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METAL BORIDES, CARBIDES AND NITRIDES, AND COMPLEMENTARY REFRACTORIES: AN ANNOTATED BIBLIOGRAPHY

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Compiled by
JACK B. GOLDMANN

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Lockheed
MISSILES & SPACE COMPANY
A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION
SUNNYVALE, CALIFORNIA

ABSTRACT

The metal borides, carbide and nitrides, and complementary refractories which are related to the field of aerospace materials from the basis of this annotated bibliography. The references which are included appeared in print during the period, January 1961-May 1962. Citations are arranged alphabetically by author.

Search completed July 1962.

Availability notices and procurement instructions following the citations are direct quotations of such instructions appearing in the source material announcing that report. The compiler is well aware that many of these agencies' names, addresses and office codes will have changed; however, no attempt has been made to update each of these notices individually.

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This selective bibliography has been prepared in response to a specific request and is confined to the limits of that request. No claim is made that this is an exhaustive or critical compilation. The inclusion of any reference to material is not to be construed as an endorsement of the information contained in that material.

1. Aagaard, L.

PROCESS FOR PRODUCING TITANIUM CARBIDE.

U. S. Patent No. 3, 004, 832. 17 October 1961.

Comminuted TiC is formed by hydrolyzing a titanium sulfate solution in the presence of a carbon dispersion, adding a soluble inorganic phosphate to form titanium phosphate, and calcining.

2. Accary, A. and Trouve, J.

Application of microscopic methods for the study of the reaction between uranium carbide and metallic zirconium. SOCIÉTÉ CHIMIQUE DE FRANCE. BULLETIN no. 1, p. 26-30. January 1961. (In French)

A micrographic investigation to study the kinetics of the reaction in the solid state between UC and zirconium, resulting in CZr and uranium, showed the appearance of a metallic uranium matrix in the primary carbon and formation of an intermediate zone consisting of a mixed carbide of uranium and zirconium. It was concluded that the kinetics of the reaction is controlled by a diffusion phenomenon, probably of the carbon in the ZrC.

3. Adachi, A. and Mizukawa, K.

Influence of heat treatment on the behavior of titanium nitride. ŌSAKA DAIGAKU KŌGAKU HŌKOKU, v. 11, p. 351-354. October 1961. (In Japanese)

Ferrotitanium samples of various nitrogen levels were heated at 1400° C in argon to effect complete solution of titanium nitride, and then quenched. The precipitation of nitride from the supersaturated solution was studied for different isothermal treatments. Relations were analytically established between the heating temperature and the nitrogen and titanium levels, and it is shown that TiN is more stable than AlN. Graphs are presented.

4. Adams, R. P.

Hafnium carbide. In U.S. Bureau of Mines.
Albany Metallurgy Research Center, Ore.
QUARTERLY METALLURGICAL PROGRESS
REPORT no. 13, 1 Oct - 31 Dec 61. Report
USBM-U-887, p. 15. Dec 61. (Contract AT(11-1-599)

HfC castings with 5.46-10.97 wt-% C were produced to study physical properties, density, microhardness, electrical resistivity and tensile strength at high temperatures. Preliminary measurements of melting point were made.

5. Agte, C. and Blum, G.

Titanium carbide-base high-temperature materials.
NEUE HUETTE v. 6, no. 3, p. 139-146. March
1961. (In German)

Titanium carbide materials, with a Ni-Co-Cr binding component, acquire higher scaling resistance when the carbide component, instead of TiC, is made of 80% TiC + 20% TaC/NbC. The heat resistance remains the same. The scaling resistance of these materials, designated as "TZ-alloys," becomes still more improved through an addition of 1-5% Cr_3C_2. Some of the mechanical properties are also somewhat improved thereby, specifically resistance to bending at elevated temperatures, creep resistance, and impact strength. On the other hand, resistance to temperature changes becomes somewhat lower. Similar effects are produced by an addition of a small amount of TiB_2.

6. Akishin, P. A. and Khodeev, Yu. S.

Mass spectrometric study of the composition of
vapor above nitrides of zirconium, titanium and
boron. ZHURNAL NEORGANICHESKOI KHIMII
v. 7, no. 4, p. 941-942. April 1962. (In Russian)

According to literature data, no ZrN, TiN or BN molecules have been observed in the gaseous phase above solid samples of the nitrides at elevated temperatures. The present authors attempted to detect these molecules mass spectrometrically at temperatures up to 2100°C. They found only ions of the metals, of nitrogen, and of metal oxides (from impurities). However, a determination of the sensitivity of the instrument (by observing the evaporation of gold) showed that the upper limits of observable partial pressures of ZrN, TiN and BN vapors at maximum temperatures of the experiments were lower than the pressure of nitrogen ions by 5-6 orders of magnitude and, consequently, could not be detected by mass spectrometry.

7. Alekseev, V. I. and Shvartsman, L. A.

The free energy of formation of certain carbides of vanadium and chromium. PHYSICS OF METALS AND METALLOGRAPHY v. 11, no. 4, p. 63-67. April 1961.

For the system V_4C_3-V_2C-H_2-CH_4 (methane forms from the other components) the author measured the equilibrium states among the phases. By combining the results with data on equilibria in the system C (graphite) -H_2 -CH_4, it was possible to derive the equation for the temperature dependence of the free energy of formation of V_4C_3 from its elements.

8. Alyamovskii, S. I., Gel'd, P. V. and Matveenko, I. I.

Cubic phases of vanadium carbides. JOURNAL OF STRUCTURAL CHEMISTRY v. 2, no. 4, p. 412-415. July-August 1961.

Densitometric and x-ray diffraction studies of the V-C system confirm the existence of δ and ϵ carbide phases of cubic structure. Defectiveness in the carbon and vanadium sublattices is discussed. δ occurs in the $VC_{0.63-0.79}$ range and in the $VC_{0.79-0.92}$ range. Data are tabulated.

9. Amstein, E. H.

PRODUCTION OF REFRACTORY CARBIDES. BORIDES AND THE LIKE. U. S. Patent no. 3,019,084. 30 January 1962.

Titanium and zirconium borides and carbides of low free carbon content may be produced continuously by preparing a solid reaction mass of mixed metal oxides with carbon or boron and carbon, continuously introducing the mass into a reaction chamber and through a hot zone at 2000° - 3000°C while removing the evolved CO via an outlet located in a 1500°C zone, continuously passing solid reaction products through another outlet, and cooling them fast enough to prevent back reaction. A diagram is shown.

10. Antony, K. C. and Cummings, W. V.

METALLURGICAL STABILITY OF SEVERAL

BORIDE DISPERSION SYSTEMS. General Electric

Co., Atomic Power Equipment Department, Pleasanton,

Calif. Report GEAP-3530. 20 September 1960. 28p.

(Contract AT(04-3)-189)

The metallurgical stability (compatibility) of 80 different boride-metal systems was determined experimentally. Specifically, the compatibility of some MB_2 borides (HfB_2, TiB_2, VB_2, ZrB_2), MB_4 borides (B_4C, YB_4), and MB_6 borides (CaB_6, EuB_6, SmB_6, and YB_6, and YB_6) with the metals Ti, Zr, Fe, stainless steel (304), Ni, Cu, Ag, and Al, respectively, was determined using the methods of x-ray diffraction and metallography. Determinations were made on disperse powder samples at temperatures and times consistent with anticipated fabrication parameters.

11. Arai, Z, *et al*

Synthesis of titanium nitride from titanium

powder and nitrogen or ammonia. NAGOYA

KOGYO GIJUTSU SHIKENJO HOKOKU, v. 11,

no. 2, p. 119-125. February 1962.

(In Japanese)

Heating titanium powder to 1000° - 1400°C for 1-7 hours in a stream of nitrogen or ammonia gave products which were examined by x-ray and microscopy. Ammonia produced the nitride twice as fast as nitrogen in the 1300° -1400°C range, and the reaction rate was more temperature dependent. Black NaCl-type crystals were obtained. Data are tabulated.

12. Armstrong, J.R., Northrup, J.B. and Long, R.A.
TUNGSTEN TO GRAPHITE BONDING. Narmco
Industries, Inc., San Diego, Calif. Final summary
report. 13 Dec 1961. 38p. (Contract DA 04-495-
ORD-3028) ASTIA AD-270 115.

The reactions of various metallic carbides with W and with graphite were studied for the purpose of developing a W to graphite bond system for use of temperatures up to 5000°F. A bond composition and process was developed that yielded good bonds; however, the desired reproducibility was not achieved. The bond composition developed also formed an excellent coating for graphite, having good thermal shocker resistance and adherence at temperatures up to at least 5000°F.

13. Aronsson, B.
BORIDES AND SILICIDES OF THE TRANSITION
METALS. U.S. Air Force. Office of Scientific
Research. Technical Note 60-683. 1 July 1960.
114p. PB 171121.

Transition metal systems (Group IVb-VIb) with boron and/or silicon are discussed as to phase features and structures and the solid solubility of boron and silicon in the metals. Physical, chemical and crystallographic data are presented for the silicides, borides and silico-borides of the metals. Some ternary systems involved carbon or nitrogen.

14. Aronsson, B.
Borides and silicides of the transition metals.
ARKIV FOER KEMI v. 16. no. 4-5, p. 379-419.
1961. (In English)

Recent studies of transition metal borides, silicide and silico-borides are critically reviewed under the categories of crystallographic data, physical and chemical properties, crystal structure, bonding, and sililarities to interstitial phases. Available data on the TiB system are confusing, and the existence of TiB (or ZrB and HfB) phase seems dubious. The V-B system may contain more phases than have been noted. Crystallographic data on the Ti-Si system are meager and inconsistent, but the orthorhombic structure of ZrSi and HfSi has been confirmed. Other zirconium and hafnium silicides, and the lanthanon silicides, remain insufficiently characterized. It is concluded that borides and silicides can not be included among the interstitial phases, although bonding of the phases is similar. Numerous tables are presented.

15. Aronsson, B.

Borides. Part A: Basic factors. MODERN MATERIALS

v. 2, p. 143-190. 1960.

A review of information on metal borides discusses and tabulates data on borides of titanium, zirconium, hafnium, molybdenum, vanadium and the lanthanons. Mutual solubilities of TiB_2, ZrB_2 and HfB_2 are complete between any pair. A general mutual solubility with the foregoing and each other is noted for VB_2 and Mo_2B_5. Systems in which silicon is a ternary addition have found to be more complex than ternary systems involving carbon. Ternary systems involving nitrogen are very high temperature sensitive and equilibria are difficult to attain.

16. Baskin, M. L., Tret'yakov, V. I. and Chaporova, I. N.

Diffusion of niobium in titanium carbide and in TiC-NbC solid solution of equimolecular composition.

FIZIKA METALLOV METALLOVEDENIE v. 12,

no. 6, p. 860-864. December 1961. (In Russian)

The activation energy of diffusion of niobium in TiC and in equimolecular TiC-NbC solid solution, as well as the temperature dependence of the diffusion coefficients, were determined at 1935° -2280°C by measuring the penetration of β radioactivity of Nb^{95}, that isotope being absorbed from a surface covering by a 5 mm thick sample of TiC or TiC-NbC. The results were: 1) diffusion in TiC activation energy 84,000 cal/mol, $D=2.4 \exp(-84{,}000/RT)$ cm^2/sec; 2) diffusion in TiC-NbC: activation energy 120,000 cal/mol, $D=470 \exp(-120{,}000/RT)$ cm^2/sec.

17. Bassani, F. and Celli, V.

Energy-band structure of solids from a perturbation on the "empty lattice." JOURNAL OF THE PHYSICS AND CHEMISTRY OF SOLIDS, v. 20,

p. 64-75. June 1961.

A simple perturbation method for obtaining the energy-band structure of solids is described. The unperturbed Hamiltonian consists of the kinetic part of a uniform potential; the perturbing operator is the crystal potential plus a term which originates from the requirement that valence and conduction states by orthogonal to the inner states. This amounts to an approximation to the O.P.W. method. Reasons are given for the validity of such a simple scheme and applications are made to the case of the diamond lattice and of the zincblende lattice. It is shown how features of the energy-band structure depend on the symmetry of the lattice, on the lattice parameter and on the "core states" of the atomic components. Numerical results obtained for diamond, silicon and boron nitride are in fair agreement with recent calculations. An energy-band structure consistent with experimental information is obtained for Ge and GaAs by fixing the values of a few parameters.

18. Beck. W.

Electrode potential and corrosion behavior of

some borides of molybdenum and zirconium.

PLANSEEBERICHTE FUER PULVERMETALLURGIE

v. 9, nos. 1/2, p. 96-108. April 1961.

MoB is electrolytically decomposed in 0.1 N KCl by local cell currents set up between anodic and cathodic areas of MoB and residual carbon. Molybdenum is converted to a low oxide and boric acid forms. The oxide thickens with time, causing a decrease in the rate of attack. β-MoB is more resistant than d-MoB, while Mo_2B_5 and Mo_2B are intermediate. ZrB_2 and ZrB_{12} behave in a more complex way and corrode at a very low rate. The latter is the less stable. Graphs are shown.

19. Belforti, D., Blum, S. and Bovarnick, B.

Highly oriented boron nitride. NATURE v. 190,

p. 901(L). 3 June 1961.

The structure of boron nitride prepared by vapor phase pyrolysis and deposition in a hot target is described. Using boron bearing gases and regulating the parameters of the treatment, the deposit can be controlled. The x-ray diffraction patter shows the deposit to be composed of highly-oriented crystallites parallel to the deposition surface. The dimensions of a unit cell were measured, and the density was 2.26 gm/cm^3 as against 2.27 gm/cm^3 for normal boron nitride. Observed impurities were Mg, Mo, and Si at levels of 10 ppm or less. One-half mm pieces were translucent and white or yellow; the microstructure shows columnar cones similar to those of pyrolytic graphite. The technique of pyrolytic preparation produces samples with highly oriented structures which may be used in place of single crystals for investigating some properties of materials.

20. Belikov, A. M. and Umanskii, Ya. S.

Investigating the anisotropy of thermal vibrations of atoms in certain metal carbides and diborides of transient groups with hexagonal lattice. SOVIET PHYSICS-CRYSTALLOGRAPHY v. 4, p. 684-686. 1959.

Measurement of the thermal expansion coefficient (alpha) of the carbides and borides in the basic plane and perpendicular to it, and evaluation of the magnitude m (O squared) of the binding force of metallic atoms of carbides and dioborides are discussed. The magnitude m (O squared) in the first approximation is proportional to the coefficient of quasi elastic force which returns the atoms into equilibrium position during thermal vibrations; m is the reduced mass of the atom and O the characteristic temperature of thermal vibrations. The displacement of interference maxima from the differently oriented crystallographic planes, and the weakening of their integral intensity during heating were used as a basis for calculating alpha values and characteristic temperatures along the axes.

21. Benn, W. R.

METAL BORIDES AND CARBIDES - MATERIALS OF THE FUTURE. Union Carbide Metals Co., Niagara Falls, New York. May 1960. 6p.

Discusses borides and carbides - their properties and potential applications; transition metal borides; improvements in impact strength; available price information on borides and carbides; addition of other materials, such as metal binders, with the compound; transition metal carbides; titanium carbide; other carbides; other uses for borides and carbides; unconventional fabrication techniques, and further test research that is needed.

22. Binder, I., LaPlaca, S. and Post, B.

Some new rare earth borides. In Kohn, J. A., Nye, W. F. and Gaulle, G. K., eds. BORON: SYNTHESIS, STRUCTURE AND PROPERTIES. N.Y., Plenum Press, 1960. p. 86-93.

Dysprosium, holmium, erbium, thulium, luetetium and yttrium sesquioxides react with boron at 1400° - 1500°C under helium to give the dodecarborides. They are isostructural with UB_{12} and ZrB_{12} and contain four formula weights per f. c. c. unit cell. Lattice parameters are tabulated. The atomic size factor is critical in forming these borides, the larger lanthanon atoms being unable to form dodecaborides. X-ray diffraction data are tabulated.

23. Blok, N. I., et al

Boride phases in nickel-chromium base alloys.

INDUSTRIAL LABORATORY v. 25, no. 9,

p. 1103-1107. September 1959.

Conclusions: 1) a method was developed for electroyltic separation of boride pases from Ni-Cr-base alloys. (2) EI437 type alloys revealed chromium boride with tetragonal crystalline structure, corresponding to formula $(Cr, Ni)4B_3$ or $(Cr, Ni)5B_4$, and (3) ZH83 and EI617 type alloys as well as composite alloyed alloys of the ZHS_3 type revealed boride with approximate formula $(Mo, Cr, W, Ni)4B_5$, or $(Mo, Cr, W, Ni)5B_4$.

24. Calvert, E. D., Kirk, M. M. and Beall, R. A.

CHEMICAL REACTIONS IN THE ELECTRIC ARC:

REACTIVE METAL CARBIDES. U. S. Bureau of

Mines. Report of Investigations No. 5951. 1962. 13p.

Preparation of zirconium and hafnium carbides by electric arc reduction of the oxides with carbon is discussed on the basis of laboratory tests. The balance of the products can be changed only by altering the carbon-oxide ratio. Reactive carbide crystals grow at the cathode, usually in the form of trees, probably by migration in the arc plasma. High hardness and melting point were observed.

25. Cape, J. A. and Taylor, R. E.

THERMAL PROPERTIES OF REFRACTORY MATERIALS.

Atomic International, Canoga Park, Calif. WADD

TR-60-581, Part II. July 1961. 22p. (Contract

AF 33(616)-6749)

Refinements in the transient-thermal-property apparatus are described. With these modifications, the apparatus has been used to determine the thermal diffusivity of tungsten boride from about 1300° to 1600° C. The measured values increase from about 0.054 to 0.058 cm^2/sec over this temperature interval. The techniques and apparatus for measuring the specific heat of brittle conductors by pulse heating are also described. Resistivity and specific-heat data for uranium silicide of several compositions are reported. The thermal conductivity of titanium carbide was measured over the temperature region 400° to 1200° C. The steady-state radial heat flow method was used. The results obtained are in marked contrast to values reported in the literature.

26. Childs, E. E.

General properties and uses of borides, carbides,

nitrides and silicides. INDUSTRIAL HEATING v. 28,

p. 2263-2265. November 1961.

Because of the increasing importance of borides, carbides, nitrides and silicides for present and future applications, a paper presented during the 63rd Annual Meeting of the American Ceramic Society in Toronto in April 1961, is a significant contribution. It reviews the history, synthesis, fabrication, properties, and uses of these refractory materials and includes a bibliography consisting of 15 books, 7 Government reports, and 53 papers.

27. Childs, E. E.

A SELECTED BIBLIOGRAPHY CONCERNING THE

PROPERTIES AND USES OF BORIDES, CARBIDES,

NITRIDES AND SILICIDES. Melpar, Inc., Falls Church,

Va. Paper no. TP-1-31. November 1961. 15p.

This selected bibliography includes references on properties and compounds of borides, carbides, nitrides and silicides. The introduction gives the sources which were covered in order to arrive at the list of references. The history of these compounds, the methods of synthesis, fabrication, and properties are also included.

28. Clougherty, E.V., Lothrop, K.H. and Kafalas, J.A.

A new phase formed by high-pressure treatment:

face-centered cubic molybdenum monocarbide.

NATURE v. 191, no. 4794, p. 1194. 16 September 1961.

Alpha-MoC may be formed at 40-70 kilobars and 1800°-2500°C from equivalent mixtures of carbon and molybdenum or Mo_2C. The phase is retained at 1 atm and has an f.c.c. structure of the NaCl type with alpha = 4.27 A. Molybdenum carbide phase data are tabulated.

29. Coles, B. R., et al

Electrical resistivity and paramagnetic resonance

in gadolinium hexaboride. PHYSICAL SOCIETY.

PROCEEDINGS v. 79, no. 507, p. 84-86. 1 January 1962.

Magnetic susceptibility measurements in GdB_6 have been interpreted in terms of an antiferromagnetic interaction between $4f^7$ ion cores via a conduction electron. Electrical resistivity data are presented which show the spin-disorder contribution to be expected. A large effect is attributed to short-range order above the Neel temperature. The observed electron spin resonance has the expected properties.

30. Cotter, P. G.

PREPARING ZIRCONIUM DIBORIDE DIRECTLY FROM

ZIRCON. U.S. Bureau of Mines. Report of Investigations

No. 5770. 1961. 9p.

A study seeking a less expensive synthesis of ZrB_2 showed that it could be made directly from zircon without going through the ZrO_2 step, and that the quality obtained was comparable to that of commercial methods. Zircon sands were digested over night in 10% HCl, washed, fired at 150° C and mixed with 13% B_4C and 11% lampblack. The mixture was ballmilled, compacted, and reacted in a vacuum induction furnace. Reaction begins at 1350° C and is self-propagating. The zircon particle shapes are retained in the ZrB_2 product. Residual carbon and silica are not excessive. Micrographs are shown.

31. Dolloff, R. T.

RESEARCH STUDY TO DETERMINE THE PHASE EQUILIBRIUM RELATIONS OF SELECTED METAL CARBIDES AT HIGH TEMPERATURES. National Carbon Co., Parma, Ohio. WADD TR 60-143. July 1960. 22p. (Contract AF 33(616)-6286)

The work here reported is the result of an investigation of phase equilibria in the ternary system, silicon-boron-carbon. Techniques for extending the high-temperature range of measurements have been developed. Accurate phase diagrams for the silicon-carbon and the boron-carbon binaries have been obtained and details of the ternary system have been determined in the high-carbon-content region. The data were obtained by high-temperature differential thermal analysis and by photoelectric thermal analysis, both supplemented by metallographic, x-ray and chemical techniques.

32. Eckstein, B. H. and Forman, R.

Preparation and some properties of tantalum carbide. JOURNAL OF APPLIED PHYSICS v. 33, no. 1, p. 82-87. January 1962.

Small tantalum carbide objects may be made by heating the objects made from tantalum in dilute hydrocarbon atmospheres at temperatures > 2000° K. Carburization proceeds quite rapidly above 2300° K by diffusion of carbon initially deposited on the surface into the metal, principally along grain boundaries, to form a thin layer of Ta_2C which is quickly converted to the TaC. The latter has a tensile strength of 21-25 kg/mm^2, a work function $\phi = 3.17$ ev, an emissivity of 0.40-0.46 between 2400° and 3500° K. rising with increasing temperature, and a resistivity $\rho = 102 + 0.0178\ T$ (°K) ohm cm between 1400° and 3500° K.

33. Engelke, J. L., Halden, F.A. and Earley, E.P.

SYNTHESIS OF NEW HIGH TEMPERATURE MATERIALS.

Stanford Research Institute, Menlo Park, Calif.

WADC-TR-59-654. Period covered: June 1958 to June 1959. December 1959. 45p. (Contract AF 33(616)-5888; Project No. 7350) ASTIA AD-236 030.

A number of mixed transition metal carbide, borides, and nitrides, were prepared and examined in terms of melting point, structure, and oxidation resistance. None of the measured melting points was higher than the value reported for HfC-4TaC (3940°C). The melting point for a series of solid solutions between HfC and NbC increased regularly with hafnium content. A material with the composition Mo_2BC, when heated in an air stream, was found to lose weight rapidly without loss of metallic character, suggesting its possible use as an ablation material. A cubic modification of hafnia was obtained in material sprayed from a plasma arc. A low coefficient of thermal expansion and high melting temperature make this a material of interest. An implosive-shock technique for compound synthesis, which subjects materials to extremely high temperature-pressure conditions for short periods of time, was developed. The method was used successfully to synthesize boron phosphide.

34. Epprecht, W.

Crystal chemistry of metal carbides and their importance in metallurgy. CHIMIA v. 5, p. 49-60. 1951. (English Trans. AEC-tr-5022. 37p.)

The crystal chemistry of selected metal carbides is examined. Included are discussions of lattice structures and the effects of carbides in alloys.

35. Eremenko, V.N. and Naidich, Yu. V.

The wetting of borides and carbides with liquid metals. RUSSIAN JOURNAL OF INORGANIC CHEMISTRY, v. 4, no. 9, p. 931-934. September 1959.

The wetting of solid borides and carbides by liquid metals has been studied in relation to their properties, particularly the strength of the bond between the atoms in the boride. The experimental results on the wetting of carbides by liquid metals have been analysed and it has been shown that only the transition metals wet them well. The above observations can be used in the preparation of cermets.

36. Espenschied, H.

METHOD FOR THE PRODUCTION OF ZIRCONIUM BORIDE.

U. S. Patent No. 2, 964, 388. 13 December 1960.

Zirconium boride is produced by slurrying together 1 mole of uncalcined zirconia hydrate, 5 moles of carbon and 2 moles of B_2O_3 as boric acid, agitating and drying, reacting under inert atmosphere at a temperature sufficient to complete the reaction and form a comminuted product of 1-20 μ particle size. The zirconia hydrate is precipitated from a basic zirconia salt solution.

37. Espenschied, H.

TITANIUM BORIDE AND METHOD FOR MAKING SAME.

U.S. Patent no. 2, 973, 247. 28 February 1961.

Slurry uncalcined titania hydrate pulp with carbon and an oxidic compound of boron and heating in the 1350°-1750°C range in inert atmosphere produces titanium boride of 1-15 micron particle size.

38. Ewing, R. A. and Sunderman, D. N.

EFFECTS OF RADIATION UPON HAFNIUM DIBORIDE.

Battelle Memorial Institute, Columbus, Ohio.

Report BMI-1521. 14 June 1961. 10p. (Contract

W-7405-ENG-92)

HfB_2 containing O and 55% B^{10} were irradiated at 400°-600°F. X-ray diffraction disclosed degradation to amorphous structures, indicating that the materials are unsuitable for control-rod use. Retention of helium appears to be poor.

39. Eyring, L., Schuldt, H.S. and Vorres, K. S.

PHASE EQUILIBRIA, KINETIC AND THERMODYNAMIC STUDIES OF SOME RARE EARTH AND OTHER METAL OXIDE AND NITRIDE SYSTEMS. Iowa State University, Iowa City. Technical progress report on Project No. 5. 15 May 1959. 139p. (Contract AT(11-1)-72)

Oxidation kinetics of seven lanthanons were studied. Cerium oxidized most rapidly and praseodymium more rapidly than neodymium, lanthanum, gadolinium, samarium and ytterbium. Several oxide phases are possible in the first two. Rate laws and temperature ranges are tabulated. Lanthanon-lanthanon nitride systems were also studied. Lattice constants of some lanthanon nitrides change on annealing at high temperature, and in these cases it is shown that nitride formation is incomplete and that the nitrides dissolve considerable metal. Kinetics of vacuum reduction of mixed lanthanon oxides is being studied. Graphs are shown.

40. Fisher, E.D. and Baskey, R. H.

PROCESS TO PRODUCE VOID FREE REFRACTORY BORIDE PRODUCT. U.S. Patent no. 2, 974,040. 7 March 1961.

A non-porous refractory cermet product is formed by mixing nickel, silver and a boride of molybdenum, vanadium or titanium, compacting to somewhat less than theoretical density, and heating the compact in contact with silver to further impregnate it.

41. Forney, G.J. and Marshall, J. J.

INVESTIGATION OF TITANIUM BORONITRIDE AND TANTALUM BORONITRIDE MATERIALS SYSTEMS. Electro Thermal Industries, Inc., Pearl River, N.Y. Quarterly report no. 2. Report no. WAL TR-371.9/2. January 1961. 32p. (Contract DA-30-069-ORD-3126, ORD Proj. TB4-004, and DA Proj. 5B93-32-004). ASTIA AD-253 669.

Continuing the investigation of the titanium boronitride system, efforts were directed in major part of Phase 2, effect of composition on properties. Compositions containing 0, 1/2, 1-1/2, 2, 3, 4, and 6 moles excess boron nitride were selected for study. It was evident that blends containing 3 or more moles excess had insufficient cohesiveness to be of any practical value. Consequently, the balance of the investigation upon compositions was devoted to the 1/2, 1, 1-1/2 and 2 mole blends. The investigation was conducted at reactor pressures of 20,000 and 30,000 psi. It was concluded that: (1) Density decreases with increasing excess boron nitride in the blend; (2) Density increases as the reactor pressure increases for each composition; (3) Electrical resistivity increases with decreased specimen density for each composition; and (4) Preheat energy requirements are not directly proportional to increased mass, due to heat losses at a greater rate from small charges.

42. Funke, V. F., Tumanov, V. I. and Trukhanova, Z. S.

Influence of alloying elements on the structure and properties of tungsten carbide-cobalt alloys. AKADEMIIA NAUK SSSR. IZVESTIIA. OTDELENIE TEKNICHESKIKH NAUK. METALLURGIIA I TOPLIVO no. 5, p. 101-108. September-October 1961.

The limiting bending strength of WC-TiC-Co alloys (consisting of carbide and cobalt phases) decreases when the TiC content increases from 0 to 30%, and remains almost constant at higher TiC contents. Increasing the cobalt phase content up to 25 vol-% produces considerable strength increases in alloys with 5-15% TiC, and only insignificant increases in alloys with 30% and more TiC. Adding molybdenum (e.g. 4.6%) to WC-Co alloys lowers their strength, although to a smaller degree than do other additions (aluminum, chromium).

43. Funke, V. F., Yudkovskii, S. I. and Samsonov, G. V.

Some characteristics of the vacuum-thermal process for production of titanium boride. JOURNAL OF APPLIED CHEMISTRY OF THE USSR. v. 33, no. 4, p. 832-836. April 1960.

The effect of increasing the charge in TiB_2 production by the vacuum-thermal process, and the influence of impurities in the starting materials TiO_2 and B_4C were studied. Larger charges increase the gas pressure from carbon monoxide and shift the optimum process temperature to 1700°C. More time is also required. Lower temperatures and lesser times lead to higher carbon contents. A stoichiometric excess of carbon in B_4C is beneficial. Other impurities have no significant effects. Data are tabulated.

44. Goldsmith, A., Waterman, T. E. and Hirschorn, H. J.

THERMOPHYSICAL PROPERTIES OF SOLID MATERIALS.

VOLUME IV. CERMETS, INTERMETALLICS, POLYMERICS,

AND COMPOSITES. Armour Research Foundation, Chicago, Ill.

WADC-TR-58-476 (Vol. IV) (Rev.) November 1960. 798p.

(Contract AF 33(616)-5212)

Thermophysical property data, and their variation with temperature, are presented for a great number of solid materials, based on literature published during the period from 1940 to 1957. Each reported value is shown and annotated, and recommended "most probable value" curves are given. Materials covered include cermets, intermetallics, polymerics, and composite materials. Except for materials in the last two categories, only those melting above 1000° F are included. Properties covered include the following: melting point, density, latent heats, specific heat, thermal conductivity, thermal diffusivity, emissivity, reflectivity, thermal expansion, vapor pressure, and electric resistivity.

45. Goodman, E., Bargero, G. F. and Huminik, J.

ELECTRODEPOSITION OF EROSION AND OXIDATION

RESISTANT COATINGS FOR GRAPHITE. Value Engineering

Co., Alexandria, Va. Quarterly progress report no. 3,

23 August - 22 November 1961. 18 December 1961. 5p.

(Contract NOw 61-0670-c) ASTIA AD-268 767.

No automatic release to Foreign Nationals.

A literature survey resulted in the selection of the following ceramics for inclusion in the program: Ta and Hf borides and carbides, Nb and Si carbides B and Si nitrides, Zr and W borides and Zr oxide. Twelve cermet coatings in 3 particle size ranges were coated on ATJ graphite blocks. Variations in thickness existed not only between different ceramics, but also between different particle ranges of the same ceramic. Cermet coatings with satisfactory appearance were produced from baths at room temperature or 100 F. Oxyacetylene flame and high temperature oxidation tests were performed on graphite blocks coated with various cermet compositions. A sample with a W boride coating had a long life of 11.5 min. Hafnium carbide and a Zirconium boride plus 10% $MoSi_2$ coatings gave superior performance. Preliminary erosion and metallographic tests were conducted.

46. Gorbunov, N.S. et al

Neutron diffraction investigation of the carbide and the nitride of titanium. AKADEMIIA NAUK SSSR. IZVESTIIA. OTDELENIE KHIMICHESKIKH NAUK, no. 11, p. 2093-2095. November 1961.

(In Russian)

X-ray analysis does not indicate with sufficient sensitivity the position of the non-metal atoms in crystals of carbides and nitrides of transition elements. In an attempt to supplement x-ray data with neutron diffraction observations, the authors were able to establish that in $TiC_{0.25}$ (carbon deficit) and in the carbide close to TiC, titanium atoms may occupy any available vacant positions. On the other hand, whereas in TiN and $Ti_{0.85}N$ the non-metal atoms actually occupy the empty places in the octahedra, in $TiN_{0.25}$ the latter are occupied statistically.

47. Grala, E.M.

Freeze casting titanium carbide. In Leszynski, W., ed. POWDER METALLURGY New York, Interscience, 1961. p. 507-524.

Full-size TiC turbine blades were cast by preparing a very thick slip of TiC powder and a little binder, casting into a mold by vibration, centrifuging to densify the casting homogeneously, freezing the mold assembly in a kerosene bath to retain the shape, drying by sublimation in absorbent, and vacuum sintering. The porous blades appear to be flawless. A blade infiltrated with S-590 alloy was measured for density and hardness. The method is convenient, saves powder and eliminates machining, and appears applicable to casting intricate shapes from a variety of powders. Micrographs and photographs are shown.

48. Greenwood, N. N. and Osborn, A. J.

Chemical and magnetic properties of lanthanum dicarbide and sesquicarbide. CHEMICAL SOCIETY JOURNAL p. 1775-1782. April 1961.

LaC_2 and La_2C_3, prepared by heating the dihydride with graphite, were studied to determine the disposition of the third valence electron in LaC_2, which otherwise resembles CaC_2. LaC_2 is diagmagnetic and La_2C_3 paramagnetic. Gases evolved on hydrolysis by water or dilute H_2SO_4 or HNO_3 were observed by mass spectroscopy, and determined by gas-liquid chromatography. Secondary reactions complicate the interpretation of results with anhydrous H_2SO_4 and HSO_3Cl. Data are tabulated.

49. Haszko, S. E.

Rare-earth gallium compounds having the aluminum-boride structure. AMERICAN INSTITUTE OF MINING, METALLURGICAL AND PETROLEUM ENGINEERS. METALLURGICAL SOCIETY. TRANSACTIONS v. 221, no. 1, p. 201-202. February 1961.

Lanthanon digallides were prepared and crystallographic data were obtained. The AlB_2 structure is obtained except for $CeGa_2$ and $PrGa_2$, with possible semiconducting behavior. Relative intensity data were computed for $DyGa_2$. $EuGa_2$ and $YbGa_2$ could not be prepared. Divalency or large atomic size may be implicated.

50. Hergenrother, K. M.

METHOD OF PURIFYING SILICON CARBIDE. U. S. Patent 2, 996, 415. 15 August 1961.

A method for removing metallic impurities, especially aluminum, from silicon carbide is described. The silicon carbide is dissolved in a melt of chromium containing oxygen, preferably as an oxide of chromium, and a crystal is grown from the melt. The oxygen reacts with the aluminum at the temperature of the melt-crystal interface and forms an oxide with a high heat of formation, thus removing the aluminum from the silicon carbide. The chromium also removes traces of silicon or carbon impurities in the silicon carbide. Other impurities such as zirconium and titanium can also be removed by forming an oxide with a high heat of formation. Junctions can be formed by controlling the amount of oxygen in the chromium.

51. Hoke, R. M.

PREPARATION OF METAL BORIDES. U. S.

Patent No. 3,032,399. 1 May 1962.

A dry reaction of alkali borohydride with halides, oxides, or oxy-ions of Group IVb, Vb or VIb metals at temperature substantially above 300°F produces a mixture from which the metal borides may be recovered by lixiviating the byproducts. An inert atmosphere is necessary for the reaction.

52. Hollander, L. E., Jr.

Electrical conductivity and thermoelectric

effect in single-crystal TiC. JOURNAL OF

APPLIED PHYSICS v. 32, p. 996-997. June 1961.

Measurements of the temperature dependence of resistivity, thermoelectric power, and hydrostatic piezoresistivity on TiC single crystals are reported. The resistivity of all samples was $200 \pm 20\ \mu$ ohm-cm and is affected by at least three factors: non-stoichiometric composition, effects of oxygen in the lattice, and stress concentrations. The thermoelectric power $\Delta V / \Delta T$ referenced against Cu at room temperature is $7.8 \pm 0.6\ \mu v/^{\circ}C$ and indicates n-type conduction. No hydrostatic piezoresistivity was observed. P vs T and thermoelectric data indicate that single crystal TiC has metallic-type conduction and that the predominant charge carriers are electrons.

53. Hopkins, B. J. and Ross, K. J.

The work function of zirconium carbide. PHYSICAL

SOCIETY. PROCEEDINGS v. 79, no. 508, p. 447-448.

1 February 1962.

Variations in anode work function that occur in diodes containing ZrC or $ZrC-U_2C$ mixtures as cathodes were studied. The analytical method used gave the work function as 3.62 ev.

54. Hoyt, E. W., Chorné, J. and Cummings, W. V.

CORROSION BEHAVIOR OF SOME METAL BORIDES.

General Electric Co., Vallecitos Atomic Laboratory,

Pleasanton, Calif. Report GEAP-3548. 18 October

1960. 20p. (Contract AT(04-3)-189)

Results are presented of tests in which metal borides were subjected as powders and dense solids to boiling water and 400°C stream. Results indicate that the use of boron-bearing materials as control elements in water cooled or moderated reactors is limited to some extent by their corrosion behavior.

55. Hudson, R. G. et al

Vaporization characteristics of uranium-zirconium

carbides. ELECTROCHEMICAL SOCIETY.

JOURNAL v. 109, no. 3, p. 77C. March 1962.

Life expectancy of U-ZrC cathodes of thermionic devices was studied by measuring vaporization in the 1850° -2100° C range vs. composition, heating time, quality of vacuum and concentration of cesium. Composition of the condensate was studied. This paper was presented at the Spring meeting of the Electrochemical Society in Los Angeles, 6-10 May 1962.

56. Huminik, J., Jr., and Bargero, G. G.

DEVELOPMENT AND TESTING OF ELECTRODEPOSITED

CERMETS. Value Engineering Co., Alexandria, Va.

August 1961. 23p.

The program presently includes coating on the refractory metals and graphite with any of the following ceramics in a chromium matrix:

Tantalum Carbide
Tantalum Boride
Hafnium Boride
Niobium Carbide
Hafnium Carbide
Boron Nitride
Silicon Nitride
Silicon Carbide
Zirconium Boride
Zirconium Boride plus Molybdenum Silicide
Zirconium Oxide
Tungsten Boride

The present Navy-sponsored research effort is concentrating on the following specific areas utilizing graphite as the substrate: (1) Effect of various thicknesses on performance (0.003 to 0.050 inch). (2) Effect and uniformity of particle shape and size. (3) Effect of heat treatment on electrodeposited cermet coatings. (4) Effect of particle concentration in final coating.

57. Imai, Y. and Kumazawa, M.

Study on sintering process of titanium carbide

by measuring the change in electrical resistivity.

TOHOKU DAIGAKU KENKYUSHO v. 13, no. 4,

p. 225-231. August 1961. (In English)

TiC cermet sintering processes were studied by measuring electrical resistivity changes. Primary sintering in the 25° - 800° C range is governed by release of internal stresses, increase of contact areas and escape of vaporized lubricant and included gases. Resistivity increases markedly between 200° and 750° C. In sintering above 800° C diffusion is the main mechanism. Liquid phase produces anomalous resistivity at 1200° C. Increased resistivity above 1300° C is attributed to solubility of carbide for metal binder. Effects of additive carbides were observed. Graphs and x-ray diffraction patterns are shown.

58. Ingold, J.H.

Thermionic properties of HfC. JOURNAL OF

APPLIED PHYSICS v. 32, p. 2651. December 1961

Thermionic emission properties of bulk HfC were measured over the range 1300° to 2100° K.

59. Juza, R. and Haug, J.

Preparation and properties of ternary nitrides of

chromium, molybdenum and tungsten of composition

Li_9MoN_5. ZEITSCHRIFT FUER ANORGANISCHE

UND ALLGEMEINE CHEMIE v. 309, n. 5/6,

p. 276-282. April 1961. (In German)

Mixtures of lithium nitride with powdered molybdenum (or better, $MoN_{0.75}$) react with nitrogen at 660° C to form the ternary compound Li_9MoN_5. Molybdenum is in its hexavalent state, and compounds involving lower-valency molybdenum are not formed. Li_9MoN_5 enters into solid solutions with lithia up to 44 mol-% Li_2O.

60. Kane, J. S., Carpenter, J. H. and Krikorian, O. H.

METHOD FOR COATING GRAPHITE WITH NIOBIUM CARBIDE. U.S. Patent No. 3, 017, 286. 16 Jan 62.

The process comprises contacting niobium metal powders randomly with a quantity of graphite, the distance between the particles not exceeding 1 in., degassing the metal and the graphite surfaces by applying a vacuum pressure lower than 10^{-3} mm Hg thereto while heating to $< 1400°C$ for 10 min, further heating the metal and graphite to $> 2500°$ within 15 min while continuing to pump thereon at a rate of 50 liters/sec/in.^{2} of graphite surface, the vacuum pressure being maintained between 10^{-3} and 10^{-4} mm Hg, whereby the niobium powders melt, flow and wet the graphite surfaces, continuing to heat the graphite-niobium combination until carburization takes place.

61. Kato, H. and Copeland, M. I.

Hafnium-carbide phase diagrams. In U. S. Bureau of Mines. Albany Metallurgy Research Center, Ore. QUARTERLY METALLURGICAL PROGRESS REPORT no. 13, 1 Oct - 31 Dec 61. Report USBM-U-887, p. 8. December 1961. (Contract AT(11-1)-599)

The Hf-C system has been studied up to 6% C by microscopy and melting point measurement. A eutectic point occurs at 0.7% C. The two phases observed are HfC and a lamellar eutectic structure of Hf+HfC. Heat treatment and metallographic investigations are planned.

62. Kato, H. and Copeland, M. I.

Hafnium-carbide phase diagrams. In U. S. Bureau of Mines. Albany Metallurgy Research Center, Ore. QUARTERLY METALLURGICAL PROGRESS REPORT no. 12, 1 July 1961 - 30 Sep 1961. Report USBM-U-863, p. 6. September 1961. (Contract AT(11-1)-599)

The phase transformation temperature of hafnium was determined to be 1755°C by induction heating and thermocouple measurement. Making homogeneous alloys of hafnium with up to 6% C is being attempted. Arc-melting does not produce homogeneity. Future plans are discussed.

63. Kingery, W.D., Niki, E. and Narasimhan, M.D.

Sintering of oxide and carbide-metal compositions in presence of a liquid phase. AMERICAN CERAMIC SOCIETY. JOURNAL v. 44, no. 1, p. 29-35. January 1961.

Microstructural changes in TiC-Ni cermets and the rate of densification during sintering were observed. Spheroidal grains are present. Densification occurs by a solution-precipitation process in which the liquid phase must wet the solid and penetrate between grains, must have some solubility for the solid, and must be fluid enough for these processes to occur rapidly. Densification curves were obtained but fractional shrinkage made quantitative analysis impractical.

64. Kisly, P.S. and Samsonov, G.V.

High-temperature semi-conductor thermocouples. PLANSEEBERICHTE FUER PULVERMETALLURGIE v. 8, p. 200-206. 1961. (English trans. by L. F. Secretan. AERE-Trans-874. 8p.)

It is shown that a series of high-temperature semi-conducting compounds of the type of boron carbide and chromium silicide with metal-like compounds show high values and a linear temperature relation of the EMF over the range of from 300 to 400°C up to 2000 to 2200°C, which makes it possible to make high-temperature thermocouples of the semi-conductor type. A high-temperature thermocouple was made from molybdenum disilicide and boron-saturated graphite. The EMF of this thermocouple rose linearly over the range from 400 to 2000°C from 4 to 45 μV, and stayed constant in the course of time. A series of thermocouples was made from boron-saturated graphite with carbides and borides of high-melting metals. They also showed a linear relation between EMF and temperature. It is shown that it is possible to make thermocouples with pre-determined electrical and mechanical properties.

65. Klibus, A. Kh. and Nazarchuk, T.N.

Photometric determination of nitrogen in titanium carbide and boride and in other refractory materials. JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR. v. 16, no. 1, p. 80-84. January-February 1961.

The extraction with various organic solvents of a dye formed by the thymolhypobromite reaction of nitrogen has been investigated. n-Butyl alcohol exhibits the most intensive color. The optimum pH value for formation of indothymol is 11. Acid sample solutions should be neutralized with NaOH before addition of thymol and hypobromite. The above procedure has been applied to the photometric determination of small amounts of nitrogen (0. 1. -1%) in titanium carbide and boride.

66. Kopylova, V.P.

Chemical stability of carbides of transition elements of the fourth, fifth and sixth groups. ZHURNAL PRIKLADNOI KHIMII v. 34, no. 9 p. 1936-1939. September 1961. (In Russian)

The chemical stability of Mo_2C, HfC, ZrC, TiC increases in that order. Among acids and their mixtures, the mixture of concentrated HNO_3 and HF (4:1) is the most agressive medium both at room temperature and on heating. Although generally resistant to the action of dilute alkalies, the above carbides are attacked by them in mixtures with oxidizing agents such as Br_2 or H_2O_2.

67. Kornilov, I. I. et al

Interaction of titanium carbide with a six-component nickel solid solution. RUSSIAN JOURNAL OF INORGANIC CHEMISTRY. v.3. no. 3, p. 226-238. March 1958.

Difficulties in establishing diagrams of many-component systems can be avoided in certain cases by creating conditions when, as a result of the tendency of the components to form solid solutions or compounds, a "quasi-ternary" or "quasi-binary" system is produced. As an example for this method the author presents the study of the system Ni-Cr-W-Mo-Nb-Ti-Al-C in which the following three-phase equilibrium can be obtained: 8-component liquid ⇄ 8-component solid solution + compound TiC. For alloys rich in nickel this permits the establishment of the phase diagram of a quasi-binary system 8-component nickel solid solution - TiC. The diagram is of the eutectic type, analogous to that of the system Ni-TiC.

68. Kosolapova, T. Ya., and Samsonov, G. V.

Preparation of chromium carbide Cr_7C_3.

JOURNAL OF APPLIED CHEMISTRY OF THE USSR.

v. 32, no. 7, p. 1539-1542. July 1959.

Pure Cr_7C_3 was prepared by heating a pressed Cr-C mixture (containing 22.8% C and a small amount of dextrin as binder) in an H_2 atmosphere according to the following schedule: raising the temperature from 800° to 1300° in 20 min, maintaining at 1300° for 1.5 hr, crushing, and heating again for 15 to 20 min in an H_2 atmosphere at 1300°. The use of a lower than stoichiometric amount of C is necessary to prevent the formation of higher carbides.

69. Kotel'nikov, R. B.

Contribution to the question of the formation of continuous series of solid solutions in the systems formed by carbides, nitrides, borides and silicides of metals of the transition groups.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY

v. 3, no. 4, p. 1-8, April 1958.

Difficulties encountered in experimental studies of systems with exceptionally hard, brittle and heat-resisting components motivated this discussion of the existing literature, with a view to predicting the properties of such systems. The various conditions of crystallographic or chemical similarity between components, favoring the formation of continuous solid solutions, are reviewed, special attention being given to carbides, nitrides, borides and silicides of transition metals, including titanium, zirconium, hafnium, molybdenum and vanadium. Among other results it is predicted that the system TiB_2-CrB_2 should furnish a continuous series of solid solutions, while ZrB_2-CrB_2 could present only a limited mutual solubility of the metals themselves). The author confirmed his prediction experimentally.

70. Kotlyar, E.E. and Nazarchuk, T. N.

Determination of titanium in alloys of titanium carbide with niobium. JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR. v. 16 no. 5, p. 622-624. September-October 1961.

The authors observed that the reduction of pentavalent niobium by aluminum can be inhibited by NH_4F and citric acid. Accordingly, when Nb(V) and Ti(V) are treated simultaneously with aluminum under the above conditions, titanium alone will be reduced (to Ti(III)). This fact is utilized in determinations of titanium in TiC-Nb alloys. The sample is dissolved in HF + HNO_3 and, after evaporation, H_2SO_4, NH_4F, citric acid and aluminum are added. After dissolution of the latter, titanium is titrated with amonium-iron alum in the presence of KSCN.

71. Kotlyar, E.E. and Nazarchuk, T.N.

Determination of titanium in titanium carbide-vanadium alloys. ZHURNAL ANALITICHESKOI KHIMII. v. 16, no. 6, p. 688-691. November-December 1961. (In Russian)

The separation of titanium and vanadium, required in the analysis of TiC-V alloys, can be achieved by precipitation of vanadium with sodium diethyl-dithiocarbamate in the presence of masking agents like tartaric, citric, or oxalic acids or ammonium fluoride. For this operation, the alloy sample is dissolved in a mixture of sulfuric and nitric acids.

72. Koval'chenko, M.S., Samsonov, G.V. and Yasinskaya, G.A.

Alloys of borides of transition metals with other metals. RUSSIAN METALLURGY AND FUELS No. 2, p. 76-81. March-April 1960.

Refractory boride cermets are discussed in general. The systems ZrB_2-Mo, TiB_2-Mo, CrB_2-Mo, TiB_2-Cr and ZrB_2-Cr were studied, using visual polythermal methods, x-ray diffraction, incipient melting and hardness measurements. Shrinking curves are plotted, and hypothetcial phase diagrams are constructed. Melting does not begin until high temperatures are reached. All systems have at least two eutectics and some intermediate phase maxima.

73. Koval'chenko, M. S. and Samsonov, G. V.

Relaxation phenomena during the hot compacting of molybdenum carbide. PHYSICS OF METALS AND METALLOGRAPHY v. 12, no. 1, p. 126-128. July 1961.

In manufacturing compact masses of heat resistant compounds (carbides, borides, nitrides, etc.) by powder sintering under pressure, a certain role is played by the final removal of the pressure, since it produces the relaxation phenomenon of increased volume and therefore, decreased compactness (density relaxation). Experimenting on pressure sintering of Mo_2C at 2000° -2300°C and 115 kg/cm^2, the authors observed that, with increasing temperature, the duration and the effect of the relaxation decreased. Higher temperature increases the plasticity, and, thereby, reduces the period during which the activation energy (75,200 cal/mol) could be supplied for the transition from a disordered state to an ordered one.

74. Kramer, B. E., Levinstein, M. A. and Grenier, J. W.

THE EFFECT OF ARC PLASMA DEPOSITION ON THE STABILITY OF NON-METALLIC MATERIALS. General Electric Co., Cincinnati, Ohio. Final report April 1960 - May 1961. May 1961. 57p. (Contract NOa(s) 60-6076-c) ASTIA AD-264 602.

The oxides of Al, Cr, Zr Ce, Hf and mixtures of Zr and Nb; the carbides of Hf, Ta and Zr; the nitrides of Ti and Ta; and the boride of Zr can be sprayed on a graphic substrate without chemical or microstructure alteration; the operating conditions for the deposition of these materials were determined. Properties useful in design data: the coefficient of thermal expansion, density, compressive strengths, electrical resistance and hardness were obtained.

75. Kreimer, G. S., Vakhorskaya, M. R. and Baranov, A. I.

The strength, toughness and hardness of two-phase powder-metallurgical hard alloys: titanium carbide-tungsten carbide-cobalt. PHYSICS OF METALS AND METALLOGRAPHY v. 10. no. 5, p. 61-71. November 1960.

The strength and impact resistance of TiC-WC-Co alloys are not dependent on the cobalt content (up to 15% Co) or on the temperature within the 20°-500°C range. However, both are found to decrease with increase in the average grain size of the TiC-WC solid solution. The hardness decreases with increased temperature and cobalt content and with decrease in grain size, as a result of the increased plasticity. Data are presented in graphs and tables.

76. Krikorian, N.H., Farr, J.D., and Whiteman, W.G.

METHOD OF JOINING CARBIDES TO BASE METAL.

U.S. Patent no. 3, 020,632. 13 February 1962.

ZrC powder masses may be joined to a niobium or tantalum surface by carburizing the surface and sintering the powder mass to the base at 1700°-2200°C in a non-oxidizing atmosphere while they are held in contact.

77. Krikorian, N.H., Witteman, W.G. and Bowman, M.G.

Mutual solid solubility of hafnium carbide and

uranium monocarbide. ELECTROCHEMICAL SOCIETY.

JOURNAL v. 109, no. 3, p. 78C. March 1962.

HfC-UC shows complete solid solubility at 2000°C, in contrast to the miscibility gap reported by other workers. X-ray and other data are presented. This paper was presented at the Spring meeting of the Electrochemical Society in Los Angeles, 6-10 May 1962.

78. Krupka, M.C.

HIGH TEMPERATURE VAPORIZATION BEHAVIOR AND

THERMODYNAMIC PROPERTIES OF HAFNIUM DIBORIDE.

Los Alamos Scientific Laboratory, New Mexico.

Report LA-2611. 16 April 1962. 137p.

HfB_2 vaporization was studied with a tungsten effusion cell up to 2500°K, above which it could not be used because of the occurrence of a eutectic. The reaction between HfB_2 and Tungsten does not significantly effect the results. $HfB_{1.955}$ is the composition of congruent vaporization up to 2730°K. Analytical treatment of results is discussed, and numerous graphs, tables and photographs are included.

79. Kugai, L.N. and Nazarchuk, T.N.

Analysis of the borides of the transitional and rare earth elements. JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR. v. 16, no. 2, p. 213-216. March-April 1961.

A method for determining free boron in ZrB_2 is based on the difference in oxidation of free and bound boron with a mixture of perhydrol and HNO_3. Free boron in borides of titanium, zirconium and the lanthanons cannot be determined through the use of acid solutions of cerium sulfate and potassium iodate, since the borides themselves are soluble in those solutions. Hexaborides of rare earths can be determined by dissolving in HNO_3 and titrating with complexone III, using arsenazo as the indicator.

80. Kumazawa, M.

On the reducing process of free carbon included in titanium carbide. TOHOKU DAIGAKU KENKYUSHO v. 13, no. 4, p. 232-237. August 1961. (In English)

The quality of TiC is affected by the amount of the free carbon content. The content may be reduced by use of an apparatus in which a sulfur-argon gas mixture generated at 150°C is reacted with TiC in the 600° -1200°C range. 75% of the free carbon is removed after 50 hours at 1200°C. A sulfur vapor generated at 100°C is less effective. X-ray and chemical analysis show that TiC-TiS solid solutions form and that TiC decarburizes. Graphs are shown.

81. LaPlaca, S. and Post, B.

BINARY DODECABORIDES. Polytechnic Institute of Brooklyn, New York. ONR TR-2. (1961?) 8p. (Contract Nonr 839(12)

Cubic dodecarborides of Dy, Ho, Er, Tm, Lu, and Y, isomorphous with UB_{12} and ZrB_{12}, have been prepared by the reaction of metal sesquioxides with excess amorphous boron at 1400° - 1500°C in a protective helium atmosphere. The boron atoms are linked in a rigid three-dimensional network with metal atoms in large cubo-octahedral holes. The stability of the structure appears to be a sensitive function of the effective size of the metal atom; it could not be prepared when metal atoms larger than Dy or smaller than Zr were used. Coefficients of thermal expansion of HoB_{12} and ErB_{12} have been measured by x-ray diffraction methods.

82. LaPlaca, S., and Post, B.
THE CRYSTAL STRUCTURE OF RHENIUM DIBORIDE. Polytechnic Institute of Brooklyn, New York. ONR Tr-3. (1961?) 6p. (Contract NOnr 839(12).

The crystal structure of ReB_2 has been determined from powder data. The unit cell is hexagonal; a = 2.900 and c = 7.478 A; there are two ReB_2 units per unit cell. The structure may be described in terms of alternating layers of rhenium and boron atoms; the former are planar, the latter are puckered.

83. Lassner, E. and Scharf, R.
Determination of titanium, niobium and tantalum in cemented carbides. CHEMIST-ANALYST v. 50 no. 3, p. 69-71. September 1961.

Determination of titanium for production of cemented carbides may be accomplished without separating binder metals by dissolving the sample in HF-HNO_3, fuming with H_2SO_4, and double precipitation with cupferron. After gravimetric assay of total metal, titanium may be determined by chelometric titration with diaminocyclohexanetetraacetate. Other methods are discussed. Data are tabulated.

84. Latva, I. D.
Ceramics and intermetallics. In Aeronautical Systems Division. Wright-Patterson Air Force Base, Ohio. MATERIALS SYMPOSIUM, SEPT 13-15, 1961, HOTEL WESTWARD HO, PHOENIX, ARIZONA, p. 679-709. July 1961. (ASD-TR-61-322)

A survey is made of developments, applications, and future requirements of refractory ceramics and intermetallic compounds of interest in aerospace structural and non-structural components. The materials discussed include borides, carbides, beryllides, nitrides, silicides, and oxides. Brittle behavior and effects of microstructure of the materials are discussed.

85. Leitnaker, J. M., Bowman, M. G. and Gilles, P. W.
High-temperature evaporation and thermodynamic properties of zirconium diboride. JOURNAL OF CHEMICAL PHYSICS v. 36, no. 2, p. 350-358. 15 January 1962.

Vapor pressures of zirconium over zirconium diboride have been measured by the Knudsen technique over the temperature range 2150° to 2475°K. A new type of apparatus was constructed and used successfully in the study. Zirconium diboride was determined to evaporate congruently at a composition of $ZrB_{1.906(+0.025 \text{ or } 0.010)}$ by heating solid pressed plugs of both zirconium-rich and boron-rich material to constant composition at 2400°C to 2500°C. The overall reaction is

$$ZrB_{1.906(S)} = Zr(g) + 1.906\ B(g)$$

Three series of measurements were made using tungsten crucibles and different orifice sizes. Second-law and third-law treatments of the data did not agree. Thermodynamic calculations were made which indicated that water vapor at low background pressures would produce volatile oxides of both zirconium and boron. This reaction was investigated by adding water vapor to the system and the increased transport of zirconium was clearly demonstrated. Accordingly, each pressure measurement was corrected by a factor β, constant for each series, related to the background pressure. From the corrected pressures, values of $\Delta H_O°$ for the reaction were computed by the third-law treatment. From the three series a vaporization coefficient of 0.025 ± 0.010 was computed, leading to an equilibrium $\Delta H_O°$ of 458.3 ± 6.5 kcal/mole for reaction or a partial pressure of Zr over $ZrB_{1.906}$ of 2.38×10^{-10} atm±20% at 2000°K. The variance between this and an expected value of 477.4 kcal/mole is presumed to be related, at least in part, to discrepancies in the heat of vaporization of zirconium. The results verify the prediction that the Zr-Br system exhibits a congruently evaporing composition in many high-temperature systems will occur at nonstoichiometric compositions.

86. Leitnaker, J. M.
THERMODYNAMIC PROPERTIES OF REFRACTORY BORIDES I. EVAPORATION BEHAVIOR AND VAPOR PRESSURE OF ZIRCONIUM DIBORIDE; II. PHASE STUDIES IN THE TANTALUM-BORON SYSTEM BETWEEN Ta and TaB. Ph. D. Dissertation.
Kansas. University. 1960. 269p.

Vapor pressures of zirconium over ZrB_2 were measured in the 2150° -2475°K range by the Knudsen method. Discrepancies between observed and calculated Third Law enthalpy values are explained on the basis of inconsistencies in the heat of vaporization of zirconium.

87. Leitnaker, J. M., Krikorian, N. H. and Krupka, M. C.

Unusual ternary behavior of transition metal borides.

ELECTROCHEMICAL SOCIETY. JOURNAL v. 109,

no. 1, p. 66. 1962.

All Group IVb diborides react with molybdenum and the products show nearly identical x-ray diffraction patterns of an orthorhombic phase. Lattice parameters of the TiB_2-Mo phase, which forms as low as 1600°C, are $a = 3.185$ A, $b = 8.475$ A, $c = 3.075$ A. When heated with tungsten powder, TiB_2 forms a similar ternary phase, but ZrB_2 forms no intermediate phases, while HfB_2 appears to form a ternary phase although equilibrium is not attained. A solid solution between Group IVb monoborides and molybdenum or tungsten monoborides is suggested.

88. Lersmacher, B, and Scholz, S.

Pressure sintering of hafnium, zirconium and

tantalum carbides without a binding phase.

ARCHIV FUER DAS EISENHUETTENWESEN v. 32,

no. 6, p. 421-429. June 1961. (In German)

In pressure sintering of zirconium and hafnium carbides, the maximum intensity obtained by relatively protracted compression (e.g. 1 hr) does not increase monotonically with the temperature, but decreases after a certain temperature has been reached. This phenomenon is due to the fact that the diffusion of the pores is hindered by the growing grains. The rate of the density increase is furthered considerably by addition of up to 1% nickel, cobalt, manganese or FeMn. In the case of cobalt and nickel, this relationship is explained by the formation of a liquid phase.

89. Lewis, D. R.

METALLOGRAPHY OF THE BORIDES. General Electric

Co., Vallecitos Atomic Laboratory, Pleasanton, Calif.

Report GEAP-3626. 11 January 1961. 21p. (Contract

AT(04-3)-189)

Metallographic procedures were studies for TiB_2, ZrB_2, SmB_6, YB_4, HfB_2, EuB_6, and DyB_6 bodies. It is recommended that high density boride bodies used in AEC control rod program be processed as follows: sectioning with a smooth, diamond metal bonded saw of 120 grit when necessary; use of Precisionite or type 15-95-E Formvar for mounting; grinding first on a 180 grit and then a 400 grit diamond wheel (final grinding with a 600 grit wheel is optional); diamond polishing on a vibratory polisher; etching with aqueous $Hf-HNO_3$; using short etching intervals; and, except of anisotropic borides, metallographic examination underbright field illumination at magnifications of 250X or over. Grinding on SiC paper is a simple test of whether bonding has occurred. Electrolytic etching appears useful but no procedures were established. Micrographs are presented.

90. Litz, L. M.

Graphite, carbide, nitride and sulfide refractories.

In INTERNATIONAL SYMPOSIUM ON HIGH

TEMPERATURE TECHNOLOGY, ASILOMAR, CALIF.

1959. PROCEEDINGS p. 90-112. N.Y., McGraw-

Hill, 1960.

A section discusses properties and preparation of transition metal carbides and nitrides, and lanthanon sulfides, TiS, VS, HfS and Zr_4S_3. Physical properties are tabulated. TiC-base cermets are also covered. Standard free energy curves are plotted for several materials, and show substantial thermal stability for the sulfides. The compounds have been studied as crucible materials.

91. Liu, T. S. and Stowell, E. Z.

PARAMETRIC STUDIES OF METAL FIBER

REINFORCED CERAMIC COMPOSITE MATERIALS.

Final Report, January 1960 – January 1961. Southwest

Research Institute, San Antonio, Texas. 26 January 1961.

73p. (Contract NOaa 60-6077-c)

The purpose of this program was to conduct a theoretical study of the various parameters which effect the mechanical characteristics of metal fiber reinforced ceramic composite materials. In addition, a survey of properties of potential fiber and matrix materials was made so that promising combinations needing intensive investigation can be defined in specific terms. Certain room temperature mechanical behavior of metal fiber reinforced ceramics (MFRC) were predicted using an inclusion concept and from geometric, elastic, statistical distribution and plastic strength considerations. Certain elevated temperature mechanical behaviors of MFRC were predicted using a universal visco-elastic concept. A survey of pertinent physical, chemical and mechanical properties was made on refractory metals, metal oxides, carbides, borides, nitrides, silicides, sulfides and single crystal whiskers. Areas of research for the development of fiber reinforced materials in general and of MFRC in particular were recommended.

92. Love, R. W. and Alliegro, R. A.

Important properties of zirconium and titanium boride as electrode materials. ELECTROCHEMICAL SOCIETY. JOURNAL v. 108, no. 3, p. 68C. March 1961.

Chemical and physical characteristics of TiB_2 and ZrB_2 are discussed. Manufacturing process as a variable affecting characteristics is considered. The possible impact of diborides as electrode materials on aluminum manufacturing is noted and results obtained from operating a laboratory aluminum cell are reported. Other areas of application are reviewed. This paper was presented before the 119th meeting of the Electrochemical Society, in Indianapolis, 30 April - 3 May 1961.

93. Lowrie, R.

RESEARCH ON PHYSICAL AND CHEMICAL PRINCIPLES AFFECTING HIGH TEMPERATURE MATERIALS FOR ROCKET NOZZLES. Union Carbide Research Institute, Tarrytown, New York. Semi-annual progress report, 1 July - 31 December 1961. 31 December 1961. 64p. (Contract DA 30-069-ORD-2787) ASTIA AD-270304.

Studies of the influence upon rocket-nozzle erosion of chemical reaction between the nozzle and the exhaust were made. Refractory carbides and borides, several grades of graphite, and W were exposed to CO, CO_2, H_2, H_2O, HCl, and BF_3. The CO reacted only slightly with any of the materials, H_2 reacted appreciably only with graphite, and CO_2 and H_2O oxidized all the refractory solids (W had the best resistance). Quantitative measurements were made of the reactions of H with graphite and of H with TiC. The vaporization of ZrB_2 was studied with the mass spectrometer. A report was written on the spectra of B O and B O molecules trapped in Ar and Xe matrices. Experiments were made with C vapor trapped in Ne and Xe matrices for comparison. The dynamic elastic constants of mon-crystalline W were determined at room temperature. Similar determinations on single crystals of ZrC and TiC are reported.

94. Lowrie, R.

RESEARCH ON PHYSICAL AND CHEMICAL PRINCIPLES AFFECTING HIGH TEMPERATURE MATERIALS FOR ROCKET NOZZLES. Union Carbide Research Institute, Tarrytown, New York. Quarterly progress report 1 January - 31 March 1962. 31 March 1962. 50p. (Contract DA 30-069-ORD-2787) ASTIA AD-274 186.

Reactions of several new materials (HfB_2, HfC and solid solutions of TiC/ZrC and ZrC/Nb with possible rocket exhaust components) were studied. Only HfC in oxidizing atmospheres appeared to have attractive qualities. Preliminary kinetic studies were conducted with TiC and ZTA graphite in mixtures of CO_2-CO-Ar. Corrosion of both materials depend linearly upon the CO_2 partial pressure; the graphite corroded nearly linearly with time. New phases were observed in corroded carbide and boride samples. Vaporization studies were made to calculate the heat of formation of ZrB_2; results thus far indicate a value near -45 kcal/mole. Thermal expansion data on ZrC, TiC and W are in good agreement with literature sources. Studies of the compatibility of TiB_2 with W, Ta and Mo showed that Ta and W did not react significantly with TiB_2 up to 2100 C but Mo did.

95. L'vov, S. M., Nemchenko, V. P. and Samsonov, G. V.

Electrical properties of titanium carbide-titanium nitride alloys. UKRAINS'KII FIZICHNII ZHURNAL v. 7, no. 3, p. 331-335. March 1962. (In Ukrainian)

Since carbon and nitrogen atoms differ considerably in their ionization potentials, the relative concentration of these atoms in mixed crystals of TiC-TiN alloys should be reflected in the conductivity and other electrical properties. It is found from measurements of the conductivity and its temperature dependence, of the Hall coefficient and of the thermo emf, that the conductivity of TiC-TiN alloys, including the boundary phases, is due mainly to electrons arising from the 4s shell of titanium. However, a certain role is also played by vacancies in the 3d shell, this role increasing with the concentration of TiN in the alloy.

96. L'vov, S. N., Nemchenko, V. F. and Samsonov, G. V.
Some regularities in the electrical properties of borides, carbides and nitrides of transition metals of Groups IV-VI of the periodic system. SOVIET PHYSICS - DOKLADY v. 135, no. 3, p. 577-580.
21 November 1960.

A study was made of the Hall effect, electrical resistivity and thermoelectromotive force of transition metal carbides, nitrides and borides. Results show that the Hall coefficient of these compounds is generally negative, decreasing in absolute value from the Group IV to Group VI metals and in some instances becoming positive. In most of the compounds studied, the sign of the thermoelectromotive force agrees with that of the Hall constant. Tests substantiated earlier finding that the majority of the transition metal diborides have a smaller electrical resistivity than the carbides. Data are tabulated.

97. Lynch, C. T., et al
INVESTIGATION OF SINGLE-CRYSTAL AND POLYCRYSTALLINE TITANIUM DIBORIDE: METALLOGRAPHIC PROCEDURES AND FINDINGS. U. S. Air Force. Materials Central, Wright-Patterson Air Force Base, Ohio. TR 61-350. November 1961. 41p.

Single-crystal and polycrystalline TiB_2 was examined to develop applicable metallographic techniques for sectioning, mounting, grinding, polishing, and etching of TiB_2 specimens. This work demonstrates the usability and practicability of using various SiC papers together with different grades of diamond paste on polishing wheels in preference to using cloths. It has been found that H_2SO_4, as a constituent of etchants. produces more reliable and more consistent results than HF. The same is true of H_2SO_4 when used as a constituent of electrolytes. Single-crystal TiB_2 was found to have a Widmanstatten structure while polycrystalline TiB_2 had a "needle-like" pattern.

98. McMullen, J.C. and McKee, W.D.

Zirconium diboride prepared directly from zircon.

AMERICAN CERAMIC SOCIETY. BULLETIN v. 41,

no. 4, p. 255. April 1962.

Zircon was reacted with carbon and B_2O_3 in a submerged electrode arc furnace to give reasonably pure ZrB_2. The reaction depends on the volatility of SiO. This paper was presented at the 63rd annual meeting of the American Ceramic Society of New York, 29 April - 3 May 1962.

99. Maduk, E.A. and Ricker, R.W.

REFRACTORY AND METHOD OF MAKING THE SAME.

U.S. Patent No. 3, 011, 982. 5 December 1961.

A refractory composition based on aluminum nitride contains 35-50 wt-% titanium cyanonitride. It has low electrical resistivity and chemical resistance to molten cryolite and molten aluminum.

100. Mah, A.D., et al

THERMODYNAMIC PROPERTIES OF ALUMINUM

NITRIDE. U. S. Bureau of Mines Report No. RI 5716.

1961. 8p.

Relatively pure aluminum nitride (AlN) recently has been prepared in sufficiently large amounts to permit a variety of experimental studies. Several mechanical and chemical properties have been investigated, which show that this substance has good potentialities as a container for liquid aluminum, gallium, and boric oxide. The present work by the Bureau of Mines was undertaken to obtain thermodynamic date pertinent to the calculations regarding thermal stability and reactivity of aluminum nitride. The thermodynamic values show aluminum nitride to be quite stable regarding decomposition.

101. Mandorf, V., Hartwig, J. and Seldin, E. J.

High temperature properties of titanium diboride.

JOURNAL OF METALS v. 13, no. 3, p. 233. March 1961.

No abstract given.

102. Mandorf, V., Jr.

TITANIUM DIBORIDE ARTICLE. U.S. Patent No. 3, 003,885. 1 February 1960.

TiB_2 of about 7μ size is mixed with 3-10% transition metal or boron nitrides and a fugitive binder, cold pressed to shape under 10-20 tsi, and hot pressed at 2000°-2300°C under 1 tsi.

103. Markovskii, L. Ya. and Kaputovskaya, G.V.

Chemical resistance and hydrolytic decomposition of some transition metal diborides on reaction with acids. JOURNAL OF APPLIED CHEMISTRY OF THE USSR. v. 33, no. 3, p. 574-581. March 1960.

The thermal and electrical properties of TiB_2 and ZrB_2 and their high slag resistance has prompted studies of their chemical properties. Chemistry of solution processes of the borides in acids was studied for the powdered and sintered forms in HCl, H_2SO_4, HF and HNO_3. Electrolytically prepared borides dissolve, but to a lesser degree than those prepared by boron carbide or carbothermal methods. Hot or cold HCl solution produced boron hydride intermediates and $TiCl_3$ or $ZrOCl_2$, TiB_2 dissolving more slowly. Slight heating makes ZrB_2 react vigorously. ZrB_2 does not react with cold H2SO4 or HNO_3. TiB_2 was hardly attacked by cold, concentrated H_2SO_4, but HNO_3 dissolved it under all conditions. 15-17% was dissolved by HF. Data are tabulated.

104. Matkovich, V.I. and Rogers, H.H.

The formation of chromium or molybdenum stabilized tungsten silicon carbide. ELECTROCHEMICAL SOCIETY. JOURNAL v. 108. no. 3, p. 261-262. March 1961.

An attempt to form W_4Si_3C isostructural with Mo_4Si_3C is described. The pure compound could not be formed, but it may be prepared in the presence of 11.5 at-% Mo to 4.6 at -% Cr. It is assumed that W_4Si_3C is stabilized by solid solution with other Group VIa silico-carbides. Data on unit cell sizes are tabulated.

105. May, C. E. and Hoekstra, P. D.

STABILITY OF REFRACTORY COMPOUNDS IN HYDROGEN BETWEEN 4500° and 5000° F, AND THEIR COMPATIBILITY WITH TUNGSTEN. U.S. National Aeronautics and Space Administration, Washington, D. C. Report no. TN-D-844. May 1961. 12p. ASTIA AD-257 063.

The present work is a continuation of work described in NASA Memorandum 3-5-59E (ASTIA AD-213048). Each refractory compound was placed in a W cup which was inductively heated in a H atmosphere to temperatures between 4500° and 5000° F. Changes in pressure, weight, and crystal structure were taken as indications of reaction. HfC, TaC, TiC, ZrC, HfN, ZrN, and ZrO_2 showed weight loss due to volatilization, decomposition, or reaction with H; reaction to TaN was indicated from diffraction data. Any reaction occurring for TaB2, WB, and NbC was less than the minimum detactable amount. Most of the compounds (except the nitrides)were found to be incompatible with the W container. This prevented the determination of the degree of stability of some of the materials in H. These results are compared with the earlier work at Lewis Research Center on the stability of these materials in H between 4000° and 4500° F.

106. May, F.H.

PURIFICATION OF TITANIUM BORIDE. U.S. Patent no. 3, 013,862. 21 July 1960.

Crude TiB_2 contaminated with oxygen or free or combined carbon may be purified by mixing with sufficient B_2O_3, titanium and carbon to react with the contaminants, heating at 1600 -1750°C in inert atmosphere, and recovering TiB_2.

107. Meerson, G.A. and Krein, O.E.

Conditions under which vanadium carbide is produced in a vacuum. RUSSIAN JOURNAL OF INORGANIC CHEMISTRY v. 5, no. 9, p. 938-941. September 1960.

Study of the formation of VC from V_2O_3 and carbon (lamp black) in vacuum showed that at 1500°-1800°C and 0.1-1.10 mm Hg the carbide formed contained no oxygen. However, the content of chemically bound carbon in the product was 15.5-17.8% instead of the theoretical 19.05%, a fact pointing to the formation of a VC-V solid solution. The above content in bound carbon is thus a maximum independent of the amount of free carbon present, under the conditions indicated.

108. Meerson, G. A., Kiparisov, S.S. and Chen, S. L.

Influence of cyclic temperature changes on the sintering of titanium carbide. AKADEMIIA NAUK USSR. IZVESTIIA. OTDELENIE TEKHNICHESKIKH NAUK. METALLURGIIA I TOPLIVO No. 6, p. 52-55. November-December 1961. (In Russian)

Cyclic temperature changes during sintering of powdered titanium carbide (the cycle consisting, e.g., of heating at 2800°C for 3 minutes, followed by cooling to 400°C) accelerates considerably the process of densification, as compared with the usual isothermal hot compression. Another possibility of intensifying the densification is to activate the surface of the powder particles by pickling with a mixture of HF and HNO_3 prior to isothermal heating (e.g. at 2900° C).

109. Meerson, G. A. and Krein, O. E.

The preparation of hafnium carbide. RUSSIAN JOURNAL OF INORGANIC CHEMISTRY, v. 5, no. 5, p. 559-561. May 1960.

Because of the high affinity of hafnium for oxygen, complete removal of the latter in the reduction of hafnium dioxide by carbon required temperatures of approximately 2000°, even in vacuum. When the total quantity of carbon in the charge (HfO_2 + C) is sufficiently high, a product of the approximate composition HfC can be obtained at 2200° in vacuum. With insufficient carbon in the charge, the combined carbon in the carbide is less than the theoretical, but the sum of Hf + C is 100%, and the specimens retain the HfC structure, with smaller parameters. This indicates the existence of a region of homogeneity close to HfC, with a lower carbon content, a defect lattice with vacant carbon sites. The saturation of hafnium carbide with combined carbon is favored by a residual CO pressure of several mm Hg. Very low pressures lead to the formation of carbide which is not saturated with carbon, as is found in the preparation of titanium carbide. Under the above conditions, hafnium carbide of composition close to HfC is made quickly in approximately 1 hours.

110. Meerson, G. A. et al

Some properties of alloys of the borides of the refractory metals of the transition groups.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY.

v. 3, no. 4, p. 92-101. April 1958.

The following properties of TiB_2, ZrB_2, CrB_2 and W_2B_5, as well as of alloys TiB_2-CrB_2, TiB_2-W_2B_5 and ZrB_2-CrB_2 (as a function of their composition), were measured: crystal structure parameters, mean grain size, microhardness, specific electrical conductivity, coefficient of linear thermal expansion, compression strength limit, and bending strength limit.

111. Meerson, G. A. et al

Study of conditions of chlorination of titanium-niobium carbide. IZVESTIIA VYSSHIKH UCHEBNYKH ZAVEDENII. TSVETNAYA METALLURGIIA v. 3 no. 5, p. 108-115. 1960. (In Russian)

Carbides of titanium and niobium, prepared directly from ore concentrates, can be used for the production of chlorides of those metals. In the present work the authors studied the chlorination of a combined carbide TiC-NbC obtained from a corresponding concentrate and containing silicon, nitrogen and oxygen. The process involves the formation of an outer layer of graphite which, up to 400°C, does not affect the reaction velocity, while at 600°-800°C, the reaction becomes somewhat inhibited by the presence of the intermediate layer. Experiments with a furnace of semi-industrial type demonstrated the possibility of conducting the chlorination in a "boiling layer" process and, since the reactions are strongly exothermic, no external sources of heat are required.

112. Metallic Surfaces Research Laboratories, Ltd.

(Gt. Brit.) BORIDE COATINGS ON METAL SURFACES. British Patent No. 861 644.

22 February 1961.

Transition metals or copper may have conferred on them a hard, refractory and wear and corrosion-resistant boride coat by first diffusion with the metal a Group IVb, Vb or VIb metal, silicon or aluminum and then subjecting to boron diffusion.

113. Meyerson, G. A. et al

Certain properties of boride alloys of refractory transition metals. In KONFERENTSIYA PO KHIMII BORI I YEGO SOYEDINENII, p. 58-73. 1955. (In Russian) (English trans. by Aerospace Technical Intelligence Center, Wright-Patterson Air Force Base, Ohio. Trans no. MCL-476, 1 November 1960. 26p.)

ASTIA AD-257 671.

TiB_2 - CrB_2, TiB_2 - W_2B_5, and ZrB_2 - C_6B_2 systems were studied. After taking into account the properties of the initial borides and the possible technical use of their alloys, the research was conducted along the following basic lines: (1) the study of the phase composition and structures of the products of the diffusion reaction of the initial borides; (2) the study of the microhardness of the phases; and (3) the study of the corrosion resistance and the structure of scales of various compositions.

114. Minkevich, A. N.

Surface layers of diffusion borides on various metals. METALLOVEDENIE I TERMICHESKAYA OBRABOTKA METALLOV no. 8, p. 9-15. August 1961. (In Russian)

Experimenting with various metals showed that, under equal conditions of boridizing, the depth of the boride layer is greatest in the case of molybdenum, least in the case of zirconium. According to x-ray analysis, the phase compositions of the layer on molybdenum was Mo_2B (weak lines) and Mo_2B_5. On zirconium it was Zr_2B (weak lines) and ZrB_2. Also studied were changes in the microhardness in the layer with the distance from the surface, effect of the temperature and the duration of the process on the depth and the surface microhardness of the layer, and decreases in the hardness of the boride layers, produced by vacuum heating at various temperatures (up to 800°C).

115. Modylevskaya, K. D., Lyutaya, M. D. and Nazarchuk, T. N.

The sintering method in the analysis of boron carbide, boron nitride, and borides of metals. INDUSTRIAL LABORATORY v. 27, no. 11, p. 1350-1351. November 1961.

A method is proposed for decomposing boron carbide, boron nitride and borides of metals by sintering with CaO MgO and $BaCO_3$. The optimum conditions for sintering are 900 -1000°, 1-2 hr and for chromium boride 3 hr. The method does not require the use of platinum crucibles.

116. Montgomery, W. E.

Titanium carbide cermets - what about 'em? CUTTING TOOL ENGINEER v. 13. no. 12, p. 10-13. December 1961.

TiC, previously used as an addition to tungsten-base carbide cutting material, is now used as a base for ceramic cutting tools. Among the properties TiC possesses which make it valuable as a cutting tool material are wear resistance, retention of hardness and transverse rupture strength at high temperatures, thermal shock resistance, oxidation resistance, and high modulus of elasticity. The necessity of brazing and consequent loss of strength is obviated by the concept of indexable, disposable inserts. TiC-base cermet tools are most suited to high-speed finishing operations but perform well in a variety of cutting operations, e.g. instances in which fine finishes or interrupted cuts are required. Illustrations are shown.

117. Mordike, B. L.

The frictional properties of carbides and borides at high temperatures. WEAR v. 3, no. 5, p. 374-387. September-October 1960.

TiC and VC specimens were studied for frictional properties vs. temperature by sliding on the same and other carbides and on graphite. ZrB_2 and TiB_2 were similarly studied. The coefficient of friction first decreases, then, at a critical temperature in the 800° -1400°C range, increases rapidly, due to sintering, except where graphite is concerned. Results are explained in terms of the adhesion theory of friction.

118. Moskowitz, D. and Humenik, M., Jr.

A note on vacuum sintered fine-particle titanium carbide. PLANSEEBERICHTE FUER PULVER-METALLURGIE v. 9, nos. 1/2, p. 60-64. April 1961.

TiC powder specimens leached from micron-sized powders show a high degree of densification at temperatures as low as the 1250° -1500° C range. Electrical resistivity, when corrected to full density, is lower than has been previously reported. Repeated leaching removes surface oxygen, thereby increasing the combined carbon content. Graphs and a micrograph are shown.

119. Moskowitz, L.

REACTION RATE OF BORON CARBIDE AND ZIRCALOY-2

Knolls Atomic Power Laboratory, Schenectedy, N. Y.

Report KAPL M-LM-1. 15 May 1959. 27p. (Contract W-31-109-ENG-52) (Decl. 1 Sep 1960).

Zircaloy-B_4C reaction rates were studied at 1200° F and in the 1350° -1750° F range at 100° F increments, using hot-extruded powder specimens. After an initial period, a diffusion controlled reaction occurs with an activation energy of 33.3 kcal/g. atom up to 1550° F. Above 1650° F a less temperature-dependent reaction predominates and has a nearly constant rate. Particle size and moisture absorption are unimportant. Data are tabulated.

120. Mukaseev, A. A. et al

Machinability of carbides of ultrasonic vibrations.

RUSSIAN ENGINEERING JOURNAL v. 41, no. 3, p. 53-55. March 1961.

An investigation was made of ultrasonic machining of the carbides, nitrides, borides and silicides of the transition metals. Specimens with a porosity ranging from 0-25% were prepared from refractory powder to determine the effect of porosity on the applicability of ultrasonic machining. An unsuccessful attempt was made to correlate the K factor (the ration of material wear to cutting tool wear) with hardness and other properties. However, the dependence of K on the density was clearly demonstrated on samples of W_2B, $MoSi_2$ and ZrC. Ultrasonic machinability increases markedly with porosity. It was also found that, during ultrasonic cutting, destruction occurs chiefly along grain boundaries. Data are tabulated.

121. Mukherjee, A.K. and Martin, J.W.

Hardening of a molybdenum-zirconium alloy by nitride dispersions. JOURNAL OF THE LESS-COMMON METALS v.3, no. 3, p. 216-220. June 1961.

Nitriding Mo-1Zr in the 1100° -1500° C range produces a stable ZrN dispersion and confers a high microhardness. Nitriding with ammonia gives a higher microhardness than with nitrogen because the diffusion front moves faster and leaves less time for particle growth. The diffusion rate obeys a parabolic law, and the structure coarsens with a depth of penetration because the diffusion front slows. Nitriding at 1500°C produces a dark-etching layer, as it does in Mo-Ti alloys, but the dispersed phase precipitates as rectangular plates on three mutually perpendicular crystallographic planes. Graphs and micrographs are shown.

122. Nalon, G. C. and Brierley, R. G.

How to choose the right carbide. METALWORKING PRODUCTION v. 105, no. 33, p. 64-68. 16 August 1961; AMERICAN MACHINIST v. 105 no. 12, p. 95-98. 12 June 1961.

Adding TiC to tungsten carbide for cutting tools has the effect of reducing, seizing, galling, welding, cratering and crater depth. Wear land is reduced, but tool life is affected by the lowering of transverse rupture strength. High-speed finishing tools require a higher TiC content (30% and up) than roughing or intermediate grades. The decreased abrasive wear resistance caused by TiC additions may make tantalum carbide additions more advantageous. Graphs are shown.

123. Nazarchuk, T.N. and Pechentkovskaya, L.E.

Colorimetric determination of free carbon in molybdenum and tungsten carbides. INDUSTRIAL LABORATORY v. 27, no. 3, p. 258-261. March 1961.

The colorimetric determination of free carbon in WC was achieved by absorption of bromothymol blue, methyl orange and methyl violet, and in Mo_2C by absorption of bromothymol blue. The determination, carried out with an accuracy of about 5%, required 20-30 minutes. For purposes of comparison, free carbon was also determined in WC and Mo_2C by the ordinary gas-volume method. Data are tabulated.

124. New carbide put on market.

STEEL v. 149, no. 5, p. 71. 31 July 1961

The value of TiC tool bits and cutters is demonstrated by reports from three firms. The material used is VR-65, the manufacture and sale of which is now licensed to Vascoloy-Ramet Corp., Waukegan, Ill. The latter reports that TiC tools cut stainless and other steels and cast iron. The faster cutting permitted gives improved finishes, while edge wear and crater resistance are superior. Tool geometry can be the same as for other carbide tools, but negative rakes are recommended for rough or interrupted cutting.

125. Niki, E. et al

A study of the sintering of nickel-bonded

titanium carbides. KOGYO KYOKAISHI v. 69,

no. 786, p. 169-177. June 1961. (In Japanese)

Powders of TiC alone and with 10, 20, 30, 40, 50 and 75 wt-% Ni were sintered, and the linear shrinkage was measured. Except for TiC-75Ni, the shrinkage is slight up to 1200° C, increases abruptly in the 1200° -1350° C range, and varies logarithmically with time up to 1500° C. Abrupt shrinkage is attributed to a liquid phase. Increasing the nickel content changes the carbides from spheroid to polygonal shape. Graphs and micrographs are shown.

126. Noguchi, S. and Sat, T.

Thermoelectric power of titanium and vanadium

carbides. NIPPON BUTSURI GAKKAI v. 15, no. 12

p. 2359. December 1960. (In Japanese)

The thermoelectric power of TiC and VC was measured at -196° and 25° C to obtain information on the behavior of their conduction electrons. Results are compared with those from measuring Hall coefficient, and show that one more conduction electron per carbide molecule is available in VC. Data are tabulated.

127. Norton, J. T.

(NO TITLE) Massachusetts Institute of Technology,

Cambridge, Mass. Final report. November 1960.

6p. (Contract NOnr-184124, Proj. NR 039-008)

ASTIA AD-247 862

A study was made of the solubility relationships of the monocarbides of V, Ti, Cb, Ta and Zr. The carbides were combined in pairs, and with the exception of the VC-ZrC system continuous solid solution series were formed. The limited solubility in the VC-ZrC system was attributed to the size factor. Consideration was given to the mutual solubility of Be_2C and ZrC; there was no evidence of solid solution, and above 1400°C the Be evaporated rapidly. Solubility relationships were studied for TiC-VC-ZrC, TaC-VC-ZrC, and CbC-VC-ZrC. Isothermal sections of these pseudo ternary systems at 2000°C showed a 2-phase field surrounded by a single-phase field. X-ray diffraction and metallographic studies were made of the ternary Ti-Ta-C system, in particular the isothermal section at 1800° C; note was made of the extent of the cubic single-phase region extending across the diagram. Isothermal sections of Mo-W-C and Mo-Ti-C were studied at 1700° C. In the Mo-W-C system, a narrow single-phase field extended across the diagram from Mo_2C to WaC. In the Mo-Ti-C system, a cubic single-phase field of considerable extent was observed. WC was sintered with 25-wt% compositions ranging from pure Cu to pure Ni. The surface energy changed abruptly from the value of pure Cu when the first amount of Mo was added and then remained constant. The solubility varied linearly from zero for pure Cu to about 37-wt% for pure Ni. The feasibility of determining the ratio of grain boundary diffusion to lattice diffusion with an electron microbeam probe was investigated. In this method, Zr was diffused into the face of an Ag bicrystal with a grain boundary perpendicular to the face.

128. Norton, J. T.

STUDIES OF THE REFRACTORY METAL CARBIDES.

Massachusetts Institute of Technology, Cambridge,

Mass. Final report. November 1960. 10p. (Contract

NOnr-1841(24)) ASTIA AD 247 862. PB-157587.

Solubility relationships in the Ti-Ta-C, TiC-VC-ZrC, TaC-VC-ZrC, NbC-VC-ZrC and Be_2C-ZrC were studied. Of particular interest were solubility of pairs of carbides in the three carbide system and the 1800° C isothermal section of Ti-Ta-C. Sintering carbides in the presence of liquid metal and the 1700°C isothermals of Mo-W-C and Mo-Ti-C were also studied.

129. Nussbaum, L.

HARD METAL CARBIDE PRODUCTS. U.S. Patent No. 2, 971, 839. 14 February 1961.

A manufacturing process for TiC-base cermets consists of mixing comminuted and recrystallized TiC (and any other carbide) with 7-45% binder of chromium and equal or lesser amounts of nickel, heating to liquify the binder, comminuting the cooled mixture, and pressing and sintering into the desired form.

130. Nussbaum, L.

SINTERING HARD METAL CARBIDE PRODUCTS AND THEIR PRODUCTION. Canadian Patent No. 617, 587, n.d.

Comminuted TiC crystals with a lesser amount of W_2C and/or NbC crystals are intimately mixed with enough nickel and chromium powders to form a liquid binder-carbide eutectic with a part of the carbides. The heated mixture is cooled, comminuted, and pressed and sintered into the forms of desired products.

131. Orne, N.

METHOD OF PRODUCING METAL BORIDES. U.S. Patent No. 3, 004, 830. 17 October 1961.

Titanium, zirconium and molybdenum borides are produced by forming a comminuted mixture of their oxides, carbon and boric acid, and passing an electric arc through a cup-shaped charge in a furnace such as that described. The arc causes a vitrified wall and a pressurized, protective CO atmosphere to form while causing the boride to form and melt into the bottom of a cavity.

132. Paderno, Yu, B. and Samsonov, G.V.

Electrical properties of alkaline earth, rare earth, and thorium hexaborides. ACADEMY OF SCIENCES, USSR. PROCEEDINGS. PHYSICAL CHEMISTRY SECTION v. 137, nos. 1-6, p. 293-294. March-April 1961.

Lanthanon hexaborides are acquiring practical importance as materials for cathodes in high-powerful electronic devices. The authors measured systematically (using the same sample in measurements of different properties, and taking into account the degree of porosity of the samples) the following properties of the above substances: specific electrical resistivity and its thermal coefficient, Hall effect, and thermo-emf. It was found that, with the exception of SmB_6, electron conductivity plays an essential part in the electrical properties of the materials examined.

133. Paderno, Yu. B., Samsonov, G.V. and Fomenko, V.S.

The electrical properties of lanthanum boride. PHYSICS OF METALS AND METALLOGRAPHY v. 10, no. 4, p. 143-145. October 1960.

Sintered lanthanum hexaboride is used in manufacturing cathodes for high-power electronic equipment. The authors measured the electrical resistivity of samples of this material as a function of their degree of porosity (up to 37%). Measurements of thermoelectromotive force showed, as expected, its independence of the degree of porosity. Determination of the temperature dependence (up to 2000°C) of the resistivity of a sample with 2% porosity demonstrated that lanthanum boride is a metal-type conductor whose temperature coefficient of resistivity is considerably smaller than that of lanthanum metal, a fact attributable to the greater rigidity of the crystal lattice of the boride as well as to the change of the energy level of electrons taking place during the formation of the compound.

134. Paderno, Yu. B., Fomenko, V.S. and Samsonov, G.V.

Some properties of neodymium hexaboride and its preparation. UKRAINSKII KHIMICHESKII ZHURNAL v. 26, no. 4, p. 409-411. 1960. (In Ukrainian)

NdB_6 was obtained by reduction of Nd_2O_3 with B_4C or boron in a vacuum furnace at 1100° -1800° C. The end product was a finely divided powder, from which solid specimens were prepared by hot pressing at 2000° C at a pressure of 175-200 kg/cm^2. Determinations were made of the thermoelectromotive force, microhardness and electrical resistivity of NdB_6. The minimum porosity was 3% and the melting temperature was found to be 2540°C. Data are tabulated.

135. Paderno. Yu, B. and Samsonov, G. V.

Thulium borides. JOURNAL OF STRUCTURAL

CHEMISTRY v. 2, no. 2, p. 202-203.

March-April 1961.

The possibility of forming borides by reducing Tm_2O_3 with boron was studied. X-ray diffraction of the product mass showed characteristic structures of tetra and hexaborides (h.c.p. and cubic, respectively). Lattice constants are a = 7.04 kX and c = 3.98 kX, and a = 4.102 kX, respectively. Data are presented in a graph and table.

136. Palenik, G. J.

RARE EARTH CARBIDES: STRUCTURAL AND

HYDROLYTIC STUDIES. Ph. D. Dissertation.

University of Southern California. 1960. 119p.

Lanthanon carbides were prepared in a special high temperature furnace and studied by x-ray diffraction. Lanthanum, cerium and praseodynmium form MC_2, b.c.c. M_2C_3 and f.c.c. MC compounds while deodymium forms only MC_2. Isomorphisms, axial lengths and unit cells were determined. The hydrocarbon species obtained by reacting LaC_2, CeC_2 and CeC with water vapor depends on the reaction temperature. The reaction mechanism is discussed.

137. Philipp, W. H.

STABILITY OF TITANIUM NITRIDE AND TITANIUM

CARBIDE WHEN EXPOSED TO HYDROGEN ATOMS

FROM 298° to 1950° K. Lewis Research Center,

Cleveland, Ohio. NASA TN D-1053. August 1961, 15p.

Titanium nitride and titanium carbide deposited on tungsten wires were exposed to hydrogen atoms (10^{-4} atm pressure) produced by the action of microwave radiation on molecular hydrogen. The results of these experiments in the temperature range 298° to 1950° K indicate that no appreciable reaction takes place between atomic hydrogen and TiN or TiC. In order to interpret the stability of TiN and TiC in H atoms more fully, the stability of TiN and TiC in vacuum and H_2 gas was also studied. The thermodynamic computations conform in order of magnitude to the experimentally found rates of decomposition of TiN and TiC in vacuum and are also consistent with the fact that no appreciable reaction is found with these compounds in molecular H_2 at a pressure of 10^{-3} atmosphere in the temperature range 298 to 2000°K. When TiN or TiC was heated in atomic H or molecular H_2, no reaction products other than those obtained from the simple decomposition of the nitride and carbide were observed. The gaseous products were analyzed in a mass spectrometer.

138. Pollack, B. D.

THE VAPORIZATION BEHAVIOR AND THERMODYNAMIC STABILITY OF ZIRCONIUM CARBIDE AT HIGH TEMPERATURE. Atomics International Division of North American Aviation, Inc., Canoga Park, Calif. Report NAA-SR-5439. 1 January 1961. 19p. (Contract At-11-1-GEN-8)

The nature of the vaporization process of ZrC in the 2620° -2747° K range was studied by two methods. Agreement in results shows that accommodation coefficients must be near unity and that molecular species are unimportant. Free energy functions were estimated and used to derive a heat of formation. Data are tabulated.

139. Pollock, B. D.

The vaporization behavior and thermodynamic stability of zirconium carbide at high temperature. JOURNAL OF PHYSICAL CHEMISTRY v. 65 no. 5, p. 731-735. May 1961.

Knudsen and Langmuir methods were used to study ZrC vaporization in the 2620° - 2747° K range. Stoichiometric excesses of either component are preferentially vaporized in vacuo, indicating a constant subliming composition. A molecular ZrC vapor is absent. Thermodynamic values were calculated.

140. Popova, O. I. and Kabannik, G. T.

Dissolution in acids and methods of analysis of the nitrides of titanium, zirconium, niobium and tantalum. RUSSIAN JOURNAL OF INORGANIC CHEMISTRY v. 5 no. 4, p. 447-449. April 1960.

The solubility of nitrides of titanium, zirconium, niobium, and tantalum in various acids and mixtures of them in the cold and on heating, and in solutions of alkalis with hydrogen perioxide, has been studied. It has been shown that the most resistant to the various solvents is tantalum nitride and the least zirconium nitride. The information about the solubilities of these nitrides has been used in dissolving the samples for analysis. Methods of analysing the nitrides have been given.

141. Portnoi, K. I., Levinskii, Yu. V. and Fadeeva, V.I.

The nature of the interaction of some heat resistant

carbides and their solid solutions with carbon.

AKADEMIIA NAUK SSSR. OTDELENIE TEKHNICHESKIKH

NAUK. METALLURGIIA I TOPLIVO no. 2, p. 147-148.

March-April 1961. (In Russian)

While the metal corner of Me-C diagrams (Me=Ti, Zr, Hf) has been carefully investigated, little is known of the carbon corner. The authors made fusibility metallographic and x-ray observations of the pseudobindary systems TiC-C, ZrC-C, and HfC-C, and demonstrated the eutectic character of the interaction at work. Eutectic diagrams were also found for the pseudoternary systems TiC-ZrC-C, NbC-TiC-C, NbC-ZrC-C, TaC-TiC-C and TaC-ZrC-C. The dependence of the temperature of formation of binary eutectics in these systems on the composition of the carbide phase was determined.

142. Portnoi, K.I. and Levinskii, Yu. V.

Preparation of technical zirconium nitride.

JOURNAL OF APPLIED CHEMISTRY OF THE U. S. S. R.

v. 34, no 7, p. 1355-1359. July 1961.

Pure zirconium nitride can be obtained by treating zirconium with dry nitrogen. However, this process requires high temperatures (1200° -2000° C). The authors submit wet zirconium powder to nitridation at 450° -600° C and obtain (after 15 minutes) zirconium oxynitride, a product which in many cases can be used in place of zirconium nitride. Heat developed in the reaction between zirconium and water vapors is utilized in the process.

143. Portnoi, K. I.

Properties of boride-base materials and other high melting compounds. AKADEMIIA NAUK SSSR. INSTITUT METALLOV IM A. A. BAIKOVA. ISSLEDOVANIE SPLAVOV TSVETNYKH METALLOV No. 2, p. 197-204. 1960. (In Russian); (English Trans. NP-tr-510) p. 29-38.

The high-temperature properties of boride-base materials and metal systems containing carbides and silicides are reviewed.

144. Portnoi, K. I., Samsonov, G. V. and Frolova, K. I.

Some properties of alloys of titanium boride and chromium-titanium boride with boron carbide. PLANSEEBERICHTE FUER PULVERMETALLURGIE v. 8, no. 4, p. 195-199. January 1961. (In German)

In the expectation that the addition of other borides will reduce the brittleness of B_4C and improve its heat resistance, the authors experimented with additions of TiB_2 and of $(Ti, Cr)B_2$ mixed crystals. In both cases eutectic crystallizations take place which, as is known, inhibit the growth of crystals. It was found that the scale formation in alloys of the system B_4C-TiB_2 is too intensive. Accordingly, such alloys are not fit for prolonged service. As to alloys of the system B_4C-$(Ti, Cr)B_2$, they were found to possess a somewhat higher resistance to oxidation.

145. Portnoi, I. I., Samsonov, G. V. and Frolova, K, I.

Some properties of titanium boride and double titanium-chromium boride with boron carbide. JOURNAL OF APPLIED CHEMISTRY OF THE USSR. v. 33, no. 3, p. 582-586. March 1960.

While exceptionally hard, B_4C is brittle, easily oxidized, and not sufficiently heat resistant. It could be expected that these defects might be neutralized by allowing B_4C with other hard substances, more heat and oxidation resistant and of higher heat conductivity. Moreover, a eutectic structure of the alloy would ensure fine granulosity and consequently, sufficient mechanical strength. In experimenting with B_4C-TiB_2 and B_4C-(Ti, Cr)B2 alloys, the authors observed that their structure is essentially two-phase and eutectic, with the phase microhardness practically independent of the relative contents of components (except when below 10% or above 90%). However, the oxidation and heat resistances, while somewhat higher than in B_4C, are insufficient to guarantee long life, especially for B_4C-$(Ti, Cr)B_2$.

146. PROPERTIES AND STRUCTURE OF BORIDES (SELECTED ARTICLES) Metals and Ceramics Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Report on Refractory Inorganic Nonmetallic Materials. ASD TR-61-514. January 1962. 21p. (Proj. 7350) (English trans. by F.W. Vahldiek and S.A. Mersol) ASTIA AD-273 601

Of the four translations included in this report, two concern SiB_6, the x-ray determination of the SiB_6 structure, and some problems on the chemical compounds involving boron and silicon. The third is a treatise on the heats of formation of the borides of some transition metals, with certain references to their carbides and nitrides. The fourth comprises a discussion of the pressing and sintering of TiB_2 and CrB_2 powders.

147. Ransley, C.E.

Refractory carbides and borides for aluminum reduction cells. JOURNAL OF METALS v. 14, no. 2, p. 129-135. February 1962.

TiC has been found to be a suitable material for cruicibles used in aluminum reduction, and many patents have been published for the use of transition metal carbides and borides in cell structures. TiC has a high electrical resistivity, and that of TiB_2 is also good if it is of high purity. The thermal conductivity and mechanical strength of TiB_2 approach those of iron, and mediocre resistance to mechanical and thermal shock should not obviate its use. The rate of dissolution under cathodic conditions is negligible.

148. Ricker, R.W. and Wallace, P.F.

REFRACTORY AND METHOD OF MAKING THE SAME

U. S. Patent No. 3, 011, 983. 5 December 1961.

A refractory composition of titanium cyanonitride base contains 15-30 wt-% AlN and has low electrical resistivity and chemical inertness to molten cryolite and molten aluminum.

149. Rose, M.V. and Marshall, J.J.

INVESTIGATION OF TITANIUM BORONITRIDE AND TANTALUM BOROCARBIDE MATERIALS SYSTEMS.

Electro-Thermal Industries, Inc., Pearl River, New York.

Report no. WAL TR-371.9/1. October 1960. 36p.

(Contract DA 30-069-ORD-3126, Projs. TB4-004 and 5B93-32-004) ASTIA AD-249 818.

Specimens containing one mole excess BN (representing low BN contact materials) were successfully produced with conditions: (1) Refractory container pressure - 3100 psi, (2) 5/8 in. diam with charge compacting pressure - 26,600 psi, and (3) Reactor pressure - 20,000 psi. Specimens containing three moles excess BN (representing high BN content materials) were successfully fired using 3/4 in. diam charge with a compacting pressure of 3100 psi. Soundness appears to be a function of reactor pressure. Up to a reactor pressure of 40,000 psi, the density generally increased with reactor pressure. Above 40,000 psi, the density appears to increase slightly with reactor pressure. Electrical resistivity was 76.4 x 10^{-6} ohm-cm for one mole excess BN specimens and, 305 X 10^{-6} ohm-cm for three mole excess specimens. Compressive strengths were 60,000 psi for one mole excess BN and 5,000 psi for three moles excess BN. Energy input for the firing to the TiBN systems will increase as the moles excess BN is increased.

150. Rudy, F. and Benesovsky, F.

Electrical conductivity of high-melting, hard carbides and mixed crystals of carbides. PLANSEEBERICHTE FUER PULVERMETALLURGIE v. 8, no. 2, p. 72-82. August 1960.

Using an eddy current method, resistivity curves of binary systems composed of TiC, ZrC, HfC, VC, NbC and TaC were plotted. As a general result, the values measured were lower than those found in the literature. The continuous resistivity vs. composition curves have maxima in cases (e.g. ZrC-NbC, ZrC-TaC, HfC-VC, HfC-NbC, VC-TaC) were mixed crystals of the components are formed, thus determining a field of heterogeneity.

151. Ruppert, W. and Schwedler, G.

PROCEDURE FOR THE PRODUCTION OF COATINGS OF HARD, HIGH-MELTING NITRIDES. German Patent No. 1,089,240. n.d. (In German)

Coatings made of the nitrides of the metals of Groups IV and V of the periodic system are prepared by gas-plating with ammonia and halides of the nitride-forming metals. The object to be coated is heated to 700°C and the plating chamber is brought to a temperature above 650° C. The reaction between the ammonia and the metal halides is carried out in the plating chamber.

152. Rybal'chenko, R.V., Chaporova, I. N. and Tret'yakov, V.I.

Effect of carbon on the solubility of titanium carbide in cobalt, and some properties of Ti-C-Co alloys. ZHURNAL NEORGANICHESKOI KHIMII v. 6, no. 11, p. 2517-2527 November 1961. (In Russian)

The carbide in TiC-Co alloys contains varying amounts of dissolved carbon. The latter migrates into the cobalt phase to form a solid solution. A study was made to clarify the effect of the concentration of this solution on the strength of the binding cobalt phase. It was found that the microhardness of the latter remains approximately constant with increasing carbon content up to the appearance of the free carbon phase in the eutectic Co + C, in which case the microhardness decreases considerably. In general, increasomg carbon contents in the TiC-C-Co alloys, through the precipitation of the carbon phase, lessens the strength of the binding cobalt phase by decreasing its hardness, by favoring formation of fissures at the sites of carbon inclusions, and by decreasing the fusion temperature (as in the ternary eutectic TiC + C + Co).

153. Rybal'chenko, R. V., Tret'yakov, V. I. and Chaporova, I. N.
Influence of tantalum carbide on the composition and properties of the cobalt phase in titanium carbide-tungsten carbide-cobalt alloys. AKADEMIIA NAUK SSSR. IZVESTIIA. OTDELENIE TEKHNICHESKIKH NAUK. METALLURGIIA I TOPLIVO no. 4, p. 83-89. July-August 1961. (In Russian)

Alloys of cobalt with solid solutions TiC-WC (I) were compared with alloys of cobalt with solid solutions TiC-WC-TaC (II). The temperature of the eutectic Co-(TiC-WC-TaC) in II is higher by about 100° C than that of eutectic Co-(TiC-WC) in I. Alloys II are harder than alloys I from room temperature up to 400° C, this difference disappearing above that point. It is important to note that the above differences between I and II disappear, or are considerably smaller, in the presence of a free carbon phase.

154. Sakurai, J. et al
Thermal conductivities of mono-carbides in transition metals. NIPPON KINZOKU GAKKAISHI v. 25, no. 4, p. 289-292. April 1961. (In Japanese)

Thermal conductivities of TiC, ZrC, C and VC were measured at 0° C and liquid oxygen temperatures. Lattice contributions are larger than conduction electron contributions, according to calculations of the Wiedemann-Franz ratio. Graphs and tables are shown.

155. Samsonov, G. V. and Verkohoglyadova, T. S.
Hardness of transition-metal nitrides. JOURNAL OF STRUCTURAL CHEMISTRY v. 2, no. 5, p. 569-571. September-October 1961.

Microhardiness data are tabulated from $TiN_{0.50-0.97}$ compositions, $ZrN_{0.91}$, $VN_{0.338}$ and $VN_{0.74}$. Microhardness of TiN varies linearly with nitrogen concentration, but the more metallic VN is the harder. An electron structure different from that of the metals is inferred, probably because of ionic bonding. Results are plotted against the acceptor capacity of the transition metals.

156. Samsonov, G. V. and Verkhoglyadova, T. S.

The physical properties of titanium nitride in the region of homogeneity. SOVIET PHYSICS - DOKLADY v. 6, no. 5, p. 429-430. November 1961.

TiN occupies a wide homogeniety field between 30-50 at-% N. It seems plausible to assume that changes in the nature of the chemical bond may occur with this range which may be reflected in the physical properties. Plotting microhardness and electrical resistivity as functions of the nitrogen content and resistivity as a function of the temperature for various nitrogen contents revealed an increasing significance of ionic bonds with decreasing nitrogen content within the homogeneity range. This is correlated with the increasing number of covalent Ti-Ti bonds, while the number of covalent Ti-N bonds is decreasing. These changes result in a widening energy gap in the crystal lattice of TiN.

157. Samsonov, G. V. and Verkhoglyadova, T. S.

Physical properties of transition metal nitrides. AKADEMIIA NAUK S. S. S. R. DOKLADY v. 142, no. 3, p. 608-611. 21 January 1962. (In Russian)

Nitrides of transition metals combine features of intermetallic and ionic compounds, the preponderance in each case being a function of the degree of filling of the d shell of the metal atom, and of the principal quantum number N of this shell. These data determine the electron-accepting strength of the metal and, accordingly, the number of transitions of valence electrons of nitrogen into the d shell of the metal, with the resulting formation of hybrid spd states at the expense of polarized metal-nitrogen bonds. It is from these viewpoints that the authors examine the results of their measurements of physical properties of nitrides of titanium, zirconium, hafnium, vanadium and molybdenum, specifically their thermoelectric coefficient, electrical resistivity, Hall coefficient, heat conductivity and microhardness.

158. Samsonov, G. V. and Verkhoglyadova, T. S.

Physical properties of zirconium nitride in the homogeneity field. AKADEMIIA NAUK UKRAINS'KOI R. S. R. DOPOVIDI no. 1, p. 48-50. 1962. (In Ukrainian)

It is found by x-ray analysis that the limits of the homogeneity field of ZrN in the Zr-N diagram lie at 40 and 50 at-% N. A decrease in the nitrogen content is accompanied by an increasing influence of ionic interatomic forces in the crystal lattice. This phenomenon is stronger in the homogeneity field of ZrN than in the analogous TiN Field.

159. Samsonov, G.V. and Paderno, V.N.

Preparation and certain properties of hafnium carbide. JOURNAL OF APPLIED CHEMISTRY OF THE U.S.S.R. v. 34, no. 5, p. 931-936. May 1961.

Reduction of HfO_2 with carbon involves the formation of intermediate oxides Hf_2O_3 and HfO. Carbide close to the composition HfC is obtained by heating twice at 1900° C a mixture of HfO_2 with carbon in the stoichiometric ratio. After the first heating the product should be submitted to grinding. Relatively dense samples of the carbide are prepared by compressing the powder at 3000° C. Various data on the chemical stability (in cold and hot acids) and physical properties of hafnium carbide (electrical resistivity, characteristic temperature, elasticity modulus, thermal expansion coefficient, etc.) are presented.

160. Samsonov, G.V., Makarenko, G.N. and Kosolapova, T. Ya.

Preparation and properties of yttrium monocarbide. JOURNAL OF APPLIED CHEMISTRY OF THE U.S.S.R. v. 34, no. 7, p. 1381-1384. July 1961.

YC was obtained by reducing Y_2O_3 with carbon, taken in the stoichiometric ratio at 1900° C. The monocarbide melts at 1950° ± 20° C, its microhardness is 120 kg/mm^2, coefficient of thermal expansion is very low (1.36×10^{-6}), and its electrical resistivity is 4×10^4 μohm·cm. It oxidizes rapidly in air, is readily decomposed by water and dilute acids and alkalis, but is only slowly attacked by concentrated acids.

161. Samsonov, G.V., Paderno, Yu. B. and Kreingol'd. S.U.

Preparation of lanthanum hexaboride. JOURNAL OF APPLIED CHEMISTRY OF THE USSR. v. 34, no. 1, p. 8-13. January 1961.

LaB_6 was prepared by reacting La_2O_3 containing 1% of other lanthanon oxides with boron or B_4C (prepared by not pressing a mixture of amorphous boron and carbon black. In both cases powders were mixed, pressed into briquets and heated in a vacuum furnace. Formation of LaB_6 began at 1200° -1300° C and was terminated in an hour at 1500-1600° C. A carbon-free powder was obtained which is essential to certain fields of LaB_6 application.

162. Samsonov, G. V., Yasinskaya, G. A. and Shiller, E. A.

The reaction of certain oxides and carbides with refractory metals at high temperatures. OGNEUPORY v. 7, p. 335-338. 1961. (In Russian) (English trans. by Foreign Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, 6 October 1961. 7p.) ASTIA AD-265 808.

Results are presented of an investigation of the contact reaction of BeO, MgO, ZrO_2, and metal carbides (Zr, Hf, Nb and Ta) with Nb, Mo, and W at temperatures up to 2100° C. Oxides of chemically pure Be and Mg and ZrO2, stabilized with CaO, ZrC, HfC, NbC, and TaC of stoichiometric composition, and also industrially pure refractory metals were used. An oxide or carbide was pressed, after heating for 3 to 5 min on a hot forging press, onto a refractory metal sample. The products obtained were kept in a vacuum furnace with a graphite heater at temperatures from 1000 to 1600 to 2100°C for 0.5 to 5 hours. After extraction the ends were ground, polished, and examined metallographically. Tungsten had the greatest stability with BeO, Mo and W with MgO, and Mo with stabilized ZrO_2.

163. Samsonov, G. V.

Zirconium boride tips for immersion thermocouples. REFRACTORIES Nos. 1-2, p. 57-59. January-February 1961.

The resistance of submerged zirconium boride thermocouple tips, used in automation of metallurgical processes, was tested in molten iron and steel at 1400° -1450° C. After two hours of service the tips became slightly coated with slags, but did not corrode and preserved their initial structure. Tips tested in molten brass at 850° -50° C for 86 hours did not show any signs of deterioration. The same results were obtained when molten bronze was substituted for brass.

164. Samuel, R. L. and Lockington, N. A.

PROCESS FOR THE PRODUCTION OF METALLIC BORIDES ON THE SURFACE OF METALS. U. S. Patent No. 3, 029, 162. 10 April 1962.

A diffusion coating is applied to metal articles by first diffusion coating with titanium, zirconium, vanadium or molybdenum, and then heating in a coating pack containing a source of boron and volatilizable halide as a boron carrier.

165. Sanders, W. A., <u>et al</u>

Preliminary investigation of fabrication and properties of hafnium carbide. JOURNAL OF METALS v. 13, no. 3, p. 233. March 1961.

Some preliminary investigations on the fabrication and properties of hafnium carbide have been completed. Fabrication procedures for the production of high-density hafnium carbide bodies are given, and room- and elevated-temperature, mechanical- and physical-property values are presented.

166. Savost'yanova, N. A. and Shvartsman, L. A.

The solubility of vanadium carbide in gamma iron. PHYSICS OF METALS AND METALLOGRAPHY v. 9, no. 4, p. 35-39. April 1960.

A thermodynamic treatment is offered of the problem of the passage of carbides of alloying elements into a solid solution. This is done for the specific example of the solubility of vanadium carbide in gamma iron. The fact that the presence of manganese increases that solubility is interpreted as due to a lowering of the activity coefficient of carbon under the influence of manganese present in the solid solution.

167. Shaffer, P. T. B.

DEVELOPMENT OF ULTRA REFRACTORY MATERIALS. Carborundum Co., Niagara Falls, New York. Summary report 1 November 1959 - 31 October 1960.

15 December 1960. 35p. (Contract NOrd-17175)

ASTIA AD-248 027.

Structural applications of the composition consisting of a solid solution of $MoSi_2$ in ZrB_2 in (90% ZrB_2-10% $MoSi_2$) were investigated. The composition showed excellent resistance to oxidation (for 4 hours at 3540° F or at higher temperatures for shorter duration). Application is limited, however, as the melting temperature of one of the constituents is near the prescribed temperature of 3500° F. High-temperature, cross-bending strength was increased significantly by the inclusion of dispersed BN particles in the ZrB_2-$MoSi_2$ composition. Oxidation resistance was improved since the resulting oxide layers are more uniform and tightly bound than with the layer resulting from oxidation of samples containing no BN. Variation in oxidation resistance of different lots of ZrB_2 indicated presence of impurities; studies showed Si or SiC improved oxidation resistance. Mixed carbide systems consisting of mixtures of the monocarbides of group IV and V metals were investigated to clarify an anomaly. This pertains to the situation where melting temperatures within the solid solution series are higher than those of the component materials. In at least 2 of the mixed carbide systems, there was evidence that a complete series of solid solutions stable at ambient temperatures does not exist. A second phase was established by x-ray diffraction in ZrC-NbC at 3990° F, and disproportionation was indicated in the HfC-4TaC composition at 2730° F.

168. Shaffer, P. T. B.

DEVELOPMENT OF ULTRA REFRACTORY MATERIALS.

Carborundum Co., Niagara Falls, New York.

Progress report no. 23, 1 November 1960 - 31 January 1961. 3 February 1961. 6p. (Contract NOrd-17175)

ASTIA AD-250 522.

Studies were undertaken to explain anomalies such as increases in melting temperature, strength and creep resistance observed in solid solutions of ZrC, and TaC. The melting point increase in the solid solution series of Zr and Ta Carbides indicated possible formation of a compound. A range of compositions of the series was prepared from finally powdered oxides mixed and blended with stoichiometric amounts of carbon. Billets were hot pressed from the powders and 4 samplebars were sawed from each billet; physical property measurements were made of each bar before and after annealing. No significant changes, indicating formation of a compound took place in the following categories: lattice parameters, micro-hardness electrical resistivity, and Young's modulus.

169. Shaffer, P. T. B.

DEVELOPMENT OF ULTRA REFRACTORY MATERIALS. Carborundum Co., Niagara Falls, New York. Progress report no. 25, 1 May - 31 July 1961. 16 August 1961. 17p. (Contract NOrd-17175) ASTIA AD-261 471.

The study of solid solutions of TaC and ZrC was continued. The melting temperatures and calculated spectral emissivities showed a reversible change to occur on heating the pure carbidides. This change is accompanied by a marked decrease in emissivity and resistivity. The measured melting temperatures are lower than the reported values. The cause of the low melting temperatures, due possibly to non-stoichiometry or failure to correct completely for emissivity, has not been resolved. A survey was started to determine whether radome materials with improved thermal shock resistance can be developed. A few zero expansion and low expansion ceramic bodies were prepared for testing.

170. Shaffer, P. T. B. and Watts, R. L.

DEVELOPMENT OF ULTRA REFRACTORY METALS. Carborundum Co., Niagara Falls, New York. Summary report, November 1961. 38p. (Contract NOrd-17175).

Room temperature investigations of various physical, mechanical and electrical properties of solid solutions of tantalum carbide and zirconium carbide showed no evidence of discontinuous changes indicating new phases or compound formation after a wide variety of annealing treatments. Emissivity studies, however, indicate the probable existence of high-temperature phases of both tantalum carbide and zirconium carbide, though not of the solid solutions. The reported increase in melting temperature of ArC-TaC solid solutions has been confirmed.

171. Shaffer, P. T. B.

An oxidation resistant boride composition. AMERICAN CERAMIC SOCIETY. BULLETIN v. 41, no. 2, p. 96-99. February 1962.

A ZrB_2-$10MoSi_2$ solid solution composition was developed which has good resistance to thermal shock and to 4-hr exposure to 3542° F air, and moderate high-temperature strength. Test samples were prepared by hot pressing, but the material may be prepared by cold pressing and sintering and can be applied as sintered and plasma-sprayed coatings. Graphs and photographs are shown.

172. Shcherbakov, V.G. and Stegendo, Z.K.

Determination of titanium, tantalum, and niobium

in carbide mixtures. INDUSTRIAL LABORATORY

v. 26, no 2, p. 145-148. February 1960.

Analysis of TiC and tantalum and niobium carbide mixtures with possibly some other carbides may be carried out by oxalate precipitation of titanium and tantalum (and much of the niobium) to separate them from tungsten, and determining titanium volumetrically with zinc amalgam reduction using NaF addition to suppress niobium reduction. Determination of the other metals present (carried out subsequently) is described.

173. Simnad, M.T.

METHOD FOR FORMING A COATING OF MOLYBDENUM

CARBIDE ON A CARBON BODY. U.S. Patent No.

3, 028, 256. 3 April 1962.

Carbon bodies are made more corrosion- and erosion-resistant and less permeable to gases by coating with molybdenum oxide below the carburization temperature and then carburizing in inert atmosphere to form molybdenum carbide on and in the body.

174. Smirnov, M.V. and Krasnov, Yu. N.

The electrochemical behavior of titanium carbide

in a chloride melt. RUSSIAN JOURNAL OF INORGANIC

CHEMISTRY v. 5, no. 6, p. 598-602. June 1960.

Anodic dissolving of TiC in a eutectic LiCl-KCl melt at 400°-700° C and current density 0.1 a/cm^2 occurs with the formation mainly to $TiCl_4$. The dissolving takes place at an anode potential ($Ti_{1.04}C$ anode) which is more negative by 0.6-1.4 v than the potential of formation of Cl_2. There is a considerable polarization reaching 0.50-0.65 v. Other experiments furnished data for the calculation of changes of the isobar potential, enthalpy, and entropy occurring when the composition, in the Ti-C system changes within the range of the β phase (i.e. $TiC_{1.0-1.6}$).

175. Stadelmaier, H. H.

TERNARY CARBIDES AND NITRIDES OF THE TRANSITION METALS WITH METALS OF THE B SUB-GROUPS OF THE PERIODIC SYSTEM.

North Carolina State College, Raleigh, N. C. Final report, 13 October 1961. 11p. (Contract No. DA-36-034-ORD-2766RD) ASTIA AD-265251.

Among the many metal phases that exhibit close packing of the atoms, a new class, that occurs with some abundance, has been studied. The structure is characterized by the inclusion, in ordered positions, of B-metal atoms in the close-packed lattice of the transition metals manganese, iron, cobalt, or nickel, and by occupancy of the large interstices inside the transition-metal octahedra with carbon or nitrogen. There is considerable deviation from the ideal structure and composition for the cubic phases, and in some cases tetragonal distortions are observed. The work under this contract was concerned primarily with establishing the existence of such ternary compounds and in many cases their exact composition.

176. Steinitz, R.

Borides. Part B: Fabrication, properties, and applications. MODERN MATERIALS v. 2, p. 191-224. 1960.

Diborides of the transition metals are isomorphous and form solid solutions. This is untrue of the monoborides, which are unstable and hard to make. The possibility of tetra-borides among the lanthanons depends on atomic size. Production of boride powders is achieved by different methods. Those from Group Vb and VIb and lanthanons are best made by reaction of Boron and metal powders, while Group IVb borides are made by reduction of the fine oxides with carbon, boron or B_4C or, for TiB_2, by reaction of boron with the hydrides. Other largely experimental production methods are reviewed. Details in methods of fabrication by hot pressing, cold pressing and sintering, or slip casting are described. Coatings may be applied by flame spraying. Parts thus produced are machined by grinding with resin bonded diamond wheels, electrospark machining or ultrasonic drilling. Porosity of the fabrications strongly affect mechanical properties and corrosion resistance.

177. Stoner, L.

Between carbide and ceramic. MACHINE AND TOOL BLUEBOOK v. 56, no. 10, p. 141-143. October 1961.

Cutting tool materials based on TiC have a long tool life and permit a wide range of speeds, better size control and finer surface finish. TiC must not be considered exclusively as a high-speed finishing tool material. Turning and facing operations are described as examples of its use.

178. Stoner, L.

Brazing titanium carbide. MACHINE AND TOOL BLUE BOOK v. 57, no. 1, p. 121-122. January 1962.

Brazing a cemented TiC tip requires attention to cleanliness and freedom from burrs. The tip should be as thick as possible without impairing the strength of the supporting shank. Tips should not be brazed into pockets. Blanks of 0.5-1.0-in length should be brazed with a thin copper shim. Greater lengths need a thicker shim. The flow point of the brazing alloy should be high enough to withstand the heat of cutting but low enough to minimize thermal expansion effects. Photographs are shown.

179. Storms, E. K.

A CRITICAL REVIEW OF REFRACTORIES. I. SELECTED PROPERTIES OF GROUP 4a, 5a AND 6a CARBIDES. Los Alamos Scientific Laboratory, New Mexico. Report no. LAMS-2674. 15 March 1962. 87p.

Reported studies of systems of titanium, zirconium, hafnium, vanadium and molybdenum with their carbides are reviewed and cover preparation, phase relations, lattice parameter and structure, chemical stability and other properties, hardness, electrical resistivity, superconductivity, and thermodynamic properties.

180. Stowell, E. Z. and Liu, T. S.

PARAMETRIC STUDIES OF METAL FIBER
REINFORCED CERAMIC COMPOSITE MATERIALS.
Bi-monthly report no. 4, 8 July 1960 through
7 September 1960. Southwest Research Institute,
San Antonio, Texas. 8 September 1960. 11p.
(Contract NOas 60-6077-c) ASTIA AD-244 305.

The mechanical behavior of ceramic materials at elevated temperatures is described from a phenomenological standpoint. The viscoelastic characteristics of both the ceramic materials and the metals at elevated temperatures makes possible the prediction of their behavior. Summary tables on pertinent physical, mechanical and thermodynamic properties are presented for carbides, nitrides and borides.

181. Szklarz, E.G. and Giorgi, A. L.

Superconducting-transition temperatures of hafnium-
nitride and hafnium-nitride - zirconium-nitride solid
solutions. AMERICAN PHYSICAL SOCIETY. BULLETIN
v. 7, no. 3, p. 176. March 1962.

Nitrogen-rich and -deficient HfN transition points were measured. Nitrogen excesses depress the transition temperature from 6.2° K more rapidly than nitrogen deficiencies. The transition temperature of HfN-ZrN solid solutions varies smoothly in the 6.2°-10.7°K range.

182. Takamura, A.

Nitriding of titanium. NIPPON KINZOKU GAKKAISHI
v. 24, no. 9, p. 565-569. September 1960. (In Japanese)

The kinetics of nitriding titanium in a nitrogen stream at various temperatures were studied. The parabilic rate law operative to 800° C or 900° C is diffusion controlled in both the thin outer TiN layer and the diffusion layer. Solubility and diffusion coefficients are governed by temperature, but nitriding above the transformation point is impractical since surface reliefs form and deformation results. 850° C is the optimum nitriding temperature. Tables and graphs are shown.

183. Taylor, R. E.

Thermal conductivity of titanium carbide at high
temperatures. AMERICAN CERAMIC SOCIETY.
JOURNAL v. 44, no. 10, p. 525. October 1961.

Thermal conductivity measurements on TiC with the steady-state radial heat flow furnace in the 500°-2100° C range show that cylindrical samples have a somewhat linear relationship with temperature. Lack of agreement with results of Vasilos is noted. Electrical resistivity was measured in the 0° - 800° C range, and results are treated analaytically.

184. Tereshko, J. W.

The determination of boron in boron nitride,
boronated graphite rods, titanium borides and
zirconium borides using Tiron or EDTA as the
masking agent. AMERICAN CHEMICAL SOCIETY.
ABSTRACTS OF PAPERS, 141ST MEETING. p. 7B.
March 1962.

A procedure applicable to boron analysis of titanium and zirconium borides is described which is fast and accurate. Use of Tiron or EDTA chelating agents for metal interferences is featured.

185. Troitskaya, N. V. and Pinsker, Z. G.

The hexagonal nitrides of molybdenum. SOVIET
PHYSICS-CRYSTALLOGRAPHY v. 6, no. 1, p. 34-39.
January-February 1961.

Electron diffraction of Mo-N compositions disclosed two hexagonal nitride phases designated ' and ". Potential synthesis of the former indicates the displacement of molybdenum atoms from special positions in the lattice, while the latter appears to have eight nitrogen atoms randomly distributed over the 12-fold positions of the space group D_3^3d. The D_6^4h alternative was rejected. Diffraction patterns and synthesis sections are presented, and interatomic distances and other data are tabulated.

186. Vainshtein, E. E., et al

Fine structure of K absorption spectra of the metal in the homogeneity field of titanium nitride. FIZIKA METALLOV I METALLOVEDENIE v. 12, no. 3, p. 360-364. September 1961. (In Russian)

The authors measured the fine structure of the K edge of absorption x-ray spectra of titanium in the homogeneity field of the nitride. The gradual changes in the aspect of the spectra, as the nitrogen content changed from 11.7 to 22.4 wt-%, are interpreted as due to bonds of ionic character, which apparently are more prominent in the nitrides than, e.g., in the carbides of titanium. This ionic component of the bonds decreases as the composition approaches the stoichiometric TiN.

187. Wakelyn, N. T.

Coatings of titanium nitride project graphite at high temperatures. METAL PROGRESS v. 80 no. 6, p. 143-144. December 1961.

Vapor deposition of a TiN coat on graphite projected it for 60 sec at 2250° K in a Mach 2 airstream, while uncoated samples were destroyed. In coating, mixed H_2, N_2 and $TiCl_4$ gases are passed over graphite at 1475° K in a quartz reaction tube pre-purged with argon. The quality of TiN formed varied with the $TiCl_4$ used. The coating forms a protective oxide without spalling because of similar thermal expansion coefficients of nitride, oxide and substrate. Standard free energies of formation and heats of reaction are plotted.

188. Wakelyn, N. T.

TITANIUM NITRIDE: AN OXIDIZABLE COATING FOR THE HIGH-TEMPERATURE PROTECTION OF GRAPHITE. U. S. National Aeronautics and Space Administration. Technical Note D-722. February 1961, 17p.

Vapor deposition of a TiN coat on graphite protected it for 60 sec at 2250° K in a Mach 2 airstream, while uncoated samples were destroyed. In coating, mixed H_2, and N_2 and $TiCl_2$ gases are passed over graphite at 1475° K in a quartz reaction tube pre-purged with argon. The quality of TiN formed varied with the $TiCl_2$ used.

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The coating forms a protective oxide without spalling because of similar thermal expansion coefficients of nitride, oxide and substrate. Standard free energies of formation and heats of reaction are plotted.

189. Westabrook, J. H.

Silicides, borides, aluminides, intermetallics

and other unique refractories. In INTERNATIONAL

SYMPOSIUM ON HIGH TEMPERATURE TECHNOLOGY,

ASILOMAR, CALIF., 1959. PROCEEDINGS p. 113-128.

N. Y., McGraw-Hill, 1960.

Available data on transition metal borides, silicides and phosphides are presented. Among the illustrations shown are the Mo-Si, V-B, Zr-Si, Zr-Ge and Zr-Sn phase diagrams, 1300° C solid solubility sections for the pseudoternary systems involving $TiSi_2$ or $MoSi_2$ or both, the 1000° C isothermal section of the Ni-Ti-Si system, and strength property curves of $MoSi_2$ vs. temperature. Applications of the silicides are of considerable interest.

190. Westerman, R. E.

INVESTIGATION OF PYROLYTIC GRAPHITE AS

CRUCIBLE MATERIAL FOR ZIRCONIUM MELTING.

General Electric Co., Hanford Atomic Products

Operation, Richland, Wash. Report HW-72998.

March 1962. 11p.

Zirconium sponge was melted in crucibles internally coated with pyrolytic graphite. Analysis showed that the ingots contained 0.41 wt-% C and 0.07 wt-% 0, regardless of holding time. Ingots are readily freed from the coated crucibles, but the latter show no advantage over reactor-grade graphite crucibles. Micrographs are shown.

191. Whitehead, K. and Brownlee, L. D.

THE ZIRCONIUM CARBIDE-URANIUM CARBIDE SYSTEM. U.K. Atomic Energy Authority. Research Group. Atomic Energy Research Establishment. Report X/PR-2477. February 1956. 17p.

The melting point curve of the ZrC-UC system was determined. It falls smoothly from the 3535° C melting point of ZrC to the 2640°C melting point of U.C. The system consists of a complete series of solid solutions. The lattice parameter obeys Vegard's law closely in relation to composition. Data are tabulated and curves are shown.

192. Wiegand, H. and Ruppert, W.

Preparation and properties of tube drawing dies with titanium carbide coatings. METALLOBERFLAECHE v. 15, no 1, p. 1-12. January 1961. (In German).

Previous papers have considered the method of deposition of TiC coatings on steel surfaces and the properties of such TiC-steel combinations. The authors here discuss the possible causes of wear in drawing dies, and the effect on wear of protective coatings. It is shown on the basis of a detailed investigation that TiC coatings 3-10μ in thickness improve the wear characteristics of drawings dies quite satisfactorily if the base material is of sufficient strength.

193. Wilke, K. Th.

Needle-like growth of titanium nitride crystals. DEUTSCHE AKADEMIE DER WISSENSCHAFTEN ZU BERLIN. MONATSBERICHTE v. 2, no. 7, p. 425-426. 1961. (In German)

Among coarse grained titanium nitride crystal accumulations, formed upon an incadescent tungsten filament in an atmosphere of $TiCl_4$, nitrogen and hydrogen, the author observed fine whiskers of the same substance, which grow to needle-like crystals.

194. Williams, W. S. and Schall, R. D.

Elastic deformation, plastic flow, and dislocations in single crystals of titanium carbide. JOURNAL OF APPLIED PHYSICS v. 33, no. 3, p. 955. 1962.

March 1962.

Monocrystals of titanium deformed plastically in the 800° -2200°C are concluded to have slip systems like those of f.c.c. metals on the basis of dislocation etch-pit studies. The slip plane is $\{111\}$. The resolved shear stress for slip at 1100°C is large. Crystals loaded to 25°C do not deform plastically, but electropolished surfaces accommodate up to 1.2% elastic strain. Observations are consistent with a Peierls stress associated with covalent binding.

195. Williams, W. S.

The heat of formation of titanium diboride: experimental and analytical resolution of literature conflict. JOURNAL OF PHYSICAL CHEMISTRY v. 65, no. 12, p. 2213-2216.

December 1961.

Two experimental results (TiN + BN in nitrogen, and TiO_2 + B_4C + carbon) and two calculations of TiB_2 heat of formation have been reported, giving values near -70 kcal/mole. A value of -32 kcal/mole was confirmed by present studies which involved stability comparisons with other compounds and analysis of the errors in other studies. However, a refinement of the TiB + BN in nitrogen determination resulted in a value of -66 kcal/mole at the nitride transition temperature of 2150° K (reported at 1870°K). Cumulative uncertainty in the thermodynamic data used is implicated.

196. Williams, W. S.

Mondrian precipitation patterns in single crystals of titanium carbide. AMERICAN PHYSICAL SOCIETY. BULLETIN v. 6, no. 1, p. 23-24. 1 February 1961.

Large TiC monocrystals (NaCl structure) were electrolytically etched and examined by x-ray diffraction and metallography. Square, flat-bottomed pits produced are related to precipitation of excess carbon and not to dislocations. Vacuum annealing at 2000°C for an hour redistributed much of the excess carbon as platelets along a different cleavage plane.

197. Williams, W. S.

Mondrian precipitation patterns in single crystals

of titanium carbide. JOURNAL OF APPLIED PHYSICS

v. 32 no. 3, p. 552-554. March 1961.

Etching studies of TiC monocrystals produced square, flat-bottomed etch pits similar to those of LiF. Both have the NaCl structure and cleave along (100) planes. X-ray diffraction shows globular precipitates on TiC cleavage planes, and other evidence also shows that the etch pit phenomenon is due to Mondrian precipitation patterns rather than dislocations. Micrographs are shown.

198. Wong, M. M. and Kleespies, E. K.

METHOD FOR REDUCTION OF REFRACTORY METAL

OXIDE BY CALCIUM CARBIDE. U.S. Patent No. 3,016,296.

9 January 1962.

Titanium, zirconium and chromium are obtained from their oxides by reduction with CaC in the presence of a molten flux. Reduction is improved by arranging the carbide, the flux and the oxide in vertical layers within the crucible so that the carbide and oxide are separated by a layer of flux. A diagram is shown.

199. Zalabak, C. F.

THE MELTING POINTS OF TANTALUM CARBIDE AND

OF TUNGSTEN. Lewis Research Center, Cleveland,

Ohio. NASA TN D-761. March 1961. 21p.

An experimental determination was made of the melting points in the tantalum-carbon system in the range 4.26 to 5.60 weight per cent carbon. The melting points ranged from 6360 to 6970°F. A melting point of 6165°F was obtained from tungsten with a carbon content of 15 parts per million. Melting points of tungsten as low as 5790°F are attributed to carbon impurities in the region of 70 parts per million and the consequent lower solidus temperature for the tungsten-carbon solid solution. The foregoing temperatures are accurate to ± 0.7 per cent of the absolute temperature.

200. Zalabak, C. F.

Sintering of hafnium carbide with a fugitive metal binder. ELECTROCHEMICAL SOCIETY. JOURNAL v. 108, no. 8, p. 183C. August 1961.

Mechanical mixtures of HfC and cobalt powders were cold compacted and sintered to vaporize the cobalt. 95% density and 2% surface-connected porosity were achieved. Grain size and microhardness vs. process variables were studied. This paper was presented before a meeting of the Electrochemical Society in Detroit, 1-5 October 1961.

201. Zelezny, W. F.

NITRIDED METALS. U.S. Patent No. 3,011,927. 5 December 1961.

An article may be formed by mixing the powder of a Group IVb metal with its nitride, molding and vacuum heating in the 1400°-3000°F range.

202. Zhuravlev, N. N., et al

X-ray determination of the expansion of coefficients of hexaborides. SOVIET PHYSICS-CRYSTALLOGRAPHY v. 6, no. 5, p. 636-638. March-April 1962.

Lanthanon and yttrium hexaborides were subjected to x-ray powder diffraction Data on lattice constants and expansion coefficients are tabulated. Amplitudes of vibration of the hexaborides are small and very much alike.

AUTHOR INDEX

SUBJECT INDEX

BORIDES