P. Miglin and R.A. Rapp, "Hot Corrosion/Fouling of Metals Beneath Surface Deposits", Corrosion-Erosion-Wear of Materials in Emerging Fossil Energy Systems, A. Levy and P. Daniel, Eds., NACE, (1982).

86. J.P. Sauer, R.A. Rapp and J.P. Hirth, "Oxidation of Iron-Manganese-Aluminum Alloys at 850° and 1000°C", Oxid. Metals 18, (1982) 285.

87. S.F. Chou and R.A. Rapp, "Electrochemical Studies of Dopant Redoxing and Diffusion at the Pt, $O_2|CaF_2$ Interface", J. Electrochem. Soc. 130, (1983) 506.

88. R.A. Rapp, "Electrochemistry of Hot Corrosion," Proceedings of Third Japanese International Symposium on High Temperature Corrosion of Metals and Alloys, R. Tanaka, Chairman, Nov. 18-20, 1982; Supplement to Trans. Japan Inst. Met., 24 (1983), 23.

89. R. Wang and R.A. Rapp, "Potentiodynamic Corrosion Behavior for Several Fe-Mn-Al Austenitic Steels", Proceedings of Conference on Conservation and Substitution Technology for Chromium, A. Gray, Ed, October 4-7, 1982.

90. Y.K. Li and R.A. Rapp, "Internal Chloridation of Dilute Ni-Cr Alloys", Metall. Trans. 14B, (1983) 509.

91. W.C. Fang and R.A. Rapp, "Electrochemical Reactions in a Pure Na_2SO_4 Melt", J. Electrochem. Soc. 130, (1983) 2335.

92. R.A. Rapp, "A System of Supportive Coupled Electrochemical Cells Operating in Closed Loop for the Conversion of Heat into Electrical Energy", Proceedings of SERI Workshop on Thermally Regenerative Electrochemical Systems, H.L. Chum, Ed., Nat. Techn. Inf. Service, Dec. (1981).

93. T.L. Jungling and R.A. Rapp, "High Temperature Oxidation of Iron at 1200°C in a Hot Stage Environmental Scanning Electron Microscope", High Temperature Materials Chem., Z.A. Munir and D. Cubicciotti, Eds., Electrochem. Soc., (1983).

94. S. Espevik, R.A. Rapp, P.L. Daniel, and J.P. Hirth, "The Oxidation of Co-Cr-W Ternary Alloys", Oxid. Metals 20, (1983) 37.

95. G.M. Raynaud, W.A.T. Clark and R.A. Rapp, "In-Situ Observation of Copper Oxidation at High Temperatures", Metall. Trans. 15A, (1984) 573.

96. G.M. Raynaud and R.A. Rapp, "A Collision Model for Fume Formation in Metal Oxidation", Metall. Trans. 15A, (1984) 587.

97. D.A. Carey, R.A. Rapp and J.P. Hirth, "Effect of UV Illumination on the Sublimation of Basal Surfaces of Zinc Oxide", J. Chem. Phys. 79, (1983) 3160.

98. R. Wang, M.J. Straszheim and R.A. Rapp, "High Temperature Oxidation-Resistant Fe-Mn-Al-Si Alloy", Oxid. Metals 21, (1984) 71.

99. H. Erhart, R. Wang and R.A. Rapp, "In-Situ SEM Study of the High Temperature Oxidation of an Fe-Mn-Si Alloy", Oxid. Metals 21, (1984) 81.

100. R.A. Rapp, "The Oxidation of Metals Forming Cation-Diffusing Scales at Elevated Temperatures", 1983 Edward DeMille Campbell Memorial Lecture, Metall. Trans. 15A, (1984) 765.

101. G.M. Raynaud and R.A. Rapp, "In-Situ Observations of the Nucleation and Growth of Copper Oxide on Copper at Intermediate Temperatures", accepted for publication in Metall. Trans.

102. G.M. Raynaud and R.A. Rapp, "In-Situ Observation of Whiskers, Pyramids and Pits during the High Temperature Oxidation of Metals", Proceedings of International Metallographic Society Meeting, Calgary, July (1983); Oxid. Metals, 21, (1984), 89.

103. T.L. Jungling and R.A. Rapp, "High Temperature Oxidation of Iron at 1200°C in a Hot-Stage Environmental Scanning Electron Microscope", Metall. Trans. 15A, (1984) 2231.

104. L.E. Matson, H. Erhart, M.Y. Lee and R.A. Rapp, "Crystallographic and Morphological Characteristics of Oxidation Growth Pits in Wustite at 1200°C", Metall. Trans. 15A, (1984) 2241.

105. B.S. Lee and R.A. Rapp, "Gaseous Sulfidation of Pure Molybdenum at 700° - 950°C", J. Electrochem. Soc. 131, (1984) 2998.

106. R. Wang and R.A. Rapp, "Seawater and H_2SO_4 Corrosion Studies of Several Ferritic Fe-Al Base Alloys," Proceedings of Ninth International Congress On Metallic Corrosion, Toronto, June 3-7, 1984.

107. R.A. Rapp, "In Situ Studies of the High Temperature Oxidation of Metals and Alloys," Plenary Lecture, Tenth International Symposium on Reactivity of Solids, Dijon, August 27 - September 1, 1984, published in Pure and Appl. Chem. 56, (1984) 1715.

108. C.O. Park, R.W. Geist and R.A. Rapp, "Electrochemical Studies in Fused Na_2SO_4 at 900°C," Localized Corrosion; Equilibrium Diagrams, R. Frankenthal and J. Kruger, Eds., Electrochem. Soc., (1984) 228

109. Y.S. Zhang and R.A. Rapp, "Solubility of α-Fe_2O_3 in Fused Na_2SO_4 at 1200 K", J. Electrochem. Soc. 132, (1984) 734.

110. P.D. Jose, D.K. Gupta, and R.A. Rapp, "Solubility of α-Al_2O_3 in Fused Na_2SO_4 at 1200 K", J. Electrochem. Soc. 132, (1985) 735.

111. Y.S. Zhang and R.A. Rapp, "Solubilities of α-Fe_2O_3 and Fe_3O_4 in Fused Na_2SO_4 at 1200K", J. Electrochem Soc. 132, (1985) 2498.

112. R.L. Shook, R.A. Rapp, and J.P. Hirth, "Displacement Reactions between Cr and MoO_2 in a Ni-Base Alloy Matrix," Metall. Trans. 16A, (1985) 1815.

113. R.A. Rapp and G.R. St.Pierre, "New Options for the Protection of Carbon-Carbon Composites", Proceedings of High Temperature Composites Symposium, Dayton, Ohio, October 1985.

114. S. Guruswamy, S.M. Park, J.P. Hirth, and R.A. Rapp, "Internal Oxidation of Ag-In Alloys: Stress Relief and the Influence of Imposed Strain," Oxid. Metals 26, (1986) 77.

115. C.S. Lin, R.A. Rapp and J.P. Hirth, "Diffusional Breakdown of a Ag Diffusion Barrier in a Cu-Ag-Ni Diffusion Triple", Metall. Trans. 17A, (1986) 933.

116. D.S. Williams, R.A. Rapp, and J.P. Hirth, "Phase Suppression in the Transient Stages of Interdiffusion in Thin Films", Thin Solid Films 142, (1986) 47.

117. D.Z. Shi and R.A. Rapp, "The Solubility of SiO_2 in Fused Na_2SO_4 at 900°C," J. Electrochem. Soc. 133, (1986) 849.

118. C.O. Park and R.A. Rapp, "Electrochemical Reactions in Molten Na_2SO_4 at 900°C," *J. Electrochem. Soc.* *133*, (1986) 1636.

119. R.A. Rapp, "The Chemistry and Electrochemistry of the Hot Corrosion of Metals," 1986 Willis Rodney Whitney Lecture, *Corrosion* *42*, (1986) 568.

120. Y.S. Zhang and R.A. Rapp, "Solubilities of CeO_2, HfO_2, and Y_2O_3 in Fused Na_2SO_4-30 m/o $NaVO_3$ and CeO_2 in Pure Na_2SO_4 at 900°C," *Corrosion*, *42*, (1986) 348.

121. B. Pieraggi and R.A. Rapp, "Stress Generation and Vacancy Annihilation During Scale Growth Limited by Cation/Vacancy Diffusion, Norm Peterson Memorial Symposium on *Oxidation of Metals*, *and Associated Mass Transport*, M. Dayanada, S. Rothman, and W. King, Eds., TMS-AIME, Warrendale, PA (1987) 263.

122. R.A. Rapp, "Chemistry and Electrochemistry of Hot Corrosion of Metals," Plenary lecture at Internat. Symp. High Temperature Corrosion in Marseille, *J. Materials Sci. and Eng.*, *85*, (1986), 319.

123. B. Onay and R.A. Rapp, "In-Situ Observation of Copper Oxidation in a Hot Stage Environmental SEM," *Fundamental Aspects of High Temperature Corrosion II*, Electrochem. Soc., May 1986.

124. V. Ananthanarayanan, Y. Sahai, C.E. Mobley and R.A. Rapp, "Modeling of Fixed Bed Heat Storage Utilizing Phase Change Materials," *Metall. Trans.* *18B*, (1987) 216.

125. W.B. Connor, W.B. Johnson and R.A. Rapp, "Electrochemistry of Molten Salt Enhanced Carbothermic Reduction: Metal/Metal Oxide Half-Cell Reactions," Proceedings of R. Schuhmann Int. Symp. on Innovative Technology and Reactor Design in Extractive Metall., AIME, (1986).

126. M.J. Straszheim, C.E. Mobley and R.A. Rapp, "Oxidation of Iron-and Nickel-Base Microcrystalline Alloys," accepted for publication in *Oxid. Metals*.

127. M. Lee and R.A. Rapp, "Development of Scale Morphology During Wustite Growth on Iron at High Temperatures," *Oxid. Metals*, *30*, (1988) 125.

128. M. Lee and R.A. Rapp, "Coalescence of Wustite Grains During Iron Oxidation in a Hot-Stage Environmental SEM," *Oxid. Metals*, *27*, (1987) 187.

129. J. Kupper and R.A. Rapp, "Oxidation/Reduction Reactions of Sodium Molybdate in Sodium Sulfate at 1200 K," *Werkstoffe und Korrosion*, *38*, (1987) 674.

130. R.A. Rapp, D. Wang, and T. Weisert, "Simultaneous Chromizing/Aluminizing of Iron and Iron-Base Alloys by Pack Cementation," *High Temperature Coatings*, Eds. M.K. Khobaib and R.C. Krutenat, TMS-AIME, Warrendale, PA, (1987), 131.

131. S.C. Kung and R.A. Rapp, "Fundamental Study of Aluminization of Iron by Pack Cementation at 900°C," Surface and Coatings Technology, 32, (1987) 41.

132. Y.S. Zhang and R.A. Rapp, "The Solubilities of Metal Oxides in Fused Na_2SO_4 Solutions," Molten Salts VI, Eds. G. Mamantov, M. Blander, C. Hussey, C. Mamantov, M. Saboungi and J. Wilkes, Electrochemical Soc., (1987) 707.

133. D.Z. Shi, J.C. Nava, and R.A. Rapp "Electrochemical Reactions of $NaVO_3$ and Na_2CrO_4 Solutes in Na_2SO_4", High Temperature Materials Chemistry IV," Electrochemical Soc., (1987) 1.

134. S.C. Kung and R.A. Rapp, "Kinetic Study of Aluminization of Iron by Using the Pack Cementation Method", J. Electrochem. Soc., 137 (1988) 731.

135. D.M. Miller, S.C. Kung, S.D. Scarberry and R.A. Rapp, "Simultaneous Chromizing - Aluminizing Coating of Austenitic Stainless Steels", Oxid. Metals, 29 (1988) 239.

136. B. Onay and R.A. Rapp, "In-Situ Observation of the Effect of Temperature on Cu_2O Scale Morphology", Oxid. Metals, 29, (1988) 473.

137 B. Bonvalot-Dubois, G. Dhalenne, J. Berthon, A. Revcolevschi, and R. A. Rapp "The Reduction of NiO Platelets In a $NiO/ZrO_2(CaO)$", J. Amer. Ceram. Soc., 71, (1988) 296.

138. R.A. Rapp, "The Hot Corrosion of Metals by Fused Salts", Thermochemistry of Alloys, NATO-ASI (1987).

139. J. C. Nava and R. A. Rapp, "Electrochemical Reactions by $NaVO_3$ Solute in Fused Na_2SO_4", submitted for publication in J. Electrochem. Soc. (1988).

140. D. Z. Shi and R. A. Rapp, "Electrochemical Studies of Na_2CrO_4-Na_2SO_4 Melts at 1200 K", submitted for publication in J. Electrochem. Soc.

141. R. A. Rapp, "Pack Cementation Coating of Steel for High Temperature Applicatons", paper number 131, Corrosion 88, NACE.

142. B. Pieraggi and R.A. Rapp, "Stress Generation and Vacancy Annihilation", Acta Metallurgica, 36, (1988) 1281.

143. V. A. Ravi, P. Choquet, and R. A. Rapp, "Thermodynamics of Simultaneous Chromizing-Aluminizing in Halide-Activated Cementation Packs," Proceedings of MRS International Meeting on Advanced Materials, Tokyo (1988).

144. S.N.S. Reddy and R. A. Rapp, "The Electrometallurgy of Titanium", Proceedings of the Terkel Rosenqvist Symposium, S. E. Olsen and J. K. Tuset, Eds., Trondheim, Norway (1988).

BIOGRAPHICAL SKETCH

of

John Price Hirth

John Price Hirth received his B.S. and M.S. degrees in Metallurgical Engineering from The Ohio State University in 1953. He obtained his Ph.D. from Carnegie Institute of Technology in 1958. He was in the U.S. Air Force in 1953-55; a General Electric Research Fellow at Carnegie Institute of Technology, 1955-57; a Fulbright Research Fellow at Bristol University, England, 1957-58; and an Assistant Professor at Carnegie from 1958-61. Dr. Hirth was appointed Mershon Associate Professor of Materials Science and Metallurgical Engineering at Ohio State in 1961. He was named to his present post as Professor in 1964. He served as Visiting Professor at Stanford University in 1968-69.

Awards include the Hardy Gold Medal, AIME, 1960; ASM Bradley Stoughton Award, 1964; Curtis McGraw Award of the ASEE, 1967; Fellow, ASM, 1971; Cambell Lecturer, ASM, 1972; Jeffries Lecturer, ASM, 1974; Fellow, TMS-AIME, 1974; McDonald Lecturer, Canadian Metal Physics Society, 1978; Ohio State University Distinguished Research Award, 1979, IMD Lecturer and R. F. Mehl Medalist, TMS-AIME, 1980; Champion H. Mathewson Gold Medal, TMS-AIME, 1982; C. S. Barrett Lecturer and Medalist, ASM, 1986. He was elected to the National Academy of Engineering in 1974. Dr. Hirth's committee activity includes service with the Committee on Metallic Materials and Committee on Basic Research, Materials Advisory Board of the National Academy of Sciences, 1961-64; Chairman of the Physical Metallurgy Gordon Conference, 1967; Chairman, Chemistry and Physics of Metal Committee of AIME, 1967; Chairman of the ASM Transactions Committee, 1969; National Academy of Sciences Advisory Committee to the National Bureau of Standards, 1969-72; ARPA Materials Research Council, 1968 to present; Board of Overseers, Academy for Contemporary Problems, 1971 to 1975; Argonne National Laboratory Materials Science Review Committee, 1970-73; Los Alamos National Laboratory, Center for Materials Science Advisory Committee, 1982-present.

Dr. Hirth is the author or co-author of more than 290 articles, including two books appearing in the technical literature and dealing with nucleation and growth processes, dislocation theory and physical metallurgy. He has been Editor of Scripta Metallurgica since July 1974.

At Ohio State University he has served on the Graduate Council, 1969-72; the Council on Academic Affairs, 1970-73; and the Task Force on Research, which he chaired, 1976-77. He received the Fontana Teaching Award in 1969 and the MacQuigg Teaching Award in 1982. He was active with the OSU Rugby Football Club, 1971-81. He was on the Board of Directors of the Research Foundation, 1981-85. He presented the Commencement address in March, 1987, and later that year was named a Presidential Professor.

BIOGRAPHICAL SKETCH

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John Price Hirth

John Price Hirth received his B.S. and M.S. degrees in Metallurgical Engineering from The Ohio State University in 1953. He obtained his Ph.D. from Carnegie Institute of Technology in 1958. He was in the U.S. Air Force in 1953-55; a General Electric Research Fellow at Carnegie Institute of Technology, 1955-57; a Fulbright Research Fellow at Bristol University, England, 1957-58; and an Assistant Professor at Carnegie from 1958-61. Dr. Hirth was appointed Mershon Associate Professor of Materials Science and Metallurgical Engineering at Ohio State in 1961. He was named to his present post as Professor in 1964. He served as Visiting Professor at Stanford University in 1968-69.

Awards include the Hardy Gold Medal, AIME, 1960; ASM Bradley Stoughton Award, 1964; Curtis McGraw Award of the ASEE, 1967; Fellow, ASM, 1971; Cambell Lecturer, ASM, 1972; Jeffries Lecturer, ASM, 1974; Fellow, TMS-AIME, 1974; McDonald Lecturer, Canadian Metal Physics Society, 1978; Ohio State University Distinguished Research Award, 1979, IMD Lecturer and R. F. Mehl Medalist, TMS-AIME, 1980; Champion H. Mathewson Gold Medal, TMS-AIME, 1982; C. S. Barrett Lecturer and Medalist, ASM, 1986. He was elected to the National Academy of Engineering in 1974. Dr. Hirth's committee activity includes service with the Committee on Metallic Materials and Committee on Basic Research, Materials Advisory Board of the National Academy of Sciences, 1961-64; Chairman of the Physical Metallurgy Gordon Conference, 1967; Chairman, Chemistry and Physics of Metal Committee of AIME, 1967; Chairman of the ASM Transactions Committee, 1969; National Academy of Sciences Advisory Committee to the National Bureau of Standards, 1969-72; ARPA Materials Research Council, 1968 to present; Board of Overseers, Academy for Contemporary Problems, 1971 to 1975; Argonne National Laboratory Materials Science Review Committee, 1970-73; Los Alamos National Laboratory, Center for Materials Science Advisory Committee, 1982-present.

Dr. Hirth is the author or co-author of more than 290 articles, including two books appearing in the technical literature and dealing with nucleation and growth processes, dislocation theory and physical metallurgy. He has been Editor of Scripta Metallurgica since July 1974.

Curriculum Vitae

JOHN PRICE HIRTH

Education

Ph.D., Carnegie Institute of Technology, 1955-1957, dissertation title: "Evaporation of Crystals."

M.Sc., The Ohio State University, 1951-1953.

B.S., Metallurgical Engineering, The Ohio State University, 1948-1953.

Employment

1964-present	Professor, The Ohio State University
1961-1964	Mershon Associate Professor, The Ohio State University
1958-1961	Assistant Professor, Carnegie Institute of Technology
1957-1958	Research Fellow, Bristol University (England)
1953-1955	Task Scientist (Metallurgy), U.S. Air Force (1st Lt.)
1958-present	Consultant, Crucible Steel Company
1961-present	Consultant, Battelle Memorial Institute
1967-present	Member, DARPA Materials Research Council

Brief Personal History

John Price Hirth was born in Cincinnati, Ohio, December 16, 1930, and attended high school in Greenhills, Ohio at Greenhills High School. Attending Ohio State University from 1948-53, he was active in Pi Kappa Alpha Social Fraternity and a number of campus activities; he was named to the Texnikoi activities honorary and the Tau Beta Pi engineering honorary. He was married in 1953 to Martha Davis, and now has four children (Marc, Laura, Gregory, and Christina) and five grandchildren.

Current activities in addition to his technical work include participation in the hobbies of handball, golf, hiking, birding and skiing.

Research Accomplishments

Professor Hirth's scientific activities have been concerned primarily with dislocation interactions in solids, evaporation and condensation on solids, and kinetics of solid state phase transformations.

Activities at Ohio State University

1. Graduate Council, 1969-72
2. University Honors Committee, 1966-68
3. Council on Academic Affairs, 1970-73
4. Player, Coach and Referee, Rugby Football Club, 1970-81
5. Task Force on Research, Chairman, 1976-77
6. Committee on Attrition and Retention, 1980-83
7. Materials Research Laboratory, Executive Committee, 1981-86
8. Board of Directors, Research Foundation, 1981-85
9. University Promotion and Tenure Committee, 1985-87
10. In addition, he has served on numerous college and department committees.

Membership and Activities in National and Professional Organizations

1. Office of Army Research, Durham, Advisory Committee (1966-72).
2. Chairman, Physics and Chemistry of Metals Committee of AIME, 1967.
3. Member, Physical Metallurgy Committee of AIME (1960-64).
4. Member, Transactions Committee, American Society for Metals, 1966-70; Chairman 1969-70.
5. Member, Publications Committee, AIME (1961-64).
6. Chairman, Gordon Conference on Physical Metallurgy (1967).
7. Member, Publications Council, ASM, 1969-72.
8. Member, Technical Divisions board, ASM, and Materials Science Division, 1970-73; Chairman 1972-73.
9. Member, Carnegie-Mellon University Visiting Committee, 1968-78, 1984-.
10. Member, Advisory Board to Materials Research Laboratory, Cornell University, 1969-71.
11. Member, National Academy of Sciences Review Panel for the National Bureau of Standards Materials Division, 1969-72.
12. Member, Review Committee, Argonne National Laboratory, 1969-73.
13. Member and Executive Committee, Defense Advanced Research Projects Agency, Materials Research Council, 1967-.
14. Member, Board of Overseers, Academy for Contemporary Problems, 1970-75.
15. Member of Committees on (a) Metallic Materials, (b) Basic Research, (c) Ad-hoc Committee on Theoretical Strength of Crystals for National Academy of Sciences, Materials Advisory Board.
16. Editor, Scripta Metallurgica, 1974-.

17. Executive Committee, American Association for Crystal Growth, 1970-75.

18. Member, Center for Materials Science Advisory Committee, Los Alamos National Laboratory, 1982-.

19. Trustee, Alpha Sigma Mu, 1973-75.

20. Tau Beta Pi, ASEE, AAUP, AAAS.

21. Member, Editorial Advisory Boards, "Crystal Lattice Defects and Amorphous Materials" and "Journal of Nonmetals."

Honors

1. Fulbright Fellowship for study at Bristol University in England in 1957-58. Subject of his work was "Dislocations in Solids."
2. Hardy Gold Medal of AIME in 1959.
3. Mershon Associate Professor, The Ohio State University, 1961-64.
4. Bradley Stoughton Award, American Society for Metals, 1964.
5. Curtis W. McGraw Award, ASEE, 1967.
6. Visiting Professor, Stanford University, 1968-69.
7. Visiting Professor, Oslo University, Summer, 1964.
8. Mars G. Fontana Teaching Award, Ohio State University, 1970.
9. Fellow, American Society for Metals, 1971.
10. Campbell Lecturer, American Society for Metals, 1972.
11. Elected to the National Academy of Engineers, 1974.
12. Fellow of The Metallurgical Society of AIME, 1974.
13. Z. Jeffries Lecturer, American Society for Metals, 1974.
14. Visiting Professor, University of Mexico, 1976.
15. Macdonald Lecturer, Canadian Metal Physics Society, 1978.
16. University Distinguished Research Award, The Ohio State University, 1979.
17. R. F. Mehl Medal and IMD Lecturer, The Metallurgical Society of AIME, 1980.
18. Matthewson Gold Medal, The Metallurgical Society of AIME, 1982.
19. MacQuigg Teaching Award, The Ohio State University, 1982.

20. College Distinguished Research Award, The Ohio State University, 1985.

21. C. S. Barrett Lecturer and Medalist, ASM International, 1986.

22. Honorary Member, Alpha Sigma Mu, 1986.

23. Commencement Speaker, The Ohio State University, March 1987.

24. Presidential Professor, The Ohio State University, 1987-.

Publications

Books

1. Condensation and Evaporation, Pergamon Press, 1963, 192 pp., co-authored with G. M. Pound.

2. Theory of Dislocations, McGraw Hill Press, 1967, 800 pp., co-authored with J. Lothe; 2nd Edition, Wiley, 1982.

3. Deformation Twinning, Gordon and Breach, 1964, 464 pp., co-edited with H. C. Rogers.

4. Condensation and Evaporation of Solids, Gordon and Breach, 1964, 706 pp., co-edited with E. Rutner and P. Goldfinger.

5. Work Hardening, Gordon and Breach, 1966, 382 pp., co-edited with J. Weertman.

6. Hydrogen Degradation of Ferrous Alloys, Noyes, 1985, 850 pp., co-edited with R. A. Oriani and M. Smialowski.

Journal Publications

See attached list.

PUBLICATIONS - J. P. HIRTH

1. J. F. Willging, J. P. Hirth, F. H. Beck, and M. G. Fontana, "The Corrosion and Erosion-Corrosion of Some Metals and Alloys in Fuming Nitric Acid," Corrosion, 11, 71t (1955).
2. J. P. Hirth and G. M. Pound, "Evaporation of Metal Crystals," Journal of Chemical Physics, 26, 1216 (1957).
3. J. P. Hirth and G. M. Pound, "Dislocation-Spiral Kinetics of Crystal Evaporation," Acta Metallurgica, 5, 649 (1957).
4. J. P. Hirth and L. F. Vassamillet, "A Correlation Between Dislocations and Thermal Etch Pits," Journal of Applied Physics, 29, 595 (1958).
5. J. P. Hirth and G. M. Pound, "Evaporation of Silver Crystals," Transactions AIME, 215, 932 (1959).
6. J. P. Hirth and F. C. Frank, "On the Stability of Axial Dislocations in Metal Whiskers," Philosophical Magazine, 3, 1110 (1958).
7. J. Lothe and J. P. Hirth, "Dislocation Dynamics at Low Temperatures," Physical Review, 115, 543 (1959).
8. J. P. Hirth and G. M. Pound, "Coefficients of Condensation and Evaporations," Journal of Physical Chemistry, 64, 619 (1960).
9. J. P. Hirth, "On Two-Dimensional Nucleation," Acta Metallurgica, 7, 755 (1959).
10. R. W. Armstrong, J. P. Hirth, and G. M. Pound, "A Discussion of 'Self-Diffusion and Interdiffusion in Gold-Nickel Alloys': A Correlation with Absolute Rate Theory," Acta Metallurgica, 8, 55 (1960).
11. R. A. Rapp, J. P. Hirth, and G. M. Pound, "On the Condensation Coefficient in the Growth of Silver from the Vapor Phase," Canadian Journal of Physics, 38, 709 (1960).
12. M. B. Ives and J. P. Hirth, "Dissolution Kinetics at Dislocation Etch Pits in Single Crystals of Lithium Fluoride," Journal of Chemical Physics, 33, 517 (1960).
13. R. A. Rapp, J. P. Hirth, and G. M. Pound, "Condensation of Cadmium and Zinc from the Vapor Phase," Journal of Chemical Physics, 34, 184 (1961).
14. J. P. Hirth, "On Dislocation Interactions in the fcc Lattice," Journal of Applied Physics, 32, 700 (1961).
15. S. J. Hruska and J. P. Hirth, "A Discussion of the Growth and Evaporation of Potassium Whiskers," Zeitschrift fur Elektrochemie, 65, 479 (1961).

N 16. J. P. Hirth and G. M. Pound, Condensation and Evaporation-Nucleation and Growth Processes, Monograph in Progress in Materials Science, edited by Bruce Chalmers, Pergamon Press, Oxford (1963).

17. B. R. Banerjee, J. M. Capenos, J. J. Hauser, and J. P. Hirth, "Dislocation Interaction in bcc Stainless Steel," Journal of Applied Physics, 33, 556 (1961).

N 18. W. L. Winterbottom and J. P. Hirth, "Surface Diffusion Contribution to the Total Flow from Knudsen Cells," Journal of Chemical Physics, 37, 784 (1962).

19. E. J. Dulis, V. K. Chandhok, and J. P. Hirth, "Relation between Fatigue and Damping Characteristics and Microstructure of 12% Cr Steels," Transactions Quarterly ASM, 54, 456 (1961).

20. M. L. Swanson, R. F. Mehl, G. M. Pound and J. P. Hirth, "A Study of the Sorption of Zinc in Alpha-Brass Using Optical Reflectivity Measurements," Transactions AIME, 224, 742 (1962).

21. V. K. Chandhok, J. P. Hirth and E. J. Dulis, "Effect of Cobalt on Carbon Activity and Diffusivity in Steel," Transactions AIME, 224, 858 (1962).

A 22. J. P. Hirth, "Climb Barrier to Dislocation Glide in fcc Crystals," Journal of Applied Physics, 33, 2286 (1962).

23. W. L. Winterbottom, W. H. Robinson and J. P. Hirth, "Thermal Etch Pits and Dislocations in Silver," in Direct Observation of Imperfections in Crystals, edited by J. B. Newkirk and J. H. Wernick, John Wiley and Sons, Inc., New York (1962), p. 131.

N 24. J. P. Hirth, "Nucleation in Condensation from the Vapor onto a Substrate," Annals of the New York Academy of Sciences, 101, 805 (1963).

25. V. K. Chandhok, J. P. Hirth and E. J. Dulis, "Effect of Cobalt on Tempering Tool and Alloy Steels," Transactions Quarterly ASM, 56, 677 (1963).

N 26. V. Ruth, W. L. Winterbottom and J. P. Hirth, "Die Winkelabhangigkeit der mit einer Knudsen-Zelle erzeugten Molekularstrahlen," Zeitschrift fur angewandte Physik., 16, 53 (1963).

N 27. W. W. Mullins and J. P. Hirth, "The Microscopic Kinetics of Step Motion in Growth Processes," Journal of the Chemistry and Physics of Solids, 24, 1391 (1963).

N 28. J. P. Hirth, "On the Movement of Interface Dislocations During Diffusion," in Single Crystal Films, edited by M. Francombe and H. Sato, Pergamon Press, Oxford (1964), p. 173.

N 29. V. Ruth and J. P. Hirth, "Angular Distribution of Vapor Flowing from a Knudsen Cell," in Condensation and Evaporation of Solids, edited by E. Rutner, P. Goldfinger, and J. P. Hirth, Gordon and Breach, New York (1964), p. 99.

N 30. W. L. Winterbottom and J. P. Hirth, "Evaporation of Silver Crystals," in Condensation and Evaporation of Solids, ed. by E. Rutner, P. Goldfinger and J. P. Hirth, Gordon and Breach, New York, (1964), p. 347.

31. G. M. Pound and J. P. Hirth, "Theory of Heterogeneous Nucleation on Substrates," in Condensation and Evaporation of Solids, edited by E. Rutner, P. Goldfinger and J. P. Hirth, Gordon and Breach, New York (1964), p. 475.

N 32. J. P. Hirth, S. J. Hruska and G. M. Pound, "Theory of Nucleation in Deposition on Substrates," in Single Crystal Films, edited by M. Francombe and H. Sato, Pergamon Press, Oxford (1964), p. 9.

N 33. J. P. Hirth, "Evaporation of Metal Crystals," Chapter in Metal Surfaces: Structure, Energetics and Kinetics, American Society for Metals, Cleveland (1963), p. 199.

N 34. J. P. Hirth, "On the Pole Mechanism in fcc Metals," in "Deformation Twinning," edited by R. E. Reed-Hill, J. P. Hirth and H. C. Rogers, Gordon and Breach, New York (1964), p. 112.

N 35. J. P. Hirth, "The Influence of Surface Structure on Dislocation Nucleation," in The Relation Between the Structure and Mechanical Properties of Metals, National Physical Laboratory Symposium No. 15, H. M. Stationery Office, London (1963), p. 217.

36. J. Feder, J. P. Hirth, J. Lothe, K. C. Russell and G. M. Pound, "Homogeneous Nucleation in Condensation," Progress in Astronautics and Aeronautics, 15, 667 (1964).

37. R. M. Shemenski, J. P. Hirth, F. H. Beck and M. G. Fontana, "Dissolution of Iron Whiskers," Corrosion, 20, 203t (1964).

N 38. V. Ruth and J. P. Hirth, "Kinetics of Diffusion Controlled Whisker Growth," Journal of Chemical Physics, 41, 3139 (1964). Addendum, Physikalische Verhandlungen, 16, 47 (1965).

A 39. C. S. Hartley and J. P. Hirth, "Interaction of Nonparallel, Noncoplanar Dislocations," Acta Metallurgica, 13, 79 (1965).

40. K. L. Moazed and J. P. Hirth, "On the Contact Angle in Heterogeneous Nucleation Upon a Substrate," Surface Science, 3, 49 (1965).

A 41. T. Jossang, M. J. Stowell, J. P. Hirth and J. Lothe, "On the Determination of Stacking Fault Energies from Extended Dislocation Node Measurements," Acta Metallurgica, 13, 279 (1965).

N 42. T. Jossang, C. S. Hartley and J. P. Hirth, "Anisotropic Elasticity Solutions for Dislocation Barriers in Face Centered Cubic Crystals," Journal of Applied Physics, 36, 2400 (1965).

43. E. Rutner, P. Goldfinger and J. P. Hirth, "Condensation and Evaporation of Solids," Gordon and Breach, New York (1964).

44. R. E. Reed-Hill, J. P. Hirth and H. C. Rogers, "Deformation Twinning," Gordon and Breach, New York (1964).

N 45. C. S. Hartley and J. P. Hirth, "Resolution of Stresses in Single Crystal Deformation," Transactions of the Metallurgical Society of AIME, 233, 1415 (1965).

N 46. N. A. Gjostein and J. P. Hirth, "On the Surface Self Diffusion Coefficient," Acta Metallurgica, 13, 991 (1965); Discussion, Ibid. 14, 899 (1966).

N 47. J. P. Hirth, "The Kinetic and Thermodynamic Properties of Surfaces," in Energetics in Metallurgical Phenomena, Vol. II, edited by W. M. Mueller, Gordon and Breach, New York (1965).

N 48. J. P. Hirth, T. Jossang, and J. Lothe, "Dislocation Energies and the Concept of Line Tension," Journal of Applied Physics, 37, 110 (1966).

N 49. V. Ruth, K. L. Moazed and J. P. Hirth, "Effect of Beam Temperature on Heterogeneous Nucleation of Zinc from the Vapor,", Journal of Chemical Physics, 44, 2093 (1966). Addendum, Physikalische Verhandlungen 16, 48 (1965).

A 50. T. Jossang and J. P. Hirth, "The Energies of Stacking-Fault Tetrahedra in fcc Metals," Philosophical Magazine, 13, 657 (1966).

51. J. P. Hirth, "Condensation Processes," in Vapor Deposition, edited by C. F. Powell, J. H. Oxley and J. M. Blocher, Jr., John Wiley and Sons, Inc., New York (1966), p. 126.

N 52. G. M. Pound and J. P. Hirth, "Heterogeneous Nucleation on Substrates," in Series of Selected Papers in Physics, Physical Society of Japan (1966), p. 39.

A 53. J. P. Hirth and J. Lothe, "Elastic and Core Anisotropies for <111> Screw Dislocation in Cubic Crystals," Physica Status Solidi, 15, 487 (1966).

54. V. K. Chandhok, A. Kasak and J. P. Hirth, "Structures and Strengthening Mechanisms in Carbon Steel Wire," Transactions Quarterly ASM 59, 288 (1966).

N 55. T. L. Davis and J. P. Hirth, "Nucleation Rate of Vacancy Clusters in Crystals," Journal of Applied Physics, 37, 2112 (1966); Discussion, Ibid. 38, 2390 (1967).

A 56. J. P. Hirth, "Dislocation Dissociation in bcc Crystals," Acta Metallurgica, 14, 1394 (1966).

N 57. J. P. Hirth and K. L. Moazed, "Nucleation Processes in Deposition onto Substrates," in "Fundamental Phenomena in the Materials Sciences," edited by L. J. Bonis, P. L. deBruyn and J. J. Duga, Plenum, New York (1966), p. 63.

58. R. D. Gretz, C. M. Jackson and J. P. Hirth, "Nucleation in Surface Catalyzed Chemical Vapor Deposition," Surface Science, 6, 171 (1967).

59. R. E. Hook and J. P. Hirth, "The Deformation Behavior of Isoaxial Bicrystals of Fe-3% Si," Acta Metallurgica, 15, 535 (1967).

A 60. J. P. Hirth and J. Lothe, "Glide of Jogged Dislocations," Canadian Journal of Physics, 45, 809 (1967).

A 61. J. Lothe and J. P. Hirth, "Dislocation Climb Forces," *Journal of Applied Physics*, *38*, 845 (1967); Discussion, Ibid. *38*, 4916 (1967).

62. R. E. Hook and J. P. Hirth, "The Deformation Behavior of Non-Isoaxial Bicrystals of Fe-3% Si," *Acta Metallurgica*, *15*, 1099 (1967).

S 63. F. J. Fraikor and J. P. Hirth, "Vacancy Concentration and Precipitation in Quenched Pure Gold and Gold-Silver Alloys," *Journal of Applied Physics*, *38*, 2312 (1967).

64. R. D. Gretz and J. P. Hirth, "Nucleation and Growth Processes in CVD," in "Chemical Vapor Deposition of Refractory Metals, Alloys and Compounds," edited by A. C. Schaffhauser, American Nuclear Society, Hinsdale, Illinois (1967). p. 73.

N 65. J. P. Hirth, "Evaporation and Sublimation Mechanisms," in "The Characterization of High Temperature Vapors," edited by J. L. Margrave, Wiley, New York (1967), p. 453.

N 66. J. P. Hirth and K. L. Moazed, "Nucleation Processes in Thin Film Formation," *Physics of Thin Films*, *4*, 97 (1967).

N 67. J. P. Hirth and J. Lothe, "Theory of Dislocations," McGraw-Hill, New York, 1968; 2nd Edition, Wiley, New York 1982.

N 68. S. J. Hruska, J. P. Hirth and G. M. Pound, "Recent Developments in Heterogeneous Nucleation From the Vapor Phase," in "Surfaces and Interfaces I," edited by J. J. Burke, N. L. Reed and V. Weiss, University Press, Syracuse (1967), p. 305.

S 69. F. J. Fraikor and J. P. Hirth, "Vacancy Concentration in the Binary Au-Ag Alloy System," *Scripta Metallurgica*, *2*, 55 (1968).

A 70. J. P. Hirth and J. Lothe, "Interactions between Moving Dislocations," in "Dislocation Dynamics," edited by A. R. Rosenfield, G. T. Hahn, A. L. Bement and R. I. Jaffee, McGraw-Hill, New York (1968), p. 231.

A 71. R. E. Hook and J. P. Hirth, "Dislocation Arrays in Deformed Silicon Iron Bicrystals," *Transactions Japan Institute of Metals, Supplement*, *9*, 778 (1968).

A 72. M. McLean and J. P. Hirth, "Surface Self-Diffusion on Gold," *Surface Science*, *12*, 177 (1968).

N 73. M. McLean and J. P. Hirth, "Surface Self-Diffusion of Gold - 54.4 At. % Silver," *Acta Metallurgica*, *17*, 237 (1969).

N 74. M. McLean and J. P. Hirth, "On the Equilibrium Shape of Dislocation Etch Pits," *Surface Science*, *11*, 25 (1968).

A 75. L. F. Bryant, R. Speiser and J. P. Hirth, "Some Interfacial Properties of Fcc Cobalt," *Transactions of the Metallurgical Society AIME* *242*, 1145 (1968).

N 76. T. E. Dunham and J. P. Hirth, "Effusion from Knudsen Cells with Conical Channels," Journal of Chemical Physics, 49, 4650 (1968).

77. J. P. Hirth and Morris Cohen, "On the Interaction Energy between Dislocations and Interstitial Atoms in BCC Crystals," Scripta Metallurgica, 3, 107 (1969).

78. J. P. Hirth and Morris Cohen, "Comment on the Interaction Energy between Dislocations and Interstitial Atoms," Scripta Metallurgica, 3, 311 (1969).

79. A. H. Clauer and J. P. Hirth, "Climb Forces on Dislocations," Transactions of the Metallurgical Society AIME, 245, 1075 (1969).

80. J. P. Hirth and P. C. Gehlen, "Dislocation Displacement Fields in Anisotropic Media," Journal of Applied Physics, 40, 2177 (1969).

N 81. J. L. Kenty and J. P. Hirth, "Epitaxy and Heterogeneous Nucleation Theory," Surface Science, 15, 403 (1969).

82. J. P. Hirth and J. Weertman, "Work Hardening," Gordon and Breach, New York (1968).

A 83. J. P. Hirth, "Introduction to the Mathematical Theory of Dislocations," in "Mathematical Theory of Dislocations," Edited by T. Mura, American Society of Mechanical Engineers, New York (1969), p. 1.

84. J. P. Hirth and W. D. Nix, "The Thermodynamics of Dislocation Glide," Physica Status Solidi, 35, 177 (1969).

N 85. J. L. Kenty and J. P. Hirth, "The Critical Supersaturation Concept Applied to the Nucleation of Silver on Sodium Chloride," Transactions of the Metallurgical Society AIME, 245, 2373 (1969).

A 86. J. P. Hirth and J. Lothe, "Stress Fields of Dislocation Segments and Forces on Them," in "Physics of Strength and Plasticity," edited by A. S. Argon, MIT Press, Cambridge (1969), p. 39.

87. J. P. Hirth, K. L. Moazed and V. Ruth, "Heterogene Keimbildung und Epitaxie bei der Kondensation aus der Dampfphase," in "Epitaxie Endotaxie," edited by H. G. Schneider, VEB Deutscher Verlag fur Grundstoffindustrie; Leipzig (1969), p. 25.

88. J. P. Hirth and Morris Cohen, "On the Strength-Differential Phenomenon in Hardened Steel," Metallurgical Transactions, 1, 3 (1970); Discussion, Ibid. 1, 2026 (1970).

89. W. A. Tiller, G. M. Pound and J. P. Hirth, "A Critique on the Mathematical Theory of Spinodal Decomposition," Acta Metallurgica, 18, 225 (1970).

90. T. W. Chou and J. P. Hirth, "Stress Distribution in a Bimaterial Plate under Uniform External Loadings," Journal of Composite Materials, 4, 102 (1970).

91. J. P. Hirth and Morris Cohen, "Dislocation-Carbon Interactions in Iron and Martensite," Scripta Metallurgica, 4, 167 (1970).

92. A. H. Clauer, B. A. Wilcox and J. P. Hirth, "Creep Behavior of Molybdenum Single Crystals," Acta Metallurgica, 18, 367 (1970).

93. A. H. Clauer, B. A. Wilcox and J. P. Hirth, "Dislocation Substructure Induced by Creep in Molybdenum Single Crystals," Acta Metallurgica, 18, 381 (1970).

N 94. J. P. Hirth, G. M. Pound and G. R. St. Pierre, "Bubble Nucleation," Metallurgical Transactions, 1, 939 (1970); Discussion, Ibid. 2, 616 (1971).

AF 95. T. Ejima, W. H. Robinson and J. P. Hirth, "Thermal Etch Pits at Dislocations in Lithium Fluoride," Journal of Crystal Growth, 7, 155 (1970).

AF 96. J. P. Hirth, "Rate Controlling Plastic Flow Mechanisms at Low Temperatures," in "Inelastic Behavior of Solids", edited by M. F. Kanninen, W. F. Adler, A. R. Rosenfield and R. I. Jaffee, McGraw-Hill, New York, 1970, p. 281.

N 97. Z. A. Munir and J. P. Hirth, "Surface Morphology of Sublimated Crystals of Cadmium and Zinc Sulfides," Journal of Applied Physics, 41, 2697 (1970).

AF 98. J. P. Hirth, "Thermodynamics of Stacking Faults," Metallurgical Transactions, 1, 2367 (1970).

99. J. P. Hirth, W. A. Tiller and G. M. Pound, "On the Thermodynamics of Inhomogeneous Systems," Philosophical Magazine, 22, 117 (1970).

N 100. W. H. Robinson and J. P. Hirth, "Nucleation of a Disc-Shaped Hole in a Low Index Surface and at a Dislocation," Journal of Crystal Growth, 7, 262 (1970).

101. J. P. Hirth and R. G. Wells, "Disclination Structures in Bloch Wall Lattices in Ba Fe$_{12}$ O$_{19}$ and Sm Co$_5$," Journal of Applied Physics, 41, 5250 (1970).

102. A. H. Clauer and J. P. Hirth, "An Analysis of L and Y Tilt Boundary Intersections formed During Creep in Molybdenum," in "Proceedings of the Second International Conference on the Strength of Metals and Alloys," Vol. III, American Society of Metals, Cleveland, 1970, p. 1113.

AF 103. M. N. Shetty and J. P. Hirth, "Force Relations Applicable to Dislocation-Forest Intersections," Metallurgical Transactions, 2, 297 (1971).

AF 104. J. P. Hirth, K. Malen and J. Lothe, "On Simple Analytic Solutions for Anisotropic Elastic Fields of Dislocations," Scripta Metallurgica, 5, 231 (1971).

105. W. A. Tiller, G. M. Pound and J. P. Hirth, "Further Comments on Spinodal Decomposition," Acta Metallurgica, 19, 475 (1971).

N 106. J. P. Hirth, "A Dislocation Mechanism for Phase Transformation," in "Fundamental Aspects of Dislocation Theory," edited by J. A. Simmons, R. deWit and R. Bullough, National Bureau of Standards Special Publication 317, Vol. 1, 1970, p. 547.

107. J. P. Hirth, "Introduction to the Panel Discussion on Intrinsic Properties of Dislocations," in "Fundamental Aspects of Dislocation Theory," edited by J. A. Simmons, R. deWit and R. Bullough, National Bureau of Standards Special Publication 317, Vol. 1, 1970, p. 683.

A 108. W. D. Nix, R. Gasca-Neri and J. P. Hirth, "A Contribution to the Theory of Dislocation Climb," Philosophical Magazine, 23, 1339 (1971).

109. K. Nishioka, G. M. Pound, J. Lothe and J. P. Hirth, "Comments on Homogeneous Nucleation Theory," Journal of Applied Physics, 42, 3900 (1971).

A 110. P. B. Lake, G. Meyrick and J. P. Hirth, "Dual Slip in Germanium Under Compression," Metallurgical Transactions, 2, 2555 (1971).

N 111. J. P. Hirth, "Discussion of Bubble Nucleation," Transactions of the ASME-Journal of Basic Engineering, 92, 702 (1970).

N 112. T. Surek, G. M. Pound and J. P. Hirth, "Ledge Dynamics in Crystal Evaporation," Journal of Chemical Physics, 55, 5157 (1971).

SF 113. C. W. Price and J. P. Hirth, "A Mechanism for the Generation of Screw Dislocations from Grain Boundary Ledges," Materials Science and Engineering, 9, 15 (1972).

N 114. Z. A. Munir, L. S. Seacrist and J. P. Hirth, "Morphology of Thermally Etched Basal Surfaces of Cadmium Selenide," Surface Science, 28, 357 (1971).

N 115. G. Pilkington and J. P. Hirth, "Epitaxial Deposition of Silver on Molybdenite," Surface Science, 29, 363 (1972).

N 116. T. L. Davis and J. P. Hirth, "The Nucleation of Dislocation Loops in Aluminum," in "The Nature of Small Defect Clusters," edited by M. J. Makin, H. M. Stationery Office, London (1966), p. 106.

117. J. P. Hirth and G. T. Hahn, "Agenda Discussion on Dislocations and Stacking Faults," in "Interatomic Potentials and Simulation of Lattice Defects," edited by P. C. Gehlen, J. R. Beeler and R. I. Jaffee, Plenum, New York (1972), p. 561.

118. J. P. Hirth, "On Volume Effects in Vacancy Formation," in "Interatomic Potentials and Simulation of Lattice Defects," edited by P. C. Gehlen, J. R. Beeler and R. I. Jaffee, Plenum, New York (1972), p. 451.

SF 119. J. P. Hirth, "Anisotropic Elastic Solutions for Line Force Arrays," Scripta Metallurgica, 6, 535 (1972).

120. P. C. Gehlen, R. G. Hoagland, M. F. Kanninen and J. P. Hirth, "Nonlinear Effects in the Displacement Field of a Dislocation," Scripta Metallurgica, 6, 445 (1972).

121. D. W. Short, R. A. Rapp and J. P. Hirth, "Influence of Surface Charge and Surface Structure on the Sublimation of Ionic Crystals," Journal of Chemical Physics, 57, 1381 (1972).

122. P. C. Gehlen, J. P. Hirth, R. G. Hoagland and M. F. Kanninen, "A New Representation of the Strain Field Associated with the Cube-edge Dislocation in a Model of α-Iron," Journal of Applied Physics, 43, 3921 (1972).

123. J. P. Hirth, "The Influence of Grain Boundaries on Mechanical Properties," Metallurgical Transactions, 3, 3047 (1972).

SF 124. P. R. Couchman, W. A. Jesser, D. Kuhlmann-Wilsdorf, and J. P. Hirth, "On the Concepts of Surface Stress and Strain," Surface Science, 33, 429 (1972).

N 125. J. P. Hirth, "Some Comments on Heterogeneous Nucleation from the Vapor Phase," Journal of Crystal Growth, 17, 63 (1972).

N 126. T. Surek, J. P. Hirth and G. M. Pound, "The Back-Force Effect at Repeated Nucleation Sources in Crystal Evaporation and Dissolution Processes," Journal of Crystal Growth, 18, 20 (1973).

SF 127. J. P. Hirth and J. Lothe, "Anisotropic Elastic Solutions for Line Defects in High-Symmetry Cases," Journal of Applied Physics, 44, 1029 (1973).

A 128. G. J. Yurek, R. A. Rapp and J. P. Hirth, "Kinetics of the Displacement Reaction between Iron and Cu_2O," Metallurgical Transactions, 4, 1293 (1973).

N 129. K. Shinohara and J. P. Hirth, "Forces Acting on Misfit Dislocations during Interdiffusion," Philosophical Magazine, 27, 883 (1973).

N 130. K. Shinohara and J. P. Hirth, "The Behavior of Misfit Dislocations during Interdiffusion," Thin Solid Films, 16, 345 (1973).

SF 131. J. P. Hirth and R. W. Balluffi, "On Grain Boundary Dislocations and Ledges," Acta Metallurgica, 21, 929 (1973).

SF 132. J. P. Hirth, "Thermodynamics of Surfaces," in "Structure and Properties of Metal Surfaces," Maruzen, Tokyo (1973), p. 10.

SF 133. R. J. Asaro and J. P. Hirth, "Planar Dislocation Interactions in Anisotropic Media with Applications to Nodes," Journal of Physics F: Metal Physics, 3, 1659 (1973).

SF 134. R. J. Asaro, J. P. Hirth, D. M. Barnett and J. Lothe, "A Further Synthesis of Sextic and Integral Theories for Dislocations and Line Forces in Anisotropic Media," Physica Status Solidi, 60, 261 (1973).

N 135. T. Surek, G. M. Pound, and J. P. Hirth, "Spiral Dislocation Dynamics in Crystal Evaporation," Surface Science, 41, 77 (1974).

AR 136. F. B. Fletcher, M. Cohen and J. P. Hirth, "Temperature Dependence of the Strength-Differential Effect in Hardened Steels," Metallurgical Transactions, 5, 905 (1974).

A 137. J. P. Hirth, R. G. Hoagland and P. C. Gehlen, "The Interaction between Line Force Arrays and Planar Cracks," International Journal of Solids and Structures, 10, 977 (1974).

SF 138. J. P. Hirth, "Defect Structures in Grain Boundaries," Acta Metallurgica, 22, 1023 (1974).

SF 139. P. B. Lake, G. Meyrick and J. P. Hirth, "Dislocation Nodes Observed in Ge Single Crystals Recovery Annealed After Dual Slip Deformation," Metallurgical Transactions, 5, 1761 (1974).

N 140. G. J. Yurek, J. P. Hirth and R. A. Rapp, "The Formation of Two-Phase, Layered Scales on Pure Metals," Oxidation of Metals, 8, 265 (1974).

SF 141. J. E. Sinclair and J. P. Hirth, "Two-Dimensional Elastic Green Function for a Cracked Anisotropic Body," Journal of Physics F: Metal Physics, 5, 236 (1975).

SF 142. J. Lothe, R. J. Asaro, D. M. Barnett and J. P. Hirth, "Comments on the Indenbom-Alshits Theory for Dislocations in Anisotropic Media," Physica Status Solidi, 66b, K79 (1974).

N 143. K. Shinohara and J. P. Hirth, "Critical Thickness for Loss of Coherency in Epitaxial Bimetals," Japanese Journal of Applied Physics, Supplement 2, 629 (1974).

SF 144. J. P. Hirth, "Stress Averaging in the Dislocation Micromechanics Analysis of Deformation," in "Rate Processes in Plastic Deformation of Materials," edited by J. C. M. Li and A. K. Mukherjee, American Society for Metals, Metals Park (1975), p. 250.

145. R. G. Tabak, J. P. Hirth, G. Meyrick and T. P. Roark, "The Nucleation and Expulsion of Carbon Particles Formed in Stellar Atmospheres," The Astrophysical Journal, 196, 457 (1975).

N 146. K. Shinohara and J. P. Hirth, "The Behavior of Misfit Dislocations During interdiffusion," Journal of the Materials Science Society of Japan, 11, 252 (1974).

N 147. J. E. McVicker, R. A. Rapp and J. P. Hirth, "The Sublimation of Basal Surfaces of Zinc Oxide," Journal of Chemical Physics, 63, 2646 (1975).

SF 148. R. J. Asaro, J. P. Hirth and J. Lothe, "Stress Functions for Line Defects in Anisotropic Media," Scripta Metallurgica, 9, 837 (1975).

N 149. J. P. Hirth and H. H. Johnson, "Hydrogen Problems in Energy Related Technology," Corrosion, 32, 3 (1976).

AF 150. D. R. Stickle, J. P. Hirth, G. Meyrick and R. Speiser, "A New Technique for Measuring the Effects of Oxygen Activity on Surface Energies: Application to Nickel," Metallurgical Transactions, 7A, 71 (1976).

AF 151. C. E. Bauer, R. Speiser and J. P. Hirth, "Surface Energy of Copper as a Function of Oxygen Activity," Metallurgical Transactions, 7A, 75 (1976).

N 152. J. P. Hirth and R. H. Wagoner, "Elastic Fields of Line Defects in a Cracked Body," International Journal of Solids and Structures, 12, 117 (1976).

SF 153. H. Kuan and J. P. Hirth, "Dislocation Pileups near the Interface of Bimaterial Couple," Materials Science and Engineering, 22, 113 (1976).

154. T. Surek, J. P. Hirth and G. M. Pound, "On the Shape of Growth and Evaporation Spirals," Rost Kristallov, 11, 203 (1975)

N 155. J. P. Hirth, "Mechanical Failures: Implications for Science," in N.B.S. Special Publication 423, "Mechanical Failure," eds. T. R. Shives and W. A. Willard, U.S. Govt. Printing Office (1976), p. 181.

SF 156. R. H. Wagoner and J. P. Hirth, "Crack Propagation Near Cylindrical Voids," Metallurgical Transactions, 7A, 661 (1976).

SF 157. J. P. Hirth, "Obstacle Size in Dispersion Hardening by the Orowan Process," Scripta Metallurgica, 10, 755 (1976).

158. R. G. Hoagland, J. P. Hirth and P. C. Gehlen, "Point Defect-Dislocation Interactions Arising from Nonlinear Elastic Effects," in "Physics of Solid Solution Strengthening," edited by E. W. Collings and H. L. Gegel, Plenum, New York (1975), p. 101.

SF 159. J. P. Hirth, "Anisotropic Elastic Theory of Line Defects," Metal Science, 10, 222 (1976).

SF 160. J. P. Hirth and C. W. Price, "Nonlinear Contributions to the Relation between Surface Stress and Surface Energy," Surface Science, 57, 446 (1976).

161. J. P. Hirth, E. E. Hucke and R. L. Coble, "Flow Equations for Graphite," Carbon, 14, 19 (1976).

162. J. P. Hirth and D. A. Rigney, "Crystal Plasticity and the Delamination Theory of Wear," Wear, 39, 133 (1976).

163. C. W. Price and J. P. Hirth, "Surface Energy and Surface Stress Tensor in an Atomistic Model," Surface Science, 57, 509 (1976).

164. C. M. Jackson and J. P. Hirth, "Heterogeneous Nucleation in Chemical Vapor Deposition Systems," in "Advances in Epitaxy and Endotaxy: Selected Chemical Problems," edited by H. G. Schneider, V. Ruth and T. Kormany, Hungarian Academy of Sciences, Budapest, 1976, p. 79.

165. R. G. Hoagland, J. P. Hirth and P. C. Gehlen, "Atomic Simulation of the Dislocation Core Structure and Peierls Stress in Alkali Halide," Philosophical Magazine, 34, 413 (1976).

SF 166. C. W. Price and J. P. Hirth, "Dislocation-Like Relaxations of BCC Surface Ledges," Nuclear Metallurgy, 20, 377 (1976).

167. H. H. Johnson and J. P. Hirth, "Internal Hydrogen Supersaturation Produced by Dislocation Transport," Metallurgical Transactions, 7A, 1543 (1976).

N 168. S. R. Shatynski, J. P. Hirth and R. A. Rapp, "A Theory of Multiphase Binary Diffusion," Acta Metallurgica, 24, 1071 (1976).

N 169. M. J. Yacaman and J. P. Hirth, "Effects of Surface Imperfections on the Nucleation of Gold on Sodium Chloride," Thin Solid Films, 38, 215 (1976).

N 170. M. J. Yacaman, T. Ocana Z., A. M. Sonnemann and J. P. Hirth, "The Back-Force Effect and its Influence on Sublimation of Alkali Halide Single Crystal Surfaces," Journal of Crystal Growth, 37, 37 (1977).

171. J. P. Hirth and G. B. Stringfellow, "A Mechanism for Liquid-Phase Epitaxial Growth of Nonequilibrium Composition Producing a Coherent Interface," Journal of Applied Physics, 48, 1813 (1977).

SF 172. T. D. Lee, T. Goldenberg and J. P. Hirth, "Hydrogen and Plastic Instability in Deformed, Spheroidized 1090 Steel," Fracture 1977, Vol. 2, ICF4, Waterloo, Canada, 1977, p. 243.

A 173. E. M. Kennedy, R. Speiser and J. P. Hirth, "Phase Transformation in Cobalt by Dislocation Emission from Grain Boundaries," in "Physical Chemistry in Metallurgy," United States Steel Corp., Pittsburgh, 1976, p. 345.

SF 174. V. Vitek and J. P. Hirth, "Line Singularity Fields in the Presence of a Crack of Elliptical Cross Section," Scripta Metallurgica, 11, 339 (1977).

N 175. J. P. Hirth and R. A. Rapp, "The Diffusional Growth of a Scale with Variable Composition, Diffusivity and Molar Volume," Oxidation of Metals, 11, 57 (1977).

N 176. Z. A. Munir and J. P. Hirth, "Transient Phenomena in the Sublimation of Cadmium Sulfide, Journal of Electronic Materials, 6, 409 (1977).

177. J. P. Hirth and F. H. Froes, "Interrelations Between Fracture Toughness and Other Mechanical Properties in Titanium Alloys," Metallurgical Transactions, 8A, 1165 (1977).

SF 178. B. L. Adams, J. P. Hirth, P. C. Gehlen and R. G. Hoagland, "Atomic Simulation of the $a/2 \langle 111 \rangle \{110\}$ Edge Dislocation in Alpha-iron," Journal of Physics F: Metal Physics, 7, 2021 (1977).

N 179. Robert H. Wagoner and J. P. Hirth, "Vaporization Kinetics of Sodium Chloride," Journal of Chemical Physics, 67, 3074 (1977).

180. J. P. Hirth and A. H. Clauer, "Concluding Agenda Discussion-Critical Issues," in "Fundamental Aspects of Alloy Design," edited by R. I. Jaffee and B. A. Wilcox, Plenum, New York, 1977, p. 647.

181. J. P. Hirth, "The Mechanism of Shear of an Amorphous Metal," Journal of Materials Science, 12, 2540 (1977).

182. J. P. Hirth, "Nucleation, Undercooling and Homogeneous Structures in Rapidly Solidified Powders," Metallurgical Transactions, 9A, 401 (1978).

SF 183. J. E. Sinclair, P. C. Gehlen, R. G. Hoagland and J. P. Hirth, "Flexible Boundary Conditions and Nonlinear Geometric Effects in Atomic Dislocation Modeling," Journal of Applied Physics, 49, 3890 (1978).

184. J. P. Hirth, "SCC and HE from the Viewpoint of the Defect Solid State," in "Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys," NACE-5, edited by R. W. Staehle, J. Hochmann, R. D. McCright and J. E. Slater, NACE, Houston, 1977, p. 1.

185. F. H. Froes, R. F. Malone, J. C. Williams, M. A. Greenfield and J. P. Hirth, "Alloy Design and Property Interrelations of Metastable Beta Titanium Alloys," in "Forging and Properties of Aerospace Materials," The Metals Society, London, 1978, p. 143.

SF 186. T. Goldenberg, T. D. Lee and J. P. Hirth, "Ductile Fracture of U-Notched Bend Specimens of Spheroidized AISI 1095 Steel," Metallurgical Transactions, 9A, 1663 (1978).

SF 187. J. P. Hirth and B. Carnahan, "Hydrogen Adsorption at Dislocations and Cracks in Fe," Acta Metallurgica, 26, 1795 (1978).

SF 188. T. D. Lee, T. Goldenberg and J. P. Hirth, "Effect of Hydrogen in Fracture of U-Notched Bend Specimens of Spheroidized AISI 1095 Steel," Metallurgical Transactions, 10A, 199 (1979).

189. P. C. Gehlen and J. P. Hirth, "The Displacement Field Associated With Line Forces in a Cracked Orthotropic Body," Computers and Structures, 9, 589 (1978).

N 190. D. A. Rigney and J. P. Hirth, "Plastic Deformation and Sliding Friction of Metals," Wear, 53, 345 (1979).

SF 191. T. D. Lee, T. Goldenberg and J. P. Hirth, "Effect of Hydrogen on Fracture of U-Notched Bend Specimens of Quenched and Tempered AISI 4340 Steel," Metallurgical Transactions, 10A, 439 (1979).

N 192. S. R. Shatynski, J. P. Hirth and R. A. Rapp, "Solid-State Displacement Reactions Between Selected Metals and Sulfides," Metallurgical Transactions, 10A, 591 (1979).

N 193. M. J. Yacaman, Z. A. Munir, T. Ocana and J. P. Hirth, "Sublimation of Ionic Crystals in the Presence of an Electrical Field," Applied Physics Letters, 34, 727 (1979).

N 194. M. J. Yacaman, A. Gomez R. and J. P. Hirth, "Cleavage Ledges and Interface Dislocations on Suzuki Phases in Sodium Chloride," Philosophical Magazine, 39A, 709 (1979).

N 195. G. J. Yurek, R. A. Rapp, and J. P. Hirth, "Kinetics of the Displacement Reaction Between Fe and Cu_2O at Temperatures Between 800 and 1050°C," Metallurgical Transactions, 10A, 1473 (1979).

SF 196. J. P. Hirth, D. M. Barnett and J. Lothe, "Stress Fields of Dislocation Arrays at Interfaces in Bicrystals," Philosophical Magazine, 40A, 39 (1979).

N 197. J. P. Hirth and D. A. Rigney, "Microstructural Models for Friction and Wear," in "Strength of Metals and Alloys," edited by P. Haasen, V. Gerold and G. Kostorz, Pergamon, Oxford 1980, Vol. 3, p. 1483.

N 198. J. P. Hirth, "Adsorption at Grain Boundaries and Its Effect on Decohesion," Philosophical Transactions of the Royal Society of London, A295, 139 (1980).

A 199. I. H. Lin, J. P. Hirth and A. R. Rosenfield, "J Integral Analysis of Stable Crack Growth," International Journal of Fracture, 16, R11 (1980).

N 200. J. P. Hirth, "Effects of Hydrogen on the Properties of Iron and Steel," Metallurgical Transactions, 11A, 861 (1980).

N 201. S. Espevik, R. A. Rapp, P. L. Daniel and J. P. Hirth, "Oxidation of Ni-Cr-W Ternary Alloys," Oxidation of Metals, 14, 85 (1980).

A 202. I. H. Lin, J. P. Hirth and A. R. Rosenfield, "Discussion of J Integral Analysis of Stable Crack Growth," International Journal of Fracture, 16, R157 (1980).

SF 203. J. P. Hirth and J. R. Rice, "On the Thermodynamics of Adsorption at Interfaces as it Influences Decohesion," Metallurgical Transactions, 11A, 1501 (1980).

204. A. G. Evans, J. R. Rice and J. P. Hirth, "Suppression of Cavity Formation in Ceramics: Prospects for Superplasticity," Journal of the American Ceramic Society, 63, 368 (1980).

N 205. M. J. Yacaman, Z. A. Munir and J. P. Hirth, "The Influence of an Electric Field on the Sublimination Kinetics of Alkali Halide Surfaces," Journal of Crystal Growth, 49, 475 (1980).

206. B. L. Adams, G. S. Clevinger and J. P. Hirth, "An Upper-Bound Evaluation of Interactive Creep and Growth in Textured Zircaloy," Journal of Nuclear Materials, 90, 75 (1980).

207. M. J. Yacaman and J. P. Hirth, "Electrostatic Charge Effects on Surface Defects in Alkali Halide Crystals," Journal de Physique, Colloque C6, Supplement No. 7, 41, 485 (1980).

SF 208. O. A. Onyewuenyi and J. P. Hirth, "The Effect of Hydrogen on Microhardness of Spheroidized AISI 1090 Steel," Scripta Metallurgica, 15, 113 (1981).

209. J. P. Hirth, "Nucleation of Void Sheets in Creep and Hydrogen Attack," Res Mechanica Letters, 1, 3 (1981).

N 210. D. S. Williams, R. A. Rapp and J. P. Hirth, "Multilayer Diffusional Growth in Silver-Zinc Alloys," Metallurgical Transactions, 12A, 639 (1981).

A 211. I. H. Lin, J. P. Hirth and E. W. Hart, "Plastic Instability in Uniaxial Tension Tests," Acta Metallurgica, 29, 819 (1981).

212. M. F. Ashby, R. Bullough, C. S. Hartley and J. P. Hirth, "Dislocation Modelling of Physical Systems," Pergamon, Oxford (1981).

213. B. L. Adams and J. P. Hirth, "Influence of Texture and Slip Mode on Creep Constitutive Behavior of Hexagonal Metals," in "Dislocation Modelling of Physical Systems," edited by M. F. Ashby, R. Bullough, C. S. Hartley and J. P. Hirth, Pergamon, Oxford (1981) p. 368.

N 214. D. C. Langstaff, G. Meyrick and J. P. Hirth, "Hydrogen Induced Delayed Failure of High Strength Alloy Steel Wires," Corrosion, 37, 429 (1981).

N 215. Z. A. Munir and J. P. Hirth, "The Nature and Role of Surface Charge in Ceramics," in "Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems," edited by J. A. Pask and A. G. Evans, Plenum, New York (1981), p. 23.

SF 216. R. Fuentes-Samaniego and J. P. Hirth, "Diffusion of Interstitial Solute in a Potential Well Characteristic of a Moving Dislocation," Physica Status Solidi (b), 106, 359 (1981).

SF 217. M. W. Joosten, T. D. Lee, T. Goldenberg and J. P. Hirth, "Hydrogen Induced Degradation of Ductile Dispersed-Phase Alloys of Iron and of Nickel," in "Hydrogen Effects in Metals," edited by I. M. Bernstein and A. W. Thompson, Metallurgical Society of AIME, Warrendale, PA (1981), p. 839.

SF 218. J. P. Hirth and O. A. Onyewuenyi, "The Effect of Hydrogen on Surface Rumpling and Cracking in Spheroidized Steel," in "Environmental Degradation of Engineering Materials in Hydrogen," edited by M. R. Louthan, R. P. McNitt and R. D. Sisson, Virginia Polytechnic Institute, Blacksburg, VA (1981), p. 133.

SF 219. G. N. Gaidukov and J. P. Hirth, "The Influence of Thermodynamic Solution Properties on Solute Atmospheres at Dislocations," Physica Status Solidi (a), 66, 601 (1981).

220. A. J. Markworth and J. P. Hirth, "An Atomistic Model of Crack Extension by Kink Propagation," Journal of Materials Science, 16, 3405 (1981).

SF 221. J. P. Hirth, "Introduction to the Viewpoint Set on the Cold-Work Peak," Scripta Metallurgica, 16, 221 (1982).

SF 222. T. D. Lee, T. Goldenberg and J. P. Hirth, "Effect of Hydrogen on Fracture of U-Notched Specimens of Steel," in "Hydrogen in Metals," Supplement to Transactions Japanese Institute of Metals, 21, 413 (1980).

SF 223. I. H. Lin and J. P. Hirth, "On Brittle Crack Advance by Double Kink Nucleation," Journal of Materials Science, 17, 447 (1982).

224. R. Kirchheim and J. P. Hirth, "Hydrogen Adsorption at Cracks in Fe, Nb, and Pd," Scripta Metallurgica, 16, 475 (1982).

N 225. C. Tangchitvittaya, J. P. Hirth and R. A. Rapp, "Mechanism of the Solid-State Displacement Reaction between Iron and Nickel Oxide at 1000°C," Metallurgical Transactions, 13A, 585 (1982).

N 226. S. J. Czyzak, J. P. Hirth and R. G. Tabak, "The Formation and Properties of Grains in the Interstellar Medium," Vistas in Astronomy, 25, 337 (1982).

227. J. P. Hirth, E. J. Dulis and V. K. Chandhok, "The Contribution of Cobalt to the Tempering Resistance and Hot Hardness of Tool Steels and Cobalt Replacement," in "Strength of Metals and Alloys-6," edited by R. C. Gifkins, Pergamon, New York (1982), p. 185.

S 228. S. X. Xie and J. P. Hirth, "Permeation of Hydrogen, Trapping and Damage in Spheroidized AISI 1090 Steel," Corrosion, 38, 486 (1982).

S 229. J. P. Hirth and G. J. Dienes, "On the Rate of Equilibration of Diffusional Traps in Solids," Acta Metallurgica, 30, 2061 (1982).

S 230. J. P. Hirth, "Factors Contributing to Brittle Fracture of BCC Metals," in "Mechanical Properties of BCC Metals," edited by M. Meshii, The Metallurgical Society of AIME, Warrendale, PA (1982), p. 181.

S 231. O. A. Onyewuenyi and J. P. Hirth, "Plastic Instability in U-Notched Bend Specimens of Spheroidized AISI 1090 Steel," Metallurgical Transactions, 13A, 2209 (1982).

S 232. O. A. Onyewuenyi and J. P. Hirth, "Effects of Hydrogen on Notch Ductility and Fracture in Spheroidized AISI 1090 Steel," Metallurgical Transactions, 14A, 259 (1983).

233. J. P. Hirth, "Dislocations in Crystals," in "Crystallography in North America," edited by D. McLachlan, Jr., American Crystallographic Association, New York (1983), Chap. 2, p. 294.

S 234. J. P. Hirth and H. H. Johnson, "On the Transport of Hydrogen by Dislocations," in "Atomistics of Fracture," edited by R. M. Latanision and J. R. Pickens, Plenum, New York (1983), p. 771.

A 235. M. T. Miglin, I. H. Lin, J. P. Hirth and A. R. Rosenfield, "Mixed-Mode Crack Growth Using the Compact Specimen," Fracture Mechanics: 14th Symposium - Volume II: Testing and Application, edited by J. C. Lewis and G. Sines, ASTM STP. 791, American Society for Testing and Materials, Philadelphia, PA (1983), p. II-353.

A 236. M. T. Miglin, J. P. Hirth and A. R. Rosenfield, "Estimation of Transverse-Shear Fracture Toughness for an HSLA Steel," International Journal of Fracture, 22, R65 (1983).

N 237. S. Thamboo, G. W. Powell and J. P. Hirth, "The Mechanical Properties of RSR Processed Fe-Si-Al Alloys," International Journal of Powder Metallurgy and Powder Technology, 19, 211 (1983).

N 238. S. Guruswamy, J. P. Hirth and G. W. Powell, "Oxidation Behavior of Fe-Si-Al Alloys at 1173-1373K," Oxidation of Metals, 19, 77 (1983).

N 239. D. A. Carey, R. A. Rapp and J. P. Hirth, "Effect of Illumination on the Sublimation of Basal Surfaces of Zinc Oxide," Journal of Chemical Physics, 79, 3160 (1983).

S 240. S. X. Xie and J. P. Hirth, "The Effect of Hydrogen on Reversible and Irreversible Softening of Spheroidized Steel," Materials Science and Engineering, 60, 207 (1983).

A 241. M. T. Miglin, J. P. Hirth and A. R. Rosenfield, "Effects of Microstructure on Fracture Toughness of a High-Strength Low-Alloy Steel," Metallurgical Transactions, 14A, 2055 (1983).

N 242. J. P. Sauer, R. A. Rapp and J. P. Hirth, "Oxidation of Iron-Manganese-Aluminum Alloys at 850 and 1000°C," Oxidation of Metals, 18, 285 (1982).

243. J. P. Hirth, "Dislocations," in "Physical Metallurgy," edited by R. W. Cahn and P. Haasen, Elsevier, New York, 1983, Chapter 18, p. 1223.

N 244. J. P. Hirth and D. A. Rigney, "The Application of Dislocation Concepts in Friction and Wear," in "Dislocations in Solids," edited by F. R. N. Nabarro, North-Holland, Amsterdam, 1983, Vol. 6, p. 1.

N 245. S. Espevik, R. A. Rapp, P. L. Daniel and J. P. Hirth, "Oxidation of Ternary Co-Cr-W Alloys," Oxidation of Metals, 20, 37 (1983).

N 246. Z. A. Munir, E. K. Chieh and J. P. Hirth, "Ledge Configurations on Alkali Halide Surfaces Evaporated in an Electric Field," Journal of Crystal Growth, 63, 244 (1983).

S 247. R. Fuentes-Samaniego, R. Gasca-Neri and J. P. Hirth, "Solute Drag on Moving Edge Dislocations," Philosophical Magazine, 49A, 31 (1984).

S 248. R. Fuentes-Samaniego and J. P. Hirth, "Asymptotic Solutions for the Differential Equation Describing Solute Drag by Dislocations," Physica Status Solidi, 121b, 101 (1984).

S 249. G. N. Gaidukov, A. A. Podrezov and J. P. Hirth, "A Volterra-Type Dislocation Model of a Low-Angle [001] Twist Boundary in an F.C.C. Crystal," Physica Status Solidi, 82a, 355 (1984).

N 250. M. J. Yacaman, T. A. Parthasarathy and J. P. Hirth, "Hydrogen Attack in an Austenitic Stainless Steel," Metallurgical Transactions, 15A, 1485 (1984).

A 251. M. T. Miglin, J. P. Hirth and A. R. Rosenfield, "Development of Fractographic Features during Shear Failure of an HSLA Steel," Res Mechanica, 11, 85 (1984).

S 252. I. R. Kramer and J. P. Hirth, "Effect of Hydrogen on the Dislocation Density Distribution in 1090 Steel," Scripta Metallurgica, 18, 539 (1984).

253. J. P. Hirth, P. S. Pershan, J. Collett, E. Sirota and L. B. Sorensen, "Dislocation Model for Restacking Phase Transitions in Crystalline-B Liquid Crystals," Physical Review Letters, 53, 473 (1984).

254. J. P. Hirth and W. A. Tiller, "Ledge Growth Strain Accommodation and Stacking Fault Foundation During Silicon Oxidation," Journal of Applied Physics, 56, 947 (1984).

255. S. C. Chang and J. P. Hirth, "Effect of Hydrogen on Fracture of U-Notch Bend specimens of Ni-Cop Steel," Proceedings of the 3rd Asian-Pacific Corrosion Control Conference, Asian-Pacific Materials and Corrosion Association, Taipei, Taiwan, 1983, p. 305.

S 256. J. P. Hirth, "Theories of Hydrogen Induced Cracking of Steels," in "Hydrogen Embrittlement and Stress Corrosion Cracking," edited by R. Gibala and R. F. Hehemann, American Society for Metals, Metals Park, Ohio, 1984, p. 29.

S 257. R. Fuentes-Samaniego and J. P. Hirth, "Excess Solute Atmosphere Carried by a Potential Well Characteristic of a Moving Dislocation Core," Physica Status Solidi, 125b, 147 (1984).

258. J. C. Williams and J. P. Hirth, "Microstructure-Property Relations and Their Role in RSP Materials," in "Rapid Solidification Processing Principles and Technologies, III," edited by R. Mehrabian, National Bureau of Standards, Gaithersburg, Maryland, 1983, p. 135.

259. F. H. Froes, C. F. Yolton and J. P. Hirth, "Grain Growth in Beta III Titanium Alloy," in "Beta Titanium Alloys in the 80's," edited by R. R. Boyer and H. W. Rosenberg, The Metallurgical Society of AIME, Warrendale, PA, 1984, p. 185.

260. F. H. Froes, C. F. Yolton, J. P. Hirth, R. Ondercin and D. Moracz, "The Processing Window for Grain Size Control in Metastable Beta Titanium Alloys," in "Beta Titanium Alloys in the 80's," edited by R. R. Boyer and H. W. Rosenberg, The Metallurgical Society of AIME Warrendale, PA, 1984, p. 161.

261. I. H. Lin and J. P. Hirth, "Changes in Stress Intensity with Dislocation Emission From a Crack," Philosophical Magazine, A50, 1984, L-43-6.

S 262. J. P. Hirth, R. G. Hoagland and C. H. Popelar, "On Virtual Thermodynamic Forces on Defects and Cracks," Acta Metallurgica, 32, 1984, 371-9.

A 263. J. G. Schroth, R. G. Hoagland, J. P. Hirth and A. R. Rosenfield, "Tensile and Shear Fracture of an HSLA Steel," Scripta Metallurgica, 19, 1985, 215-9.

S 264. J. P. Hirth and W. D. Nix, "Analysis of Cavity Nucleation in Solids Subjected to External and Internal Stresses," Acta Metallurgica, 33, 1985, 359-68.

S 265. J. P. Hirth and H. Ehrenreich, "Charged Dislocations and Jogs in $Hg_{1-x}Cd_xTe$ and Other II-VI Compounds," Journal of Vacuum Science and Technology, 3A, 1985, 367-72.

S 266. H. Ehrenreich and J. P. Hirth, "Mechanism for Dislocation Density Reduction in GaAs Crystals by Indium Addition," Applied Physics Letters, 46, 1985, 668-70.

N 267. S. Guruswamy, J. P. Hirth and G. W. Powell, "Fracture Behavior of Rapidly Solidified Fe-Al-Si Alloys," The International Journal of Powder Metallurgy and Powder Technology, 21, 1985, 235-48.

268. E. C. Aifantis and J. P. Hirth, "The Mechanics of Dislocations," American Society for Metals, Metals Park, Ohio, 1985.

S 269. J. P. Hirth, "Crystal Plastic Effects in Constitutive Behavior," in "The Mechanics of Dislocations," edited by E. C. Aifantis and J. P. Hirth, American Society for Metals, Metals Park, Ohio, 1985, 53-6.

270. R. A. Oriani, J. P. Hirth and M. Smialowski, "Hydrogen Degradation of Ferrous Alloys," Noyes, Park Ridge, New Jersey, 1985.

S 271. J. P. Hirth, in "Hydrogen Degradation of Ferrous Alloys," edited by R. A. Oriani, J. P. Hirth and M. Smialowski, Noyes, Park Ridge, New Jersey, 1985, 131-9.

S 272. S. C. Chang and J. P. Hirth, "Hydrogen Degradation of Spheroidized AISI 1090 Steel," Metallurgical Transactions, 16A, 1985, 1417-25.

N 273. R. L. Shook, R. A. Rapp and J. P. Hirth," Displacement Reactions Between Cr and MoO_2 in a Ni-Base Alloy Matrix," Metallurgical Transactions, 16A, 1985, 1815-30.

S 274. J. P. Hirth, "A Brief History of Dislocation Theory," Metallurgical Transactions, 16A, 1985, 2085-90.

N 275. C. S. Lin, R. A. Rapp and J. P. Hirth, "Diffusional Breakdown of a Ag Diffusion Barrier in a Cu-Ag-Ni Diffusion Triple," Metallurgical Transactions, 17A, 1986, 933-44.

S 276. I. S. Jeong, W.A.T. Clark and J. P. Hirth, "Morphology and Electrical Resistance of Thin Gold Films on Air-Cleaved Potassium Chloride Surfaces," Thin Solid Films, 138, 1986, 267-78.

S 277. S. C. Chang and J. P. Hirth, "Hydrogen Degradation of Spheroidized AISI 1020 Steel," Metallurgical Transactions, 17A, 1986, 1485-7.

N 278. S. Guruswamy, S. M. Park, J. P. Hirth and R. A. Rapp, "Internal Oxidation of Ag-In Alloys: Stress Relief and the Influence of Imposed Strain," Oxidation of Metals, 26, 1986, 77-100.

A 279. M. T. Miglin, J. P. Hirth, A. R. Rosenfield and W.A.T. Clark, "Microstructure of a Quenched and Tempered Cu-Bearing High-Strength, Low-Alloy Steel," Metallurgical Transactions, 17A, 1986, 791-8.

S 280. W. Y. Shih, J. P. Hirth and D. Stroud, "Twin Boundary Energies and Entropies in Simple Metals: A Constant Pressure Monte Carlo Calculation," Physical Review, 34B, 1986, 2895-8.

281. J. P. Hirth, "On Dislocation Injection into Coherently Strained Multilayer Structures," S. African Journal of Physics, 9, 1986, 72-4.

S 282. R. G. Hoagland and J. P. Hirth, "Dilatant Center-Crack Tip Interaction Effects," Journal of the American Ceramic Society, 69, 1986, 530-3.

F 283. S. Guruswamy, J. P. Hirth and K. T. Faber, "Mechanical Properties of $Ga_{1-x}In_xAs$," Materials Research Society Symposium Proceedings, Vol. 53, 1986, 329-35.

N 284. D. S. Williams, R. A. Rapp and J. P. Hirth, "Phase Suppression in the Transient Stages of Interdiffusion in Thin Films," Thin Solid Films, 142, 1986, 47-64.

S 285. J. P. Hirth, "Microstructure and Mechanical Properties of Metals," in "Advancing Materials Research," National Academies Press, Washington, DC, 1986, 111-30.

F 286. J. P. Hirth and A. G. Evans, "Damage of Coherent Multilayer Structures by Injection of Dislocations or Cracks," Journal of Applied Physics, 60, 1986, 2372-76.

S 287. A. Chatterjee, J. P. Hirth, R. G. Hoagland, A. Choudhury and C. L. White, "Auger Analysis of Hydrogen Embrittled Grain Boundaries in a Boron Containing AISI 1520 Steel," Scripta Metallurgica, 21, 1987, 79-82.

F 288. S. Guruswamy, J. P. Hirth and K. T. Faber, "High-Temperature Hardness of $Ga_{1-x}In_xAs$," Journal of Applied Physics, 60, 1986, 4136-40.

289. M. F. Ashby and J. P. Hirth, "Perspectives in Hydrogen in Metals," Pergamon Press, Oxford, 1986, 758 pp.

S 290. V. B. Rajan and J. P. Hirth, "Effect of Hydrogen on Four-Point Bend Tests of U-Notched AISI 1090 Steel," Metallurgical Transactions, 18A, 1987, 335-40.

S 291. A. Valkonen, A. Chatterjee and J. P. Hirth, "On the Application of the Hutchinson-Tvergaard Shear Localization Equations in Plane Strain," International Journal of Mechanical Science, 29, 1987, 219-27.

S 292. J. G. Schroth, J. P. Hirth, R. G. Hoagland and A. R. Rosenfield, "Combined Mode I-Mode III Fracture of a High-Strength Low-Alloy Steel," Metallurgical Transactions, 18A, 1987, 1061-72.

293. D. J. Srolovitz, R. Eykholt, D. M. Barnett and J. P. Hirth, "Moving Discommensurations Interacting with Diffusing Impurities," Physical Review, 35B, 1987, 6107-21.

F 294. R. S. Rai, K. T. Faber, S. Guruswamy and J. P. Hirth, "Transmission Electron Microscopy Studies in Deformed $Ga_xIn_{1-x}As$," Proceedings of the 45th Annual Meeting of the Electron Microscopy Society of America, edited by G. W. Bailey, San Francisco Press, 1987, 320-21.

S 295. J. P. Hirth and I. H. Lin, "The Thermodynamic Force on Line Defects," Philosophical Magazine, A56, 1987, 89-92.

S 296. J. P. Hirth, "Hydrogen Induced Fracture," in "Chemistry and Physics of Fracture," edited by R. M. Latanision and R. H. Jones, Nijhoff, Boston, 1987, 538-51.

F 297. S. Guruswamy, R. S. Rai, K. T. Faber and J. P. Hirth, "Deformation Behavior of Undoped and In-doped GaAs in the Temperature Range 700-1100°C," Journal of Applied Physics, 62, 1987, 4130-34.

S 298. R. Kirchheim, "Stress and Solubility for Solutes with Asymmetrical Distortion Fields," Acta Metallurgica, 35, 1987, 2899.

N 299. J. P. Hirth, "Hydrogen Embrittlement of Steel," in "Environment Sensitive Fracture of Metals and Alloys," edited by R. P. Wei, D. J. Duquette, T. W. Crooker and A. J. Sedriks, Office of Naval Research, Arlington, VA, 1987, 79-87.

300. S. V. Kamat, J. P. Hirth and B. Carnahan, "Image Forces on Screw Dislocations in Multilayer Structures," Scripta Metallurgica, 21, 1987, 1587-92.