SOLIDIFIED EUTECTIC CERAM
MATRIX-METAL COMPOSITES

Final Report

Prepared under Contract N62269-76-C-0

Naval Air Development Center
Warminster, Pennsylvania 18974

for

Naval Air Systems Command
Department of the Navy
Washington, DC 20361

by

C. O. Hulse

May 1, 1977

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

⑲ **REPORT DOCUMENTATION PAGE**	**READ INSTRUCTIONS BEFORE COMPLETING FORM**
1. REPORT NUMBER ⑱ NADC-75282-30	~~2. GOVT ACCESSION NO.~~
	~~3. RECIPIENT'S CATALOG NUMBER~~ ⑨
4. TITLE (and Subtitle) ⑥ DEVELOPMENT OF DIRECTIONALLY SOLIDIFIED EUTECTIC CERAMIC MATRIX-METAL COMPOSITES. ⑭ UTRC	~~5. TYPE OF REPORT & PERIOD COVERED~~ Final Report, Apr[redacted]976 - Apr[redacted]977,
	~~6. PERFORMING ORG. REPORT NUMBER~~ R77-912587-4
7. AUTHOR(s) ⑩ C. O. Hulse	~~8. CONTRACT OR GRANT NUMBER(s)~~ ⑮ N62269-76-C-0250 new
9. PERFORMING ORGANIZATION NAME AND ADDRESS United Technologies Research Center East Hartford, CT 06108 ⑯ WR02204	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ⑰ A3200000/001A WR02204001
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Air Systems Command Washington, DC 20361	12. REPORT DATE ⑪ May [redacted]977
	~~13. NUMBER OF PAGES~~ 52
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Department of the Navy Naval Air Development Center Warminster, PA 18974 ⑫ 58p.	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited.	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	
18. SUPPLEMENTARY NOTES	

61153N

D D C

RECEIVED

DEC 29 1977

B

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

ceramic-metal	directional solidification
eutectic	gas turbine
ceramics	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The third and final year of effort to identify and develop directionally solidified ceramic matrix-metal eutectic composites for use uncoated at temperatures exceeding 1315°C (2400°F) in aircraft gas turbines is reported. The primary approach was to identify oxide-metal systems in which the metal whisker phase would form a self-protective oxide coating on exposure to air at elevated temperatures. Many different oxide-metal combinations were examined by melting prefired slugs contained in tungsten wire baskets. The specimens were melted →

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

409 252

LB

20. Continued

by radiation from a carbon susceptor inductively heated in argon. A wide range of cubic mixed oxides in combination with high-melting pure metal candidates were examined. A number of compositions were found which solidified as regular oxide-metal eutectics but difficulties with container reactivities and with the volatility of certain components prevented the fabrication of ingot samples suitable for further evaluation. Although the possibility remains that suitable eutectic systems may exist, the general conclusion from this work is that chances for the successful development of an oxide-metal eutectic system for structural use uncoated in air at elevated temperatures should now be considerably reduced.

UNITED TECHNOLOGIES
RESEARCH CENTER

UNITED
TECHNOLOGIES™

East Hartford, Connecticut 06108

Report R77-912587-4

Development of Directionally Solidified
Eutectic Ceramic Matrix-Metal Composites

Final Report

Contract N62269-76-C-0250

REPORTED BY C.O. Hulse
C. O. Hulse

APPROVED BY E.R. Thompson
E. R. Thompson, Manager
Materials Sciences

Report R77-912587-4

Development of Directionally Solidified Eutectic Ceramic Matrix-Metal Composites

TABLE OF CONTENTS

I. INTRODUCTION 1

II. PRIOR RESEARCH IN CERAMIC EUTECTICS 4

III. EXPERIMENTAL PROCEDURE 6

IV. TECHNICAL PROGRESS 9

V. SUMMARY AND CONCLUSIONS 12

VI. ACKNOWLEDGEMENTS 13

REFERENCES 14

TABLES I - VI 17

FIGURES 1 - 12

I. INTRODUCTION

This report describes the results of the third and final year of a research study directed toward the development of directionally solidified oxide matrix-metal eutectic composites for potential use in aircraft gas turbines (Refs. 1-3). This work was supported by Naval Air Development Center Contract N62269-76-C-0250, with Mr. I. Machlin of the Naval Air Systems Command, Washington, DC, as technical consultant and the Naval Air Development Center, Warminster, PA, as the contracting agency.

The temperature requirements for the materials used in gas turbine engines have continually increased until they are now so close to the melting temperatures of nickel and cobalt-base superalloys that significant further materials development appears doubtful. A reasonable response to this development is to reexamine more completely than ever before the possibilities of completely different types of materials. Pure oxide ceramics and some nonoxide ceramics such as Si_3N_4 and SiC have a number of properties which make them of interest; high melting points, good resistance to corrosion by liquids and gases, and high potential strength to weight ratios. The major limitations which currently restrict their use are low tensile strengths and an inability to plastically relieve internal or external stress concentrations. As a result, ceramics are brittle, heat shock sensitive and do not exhibit reproducible design strength values.

There are a number of circumstances which could produce improvements in the mechanical properties of ceramic-metal materials with a directional eutectic microstructure over that available from hot-pressed ceramics. An immediate possibility is that at high temperatures the minor metal phase will have the high strength characteristic of a material in whisker form and that this phase will directionally reinforce the somewhat ductile ceramic matrix in a typical composite manner. The reality of this possibility has been demonstrated in numerous metallic eutectic systems. Figure 1 shows that over a wide range of temperatures, similar Petch type equations relate strength to the spacing between phases in a eutectic (Ref. 4) just as they relate the strength to grain size in hot-pressed ceramics.

An important advantage of directionally solidified eutectics for high temperature strength applications is that their microstructure is extremely stable, practically to the melting point (Ref. 5). This stability results from the fact that their microstructures are produced directly from the molten state under conditions of thermodynamic equilibrium. If grain boundaries are present in these microstructures they are relatively few in number and generally parallel to the axis of primary reinforcement.

The strength of a eutectic composite at lower temperatures, where both phases may be more brittle, may be enhanced by a suitable selection of phases so that the matrix phase is placed in compression upon cooling due to differences in thermal expansion between the phases. A tensile stress applied to the bulk composite then will not result in a tensile stress in the continuous ceramic matrix phase until the compressive prestress is overcome. Tension is the primary failure mode of ceramic materials. The effectiveness of prestressing in increasing the strength of a ceramic matrix composite has been demonstrated (Ref. 6) and surface type prestressing is of considerable commercial importance in the glass industry. If, in addition to the prestress contribution, the matrix has a lower elastic modulus than the reinforcing phase, the amount of stress seen by the matrix phase during tensile loading of the composite will be even further reduced. A proportionately larger fraction of the applied stress is carried by the minor phase as the ratio of the modulus of reinforcing to matrix phase is increased.

The fracture of brittle materials is usually believed to involve the sudden growth of very fine flaws, called "Griffith Microcracks", which are always present in these materials. The importance of a flaw depends upon its size. Fracture normally involves the growth of the "critical" flaw which is the largest microcrack with the appropriate orientation to the applied load. Because the distribution of these flaws is random, the actual strengths of ceramics show a statistical distribution which is also a function of volume stressed. Some encouraging efforts have been made to limit the size of microcracks by the presence of a fine dispersion of second phase particles. If ceramic eutectics with a very fine, uniform microstructure can be produced, improved mechanical properties may be observed because the size of these microcracks are significantly limited.

The incorporation of a metal whisker phase into a ceramic should dramatically enhance the thermal conductivity and hence the resistance to thermal shock of the ceramic. A number of investigators (Refs. 7,8) have noted improvements in thermal shock resistance made by metal wire additions. Satisfactory resistance to thermal shock is a serious requirement for an aircraft gas turbine part.

The impact strengths of ceramics are generally so low that they are not usable in many important applications for which they might otherwise be well suited. The main mechanism by which energy is absorbed during fracture of brittle materials is through the production of new surfaces. The presence of a finely dispersed, high modulus fibrous or lamellar phase may function to deviate cracks and thus increase the amount of fracture surface produced during failure. These energies can be increased significantly if cracks are deflected so as to follow the dispersed phase-matrix interface.

The primary objective of this program is to identify and develop ceramic matrix-metal eutectic compositions which may be suitable for the production of directionally solidified in-situ composites. Interest is in eutectics which should yield ceramic matrix composites exhibiting advantageous mechanical, thermal cycling and impact properties, combined with resistance to oxidation and sulfidation, for use uncoated at temperatures of 1315°C (2400°F) and preferably higher, in aircraft gas turbines. The major emphasis in this program is the search for metal-oxide systems in which the metal phase does not react with oxygen to form a volatile species. If the volume of oxide produced is larger than the volume of metal consumed, the exposed ends of whiskers should convert to solid oxide plugs which should limit further attack. Problems of this plug cracking, spalling, etc. should be minimized because of the size of the coating and the presence of the associated oxide matrix phase. The consequent prestress of these surfaces in compression may also be an added benefit. The effects of alloying additions made to increase the oxidation resistance of the metal phase, to decrease the oxygen conductivity of the oxide matrix, to improve the ceramic/metal volume ratio, or to improve the coefficient of thermal expansion match between the matrix and the metal reinforcement were also examined. A concurrent study was to be made of systems requiring sealed containers such as MgO-W/Mo and Al_2O_3 (Cr_2O_3)-W/Mo.

The main emphasis during this year has been on a continued effort to identify an oxide-metal eutectic system which could be controlled well enough to continue with the mechanical testing and environmental stability evaluation parts of this program. Although a large number of melting and directional solidification experiments were conducted using many different candidate combinations, none of these experiments resulted in a satisfactory candidate composite system.

II. PRIOR RESEARCH IN CERAMIC EUTECTICS

The recent period of interest in refractory oxide-metal eutectic systems apparently began with the accidental discoveries by Chapman, et al and by Nelson and Rasmussen (Refs. 19 and 13) that eutectic composites containing very regular metal whiskers were formed by reaction between molten oxides and their refractory metal crucibles. Interest in these unusual microstructures was also influenced by a number of prior investigations of metal eutectic systems which had shown that in situ grown whiskers had high strengths and that these whiskers could significantly increase the strength and toughness of the matrix phase.

Most of the literature to date has been concerned with identifying the occurrence of oxide-metal eutectics. Table I presents a summary of known oxide-metal eutectic systems together with a listing of systems which contain ill-defined but possible eutectics. Table II gives a summary of systems in which no oxide-metal eutectics have been observed. The data presented in these tables is an updated version of a recent compilation by Briggs and Hart (Ref. 14).

The most extensive studies of oxide-metal eutectics has been by Prof. Chapman and associates at the Georgia Institute of Technology (Refs. 18,19). These efforts have been directed primarily toward the successful use of these materials as cold electron emitters for use in cathode ray tubes (Ref. 11). Other investigations have been reported from Oak Ridge (Ref. 21), Battelle Northwest and Battelle Geneva (Refs. 10,14), and from the Max-Plank-Institute (Ref. 15) in addition to the work at United Technologies (Refs. 1-3). The references given are not intended to be as complete as possible. Except for some reports of increases in toughness due to the presence of the metal whiskers (Refs. 9,10), the general literature has not included as yet any data on the strengths of oxide-metal eutectics.

Previous work on this program has shown that a number of potentially interesting systems which responded well to directional solidification, Gd_2O_3-CeO_2-Ta, Y_2O_3-CeO_2-Ta and Y_2O_3-CeO_2-Y, could not survive a 24 hr exposure to air at 1093°C (2000°F). The $(Cr,Al)_2O_3$-Cr system, however, showed a surface attack of only a few mils after an exposure of 60 hrs in air at 1425°C (2600°F). Figure 2 shows a polished section view of this eutectic transverse to the oxidized surface layers. A variety of alloying additions including the addition of another phase to form a "ternary" eutectic were examined within this basic system. Figure 3 shows the results of experiments conducted to measure the oxidation resistance of the "ternary" eutectic. After an initial oxidation of the exposed metal whiskers, there was practically no change in the weight of this material in static air at 1425°C (2600°F). The strengths of four samples of this eutectic grown at 1.2 cm/hr were measured in bending at 1540°C (2800°F) in argon. The average strength was 23,400 lbs/in.^{2}. The samples were completely brittle and there were jogs in the loading record suggesting cracking well below the ultimate strength. Work on this system was eventually stopped because the Cr whiskers would not grow parallel to the direction of solidification and it was not possible to prepare samples with adequately polished surfaces.

In addition to the investigations of oxide-metal eutectics, there have been prior studies of oxide-oxide eutectics at United Technologies sponsored by the Office of Naval Research (Ref. 22). Flexural strengths above 70 ksi at 1575°C were reported for the Al_2O_3-ZrO_2 (Y_2O_3) eutectic system. Other investigations of oxide-oxide eutectic systems have been conducted at Penn State University (Ref. 23), the Army Materials and Mechanics Research Center (Ref. 24) and at Lockheed (Ref. 25).

III. EXPERIMENTAL PROCEDURE

Certain requirements must be met in order to develop optimum eutectic microstructures. One important requirement is that the components must be of high purity. It is believed (Ref. 26) that the presence of impurities is the primary reason for localized constitutional supercooling and the formation of a cellular interface at the boundary between the liquid and solid during solidification. The details of the resultant colony microstructure in the final ingot have been described elsewhere (Ref. 27). These microstructures are characterized by parallel elongated volumes of relatively perfect eutectic structure with the axis of the colony oriented parallel to the direction of solidification. The material between the colonies contains a higher concentration of impurities than the eutectic material within the colonies and thus it solidifies at a lower temperature. Because of the differences in melting point, the material between the colonies solidifies after the eutectic within the colonies and the liquid-solid interface contains cusps or depressions around the colonies which would resemble cells if the liquid-solid interface could be viewed directly through the liquid. The mechanical properties of metallic eutectics with colony microstructures are almost always inferior to those obtained where a planar liquid-solid interface has been maintained. Because it was known that the presence of impurities usually results in poor microstructure, attempts were made to work primarily with high purity materials. All of the materials used in this program had purities of at least 99.95%.

Because there have only been a relatively small number of investigations of the phase equilibria between metals and oxides, it was necessary to develop some capability for determining this type of information in this program. A Russian compilation (Ref. 28) of the available phase diagrams between some metals and their own oxides has been useful. It was initially felt that rapid and convenient preliminary phase equilibria information could be obtained by melting small samples supported on refractory metal resistance heaters. However, when a refractory metal resistance strip heater is used both to hold the melt and to heat the melt, there is a good chance for some solid solution of the heater in the melt because the heater must be hotter than the melt. In order to minimize this possibility, an alternative procedure was developed in which samples were held in tungsten wire baskets suspended inside a small furnace consisting of a carbon susceptor, insulation and a controlled source of R.F. power. With this approach the tungsten wire is at the same temperature as the melt and it is used only for physical support of the melt. The melts usually did not run out of the basket because of surface tension forces. A diagrammatic view of the arrangement is presented in Fig. 4. Two baskets are shown in this figure. The contents of the upper basket are melted first and then the lower basket is traversed up into the furnace and the power increased again until it also melts.

The samples were observed continuously and their temperatures measured throughout the melting process by means of an optical pyrometer which sighted directly on the sample through a hole in the side of the furnace and susceptor. A second hole in the susceptor and in some of the insulation behind the sample permitted a good silhouette of the sample to be observed. The upper section of the sample usually had a notch or other definite sharp feature which could be observed to round off or change shape slightly during the initial melting before there was any direct contact of this part of the sample with the tungsten.

The optical pyrometer used in the above melting experiments was calibrated using a special resistance heater traceable to the National Bureau of Standards. The temperature drop due to the particular quartz window used was also measured at the same time. After melting, the samples in their baskets were usually mounted and polished so that their microstructures could be examined.

The charge rods used for melting and solidification experiments were made using hand mixed -325 mesh powders of the desired batch compositions. These mixtures were isostatically pressed into rods using a rubber balloon and isostatic pressures of about 15,000 lbs/in.^{2}. Sometimes an organic binder (polyvinyl alcohol or polystyrene) was used in order to obtain adequate green strength. The rods were then fired in a tungsten wire furnace in vacuum and/or argon to about 1500°C. After firing, the charge rods were hand-sanded to be straight. The final fired rods were typically 4 in. long and about 3/8 in. in diameter.

Most of the directional solidification experiments were conducted using CVD tungsten tubes as containers which were 6 in. long x 3/8 in. I.D. with walls which were approximately .010 in. thick. The tubes fitted on the end of a refractory metal post and were traversed by this support down through a carbon ring susceptor which created a zone of molten eutectic within the tube. A schematic of the apparatus is shown in Fig. 5. The bottom of the containment tube was self-sealed by the first melt which solidified on or near the refractory metal support post. The upper end of the tube was loosely sealed with a refractory metal cap. The use of a container was considered desirable because it corresponded closely to current foundry practice. It had the additional advantage that it tended to inhibit the loss of constituents by evaporation.

A major problem in making sound ingots was the elimination of the gases evolved during melting. These gases when entrapped would result in the formation of a number of short ingot sections with air pockets in between and/or bursting of the tungsten tubes. The use of a vibrator of variable force and frequency at the bottom of the refractory metal support rod was of some help but the best solution was to apply a weight of about 90 gms at the top of the ceramic-metal charge rod and to use smaller feed rods (i.e. 1/16 in. diameter) with triangular cross sections.

The furnace arrangements described in Figs. 4 and 5 were used within a Model J Westinghouse zone refiner designed for use with refractory metal systems. The unit includes a large chamber for work in inert gas or vacuum atmospheres and various traverse controls. A 50 kW Lepel power generator operating at ~500 K.C. supplied R.F. power to the work coil through a Lepel L.C.T.-4 step down transformer. Because ceramics are generally poor conductors, the actual heating was accomplished primarily by radiation from small, insulated carbon ring susceptors, usually about 3/16 in. thick.

In an attempt to avoid the reaction of certain systems of interest with the container, some directional solidification experiments were conducted using the floating molten zone technique. The procedure followed was the same as had been developed in a prior program sponsored by the Office of Naval Research (Ref. 22). For these runs, the ends of the charge rods were sanded into points which were inserted into the ends of ZrO_2 support tubes rigidly held by the traverse mechanism. The two ends of the charge rod, first the bottom and then the top, were fused to the support tube using the R.F. heater assembly. The zone melting was initiated in the rod just above the lower fused attachment point and the rod was slowly traversed downward. With this technique, no container is required because the short melt zone can be held in place by surface tension forces. A diagrammatic sketch which illustrates the procedure used in the floating molten zone experiments is presented in Fig. 6.

IV. TECHNICAL PROGRESS

The major effort during this year has been directed toward the identification of an oxide-metal eutectic system suitable for mechanical and environmental testing. Many different compositions were melted and examinations of polished sections were made in an effort to discover suitable high melting eutectic systems. A summary of 135 experiments of this type, using the melting facility shown diagrammatically in Fig. 4, are presented in Table III together with a comment about each experiment. Although a number of regular metal-oxide eutectics have been found, problems with excessive volatility and/or reaction with containers did not permit the preparation of aligned eutectic ingots suitable for property evaluations.

Most of the melts showed evidence of immiscibility or low solubility of the metal in the ceramic. Greater solubility of the metal in the melt was assumed when the metal phase was uniformly dispersed on a fine scale in a polished section. At the other extreme, in a melt with low metal solubility the melt was concentrated in a few large spheres or as many irregular globs. Figure 7 shows a somewhat intermediate case for a melt composition of 72 Gd_2O_3, 20 Al_2O_3 and 8 Nb with some eutectic-like microstructures together with metal present as somewhat rounded globs. Figure 8 shows another selected area in a melt of composition 19.2 MgO, 72.8 Cr_2O_3 and 8.0 W in which a regular oxide-metal eutectic microstructure was observed.

The conditions necessary for solubility of a metal in an oxide melt are not understood. It has been suggested that in some cases the melt should contain a slight excess of oxygen (Refs. 20,29). Several melting experiments were made with CO_2 additions to the usual argon atmosphere using a molybdenum susceptor and heat shields, runs W-Mp-76-92 and 93. Although these experiments were very limited in number, they did not result in improved solubility for the particular systems involved. Except in these few cases, all the melting experiments were carried out in an argon atmosphere using a graphite susceptor as the heat source. In ten experiments, W-Mp-77-17, -69, -102, -103, -105, -107, -108, -112, -113 and -114, areas of oxide-metal phase mixtures were observed which were so fine that they were at or just beyond the resolution capability of the optical microscope. These unusual observations were similar to those reported by Hart & Briggs (Ref. 14).

As mentioned earlier, most of the effort consisted of an experimental survey of systems in which eutectics might possibly exist. The oxides were selected primarily on the basis of high melting points, thermal stability, and their resistances to oxygen diffusion. The latter requirement was necessary in order to protect the whiskers from oxidation in use and this eliminates from consideration materials such as ZrO_2, HfO_2 and probably also CeO_2 and the C-type rare earths. The metals were selected primarily on the basis of melting point and their potential for forming stable oxides to provide for self-protection of the whiskers when exposed to air at elevated temperatures. This requirement eliminated most of the eutectics which had been previously reported because they contained refractory metals which would not be stable in air at elevated temperatures. Some systems containing tungsten and molybdenum were eventually considered with the thought that they might somehow be highly alloyed with other metals which would form stable oxide coatings in air at elevated temperatures.

Tungsten was also added to a number of melt compositions in an attempt to reduce the reactivity of the melts with the tungsten wire baskets and the CVD tungsten containers. Some of these tungsten additions were also made as WO_3 in an attempt to add more oxygen to the melt and thereby to improve the solubility of the metal phase. Throughout this series of melting experiments it was felt that the use of variable valent materials, such as, for example, Fe, Cr, NiO, Cr_2O_3 and Fe_2O_3 was helpful in the promotion of metal solubility. Unfortunately the use of these materials also accelerated the reactivity of the melt with the container.

In earlier work we had observed that eutectics in the $(Cr,Al)_2O_3$-Cr system formed very regular microstructures with good inherent resistance to oxidation at reasonable use temperatures. However, after considerable effort we eventually abandoned work on this system because the Cr whiskers would never grow parallel to the solidification direction, this being parallel to the C-axis of the alumina and not the direction of growth preferred by Cr. Also, we were never able to mechanically polish large areas of sample surfaces free of pits and pull outs in this system. We subsequently decided that the best chances for obtaining regular eutectic microstructures with whiskers parallel to the direction of growth were with the cubic oxide structures. Most of the remainder of the year was spent looking for regular oxide-metal eutectics with cubic mixed-oxides. The results of these melting experiments have been abstracted from Table III and are presented in summary form in Table IV.

The data contained in Table IV presents many new eutectic systems. Much of these data are the result of only one melting experiment, especially in systems where no eutectic or eutectic-like structures were observed, so some reservations about the data are in order. Figures 9 through 12 show examples of eutectic microstructures in melts of various compositions. Most of the systems which form eutectics, unfortunately, have significant problems with volatility at the temperatures required for melting. Also, at these temperatures, the systems which contained eutectic microstructures reacted with tungsten. Reactivity with tungsten tended to occur at these temperatures particularly with any system containing the oxides Cr_2O_3, MgO and CaO and with the metals Fe, Cr, NiAl and Ti. Also, in a number of cases, as noted in Table IV, additional phase or phases were observed in the polished section. Taken altogether, the combination of these problems suggests that a large amount of additional effort with questionable chances of success would need to be committed to develop a melt grown oxide-metal eutectic composite material suitable for structural use in air at high temperatures.

A modification of our usual melting procedure was required to melt compositions containing NiAl or Fe which were particularly reactive with tungsten. Our first approach was to melt the bottom ends of rods supported by tungsten wires wrapped around the cooler top of the rod. Unfortunately, the rods tended to loosen and fall when the rods shrank upon heating. It was difficult to prepare rods containing NiAl with adequate strength or as long as desired. The metal tended to "sweat out" of the isostatically cold-pressed rods at elevated temperatures. It became necessary finally to directionally fire the rods in the float zone apparatus in order to obtain the necessary properties. A better holding procedure which evolved for the melting experiments was to cut notches or to drill a hole through the fired rod for the tungsten support wires.

Because of the reactivity of melts containing NiAl or Fe, the floating molten zone technique was used to directionally solidify compositions containing these metals. Our earlier experience with this solidification technique prompted us to make a modification to the equipment under Corporate support. An air bearing support system was developed for the upper end of the rod which permitted it to rotate freely if there was any solid connection inside the molten zone between this charge rod and the growing ingot at the bottom which was caused to rotate at a fixed speed through a slip clutch. Observation of the presence or absence of rotation of the charge rod permitted an easy visual indication of the extent of melting. A summary of the floating molten zone experiments is presented in Table V. In some of these experiments, a platinum wire was embedded in a cubic oxide rod and then the rod was melted in a brief attempt to discover a precious metal-oxide eutectic. None were observed. The other experiments were not successful, again primarily because of poor metal solubilities and vaporization.

In order to be able to make a useful, shaped part by a practical process we have felt that it must be possible to support the molten eutectic within a container. Perhaps because most of the melt volume is ceramic, CVD tungsten containers fabricated at UTRC have usually been adequate for this purpose. The metal components often showed some tendency to react with the tungsten but this was not a serious problem with the lower melting systems studied earlier. Table VI presents the data for directional solidification experiments obtained during the current year. The general result of these runs was unacceptable reaction between the melts and the CVD tungsten container.

V. SUMMARY AND CONCLUSIONS

An experimental survey of many possible oxide-metal systems was made in a search for compositions which would solidify with regular eutectic microstructures. The major effort concentrated on systems containing cubic mixed oxides because it was felt that these systems provided the best chance for finding regular eutectic microstructures in which the whisker phase grew parallel to the direction of solidification. A summary of all the new eutectics discovered (Table IV) and a summary of all known oxide-metal eutectic systems is included together with a listing of systems which apparently do not contain eutectics (Tables II and IV).

A major problem encountered in this work was the lack of metal solubility in the melt. Variable valent materials added either as metals or as oxides appeared to encourage solubility. Some experiments with uncertain results were also made in which excess oxygen was added to the melts. Although a number of potentially interesting new eutectics were found, they all appeared to be associated with one or more of the following problems: (a) excessive volatility in the molten state, (b) high reactivity with tungsten containers, or (c) additional phases present in the melt. Based on these results, the chances of finding and properly preparing an oxide-metal eutectic system of practical use for structural applications exposed to air at elevated temperatures appear to be considerably reduced. Probably the best applications for the use of these remarkable composite materials will be in some nonstructural device where the preparation of large volumes of material with perfect microstructures is not mandatory.

VI. ACKNOWLEDGEMENTS

The author would like to express his appreciation to Mr. Norman Chamberlain who carried out experimental portions of this program.

REFERENCES

1. Hulse, C. O.: Directionally Solidified In Situ Eutectic Ceramic Matrix-Metal Composites. Final Report, Contract N00019-74-C-0271, United Technologies Corp. Report R75-911842-4 (March 1975).

2. Hulse, C. O.: Development of Unidirectionally Solidified Eutectic Ceramic Matrix-Metal Composites. Final Report, Contract N62269-75-C-0120, United Technologies Corp. Report R76-912084-4 (May 1976).

3. Hulse, C. O.: Preparation and Characterization of $Cr-Cr_2O_3$, $Al_2O_3-ZrO_2$ (Y_2O_3) Eutectics. Proceedings of Conference on In-Situ Composites-II, Lake George, NY, 1975, Plenum Press.

4. Thompson, E. R., E. Kraft and F. George: Investigation to Develop a High Strength Eutectic for Aircraft Engine Use. Technical Report J910803-4, United Technologies Corp. (July 1970).

5. Bayles, B., J. Ford and M. Salkind: The Effect of Elevated Temperature Exposure on the Microstructure and Tensile Strength of Al_3Ni Whisker Reinforced Aluminum, Trans. AIME, Vol. 239, p 844 (1967).

6. Hulse, C. and B. Jacob: Fiber Prestressed and Reinforced Ceramics. Technical Report F110326-1, United Technologies Corp. (1967).

7. Truesdale, R. S., J. J. Surica and J. R. Tinklepaugh: Metal Fiber Reinforced Ceramics: WADC Tech. Report 58-452, Part I (Dec. 1958), Alfred Univ.

8. Surica, J. J., W. R. Joskyns, B. R. Goss, J. H. Connor, and J. R. Tinklepaugh: Metal Fiber Reinforced Ceramics. WADC Tech. Report 58-452 (Jan. 1960), Alfred Univ.

9. Claussen, N.: Hot-Pressed Eutectics of Oxides and Metal Fibers. J. Am. Ceram. Soc., 56 [8] 442 (1973).

10. Hart, P. E.: Proceedings of Conference on In Situ Composites, Lakeville, CT, 1972, Vol. III, pp 119-27. National Academy of Sciences, Washington, DC, Publ. NMAB-308-3, 1973.
    Hart, P. E.: Unpublished work.

11. Chapman, A., J. Benzel, J. Cochran, R. Feeney, J. Hooper, and J. Norgard: Melt Grown Oxide Composites. Final Tech. Report, ARPA Contract No. DAAH01-71-C-1046, Dec. 1973, and Progress Report Nos. 4 (July 1972) and 5 (Dec. 1972).

12. Levin, E., C. Robbins and H. McMurdie: Phase Diagrams for Ceramists, p. 39, Ed. by M. Reser, the American Ceramic Society, Inc., Columbus, OH (1964).

13. Nelson, R. and J. Rasmussen: Composite Solidification in the Systems Cr_2O_3-Mo, Cr_2O_3-Re, Cr_2O_3-W and MgO-W. J. Am. Ceram. Soc., 53 [9] 527 (1970).

14. Briggs, J. and P. Hart: Refractory Oxide-Metal Eutectics, J. Am. Ceram. Soc., 59 [11-12] 530 (1976).

15. Claussen, N., G. Petzow and J. John: High-Melting Metal-Ceramic Eutectics. Plansee Proc., Paper Plansee Semin., De Re Met., 8th, 1973 (Pub. 1974), Vol. II, No. 45, ONRL Transl. No. 2873 (1974).

16. Johnson, T. and J. Benzel: Unidirectional Solidification of Stabilized HfO_2-W. J. Am. Ceram. Soc., 56 [4] 234 (1973).

17. Jen, Chi-Chin and J. Benzel: Unidirectional Solidification of the UO_2-Mo, UO_2-Nb and UO_2-Ta Systems, ibid., 57 [5] 232 (1974).

18. Chapman, A., G. Clark and D. Hendrix: UO_2-W Cermets Produced by Unidirectional Solidification. Ibid., 53 [1] 60 (1970).

19. Chapman, A. and G. Clark: Growth of UO_2 Single Crystals Using the Floating-Zone Technique. J. Am. Ceram. Soc., 48 [9] 494 (1965).

20. Chapman, A., J. Benzel, J. Cochran, R. Feeney, F. Ling and J. Norgard: Melt-Grown Oxide-Metal Composites. Final Report, ARPA Contract DAAH01-71-C-1046, Georgia Inst. Tech. (1973).

21. Holder, J. and G. Clark: Directional Solidification by Internal Zone Melting of Cr_2O_3-Mo Composites. Proceedings of Conf. on In-Situ Composites-II, Lake George, NY, 1975, Plenum Press.

22. Hulse, C. and J. Batt: The Effect of Eutectic Microstructures on the Mechanical Properties of Ceramic Oxides. Final Report, Contract N00014-69-C-0073, United Technologies Corp. Report N910803-10 (1974).

23. Kennard, F., R. Bradt and V. Stubican: Mechanical Properties of the Directionally Solidified MgO-$MgAl_2O_3$ Eutectic. J. Am. Ceram. Soc., 59 [3-4] 160 (1976).

24. Schmid, F. and D. Viechnicki: Oriented Eutectic Microstructures in the System Al_2O_3/ZrO_2. J. Mats. Sci., 5, 490 (1970).

25. Rowcliffe, D., W. Warren, A. Elliot and W. Rothwell: The Growth of Oriented Ceramic Eutectics. J. Mats. Sci., 4, 902 (1969).

26. Chadwick, G.: J. Inst. Metals, 91, p 169 (1963).

27. Chalmers, B.: Principles of Solidification, J. Wiley and Sons (1964).

28. Toropov, N., V. Barzakooskii, I. Bondar and Yu Udalov: Handbook of Phase Diagrams of Silicate Systems, Vol. II, Metal-Oxygen Compounds in Silicate Systems. Translation Pub. U.S. Dept. Commerce (1972).

29. Graves, J. A.: Unidirectional Solidification of $Y_2O_3(CeO_2)$-Mo and Y_2O_3 (CeO_2)-W Composites. Masters Thesis, Georgia Inst. of Tech. (1973).

Table I

Summary of Known Oxide-Metal Eutectics

Well Defined Eutectic		Ref.
$(Al,Cr)_2O_3$	Cr	9,1
$(Al,Cr)_2O_3-ZrO_2(Y_2O_3)$	Cr	1
$(Al,Cr)_2O_3$	Mo	10
$(Al,Cr)_2O_3$	W	10,1
CeO_2	Mo	14,11
CeO_2	W	14,11
Cr_2O_3	Cr	12
Cr_2O_3	Mo	13
Cr_2O_3	Nb	15
Cr_2O_3	Re	13
Cr_2O_3	Ta	15
Cr_2O_3	V	15
Cr_2O_3	W	13
$Cr_2O_3(CeO_2)$	Mo	11
$Fe_2O_3 \cdot Cr_2O_3-Cr_2O_3$	Fe	2
$Gd_2O_3(CeO_2)$	Mo	13
$Gd_2O_3(CeO_2)$	W	13,1
$Gd_2O_3(CeO_2)$	Ta	1
$Gd_2O_3(CeO_2)$	Y	1
GeO_2	Ge	4
$HfO_2(CeO_2)$	W	16
$HfO_2(Y_2O_3)$	W	16
HfO_2	Hf	1
$Ho_2O_3(CeO_2)$	Mo	11
$La_2O_3(CeO_2)$	Mo	11
$La_2O_3(CeO_2)$	W	11
MgO	W	13
$Nd_2O_3(CeO_2)$	Mo	11
$Nd_2O_3(CeO_2)$	W	14
Sm_2O_3	W	14
$Sm_2O_3(CeO_2)$	W	14
Ta_2O_3	Ta	1
$Ta_2O_3(CeO_2)$	Ta	1
UO_2	Nb	17
UO_2	Ta	17
UO_2	W	18
Y_2O_3	Ta	14
Y_2O_3	Y	1
Y_2O_3	W	1
$Y_2O_3(CeO_2)$	Mo	14,11
$Y_2O_3(CeO_2)$	W	11
ZrO_2	Ta	15

Ill-Defined or Possible Eutectic		Ref.
$CeO_2(ZrO_2)$	W	14
La_2O_3	Mo	11
La_2O_3	W	11
Nd_2O_3	Mo	11
Nd_2O_3	W	11
TiO_2	Cr	15
TiO_2	Mo	14
TiO_2	Nb	15
TiO_2	Ta	15
UO_2	Mo	18
$Y_2O_3(CeO_2)$	Ta	14
Y_2O_3	Mo	14
ZrO_2	W	14
ZrO_2	Z	1

Table II

Summary of Systems in Which No Oxide-Metal Eutectic Has Been Observed

Mixture		Ref.	Mixture		Ref.
Al_2O_3	Mo	10	$Nb_2O_5(TiO_2)$	Mo	14
Al_2O_3	W	10	Sm_2O_3	Mo	14
$Al_2O_3(CaF_2)$	W	14	TiO_2	W	14
$Al_2O_3(CeO_2)$	W	11	$TiO_2(Nb_2O_5)$	W	14
$(Al,Cr)_2O_3$	Ti	2	$TiO_2(ZrO_2)$	W	14
$3Al_2O_3 \cdot 2SiO_2 - ZrO_2 \cdot SiO_2$	Cr	2	$TiO_2(TiO_2)$	W	14
$Al_2O_3(TiO_2)$	Mo	14	Y_2O_3	W	14
$Al_2O_3(Y_2O_3)$	W	14	$Y_2O_3(CeO_2)$	Fe	14
$Al_2O_3(ZrO_2)$	W	14	$Y_2O_3(CeO_2)$	Nb	14
CeO_2	Ta	14	$Y_2O_3(CeO_2)$	V	14
HfO_2	W	14	$Y_2O_3(CeO_2)$	W	14
$MgO \cdot Al_2O_3$	Cr	2	$Y_2O_3(CeO_2)$	Zr	14
$MgO \cdot Al_2O_3$	Mo	13	$Y_2O_3(MgO)$	Mo	14
$MgO \cdot Al_2O_3$	Ni	13	$Y_2O_3(TiO_2)$	Mo	14
$MgO \cdot Al_2O_3$	Ta	13,2	$Y_2O_3(UO_2)$	Mo	14
$MgO \cdot Al_2O_3$	Ti	13	ZrO_2	Mo	11
$MgO \cdot Al_2O_3$	W	14	$ZrO_2(CeO_2)$	Mo	14
$MgO(CeO_2)$	Mo	14	$ZrO_2(Y_2O_3)$	Co	11
Nb_2O_5	Mo	14	$ZrO_2(Y_2O_3)$	Fe	11
Nb_2O_5	W	14	$ZrO_2(Y_2O_3)$	Ni	11

Table III

Melting Runs in Tungsten Baskets or Short Tubes
(argon atmosphere, carbon susceptor unless otherwise noted)

Run #	Material (w/o)	Remarks (°C)
W-Mp-76-31	10 NiAl 38 NiO 52 Al_2O_3	Basket collapsed, melt fell, repeated, basket failed again with only partial melting at 1850-1890°.
W-Mp-76-32	10 NiAl 64.6 Al_2O_3 25.4 SiO_2	Melted well at 1810° with some attack on W wire basket. Metal apparently immiscible (globs) with some fine metal dispersions - generally metal poor. Metal globs 2 phase, oxide crystals (apparently Al_2O_3) associated with metal globs.
W-Mp-76-33	10 NiAl 29.66 NiO 60.34 Cr_2O_3	Basket failed at 1795°, sample did not melt.
W-Mp-76-34	10 NiAl 38 NiO 52 Al_2O_3	Repeat of W-Mp-76-31 in short CVD-W tube, partially melted at 1980° but not enough for polishing and examination.
W-Mp-76-35	10 NiAl 29.66 NiO 60.34 Cr_2O_3	Repeat of W-Mp-76-33 with wire basket just over W tube. Melted 1980°, reacted with W, small slug all good rod-like eutectic. In one area a metal-metal eutectic. Major problem reactivity with W.
W-Mp-76-36	10 NiAl 38 NiO 52 Al_2O_3	Repeat of W-Mp-76-31 with wire basket over W tube, melted 1890°, poor metal solubility, metal globs, attack on tungsten wires.
W-Mp-76-37	10 NiAl 25.5 MgO 64.5 Al_2O_3	Melted 1/2" long slug at 2000°, crumbled apart in polishing; 2-phase metal globs, very poor metal solubility, many "chip-outs" of lighter oxide phase in grain boundaries.
W-Mp-76-38	10 NiAl 18.1 MgO 71.9 Fe_2O_3	Melted and reacted with tungsten tube at 1790°. Poor metal solubility, considerable volume of dark faceted phase, significant attack on tungsten.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-76-39	9.5 NiAl .5 Cr 45 Al_2O_3 45 Cr_2O_3	Partially melted at 1980° in tungsten, able to use crucible over. Metal globs but rather finely dispersed, oxide-oxide eutectic present but difficult to see, regular metal whisker eutectic structures in one area with 3-fold symmetry.
W-Mp-76-40	9.5 NiAl .5 Cr 45 Al_2O_3 45 Cr_2O_3	Melted 2040°, dense but fracture during mounting for examination. Some areas of good eutectic but metal poor. Batch volume percent metal about right but not well dissolved.
W-Mp-76-41	10 NiAl 44.58 $CaCO_3$ 45.42 Al_2O_3	Melted 1/4" long slug at 1640°, appears to be only sintered with metal globs. Apparently attacked by water.
W-Mp-76-42	10 NiAl 29.5 SiO_2 60.5 ZrO_2	Did not melt at 1800°, repeated in short CVD-W tube, poorly melted at 2130°, very porous, very poor metal solubility, crystalline oxide in glassy matrix.
W-Mp-76-44	10 NiAl 35.7 NiO 39 Al_2O_3 15.3 Cr_2O_3	Reaction with W crucible, incomplete melting at 1980°C, porous, poor metal solubility.
W-Mp-76-45	10 NiAl 34.2 NiO 37.2 Al_2O_3 14.6 Cr_2O_3	Reacted with W crucible at 2100°, difficult to see any melt structures in mounted piece.
W-Mp-76-46	10 NiAl 4 W 34.2 NiO 37.2 Al_2O_3 14.6 Cr_2O_3	Reacted with W at 2070°, crucible collapsed around partial melt, porous with poor metal solubility.
W-Mp-76-47	15 NiAl 51 Al_2O_3 34 Cr_2O_3	Reacted with W crucible at 2000°, fair metal solubility, many globs, material polishes poorly.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-76-48	10 NiAl 90 FeO·Fe_2O_3	Reacted with W at 1595°, metal apparently immiscible (globs) but many areas where metal is finely dispersed, no regular eutectic structures seen.
W-Mp-76-49	10 NiAl 30 MgO 10 NiO 50 Cr_2O_3	Incomplete melting at 2215°, metal solubility fair, two oxide phases, one much darker than the other.
W-Mp-76-50	10 NiAl 35.7 NiO 39 Al_2O_3 15.3 Cr_2O_3	Repeat of -44, tungsten tube prefired at 1730° full of graphite to form carbide barrier layer, charge attacked container at 2100°, very dense, dark, transparent, fine eutectic in grain boundaries, fairly many "pull outs" of oxide phase upon polishing.
W-Mp-76-85	15 NiAl 10 NiO 50 Cr_2O_3 25 Al_2O_3	Melted, reacted with tungsten tube crucible, melt background 2000°.
W-Mp-76-86	15 NiAl 20 NiO 45 Cr_2O_3 20 Al_2O_3	Melted well at about 1890°, generally poor solubility with globs of metal. Good eutectic structures in one area.
W-Mp-76-87	15 NiAl 30 NiO 25 Cr_2O_3 20 Al_2O_3	Generally poor metal solubility, large and small globs of metal, no eutectic structures, Mp ~1900°.
W-Mp-76-88	20 NiAl 80 NiO	Extensive reaction with W tube crucible about 1870°.
W-Mp-76-89	10 Cr 15 Fe 20 Cr_2O_3 55 Fe_2O_3	First try, slumped over tungsten tube, did not melt 1600°C, repeated with hanging rod, wire broke; second attempt, sample slipped and fell at 1700°C. Next supported rod with W wire through hole in rod. Poor metal solubilities, two oxide phases, some metal in both phases but not well dispersed.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-76-90	20 Cr 5 Fe 20 Cr_2O_3 55 Fe_2O_3	Rod suspended from tungsten wire, melted end at 1900°C. Poor metal solubility, two oxide phases, metal most soluble in boundary phase, soft to polish.
W-Mp-76-91	5 Cr 20 Fe 35 Cr_2O_3 40 Fe_2O_3	Again used prefired rod suspended from tungsten wire, melted lower end. More boundary (oxide) phase than -90, poor metal solubility. Metal tends to be in boundary phase, some metal in primary oxide phase. Primary phase tends to "chip", polishes poorly.
W-Mp-76-92	20 Cr 5 Fe 20 Cr_2O_3 55 Fe_2O_3	Used moly susceptor and shields, argon plus 8 v/o CO_2. Shields warped ~1760°, put 1/8" thick zircar sheet between shields. Sample melted 1850°, two oxide phases, practically no metal phase present, matrix very dense, metal all in boundary oxide phase.
W-Mp-76-93	5 Cr 20 Fe 35 Cr_2O_3 40 Fe_2O_3	Moly susceptor, argon plus 8 v/o CO_2. Sample melted 1800-2000°. Structures similar to -90, more (lighter) boundary oxide phase and some large metal globs. Most metal solubility in oxide boundary phase.
W-Mp-76-94	10 Cr 15 Fe 20 Cr_2O_3 55 Fe_2O_3	Sample fell from tungsten wire, fused to susceptor at about 1750°C, did not melt completely.
W-Mp-77-9	43.1 Al_2O_3 50.3 $CoCO_3$ 6.6 NiAl	Lost melt 1960°C, system dirty, repeated, melted at 2000° but also fell from basket. Metal in globs, not dispersed, ceramic has fine second phase or chip-outs during polishing.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-10	43.1 Al_2O_3 50.3 $CoCO_3$ 6.6 Mo	Shrank by 2/3 at 2040°C but did not melt, dirty.
W-Mp-77-11	43.1 Al_2O_3 53.3 $CoCO_3$ 6.6 Cr	Reacted with W basket at 1990°C. Metal in globs, poorly distributed. Globs not particularly round suggesting tendency to mix, matrix "chips".
W-Mp-77-12	43.1 Al_2O_3 53.3 $CoCO_3$ 6.6 $MoSi_2$	At 1880°C, material shrank and went through bottom of W basket.
W-Mp-77-13	43.1 Al_2O_3 50.3 $CoCO_3$ 6.6 W	Shrank and fell through basket, repeated, melted 1945° but fell through basket. Distributed globs of metal, not well mixed.
W-Mp-77-14	43.1 Al_2O_3 50.3 $CoCO_3$ 6.6 Ti	Melted 1940°. Metal in globs, not well dispersed. Apparent sub-metal (gold color) associated with globs. Matrix has darker angular phase which apparently tends to chip in polishing with a lighter grain boundary phase. No metal-oxide eutectic seen.
W-Mp-77-14.5	43.1 Al_2O_3 50.3 $CoCO_3$ 6.6 Nb	Melted 2000°, no oxide-metal eutectic. Globs of metal poorly dispersed.
W-Mp-77-15	72 Gd_2O_3 20 Al_2O_3 8 NiAl	Melted 2100°C, corrected. No oxide-metal eutectic. Dense, large-grained matrix. In these grain boundaries some evidence of oxide-oxide eutectic with some metal solubility.
W-Mp-77-16	72 Gd_2O_3 20 Al_2O_3 8 Mo	Melted 2070°C, corrected. No metal-oxide eutectic but metal dispersed and on verge of solubility. Oxide dense but with large pores.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-17	72 Gd_2O_3 20 Al_2O_3 8 Cr	Melted on third attempt at 2070°, corrected. Metal solubility on a fine scale, still some globs but no metal-oxide eutectic microstructure. Needs more metal. Evidence of massive substructure in some large grains. Solid state inversion?
W-Mp-77-18	72 Gd_2O_3 20 Al_2O_3 8 $MoSi_2$	Melted 1985°C, corrected, lost through basket. Metal globs, no solubility.
W-Mp-77-19	72 Gd_2O_3 20 Al_2O_3 8 W	Melted 2185°, corrected. Sample porous, no big globs of metal. Fine metal globs on verge of solution.
W-Mp-77-20	72 Gd_2O_3 20 Al_2O_3 8 Ti	Melted 2170°, corrected. No oxide-metal eutectic, but metal on verge of solution. Relatively small metal globs, larger globs have oxide centers, thin oxide grain boundary phase in matrix.
W-Mp-77-21	43.1 Al_2O_3 50.3 $CoCO_3$ 6.6 Mo	Melted through W basket at 1990°C, no oxide metal eutectic. Metal globs, some 2 phase, ceramic porous, appears to chip during polishing on a fine scale.
W-Mp-77-22	72 Gd_2O_3 20 Al_2O_3 8 Nb	Melted 2090°, corrected. Metal globs tending to be dispersed, oxide-metal eutectic-like structures in centers of globs, other areas, fine globs or no metal at all.
W-Mp-77-23	43.1 Al_2O_3 53.3 $CoCO_3$ 6.6 $MoSi_2$	Melted 1880°, corrected. No metal solubility, angular oxide matrix with some lighter grain boundary phase.
W-Mp-77-24	52.7 Al_2O_3 39.5 Mn_3O_4 7.8 Mo	Melted 1784°, corrected. Poor melt, volatile. Metal almost soluble, many small droplets; a small amount of second oxide phase.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-26	52.7 Al_2O_3 39.5 Mn_3O_4 7.8 Cr	Melted 1710°, corrected. Melt easily separated from basket. Dense oxide matrix, metal as globs but on edge of solubility. Second oxide phase in one area.
W-Mp-77-27	52.7 Al_2O_3 39.5 Mn_2O_3 7.8 W	Melted 1745°, corrected. Easily separated from W basket. Sample dense, metal tending to disperse but not much metal present. Apparent suboxide in grain boundaries.
W-Mp-77-28	52.7 Al_2O_3 39.5 Mn_2O_3 7.8 Ti	Melted 1670°, very volatile, melt fair, no metal phase present, three "oxides".
W-Mp-77-29	52.7 Al_2O_3 39.5 Mn_3O_4 7.8 Nb	Melted 1670°, corrected. Very volatile, melt fused to susceptor. Two oxide phases, small amount of metal, not well dispersed.
W-Mp-77-30	41.5 TiO_2 52.4 $CaCO_3$ 6.1 NiAl	Melted 1855°, corrected. Poor melt (porous), volatile.
W-Mp-77-31	41.5 TiO_2 52.4 $CaCO_3$ 6.1 Mo	Melted 1920°, corrected. Poor melt, volatile. Metal tending to dissolve but no metal-oxide eutectic. Matrix appears to contain long zones of transformed or twinned material.
W-Mp-77-32	41.5 TiO_2 52.4 $CaCO_3$ 6.1 Cr	Melted 1890°, corrected. Oxide-metal eutectic, not regular but good. Eutectic associated with grain boundaries - a slightly darker boundary phase present. Try larger metal contents.
W-Mp-77-33	41.5 TiO_2 52.4 $CaCO_3$ 6.1 W	Melted 1925°, corrected. No metal oxide eutectic. Some darker (oxide) boundary phase, metal finely dispersed but primarily in boundaries.
W-Mp-77-34	41.5 TiO_2 52.4 $CaCO_3$ 6.1 Ti	Melted 1890°, corrected, fair melt. "Metal" present as a continuous sheet at all grain boundaries; in other areas degenerate eutectic. Apparent presence of suboxide.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-35	41.5 TiO_2 52.4 $CaCO_3$ 6.1 Nb	Melted 1890°, corrected. System very dense, two oxide phases, two "metals" in grain boundaries. Indication of a suboxide matrix eutectic containing oxide whiskers.
W-Mp-77-36	55 Y_2O_3 37 Cr_2O_3 8 Mo	Melted 2180°. Good melt but tungsten basket failed. Extensive areas of good eutectic. Matrix contains some darker second phase, some cracking.
W-Mp-77-37	55 Y_2O_3 37 Cr_2O_3 8 Cr	Melted 2160°, corrected. Regular oxide-metal eutectic. Oxide tends to break up along grain boundaries which suggests another phase present.
W-Mp-77-38	55 Y_2O_3 37 Cr_2O_3 8 $MoSi_2$	Melted 1890°, corrected. No oxide-metal eutectic. Two oxide phases, little metal solubility.
W-Mp-77-39	55 Y_2O_3 37 Cr_2O_3 8 W	Melted 2135°, corrected. Regular oxide-metal eutectic. Matrix looks like 2nd phase has pulled out.
W-Mp-77-40	55 Y_2O_3 37 Cr_2O_3 8 Ti	Melted 1890°, corrected. Good melt, some good oxide-metal eutectic. Matrix appears to contain two oxides.
W-Mp-77-41	55 Y_2O_3 37 Cr_2O_3 8 Nb	Melted 1900°, corrected. Considerable oxide matrix-metal in grain boundaries.which have largely fallen out. Little metal solubility in what remains.
W-Mp-77-42	19.2 MgO 72.8 Cr_2O_3 8 Mo	Melted 2095°, corrected. About 20% regular oxide-metal eutectic, a few second oxide phase areas. Oxide tends to chip during polishing, needs about twice as much metal, attacks W.
W-Mp-77-43	19.2 MgO 72.8 Cr_2O_3 8 Cr	Melted 2200°, corrected. About 20% regular oxide-metal eutectic, lost most of melt, extensive attack on W wires. Oxide tends to chip on polishing but no cracks.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-44	19.2 MgO 72.8 Cr_2O_3 8.0 $MoSi_2$	Melted 2150°C. About 10 v/o regular oxide-metal eutectic. Also oxide-oxide eutectic present. Still some attack on W wires. Matrix chips on polishing.
W-Mp-77-45	19.2 MgO 72.8 Cr_2O_3 8.0 W	Melted 2235°C, corrected. Melt poor, porous but uncracked. Some widely scattered areas of eutectic. Extensive attack on W wires, only one oxide phase present.
W-Mp-77-46	19.2 MgO 72.8 Cr_2O_3 8.0 Ti	Melted 2115°C, corrected. Good melt, metal tends to be soluble, suggestive of eutectic, matrix tends to chip. Not much attack on W wires.
W-Mp-77-47	19.2 MgO 72.8 Cr_2O_3 8.0 Nb	Melted 2190°, corrected. Extensive areas of regular eutectic, slight second oxide phase, ingot porous, attack on W wires moderate.
W-Mp-77-48	64.3 $CaCO_3$ 28.3 Cr_2O_3 7.7 Mo	Melted 2225°, corrected, good melt, very small amount of regular oxide metal eutectic, very regular. Second oxide phase, ingot porous.
W-Mp-77-49	64.3 $CaCO_3$ 28.3 Cr_2O_3 7.7 Cr	Melted 2180°, corrected. Not completely melted. Extensive primary oxide phase and good oxide-metal grain boundary eutectic. No metal solubility in primary oxide phase.
W-Mp-77-50	64.0 $CaCO_3$ 28.3 Cr_2O_3 7.7 $MoSi_2$	Melted 2150°, corrected. Good melt, no oxide-metal eutectic. Two oxide phases, metal present as large globs.
W-Mp-77-51	64.0 $CaCO_3$ 28.3 Cr_2O_3 7.7 W	Melted 2140°, corrected. Two oxide phases, very little metal present. Very small amount of oxide-metal eutectic, extensive attack on W, ingot porous, chips on polishing.
W-Mp-77-52	64.0 $CaCO_3$ 28.3 Cr_2O_3 7.7 Ti	Melted 2150°, corrected. Good melt, two oxide phases, metal globs, porous matrix. Metal tends to good solubility in continuous oxide phase, extensive attack on W.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-53	64.0 $CaCO_3$ 28.3 Cr_2O_3 7.7 Nb	Melted 2250°, corrected. Not completely melted. Good regular oxide-metal eutectic, at least two oxide phases. Ingot porous, extensive attack on W.
W-Mp-77-54	40.8 ZnO 51.1 Al_2O_3 8.1 NiAl	Melted 1945°, corrected. No regular oxide-metal eutectic, extremely volatile, at least two oxide phases.
W-Mp-77-55	40.8 ZnO 51.1 Al_2O_3 8.1 Mo	Melted 1895°, corrected. Metal phase hard to find, at least two oxide phases, system very volatile.
W-Mp-77-56	40.8 ZnO 51.1 Al_2O_3 8.1 Cr	Melted 1900°, corrected. At least two oxide phases, finely mixed. No oxide-metal eutectic.
W-Mp-77-57	40.8 ZnO 51.1 Al_2O_3 8.1 $MoSi_2$	Melted 1810°, corrected. At least two oxide phases finely mixed. No oxide-metal eutectic. Metal phase hard to find.
W-Mp-77-58	40.8 ZnO 51.1 Al_2O_3 8.1 W	Melted 1890°, corrected. Three oxide phases, no oxide-metal eutectic, ingot porous with pull-outs, volatile.
W-Mp-77-59	40.8 ZnO 51.1 Al_2O_3 8.1 Ti	Melted 1735°, corrected. Melt volatile, no oxide-metal eutectic, at least two oxide phases, ingot porous, weak.
W-Mp-77-60	40.8 ZnO 51.1 Al_2O_3 8.1 Nb	Melted 1895°, corrected. Melted poorly, at least three oxide phases, no regular oxide-metal eutectic.
W-Mp-77-61	52.5 Y_2O_3 39.5 Al_2O_3 8.0 Mo	Melted 1870°, corrected. Poor melt, metal well dispersed but no regular oxide-metal eutectic.
W-Mp-77-62	52.5 Y_2O_3 39.5 Al_2O_3 8.0 Cr	Melted 1890°, corrected. Metal finely dispersed with metal globs, no regular oxide-metal eutectic.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-63	52.5 Y_2O_3 39.5 Al_2O_3 8.0 $MoSi_2$	Melted 1925°, corrected. Metal as globs, poor solubility.
W-Mp-77-64	55.2 Y_2O_3 39.5 Al_2O_3 8.0 W	Melted well at 1910°, corrected. Metal dispersed but no oxide-metal eutectic. Ingot porous, two oxide phases.
W-Mp-77-65	52.5 Y_2O_3 39.5 Al_2O_3 8.1 Ti	Melted well at 1890°, corrected. Metal dissolved on fairly fine scale but no regular oxide-metal eutectic. Small amount of second oxide phase.
W-Mp-77-66	52.5 Y_2O_3 39.5 Al_2O_3 8.0 Nb	Melted 1900°, corrected. Two oxide phases, metal as globs, no oxide-metal eutectic.
W-Mp-77-67	38.9 NiO 53.1 Al_2O_3 8.0 Mo	Melted 1910°, corrected. No completely melted, reacted with W wires. No oxide-metal eutectic, globs of metal over wide range of sizes, matrix dense but pitted.
W-Mp-77-68	38.9 NiO 53.1 Al_2O_3 8.0 Cr	Incomplete melting, no oxide-metal eutectic. Matrix very dense with large pores, metal globs over a wide range of sizes.
W-Mp-77-69	38.9 NiO 53.1 Al_2O_3 8.0 $MoSi_2$	Melted 1975°, corrected. No oxide-metal eutectic but some finely dispersed metal. There may be a second oxide phase associated with some metal globs.
W-Mp-77-70	38.9 NiO 53.1 Al_2O_3 8.0 W	Melted 1900°, no oxide-metal eutectic, reaction with W basket, matrix pitted.
W-Mp-77-71	38.9 NiO 53.1 Al_2O_3 8.0 Ti	Incompletely melted, no oxide-metal eutectic, reaction with W basket.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-72	38.9 NiO 53.1 Al_2O_3 8.0 Nb	Incomplete melt, no oxide-metal eutectic, reacted with W basket.
W-Mp-77-73	38.9 NiO 53.1 Al_2O_3 8.0 Mo	Repeat of W-Mp-77-67 with Ta basket, partially melted, basket failed.
W-Mp-77-74	72 Gd_2O_3 20 Al_2O_3 8 Nb	Melted 2030°C, corrected. Repeat of W-Mp-77-22. Metal distributed as isolated specks and as gobular clumps consisting of metal shell around oxide centers.
W-Mp-77-75	41.5 TiO_2 52.4 $CaCO_3$ 6.1 Cr	Melted 1820°. Repeat of W-Mp-77-32. No oxide-metal eutectic, metal present as globs and as fine metal specks, mostly associated with grain boundaries. Oxide chips on polishing.
W-Mp-77-76	55 Y_2O_3 37 Cr_2O_3 8 Mo	Melted 2180°, corrected, repeat of W-Mp-77-36, poorly melted, difficult to draw conclusions.
W-Mp-77-77	38 TiO_2 48 $CaCO_3$ 14 Cr	Melted 1820°. One small area of oxide-metal eutectic, metal solubility mostly associated with grain boundaries.
W-Mp-77-78	41.8 TiO_2 48 $CaCO_3$ 12.2 Cr	Melted 1820°. Metal as globs and also as a dispersed phase especially near grain boundaries. Probable eutectic in system but none seen.
W-Mp-77-79	34.2 TiO_2 48 $CaCO_3$ 17.9 Cr	Melted 1815°. Two small areas of regular eutectic. Metal as globs and as a dispersed phase especially at grain boundaries.
W-Mp-77-80	52.6 Y_2O_3 35.4 Cr_2O_3 12.0 NiO	Melted 2140°, 2200° corrected. Melt bridged to susceptor, repeat.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-81	52.6 Y_2O_3 35.4 Cr_2O_3 12.0 NiO	Melted 2225°, corrected. Wide areas of fine oxide-metal eutectic, matrix chips on polishing. Also two oxide phases present which form eutectic.
W-Mp-77-82	50.0 Y_2O_3 37.2 Cr_2O_3 12.8 Mo	Melted 2225, corrected. Material weak, breaking apart at grain boundaries. Some very fine eutectic.
W-Mp-77-83	52.6 Y_2O_3 35.4 Cr_2O_3 12.0 Mo	Melted 2200°, corrected. Some wide areas of fine eutectic, matrix does not polish well. Material "breaks out" at grain boundaries.
W-Mp-77-84	52.6 Y_2O_3 35.4 Cr_2O_3 8.0 Mo 4.0 W	Not properly melted at 2200°, corrected.
W-Mp-77-85	52.6 Y_2O_3 35.4 Cr_2O_3 8.0 Mo 4.0 Cr	Melted poorly at 2050°, corrected. Reacted with W basket, bridged to susceptor.
W-Mp-77-86	54 Y_2O_3 32 Cr_2O_3 8 Mo 6 WO_3	Incompletely melted at 2115°, corrected. Reacted with W basket.
W-Mp-77-87	54 Y_2O_3 32 Cr_2O_3 8 Mo 6 WO_3	Incomplete melt at 2120°, corrected with new susceptor. Bad reaction with W basket.
W-Mp-77-88	55 Y_2O_3 37 Cr_2O_3 8 Cr	Melted 2180°, corrected. Melting incomplete, porous.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-89	58 Y_2O_3 34 Cr_2O_3 8 Cr	Melted 2225°, corrected. Many areas of very fine eutectic. Oxide polishes poorly, many cracks and grain boundary failures.
W-Mp-77-90	52 Y_2O_3 40 Cr_2O_3 8 Cr	Incomplete melting 2050°, corrected. Bridged to susceptor when W basket failed.
W-Mp-77-91	53 Y_2O_3 35 Cr_2O_3 8 Cr 4 W	Melted poorly at 2095°, corrected. Metal globs, reacted with W wires. Part of melt subsequently turned into powder.
W-Mp-77-92	52 Y_2O_3 34 Cr_2O_3 8 Cr 6 WO_3	Reacted, lost W basket.
W-Mp-77-93	52 Y_2O_3 34 Cr_2O_3 8 Cr 6 WO_3	Melted 2095°, corrected. Metal not well dispersed, incomplete melting, reaction with W wires.
W-Mp-77-94	55 Y_2O_3 35 Cr_2O_3 8 W	Melted 2170°, corrected. Wide areas of oxide-metal eutectic, polishes very poorly, boundaries breaking out. Second oxide phase in boundaries does not dissolve metal.
W-Mp-77-95	51 Y_2O_3 33 Cr_2O_3 6 Cr 10 WO_3	Melted 2080°, corrected. Reacted with wires, sputtering of sample while melting. Sample tended to powder in envelope after run.
W-Mp-77-96	48 Y_2O_3 36 Cr_2O_3 16 WO_3	Melted 2150°, corrected. Incomplete melt, much sputtering from melt. Sample tended to powder in envelope.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-97	51 Y_2O_3 33 Cr_2O_3 6 Cr 10 WO_3	Repeat of W-Mp-77-95. Reacted with W, basket failed.
W-Mp-77-98	54 Y_2O_3 31 Cr_2O_3 16 WO_3	Melted 2170°, corrected. Melt fell from basket, incomplete melting.
W-Mp-77-99	18 MgO 66 Cr_2O_3 16 NiO	Good melt at 2225°, corrected. Wide areas of good eutectic, some porosity, matrix tends to chip during polishing. Major solution of W wires.
W-Mp-77-100	18 MgO 66 Cr_2O_3 8 Mo 8 W	Melted 2225°, corrected. Very wide areas of good regular eutectic, very fine spacing. Matrix tends to chip. Less tendency to react with W wires than run -99.
W-Mp-77-101	16.5 MgO 62.5 Cr_2O_3 8 Mo 13 WO_3	Melted 2225°, corrected. Wide areas of regular eutectic, microstructure not completely melted. Solution of W wires.
W-Mp-77-102	19.2 MgO 72.8 Cr_2O_3 8.0 Cr	Melted 2210°, corrected. Wide areas of extremely fine eutectic structure, many areas the metal is near the limit of optical resolution. Many large pores. Extensive reaction with W wires.
W-Mp-77-103	14.2 MgO 53.8 Cr_2O_3 16.0 Cr 16.0 W	Melted 2095°, corrected. Many large pores, some few areas of oxide-metal eutectic. Metal mostly as globs in grain boundaries. Oxide tends to chip on polishing. Wide areas of fine metal dispersions - just at the limit of optical resolution.
W-Mp-77-104	12.0 MgO 45.6 Cr_2O_3 16.0 Cr 26.4 WO_3	Melted 2190°, corrected. Some areas of good regular oxide-metal eutectic. Ingot porous with oxide tending to chip. Melt predominantly present as globs along grain boundaries or around pores.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-105	9.2 MgO 34.8 Cr_2O_3 11.0 Cr 40.0 WO_3	Incomplete melting at 2170°, corrected. Wide areas of regular eutectic as well as apparently "submicroscopic" metal dispersions. A second lighter oxide phase present. Not much attack on W wires.
W-Mp-77-106	17.5 MgO 66.5 Cr_2O_3 16.0 $MoSi_2$	Melted 1900°. Two "oxide" phases, about 50/50 v/o. Darker, continuous one somewhat angular. Metal as globs. Apparent ternary eutectic between all three phases.
W-Mp-77-107	19.2 MgO 64.8 Cr_2O_3 16.0 $MoSi_2$	Melted 1775°. Two "oxide" phases, the darker continuous one tends to be angular and present in large amount. Metal as large globs or as an extremely fine, barely resolvable dispersion in the darker matrix phase, especially in wide strips across this phase.
W-Mp-77-108	11.1 MgO 72.9 Cr_2O_3 16.0 MoSi	Melted 1760°, metal as globs, two "oxide" phases. Metal very soluble in darker matrix phase, too fine to properly resolve in the optical microscope.
W-Mp-77-109	11.5 MgO 43.5 Cr_2O_3 45 WO_3	Melted 2070°. Some areas of good, regular oxide-metal eutectic. Also, two oxide phases and/or one which produces "Widmanstatten-like" structures. Metal eutectic is with the darker oxide phase. Significant attack on W wires.
W-Mp-77-110	17.5 MgO 66.5 Cr_2O_3 16.0 WO_3	Melted 2075°, corrected. Two oxide phases which form a eutectic. Metal poorly soluble.
W-Mp-77-111	18.5 MgO 64.5 Cr_2O_3 17.0 Nb	Melted 1860. Two oxide phases which form a eutectic. Metal poorly soluble.

Table III (Cont'd)

Run #	Material (w/o)	Remarks (°C)
W-Mp-77-112	50 $CaCO_3$ 22 Cr_2O_3 8 Nb 20 WO_3	Melted 1820°. Two oxide phases, major phase acicular. Darker phase contains extremely fine dispersion of metal. Rest of metal present as globs.
W-Mp-77-113	54 $CaCO_3$ 18 Cr_2O_3 8 Nb 20 WO_3	Melted 1820°. Ingot mostly acicular crystals that appear to contain pullouts which were metallic. Second darker oxide phase contains zones of extremely fine metal dispersions, barely resolvable.
W-Mp-77-114	46 $CaCO_3$ 26 Cr_2O_3 20 WO_3 8 Nb	Melted 1845°. Similar to -113.

Table IV

Summary of Oxide-Matrix Eutectics and Possible Eutectic Morphologies Observed in Cubic Mixed Oxide-Metal Melts

Well-defined Eutectics	Melt #	Temperature (°C)	Additional Phase(s)
$NiO\cdot Cr_2O_3$-NiAl	W-Mp-76-35	1980	-
Al_2O_3, Cr_2O_3- NiAl, Cr	W-Mp-76-39	1980	yes
$NiO\cdot(Al_2O_3,Cr_2O_3)$-NiAl	W-Mp-76-50 & 86	2100	-
$CaO\cdot TiO_2$-Cr	W-Mp-76-32	1890	yes
$Y_2O_3\cdot Cr_2O_3$-Mo	W-Mp-77-36	2180	yes
$Y_2O_3\cdot Cr_2O_3$-Cr	W-Mp-77-37	2160	-
$Y_2O_3\cdot Cr_2O_3$-W	W-Mp-77-39	2135	-
$Y_2O_3\cdot Cr_2O_3$-Ti	W-Mp-77-40	1890	yes
$Y_2O_3\cdot Cr_2O_3$-Nb	W-Mp-77-41	1900	no
$MgO\cdot Cr_2O_3$-Mo	W-Mp-77-42	2095	yes
$MgO\cdot Cr_2O_3$-Cr	W-Mp-77-43	2200	no
$MgO\cdot Cr_2O_3$-$MoSi_2$	W-Mp-77-44	2150	yes
$MgO\cdot Cr_2O_3$-W	W-Mp-77-45 & 109	2235	no
$MgO\cdot Cr_2O_3$-Nb	W-Mp-77-47	2190	yes
$CaO\cdot Cr_2O_3$-Mo	W-Mp-77-48	2225	yes
$CaO\cdot Cr_2O_3$-Cr	W-Mp-77-49	2180	no
$CaO\cdot Cr_2O_3$-W	W-Mp-77-51	2140	yes
$CaO\cdot Cr_2O_3$-Nb	W-Mp-77-53	2250	yes
$CaO\cdot TiO_2$-Cr	W-Mp-77-77 & 79	1820	no
$Y_2O_3\cdot Cr_2O_3$-Mo	W-Mp-77-82 & 83	2200	no
$Y_2O_3\cdot Cr_2O_3$-Cr	W-Mp-77-89	2225	no
$Y_2O_3\cdot Cr_2O_3$-W	W-Mp-77-94	2170	yes
$Y_2O_3\cdot Cr_2O_3$-Ni	W-Mp-77-81	2225	yes
$MgO\cdot Cr_2O_3$-Ni	W-Mp-77-99	2225	no
$MgO\cdot Cr_2O_3$-Mo,W	W-Mp-77-100 & 101	2225	no
$MgO\cdot Cr_2O_3$-Cr	W-Mp-77-102	2210	no
$MgO\cdot Cr_2O_3$-Cr,W	W-Mp-77-103,104,105	2100	yes
$NiO\cdot Al_2O_3,Cr_2O_3$-NiAl	W-Mp-76-86	1890	no

Table IV (Cont'd)

Metal Solubility	Melt #	Temperature (°C)	Additional Phase(s)
$FeO\cdot Fe_2O_3$-NiAl	W-Mp-76-48	1595	no
$MgO,NiO\cdot Cr_2O_3$-NiAl	W-Mp-76-49 & 50	2215	yes
$Gd_2O_3\cdot Al_2O_3$-Mo	W-Mp-77-16	2070	no
$Gd_2O_3\cdot Al_2O_3$-Cr	W-Mp-77-17	2070	no
$Gd_2O_3\cdot Al_2O_3$-W	W-Mp-77-19	2185	no
$Gd_2O_3\cdot Al_2O_3$-Ti	W-Mp-77-20	2170	yes
$Gd_2O_3\cdot Al_2O_3$-Nb	W-Mp-77-22	2090	no
$Mn_3O_4\cdot Al_2O_3$-Mo	W-Mp-77-24	1784	yes
$CaO\cdot TiO_2$-Mo	W-Mp-77-31	1920	no
$CaO\cdot TiO_2$-W	W-Mp-77-33	1925	yes
$CaO\cdot TiO_2$-Ti	W-Mp-77-34	1890	yes
$MgO\cdot Cr_2O_3$-Ti	W-Mp-77-46	2115	no
$CaO\cdot Cr_2O_3$-Ti	W-Mp-77-52	2150	no
$Y_2O_3\cdot Al_2O_3$-Mo	W-Mp-77-61	1870	no
$Y_2O_3\cdot Al_2O_3$-Cr	W-Mp-77-62	1890	no
$Y_2O_3\cdot Al_2O_3$-W	W-Mp-77-64	1910	no
$Y_2O_3\cdot Al_2O_3$-Ti	W-Mp-77-65	1890	yes
$NiO\cdot Al_2O_3$-$MoSi_2$	W-Mp-77-69	1975	yes (?)
$CaO\cdot TiO_2$-Cr	W-Mp-77-78	1820	no
$MgO\cdot Cr_2O_3$-$MoSi_2$	W-Mp-77-108	1760	yes
$CaO\cdot Cr_2O_3$-Nb, W	W-Mp-77-112	1820	yes
No Eutectic Observed			
$3Al_2O_3\cdot 2SiO_2$-NiAl	W-Mp-76-32	1810	yes
$MgO\cdot Al_2O_3$-NiAl	W-Mp-76-37	2000	yes
$MgO\cdot Fe_2O_3$-NiAl	W-Mp-76-38	1790	yes
$ZrO_2\cdot SiO_2$-NiAl	W-Mp-76-42	1800	no
$NiO\cdot Cr_2O_3,Al_2O_3$-NiAl	W-Mp-76-87	1900	no
$Fe_2O_3\cdot Cr_2O_3$-Cr,Fe	W-Mp-76-89	1700	yes
$CoO\cdot Al_2O_3$-NiAl	W-Mp-77-9	2000	no
$CoO\cdot Al_2O_3$-Cr	W-Mp-77-11	1990	no
$CoO\cdot Al_2O_3$-W	W-Mp-77-13	1945	no
$CoO\cdot Al_2O_3$-Ti	W-Mp-77-14	1940	yes
$CoO\cdot Al_2O_3$-Nb	W-Mp-77-14.5	2000	no
$Gd_2O_3\cdot Al_2O_3$-NiAl	W-Mp-77-15	2100	yes
$Gd_2O_3\cdot Al_2O_3$-$MoSi_2$	W-Mp-77-18	1985	no
$CoO\cdot Al_2O_3$-Mo	W-Mp-77-21	1900	yes
$CoO.Al_2O_3$-$MoSi_2$	W-Mp-77-23	1880	yes

Table IV (Cont'd)

No Eutectic Observed	Melt #	Temperature (°C)	Additional Phase(s)
$Mn_3O_4 \cdot Al_2O_3$-Cr	W-Mp-77-26	1710	yes
$Mn_2O_3 \cdot Al_2O_3$-W	W-Mp-77-27	1745	yes
$Mn_2O_3 \cdot Al_2O_3$-Ti	W-Mp-77-28	1670	yes
$Mn_3O_4 \cdot Al_2O_3$-Nb	W-Mp-77-29	1670	yes
$CaO \cdot TiO_2$-Nb	W-Mp-77-35	1890	yes
$Y_2O_3 \cdot Cr_2O_3$-$MoSi_2$	W-Mp-77-38	1890	yes
$CaO \cdot Cr_2O_3$-$MoSi_2$	W-Mp-77-50	2150	yes
$ZnO \cdot Al_2O_3$-NiAl	W-Mp-77-54	1945	yes
$ZnO \cdot Al_2O_3$-Mo	W-Mp-77-55	1895	yes
$ZnO \cdot Al_2O_3$-Cr	W-Mp-77-56	1900	yes
$ZnO \cdot Al_2O_3$-$MoSi_2$	W-Mp-77-57	1810	yes
$ZnO \cdot Al_2O_3$-W	W-Mp-77-58	1890	yes
$ZnO \cdot Al_2O_3$-Ti	W-Mp-77-59	1735	yes
$ZnO \cdot Al_2O_3$-Nb	W-Mp-77-60	1895	yes
$Y_2O_3 \cdot Al_2O_3$-$MoSi_2$	W-Mp-77-63	1925	no
$Y_2O_3 \cdot Al_2O_3$-Nb	W-Mp-77-66	1900	yes
$NiO \cdot Al_2O_3$-Mo	W-Mp-77-67	1910	no
$NiO \cdot Al_2O_3$-Cr	W-Mp-77-68	1900	no
$NiO \cdot Al_2O_3$-W	W-Mp-77-70	1900	no
$NiO \cdot Al_2O_3$-Ti	W-Mp-77-71	-	no
$NiO \cdot Al_2O_3$-Nb	W-Mp-77-72	-	no

Table V

Directional Solidification by Floating Molten Zone

Run #	Material (w/o)	Remarks
W-DSF-76-3	42.3 NiO 57.7 Al_2O_3	Two inch long, 20 mil diameter Pt wire embedded in charge rod, material all melted into one mass because it was not well fused to upper ceramic support rod.
W-DSF-76-5	28.3 MgO 71.7 Al_2O_3	Two inch long Pt wire embedded in charge rod, short zone melted, no Pt solubility.
W-DSF-76-6	41.1 NiO 50.5 Al_2O_3 8.4 Cr_2O_3	Rod completely melted through, generally poor solubility but near larger globs areas with considerable very fine metal distributions.
W-DSF-76-7	10 NiAl 29.66 NiO 60.34 Cr_2O_3	Evidence of considerable metal solubility with globs of metal also present. Regular eutectic metal whisker areas also seen.
W-DSF-76-8	33.0 NiO 67.0 Cr_2O_3	Two inch long Pt wire embedded in charge rod. Fused top of charge rod at 2020°C, shattered sample when moving rods together when zone narrowed, fine metal dispersions in grain boundaries.
W-DSF-76-9	6 Cr 24 Fe 21 Cr_2O_3 49 Fe_2O_3	Could not hold zone, problems with melt evaporation, metal appeared to sweat out of ceramic.
W-DSF-76-10	16.2 NiAl 76.2 Cr_2O_3 7.6 NiO	Could not hold molten zone in place, upper and lower rods became off-set, metal appeared to have poor solubility in the ceramic.
W-DSF-76-17	16.2 NiAl 76.2 Cr_2O_3 7.6 NiO	Could not control melt, need narrower susceptor.

Table V (Cont'd)

Run #	Material (w/o)	Remarks, °C
W-DSF-76-20	6 Cr 24 Fe 21 Cr_2O_3 49 Fe_2O_3	Float zone technique with upper air bearing, used all of rod, produced 13/16" dia disk, relatively soft, metal fairly evenly distributed.
W-DSF-76-21	6 Cr 24 Fe 21 Cr_2O_3 49 Fe_2O_3	Float zone, 2 3/16" of material melted to form mushroom shaped sample, melt at 1740°C. Two oxides present, no fine scale metal distribution, no eutectic. Primary oxide shows fine "pull-outs" during polishing.
W-DSF-76-22	16.2 NiAl 38.1 Cr_2O_3 38.1 Al_2O_3 7.6 NiO	Ran out of material before zone could be controlled, no eutectic structure observed.

Table VI

Directional Solidifications in CVD Tungsten Tubes
(carbon susceptor, argon)

Run #	Material (w/o)	Remarks (°C)
W-DS-76-42	5.0 WO_3 85.5 Al_2O_3 9.5 MgO	2 cm/hr, 7/8" of good melt, air pocket and 1/4" additional ingot. Microstructure poor, metal segregated, good whiskers in one area but not finely spaced.
W-DS-76-60	75 Y_2O_3 5 CeO_2 20 Ta	After two attempts, sample came through W tube reacted with furnace.
W-DS-76-61	75 Gd_2O_3 2.5 CeO_2 22.5 Ta	Melt came through W container tube.
W-DS-77-17	55 Y_2O_3 37 Cr_2O_3 8 Mo	Melt came through crucible, extensive deposit in chamber.
W-DS-77-18	19.2 MgO 72.8 Cr_2O_3 8.0 W	Melted ~2150°, reacted with crucible, contaminated chamber.
W-DS-77-19	19.2 MgO 72.8 Cr_2O_3 8.0 Nb	Incomplete melting at 2190°.
W-DS-77-20	19.0 MgO 71.5 Cr_2O_3 9.5 $MoSi_2$	Material reacted and came through CVD-W container. Incomplete melting. Extensive material deposited throughout chamber.
W-DS-77-21	62 $CaCO_3$ 27 Cr_2O_3 7 Nb 4 W	Heated to 2120°, lost about 90% of charge through W container; heavy outgassing.
W-DS-77-22	55 Y_2O_3 37 Cr_2O_3 8 Mo	Repeat of W-DS-77-17, melting 2390, incomplete melt, came through W container.
W-DS-77-23	19.2 MgO 72.8 Cr_2O_3 8.0 Cr	Incomplete melting at 2400°, reaction with CVD-W container.

FIG. 1

TENSILE STRENGTH OF $Ni_3Al–Ni_3Cb$ EUTECTIC AS A FUNCTION OF TEMPERATURE AND (INTERLAMELLAR SPACING) $^{-1/2}$

(REF. 4)

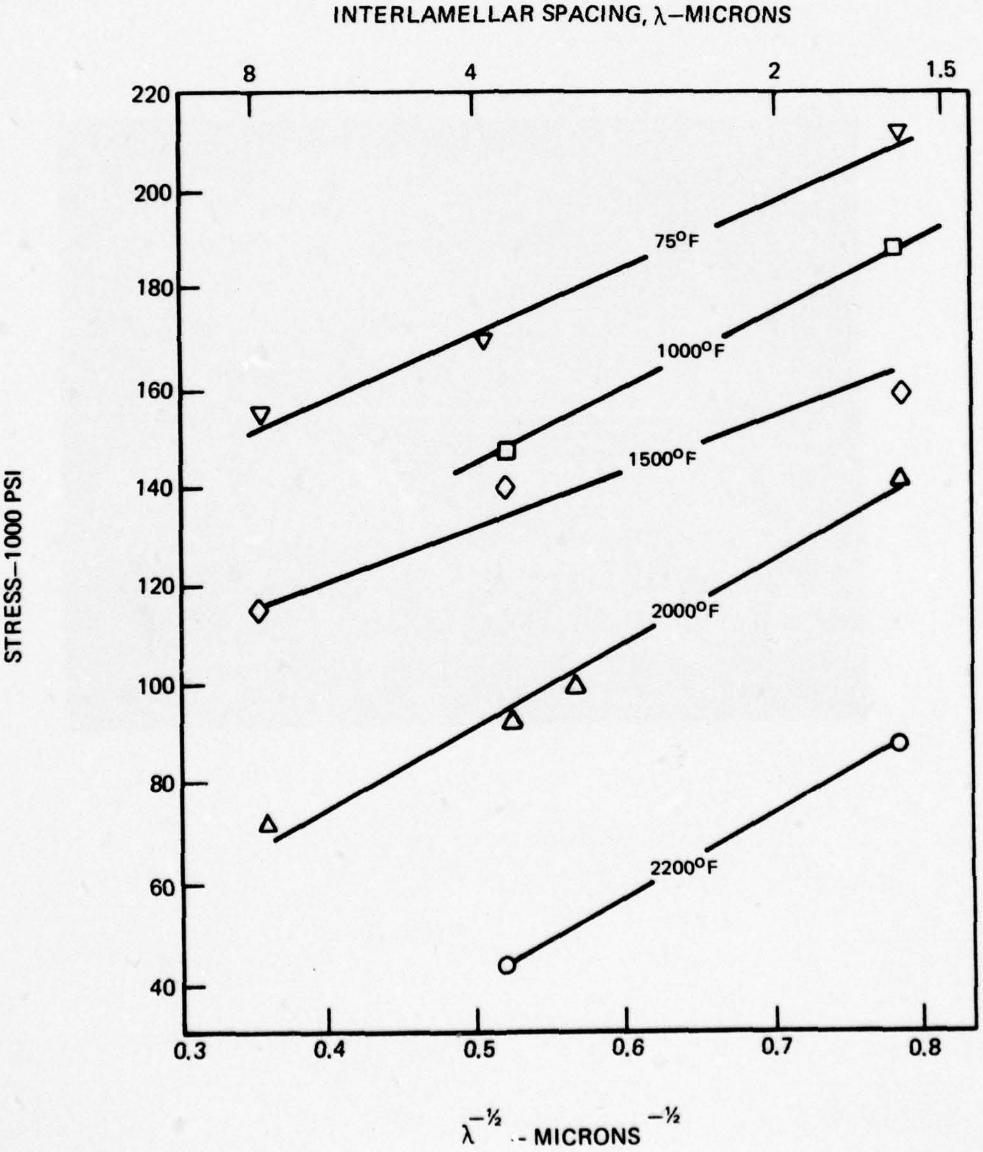
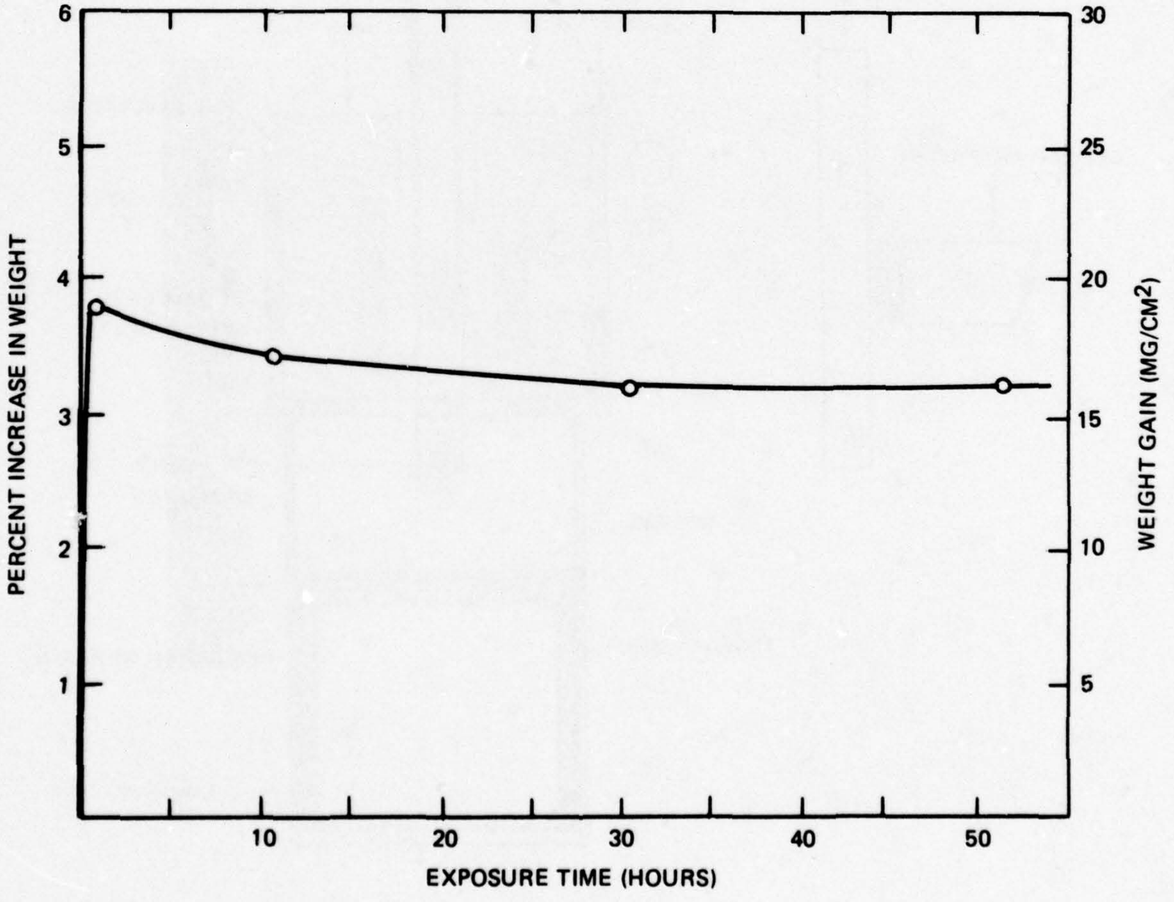


FIG. 2

POLISHED SECTION VIEW PERPENDICULAR TO EXTERNAL SURFACES (AT TOP AND RIGHT) OF $Cr-Cr_2O_3$, Al_2O_3 EUTECTIC EXPOSED TO AIR FOR 60 HOURS AT 2600 °F

WEIGHT GAIN OF DIRECTIONALLY SOLIDIFIED TERNARY EUTECTIC

24 w/o Cr, 28 w/o ZrO_2, 4.6 w/o Y_2O_3, 21.7 Cr_2O_3, 21.7 w/o Al_2O_3 IN AIR AT 1425°C



SCHEMATIC OF TUNGSTEN WIRE–BASKET MELTING POINT FURNACE

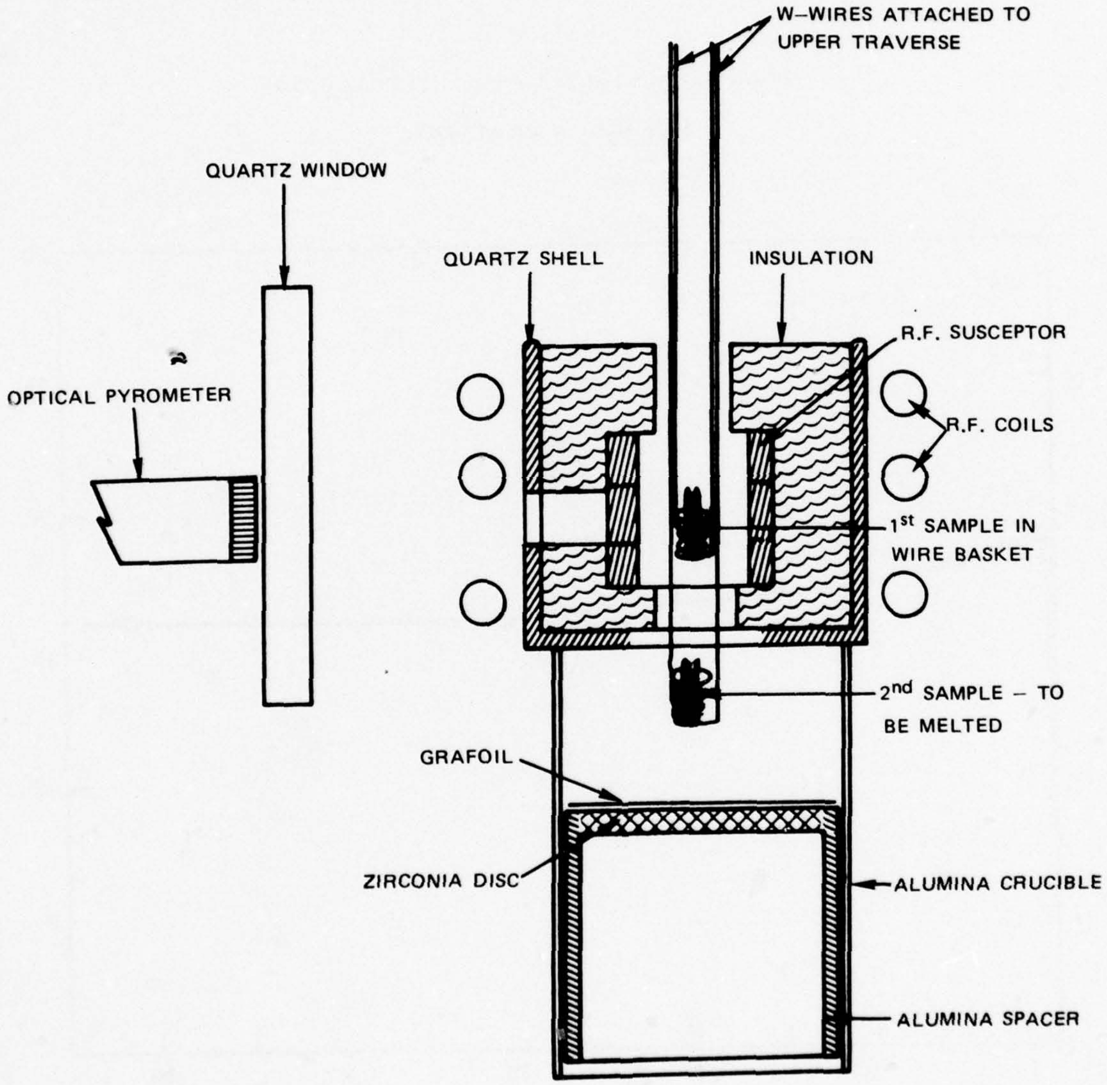
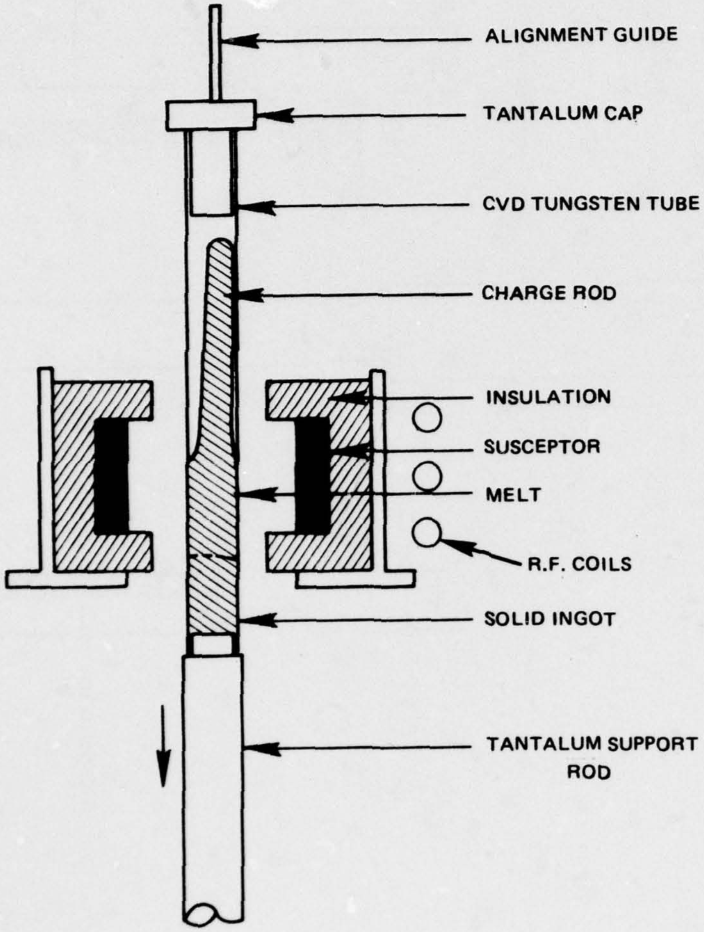


FIG. 5

FURNACE FOR DIRECTIONAL SOLIDIFICATION OF CERAMIC- METAL EUTECTICS

(VERTICAL-CENTER SECTION VIEW)



R08–137–5

FIG. 6

SCHEMATIC OF DIRECTIONAL SOLIDIFICATION EQUIPMENT FOR OXIDE–METAL EUTECTICS

VERTICAL SECTION VIEW THROUGH CENTER OF CYLINDRICAL FURNACE

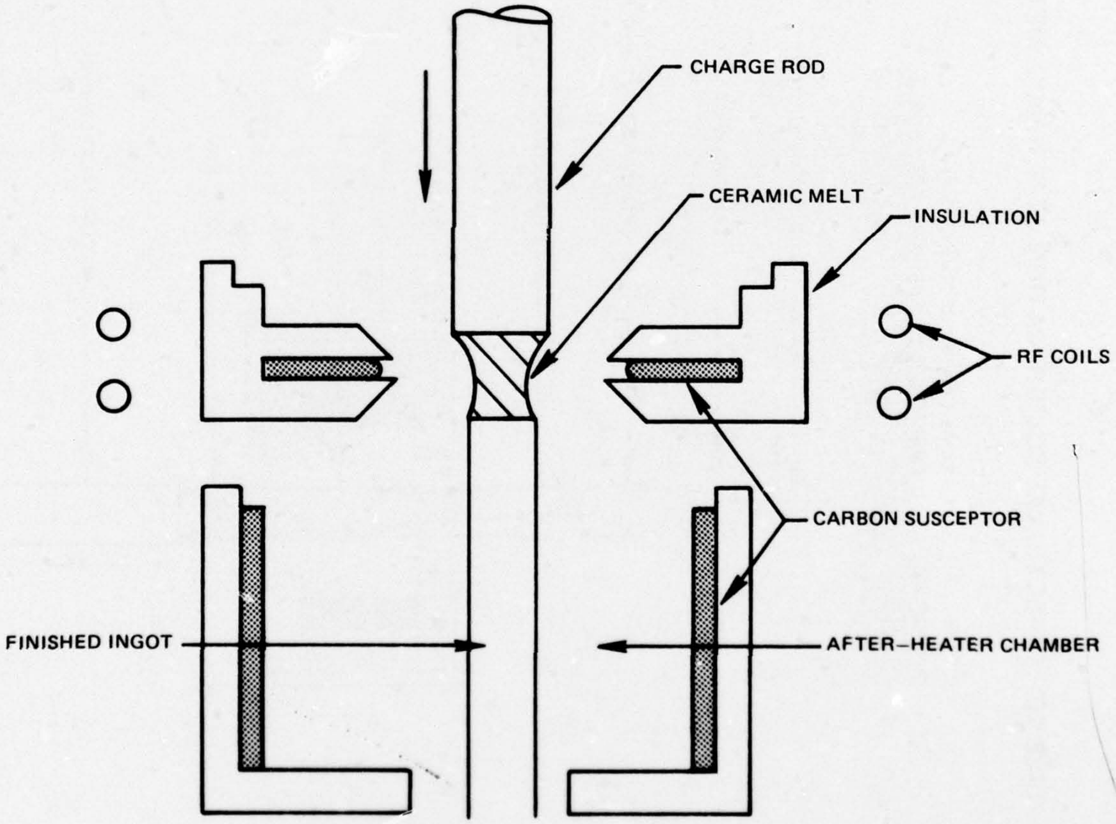
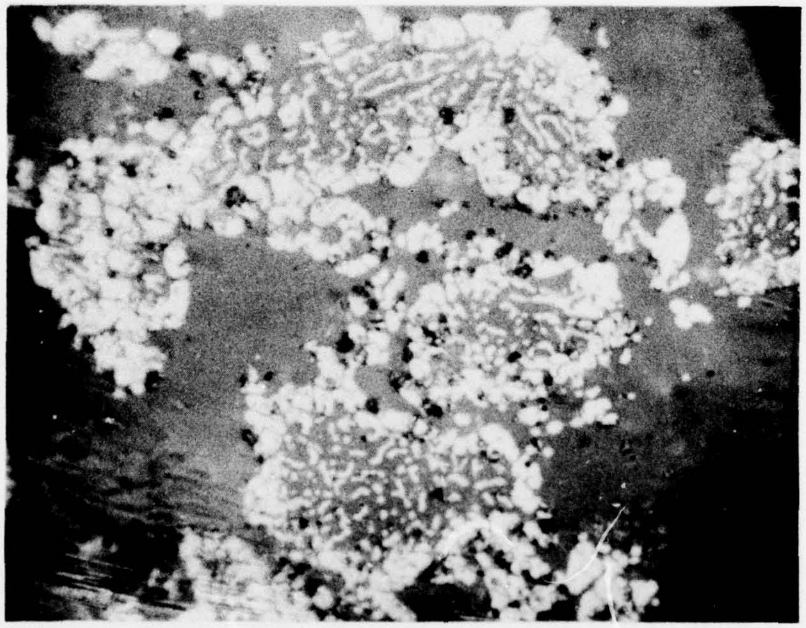


FIG. 7

AREAS OF OXIDE–METAL EUTECTIC–LIKE MICROSTRUCTURE IN MELT COMPOSITION $72Gd_2O_3$, 20 Al_2O_3 AND 8 Nb



W–Mp–77–22

FIG. 8

SELECTED VIEW OF EUTECTIC OBSERVED IN MELT
W–Mp–45–77 (19.2 MgO, 72.8 Cr_2O_3 AND 8.0W)

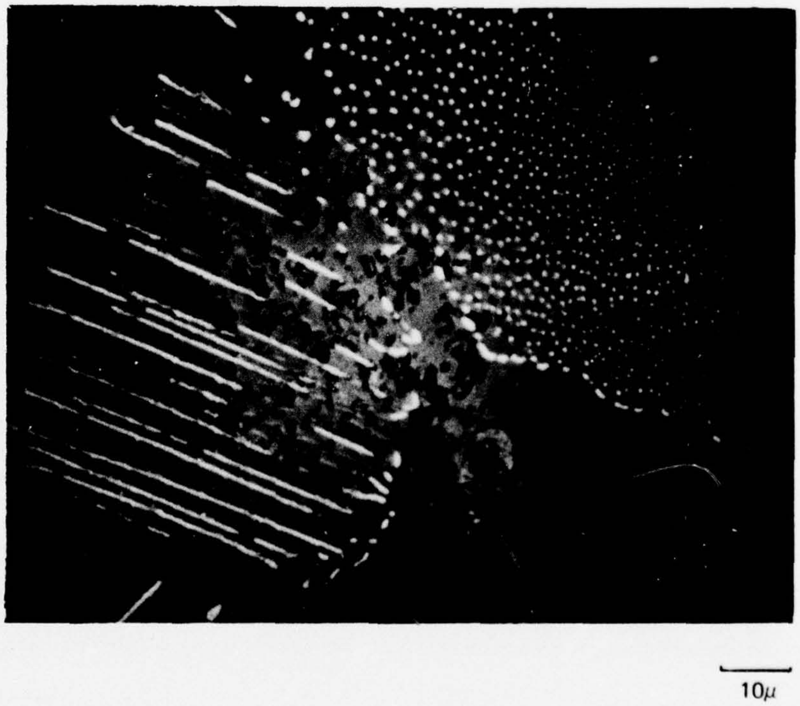
77–06–152–3

FIG. 9

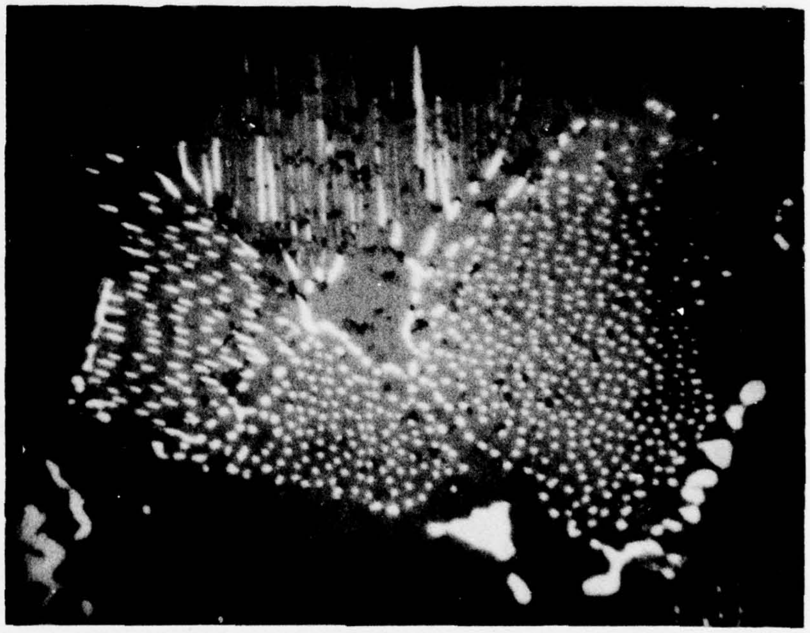
SELECTED VIEW OF EUTECTIC OBSERVED IN MELT
W–Mp–52–77 (64.0 $CaCO_3$, 28.3 Cr_2O_3 AND 7.7 Ti)

FIG. 10

SELECTED VIEW OF EUTECTIC OBSERVED IN MELT W–Mp–47–77 (19.2 MgO, 72.8 Cr_2O_3 AND 8.0 Nb)

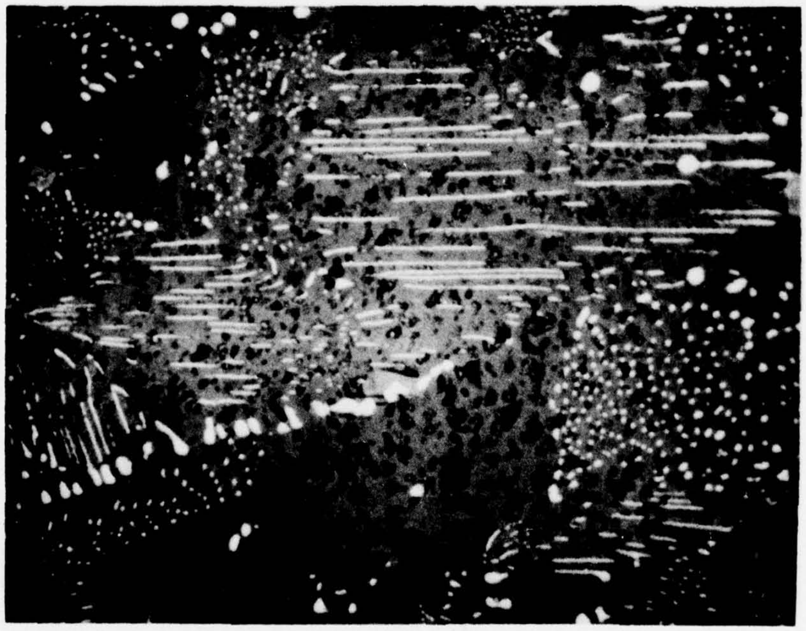


SELECTED VIEW OF EUTECTIC OBSERVED IN MELT
W–Mp–44–77 (19.2 MgO, 72.8 Cr_2O_3 AND 8.0 $MoSi_2$)



10μ

SELECTED VIEW OF EUTECTIC OBSERVED IN MELT
W-Mp-42-77 (19.2 MgO, 72.8 Cr_2O_3 AND 8.0 Mo)



DISTRIBUTION LIST

(One copy unless otherwise noted)

(3 copies plus balance after distribution)
Naval Air Systems Command
AIR 52031B
Dept. of the Navy
Washington, DC 20361

(7 copies for internal distribution by AIR 954 as follows:
AIR 954 (2 copies), AIR 536B1 (1 copy), AIR 330A (1 copy), AIR 330B (1 copy),
AIR 5361A (1 copy), AIR 5362A (1 copy)
Naval Air Systems Command
AIR 954
Dept. of the Navy
Washington, DC 20361

Commander, Naval Air Development Center (2 copies)
Code 302A, A. Fletcher (1 copy)
Code 30231, M. Thomas (1 copy)
Wasminster, PA 18974

U. S. Naval Air Turbine Test Station
Attn: J. Glatz (PE-43)
1440 Parkway Avenue
Trenton, NJ 08628

U. S. Naval Sea Systems Command
Code 035
Dept. of the Navy
Washington, DC 20362

Commander
Naval Weapons Center
Code 5516
China Lake, CA 93555

U. S. Naval Ships Engineering Center
Code 6146
Dept. of the Navy
Center Bldg., Prince George's Center
Hyattsville, MD 20782

Naval Weapons Laboratory
Attn: W. Mannschreck
Dahlgren, VA 22448

DISTRIBUTION LIST (CONTINUED)

U. S. Naval Ships Res. & Dev. Center
Code 2812
Annapolis, MD 21402

Commander
Naval Ordnance Laboratory
Metallurgy Division
White Oak
Silver Spring, MD 20910

(2 copies)
Director, Naval Research Laboratory
Code 6400 (1 copy)
Code 6360 (1 copy)
Washington, DC 20390

Office of Naval Research
The Metallurgy Program
Code 471
Arlington, VA 22217

(2 copies)
Director, Army Materials & Mechanics Res. Center
(A. Gorum - 1 copy) (P. Ahearn - 1 copy)
Watertown, MA 02172

Commander, U. S. Army Munitions Command
Frankford Arsenal
(Attn: D. Kleppinger)
Pitman Dunn Lab
Philadelphia, PA 19137

(4 copies)
Air Force Materials Laboratory
Code LLS (1 copy)
Code LLM (1 copy)
Code LLC (1 copy)
Code LT (1 copy)
Wright Patterson AFB, OH 45433

National Aeronautics & Space Adm.
Code RWM
Washington, DC 20546

DISTRIBUTION LIST (CONTINUED)

(3 copies)
National Aeronautics & Space Administration
Lewis Research Center
(G. M. Ault - 1 copy)
(H. P. Probst - 1 copy)
(Dr. R. L. Ashbrook - 1 copy)
21000 Brookpark Road
Cleveland, OH 44135

U. S. Energy Res. & Dev. Adm.
Div. of Reactor Res. & Dev.
A. Van Echo
Washington, DC 20545

Metals & Ceramics Information Center
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201

The Johns Hopkins University
Applied Physics Lab
Maynard L. Hill
Johns Hopkins Road
Laurel, MD 20810

AVCO RAD
201 Lowell St.
Wilmington, MA 01887

IIT Research Institute
Dr. N. Parikh
10 West 35th St.
Chicago, IL 60616

Detroit Diesel Allison Div.
General Motors Corp.
Materials Laboratories
Indianapolis, IN 46206

Clevite Co. Mechanical Res. Div.
Attn: Mr. A. D. Schwope
540 East 105th St.
Cleveland, OH 44108

DISTRIBUTION LIST (CONTINUED)

Chief, Materials Eng. Dept.
Dept. 93-39M
Airesearch Mfg. Co. of Arizona
420 South 36th St.
Phoenix, AZ 85034

Lycoming Div.
AVCO Corp.
Stratford, CT 06497

Curtis Wright Co.
Wright Aeronautical Div.
Wood-Ridge, NJ 07075

Bell Aerosystems Co.
Technical Library
P.O. Box 1
Buffalo, NY 14240

General Electric Co.
Aircraft Engine Group
Materials & Processes Technology Labs
Evendale, OH 45215

Solar
Dr. A. Metcalfe
2200 Pacific Highway
San Diego, CA 92112

Teledyne CAE
1330 Laskey Road
Toledo, OH 43601

Stellite Div.
Cabot Co.
Technical Library
P.O. Box 746
Kokomo, IN 46901

Materials Research Co.
Attn: Dr. S. Weinig
Orangeburg, NY 10962

DISTRIBUTION LIST (CONTINUED)

Artech Co.
Attn: Mr. Henry Hahn
2816 Fallfax Drive
Falls Church, VA 22042

Dr. Merton C. Flemings
Room 35-316
MIT
Cambridge, MA 02139

Prof. R. W. Kraft
Dept. of Met. & Materials Science
Lehigh University
Bethlehem, PA 18015

Prof. N. J. Grant
Dept. of Met. & Materials Science
MIT
Cambridge, MA 02139

Dr. Kenneth A. Jackson
Bell Telephone Laboratories Inc.
600 Mountain Ave.
Murry Hill, NJ 07974

National Academy of Sciences
Materials Advisory Board
Attn: Dr. J. Lane
Washington, DC 20418

Reynolds Metal Co.
Attn: Technical Library
Reynolds Metals Bldg.
Richmond, VA 23218

P. R. Mallory & Co. Inc.
Attn: Technical Librarian
3029 E. Washington St.
Indianapolis, IN 46206

Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

DISTRIBUTION LIST (CONTINUED)

Aluminum Company of America
Attn: Mr. G. B. Barthold
1200 Ring Bldg.
Washington, DC 20036

Prof. Alan Lawley
Head, Dept. of Met. Eng.
Drexel University
Philadelphia, PA 19104

Dr. A. I. Mlavsky
Tyco Laboratories Inc.
16 Hickory Drive
Waltham, MA 02145

Whittaker Co.
Nuclear Metals Div.
Attn: Dr. A. S. Bufferd
West Concord, MA 01718

University of California
Lawrence Radiation Laboratory
Attn: Technical Information Div.
Livermore, CA 94550

TRW Equipment Laboratories
Attn: Mr. J. A. Alexander
23555 Euclid Ave.
Cleveland, OH 44117

(3 copies)
General Electric Co.
Corporate R&D
(M. G. Benz - 1 copy)
(Dr. James D. Livingston - 1 copy)
(R. Charles - 1 copy)
P.O. Box 8
Schenectady, NY 12301

Westinghouse Electric Co.
Materials & Processing Labs
Attn: Ray Bratton
Beulah Road
Pittsburgh, PA 15235

DISTRIBUTION LIST (CONTINUED)

Dr. T. D. Chikalla
Ceramics & Graphite Section
Battelle-Northwest
Richland, WA 99352

Carl Ziveben
Bldg. 2621 Exp. Station
E. I. duPont de Nemours & Co.
Wilmington, DE 19898

NT DSC
Southwest Research Institute
Post Office Drawer 28510
San Antonio, TX 78284

Plastec
Picatinney Arsenal
Dover, NJ 07801

FINAL REPORT ONLY (12 copies)
Commander, Naval Air Development Center
Attn: A. R. Fletcher, Code 302A, FOR DDC
Warminster, PA 18974

(3 copies)
Commander, Naval Air Development Center
Attn: Code 813
Warminster, PA 18974