6-90-63-10

PHASE RELATIONSHIPS OF MOLYBDENUM, NIOBIUM AND TUNGSTEN BORIDES, CARBIDES AND SILICIDES: AN ANNOTATED BIBLIOGRAPHY

SPECIAL BIBLIOGRAPHY
SB-63-9

MAY 1963

6-90-63-10

PHASE RELATIONSHIPS OF MOLYBDENUM, NIOBIUM AND TUNGSTEN BORIDES, CARBIDES AND SILICIDES: AN ANNOTATED BIBLIOGRAPHY

Compiled by

JACK B. GOLDMANN

SPECIAL BIBLIOGRAPHY
SB-63-9

MAY 1963

Lockheed

MISSILES & SPACE COMPANY

A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION

SUNNYVALE, CALIFORNIA

NOTICE

ABSTRACT

This annotated bibliography emphasizes phase relationships and their fabrication as evidenced in the physical properties, refractories, and powder metallurgy of molybdenum, niobium and tungsten compounds which are formed with boron, carbon and silicon. The period, 1955–1962, yielded the majority of references included in this bibliography. The resources of Lockheed Missiles and Space Company Technical Information Center were utilized in the preparation and compilation of this survey.

Search completed December 1962.

CONTENTS

1. Albert, H. J. and J. T. Norton
Isothermal sections in the systems molybdenum-tungsten-carbon and molybdenum-titanium-carbon. (Isothermschnitte in den Systemen Molybdaen-Wolfram-Kohlenstoff und Molybdaen-Titan-Kohlenstoff.) PLANSEEBERICHTE FUER PULVERMETALLURGIE 41(1):2–6, Apr 1956. (In German)

It was found that the MoC phase in the system Mo-C is stable at high temperatures and decomposes into Mo_2C and carbon on cooling, and that in the isothermal section of the system Mo-W-C a single-phase field of $Mo_2C + W_2C$ exists at 1710°C. The solubility of titanium in Mo_2C in the isothermal section at 1710°C of the system Mo-Ti-C is also very low, and even lower in MoC. The solubility of molybdenum in TiC increases with increasing carbon content.

2. Alexander, P.
EVAPORATING ELEMENT WITH CARBON BASE HAVING A METAL COATING LAYER AND A SURFACE LAYER OF METAL SILICIDE AND METHOD OF MAKING THE SAME. (Assigned to Continental Can Co., Inc., Toronto.) Canadian Patent 587, 733. 24 Nov 1959.

An evaporating element for use in vacuum metalizing apparatus is provided with a molybdenum, niobium or tantalum coat bound to the carbon base by the formation of a silicide layer effected by heating metal and silicon powders in vacuum to above the fusion point of the silicide.

3. Alexander, P.
EVAPORATING ELEMENTS HAVING METAL SILICIDE COATINGS AND METHOD OF MAKING SAME. (Assigned to Continental Can Co., Inc., Toronto.) Canadian Patent 597,732. 24 Nov 1959.

A silicide-coated carbon evaporating element for use in a vacuum metallizing apparatus is produced by applying a mixture of particles of silicon and one of molybdenum, tantalum or niobium to the surface of a carbon base, and fusing the mixture at a temperature above the melting point of the resulting silicide in vacuum.

4. Allenbach, C. R. and J. C. Burbach
METHOD FOR MAKING REFRACTORY ARTICLES. (Assigned to Union Carbide Corp., Niagara Falls, N.Y.) U.S. Patent 3,002,936. 3 Oct 1961.

A refractory article is formed by sintering $MoSi_2$ powder containing 5-50% silicon nitride at the dissociation temperature of the latter and under oxidizing conditions. The Silicon is oxidized to silica.

5. Alyamovskii, S. I., P. V. Gel'd and I. I. Matveenko
Concentration regions of niobium silicide stability at 1250°C. ZHURNAL NEORGANICHESKOI KHIMII 7:836–843, Apr 1962. (In Russian)

Phase studies of Nb-Si at 1500°C indicated two stable silicides alpha-Nb_5Si_3 and $NbSi_2$; Nb_4Si was not observed. It was found that alpha-Nb_4Si_3 is a special phase with variable composition and stability ($NbSi_{0.58}$ to $NbSi_{0.66}$) at 1250°. The niobium bisilicide is a single phase ($NbSi_{1.85}$ to $NbSi_{2.20}$) developed from alpha-Nb_5Si_3 by replacement.

6. Alyamovskii, S. I., P. W. Gel'd and I. I. Matveenko
Phase components of the system Nb-Si. URAL'SKOGO POLITECHNICHESKOGO INSTITUTA IMENI S. M. KIROV. TRUDY (114): 149-151. 1961. (In Russian)

Alloys of Nb silicides were prepared by sintering briquetted mixtures of nibbium (99.6%) and silicon (99.8%) powders in a vacuum oven at 1200–1600° and were studied by microscopic and x-ray diffraction methods. Silicide phases have a considerable region of homogeneity: for a = Nb_5Si_3 from $NbSi_{0.58}$ to $NbSi_{0.66}$ for $NbSi_2$ from $NbSi_{1.85}$ to $NbSi_{2.2}$. The periods of the lattices of a = Nb_5Si_3 and $NbSi_{2.2}$ remain practically constant. The system Nb-Si contains solid solutions of substitution both for $NbSi_2$ and Nb_5Si_3. Roasting of alloys containing Nb Si at 1000–1100° caused decomposition : $Nb_4Si - Nb + Nb_5Si_3$.

7. Amberg, S.

The homogeneity region of $MoSi_2$. MONATSHEFTE FUER CHEMIE 91(3):412–425, 1960. (In German)

The lower limit of the silicon content in the homegeneity region of $MoSi_2$ was determined as 37.4 ± 1.1%. X-ray examinations always revealed the presence of Mo_5Si_3 in silicides containing up to 36% Si. Heating at 1750°C in a hydrogen atmosphere, or in the presence or absence of SiO_2 did not influence the homogeneity region or the crystal structure of the Mo_2Si phase.

8. Amberg, S.

Studies on the sintering of $MoSi_2$-Al_2O_3 cermets. POWDER METALLURGY 8:101–112, 1961.

The effect of alumina content and grain size on the porosity of hydrogen-sintered MoSi -Al_2O_3 bodies was determined by density measurements. Density is determined mainly by disilicide grain size. Fine grain bodies are oxidation-resistant but weak. Sintering in dissociated ammonia promotes formation of Si_3N_4, which decomposes on heating in air. Tables, graphs and illustrations are presented.

9. Amosov, V. M.

Ductile niobium from electrolytic powders

VYSSHIKH UCHEBNYKH ZAVEDENII. IZVESTIIA. TSVETNAYA METALLURGIIA 4:122–131, 1962. (In Russian)

The Moscow Institute of Fine Chemical Technology has conducted an experimental study to find more economical and simpler methods of consolidating Nb powders obtained by electrolysis of Nb-containing media, especially fused salts. It was shown that high-quality metallic powders of Nb and of Nb-Ta alloys with a component ratio up to pure Ta can be obtained by the electrolysis Nb_2O_5 dissolved in potassium fluotantalate or another complex fluoride with chlorides or fluorides of alkali metals. The Nb powder is double refined in an argon atmosphere and in a vacuum at ~1000°C. Prior to compacting, a calculated excess of oxygen (in the form of oxides) is added to the charge to oxidize carbon and other impurities. A pressure of 3.0 to 4.0 t/cm is adequate to produce sufficiently strong green compacts. Sintering is conducted in a vacuum at a pressure of 1.10^{-3} to 5.10^{-3} mm Hg, which is decreased to 10^{-4}-10^{-5} mm Hg toward the end of the process. The temperature is raised at a rate of about 15°C/min. The optimum final sintering temperature and duration were found to be 2300°C (max) and 4 hrs (min). After forging with 30% reduction the sintered ingots are vacuum annealed at 2300C for 1 to 2 hrs. The metal thus produced has a low impurity content and is readily rolled into strips 0.1 mm thick or less. By this method, a high-purity metal containing < 0.02% C, < 0.02% O_2, < 0.02% Ti, < 0.001% Si, and < 0.01% N_2, can be obtained with a single sintering, as compared with 3.50% C, 5.00% O_2, 0.85% Fe, 0.35% Ni, 0.10% Ti, 0.50% Si, and 0.02% N_2 in the initial powder.

10. Andersson, L. H. and R. Kiessling
Investigations on the binary systems of boron with chromium, columbium, nickel and thorium, including a discussion of the phase "TiB" in the titanium-boron system. ACTA CHEMICA SCANDINAVICA 4:160-164, 1950.

Crystal structure data are given ...

11. Aronsson, B.
The crystal structure of Mo_5Si_3 and W_5Si_3. ACTA CHEMICA SCANDINAVICA 9(7):1107-1110. 1955.

Powder photographs of the above silicides show the elementary cell of the Mo_5Si_3 phase to be body centered tetragonal with a = 9.62 A and c = 4.90 A the density 8.2. When molybdenum and silicon were sintered in a carbon-tube furnace at about 1800°C almost equal amounts of a Mo-Si-C phase and the silicide phase were obtained. Data are tabluated and graphs shown.

12. Babadzhan, A. A.
Determination of estimated rate of oxidation of MoS_2 as a function of temperature. AKADEMIIA NAUK SSSR. URAL'SKII FILIAL. INSTITUT METALLURGII. TRUDY 1:44-46, 1957. (In Russian)

Using a carbon-containing concentrate of molybdenite ore, and ignoring the influence of the grain size, it was found that oxidation becomes noticably at 360° - 400°C and is intensive at 400° - 500°C. The rate of oxidation of MoS_2 is close to that of iron sulfide and thus considerably higher than that of zinc and lead sulfides.

13. Bargainnier, R. B., et al.
DEVELOPMENT AND PRODUCTION OF IMPROVED MOLYBDENUM SHEET BY POWDER METALLURGY TECHNIQUES.
Sylvania Electric Products, Inc., Towanda, Pa.
Interim rept. no. 13, 1 Dec 1961–31 Jan 1962.
30 Mar 1962. 79p. (Contract NOa(s) 60-6018-c).
ASTIA AD-274 611.

This report includes: A STUDY OF THE BASIC FACTORS INVOLVED IN STRENGTHENING POWDER METALLURGY No-Ti-V and Mo-Ti-N ALLOY SHEET, by S. Friedman, W. Pollack, and C. D. Dickinson.

Strengthening in powder metallurgy Mo-Ti-C probably involves the solution of Ti and C during sintering followed by the formation of precipitates of TiC during fabrication. Control of fabrication temperatures by the use of an in-process solution treatment or both may be necessary to obtain optimum properties. O and N contamination during sintering is deterimental since it decreases the amount of T that goes into the solution by forming massive, stable titanium oxides and nitrides. The formation of massive Mo_2C particles at sintering temperatures above 2000° prevents a straightforward correlation of C content and strength. Strengthening in powder metallurgy Mo-Ti-N probably involves the formation of a fine dispersion of TiN by internal nitridization N additions to Mo-Ti significantly raise the recrystallization temperature. However, its effect on high-temperature strength is less than that of C. O appears to have a detrimental effect on the recrystallization temperature of Mo-Ti-N.

14. Bargainnier, R. B.
DEVELOPMENT AND PRODUCTION OF IMPROVED MOLYBDENUM SHEET BY POWDER METALLURGY TECHNIQUES. Sylvania Electric Products, Inc., Towanda, Pa. Interim rept. no. 12, 1 Oct–30 Nov 1961. 5 Feb 1962. 12p. (Contract NOa(s) 60-6018-c). ASTIA AD-272 778.

A powder-metallurgy Mo-Ti-C alloy with high-temperature properties superior to those of arc-cast Mo-O. 5 Ti-C was developed. Optimum properties were obtained by a process which involved sintering in a reducing atmosphere at about 2150°C. The mechanism which produces these outstanding properties remains to be determined. Important process variables include density of sintered billet, reactive metal and

and residual carbon content, composition of sintering atmosphere, and sintering temperature. The importance of sintering atmosphere was confirmed by test runs using vacuum sintering.

15. Bas, E. B., W. Epprecht and L. Preuss
Electron emission microscopic study of the carburization of molybdenum from a gaseous phase. ZEITSCHRIFT FUER METALLKUNDE 48(9):516–522, Sep 1957. (In German)

Transformations taking place in metallic molybdenum during carburization from a gaseous phase (carbon dioxide, vaporized benezene or butane) at low pressure were photographed in a two-stage electron emission microscope at successive stages of the process, at various temperatures, and after different thermal treatments of the product. The molybdenum preparations used were either polycrystalline or monocrystalline. The photographs show the deposition of carbon on hot molybdenum, diffusion of carbon into molybdenum, and the formation of crystals of Mo_2C within molybdenum saturated with carbon.

16. Beck, W.
Electrode potential and corrosion behavior of some borides of molybdenum and zirconimum PLANSEEBERICHTE FUER PULVER-METALLURGIE 9(1/2):96–108, Apr 1961. (In German)

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. Beta-MoB is more resistant than alpha-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.

17. Beidler, E. A., C. F. Powell and I. E. Campbell
The formation of molybdenum disilicide coatings on molybdenum. ELECTROCHEMICAL SOCIETY JOURNAL 98:21–25, Jan 1951.

Molybdenum can be rendered highly resistant to oxidation by treatment with hydrogen silicon tetrachloride atmosphere at 1000 to 1800°C so as to produce molybdenum disilicide coating at its surface; coatings 0.025 mm thick have protected base metal for over 4000 hours in air at 1000°C, and for over 30 hours at 1700°C; siliconizing of molybdenum stated to be very effective way of imparting corrosion resistance of silica glass to this highly refractory metal.

18. Belikov, A. M. and Ya. S. Umanskii
The characteristic temperatures of the heat vibration and the thermal expansion of some high metallic phases. NAUCHNYE DOKLADY VYSSHEI SNKOLY, METALLURGIIA No. 1:192–197, 1958. (In Russian)

Inclusion phases in the alloys of molybdenum with niobium and titanium were investigated. From the investigation of the carbides TiC, ZrC, NbC, and WC it may be seen that these compounds have the same combining power as metals. Data are given on the combining powers and coefficients of linear expansion of the listed metals and their metallic phases such as NbN, ZrN, Ta_2N, Tic, Mo_2C, and NbC. In the investigation of the carbides of molybdenum and tungsten as well as of all the nitrides it was found that the constant of the heat vibrations changes only little as compared to pure iron. It is assumed that in all phases the electrons of carbon actively effect the structure of the d-orbits of the metals of the fourth and fifth group. The electric conductivity of the carbides of molybdenum and tungsten is lower than the electric conductivity of pure molybdenum and tungsten metals.

19. Bender, S. L., et al.
THERMODYNAMICS OF CERTAIN REFRACTORY COMPOUNDS. VOL. I. LITERATURE SEARCH, COMPUTATIONS, AND PRELIMINARY STUDIES. Research and Advanced Development Div., Avco Corp., Wilmington, Mass. Technical Documentary Report, 1 May 1960—30 Apr 1961. May 1962. 429p. (Contract AF 33(616)-7327). (ASD-TR-61-260, Pt. 1, V. 1) NASA N62-14349.

A theoretical and experimental study over the temperature range from 298.15° to 6000°C was made of the thermodynamics oxides, borides, carbides, and nitrides of the metals in groups IVB, VB, VIB, and VIIB of the Periodic Chart in addition to silicon, boron, scandium, beryllium, magnesium, calcium, strontium and osmium.

20. Bender, S. L., et al.
THERMODYNAMICS OF CERTAIN REFRACTORY COMPOUNDS. VOL. II. BIBLIOGRAPHY OF CODED REFERENCES. Research and Advanced Development Div., Avco Corp., Wilmington, Mass. Final Technical Documentary Report, 1 May 1960—30 Apr 1961. Rept. no. RAD-TR-61-12, Pt. 1, Vol. 2. May 1962. 300p. [Contract AF 33(616)-7327] (ASD-TR-61-260, Pt. 1, Vol. 2). NASA N62-14827.

Theoretical and experimental studies were undertaken of the thermodynamics of certain refractory compounds from 298.15° to 6000°K. The list of compounds included the oxides, borides, carbides and nitrides of the metals in groups IVB, VB, VIB, and VIIB of the periodic chart in addition to those of silicon, scandium, beryllium, magnesium, calcium, strontium, and osmium. Tables of ideal gas thermodynamic functions of all of the above elements were either prepared or brought up to date. Reviews and critical analyses of the available data were completed on the oxide systems of Be, Ca, Cr, Mg, Mo, Sr, Ti, and W, the borides of Ti, and the monocarbide of Ti. Sixty-one tables of thermodynamic functions, invarious degrees of completion, were prepared on the important chemical species of the above systems. A comprehensive review of the literature was made for the existing theoretical background needed in the interpretation of high-temperature C_p data and for the improvement of methods of estimating missing data.

21. Berkowitz-Mattuck, J. B.
Oxidation kinetics in the molybdenum-silicon systems in the 1000° –2000°C temperature range. In INTERNATIONAL CONGRESS OF PURE AND APPLIED 18TH, MONTRÉAL, 1961. ABSTRACTS OF SCIENTIFIC PAPERS. Toronto, Canada, Univ. of Toronto Press, 1961. p.118.

The oxidation of molybdenum and $MoSi_2$ was studied in the 800° –1700°C range at oxygen partial pressures of 10^{-2}–10^{-3} atm. Molybdenum oxidizes linearly at the lower pressures, but at 1226°C and the higher pressures a MoO_2 film forms and ruptures. At 1660°C and the higher pressures, $MoSi_2$ oxidizes rapidly at first but more slowly with time due to formation of a silica diffusion barrier.

22. Bigeon, J.
Molybdenum and its applications in chemical technology. INDUSTRIE CHIMIQUE 46(503): 185–193, Jun 1959. (In French)

A review of applications of inorganic and organic compounds of molybdenum contains data on metallurgical uses of molybdenum disilicide, carbides and borides.

23. Blanchard, R. and J. Cueilleron
Study of the tungsten-silicon melting diagram. (Etude du Diagramme de Fusion Tungstène-Silicium.) ACADEMIE DES SCIENCES. COMPTES RENDUS 244:1782–1785, 25 Mar 1957. (In French)

Diagram established by determination of melting points, chemical analysis, metallographic and x-ray examination of a very large number of tungsten-silicon alloys.

24. Blum, A.
Furnaces, supports, and atmospheres for the sintering of some borides, nitrides, and silicides. PLANSEEBERICHTE FUER PULVERMETALLURGIE 10:72–77, 1962. (In English)

...$MoSi_2$ and WSi_2 react reading with C in both solid and gaseous form. Sintering of $MoSi_2$ and WSi_2 must be carried out in furnaces having SiC resistors and supports of Al_2O_3 or ZrO_2. A suitable furnace atmosphere is predried H, He, or Ar.

25. Booss, H. J.
The stability of ceramics with respect to gases. II. Revision of known data. METALL 16:668–671, Jul 1962. (In German)

Data published since 1956 on the stability of metallic oxides and carbides with respect to gases are tabulated. The metals reviewed are Si, Ti, Zr, Th, Ta, Cr, Mo, and W. The decarburization of WC, the reduction of ThO_2 by W_2C, reduction of WO_3 , and the precipitation of Ti from the gaseous phase are also discussed.

26. Brame, E. G., Jr., J. L. Margrave and V. W. Meloche
Infra-red spectra of inorganic solids – II. Oxides, nitrides, carbides and borides. JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY 5:48–52, 1957.

A series of oxide, nitride, carbide, and boride samples were scanned in the rock-salt region of the infra-red. The KBr disk technique was employed for the examination, The spectra showed certain characteristic bands for each of the sets of compounds studied. Changes in band position for the major bands were noted with changes in mass for a number of the samples.

27. Brauer, G. and R. Lesser
Carbon nitride of niobium. ZEITSCHRIFT FUER METALLKUNDE 50:487–492, Aug 1959. (In German)

Phases and phase boundaries in the ternary system niobium-niobium carbide-niobium nitride are determined by chemical and x-ray methods. Between 1250 and 1450, the four phases α, β, τ, δ were observed. The phase diagram is discussed.

28. Brauer, G. and R. Lesser
Karbidphasen des Niobs. ZEITSCHRIFT FUER METALLKUNDE 50:8–10, 1959. (In German)

Carbide phases of columbium; formulas, lattice structures, and lattice constants obtained by chemical and x-ray analysis of columbium/columbium carbide system at 1800–2000°C; in addition to alpha, beta and delta phases, zeta phase was observed between beta and delta; experimental details will be published in a later report on investigation of Cb-CbC-CbN system.

29. Brauer, G., H. Renner and J. Wernet
Niobium carbides. ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE 277:249–257, Dec 1954. (In German)

From iobium dioxide, niobium carbide was prepared with the composition between $NbC_{1.00}$ and Nb and the existing phase relation investigated. There exists three phases in the system Nb-C: tje monocarbide phase of $NbC_{0.50}$ to $NbC_{0.72}$ homogeneous with rock salt lattice, the subcarbide phase of $NbC_{0.50}$ to $NbC_{0.72}$ homogeneous with hexagonal dense dense spherical packing of the Nb atom, and the Nb metal phase with a dissolving power for C with the structure $NbC_{0.02}$.

30. Brewer, L., et al.
High-melting silicides. AMERICAN CERAMIC SOCIETY. JOURNAL 33(10):291–294, 1950.

The tantalum-silicon, molybdenum-silicon, and tungsten-silicon systems have been investigated for solid phase stable above 1900°K. Three new tantalum silicide phases, two new molybdenum silicide phases, and one new tungsten silicide phase are reported beside the MSi_2 phases previously known. The crystal structure of Mo_3Si is described. Lower limits for eutectic temperatures are given for these three systems, and the relative stabilities of metallic silicides of groups III through VII are discussed.

31. Brewer, L. and O. Krikorian
REACTIONS OF THE REFRACTORY SILICIDES
WITH CARBON AND WITH NITROGEN.
California Univ. Radiation Laboratory, Berkeley.
UCRL rept. no. 2544, 29 Apr 1954. 60p.
(Contract W-7405-eng-48b).

The silicides of Ti, Zr, Ce, and Nb were investigated to determine the phases present at temperatures around 2000°K. The reactions of silicides of Ti, Zr, Ce, Nb, Ta, Mo, and W with carbon were studied at these temperatures. A limited amount of work was done on the reactions of some of the silicides of nitrogen. The data have been used to establish ternary phase diagrams for the systems and to obtain upper and lower limits for the heats of formation of the silicides.

32. Brewer, L., et al.
A study of the refractory borides. AMERICAN
CERAMIC SOCIETY. JOURNAL 34:173−179, 1951.

The phases of the binary systems of boron with ... Nb ... Mo, W ... were determined by x-ray examination of samples prepared by heating various mixtures of boron and the respective metal to elevated temperatures in the atmosphere of argon. Data were obtained on the sintering behavior and stability at high temperatures of many of the phases. Several phases have promising refractory properties for use under inert or reducing conditions.

33. Brewer, R. C.
Cemented borides as tool materials.
ENGINEERS' DIGEST 20(5):205−208.
May 1959.

Molybdenum and titanium borides can be developed for cutting tool purposes, but much development work remains; e.g., optimum tool geometries must be determined. A binder is necessary to confer mechanical strenght. A liquid phase acting as a binder may be produced from a eutectic of two borides in some cases; e.g., Mo_2B-Mo_2Nib_2. Intermediate compound bonding occurs in some types of cermets. General data are given for ball-milling, compacting and sintering the powders. Boride tools do not have serious cratering but require about 10 percent greater power consumption. Graphs are shown.

34. Butorina, L. N.
An electron diffraction study of the tungsten carbide WC. SOVIET PHYSICS – CRYSTALOGRAPHY 5(2):216–220. Sep–Oct 1960.

The crystal structure of the carbide WC has been studied by the method of sections of F^2 and F series based on electron diffraction patterns with electron scattering kinematic and intermediate character.

35. Campbell, I. E., B. W. Gonser and C. F. Powell
HIGHLY REFRACTORY BODIES. (Assigned to Fansteel Metallurgical Corp., Chicago, Ill.) Canadian Patent 535,806. 15 Jan 1957.

A refractory molybdenum body is produced with an outer layer of $MoSi_2$; the body is oxidation-resistant above 1000°C. A graph is shown.

36. Chelius, J.
Major refractory metals. INDUSTRIAL RESEARCH 4(8):36–39, Sep 1962.

Review of the physical properties of W, Cb, Ta and Mo including solubility of oxygen, hydrogen, and nitrogen, corrosion resistance, high temperature strength and thermal conductivity.

37. Chrétien, A. and J. Helgorsky
On new boride compositions of molybdenum and tungsten, MoB and WB . ACADEMIE DES SCIENCES. COMPTES RENDUS 252(5):742–744, 30 Jan 1961. (In French)

The new compound MoB_4 was readily prepared by direct combination of the elements at elevated temperatures. Mo_2B_5 is also formed, reacting in turn with additional boron to produce MoB_4. The yield of the latter relative to Mo_2B_5 is found to increase with increasing temperature, with an optimum at 1400°C. MoB_4 dissociates at 1600°C to give the lower borides Mo_2B_5 and MoB. The MoB_4 crystal is tetragonal, with a = 6.34 Å and c = 4.50 Å. Data are tabulated.

38. Clougherty, E. V. and K. H. Lothrop
Monocarbide phases of molybdenum.
JOURNAL OF METALS 14:21, Sep 1962.

High-pressure, high-temperature synthesis experiments in the Mo-C system have revealed evidence for a cubic phase, α-MoC, a complex hexagonal phase, η-MoC, and a simple hexagonal phase, γ-Mo. Available information in the literature was combined with the results of the present investigation of the variation of pressure, temperature, and stoichiometry (to provide data for a thermo-dynamic analysis) on the relative stability of the so-called mono-carbide phases. All the monocarbide phases are metastable at ambient temperature and pressure. Microstructural and micro-hardness data for all phases are presented. This work was sponsored by the Metals and Ceramics Laboratory Materials Central, Aeronautical Systems Div., U. S. Air Force.

39. Clougherty, E. V., K. H Lothrop and J. A. Kafalas
A new phase formed by high-pressure treatment: face-centered cubic molybdenum monocarbide.
NATURE 191(4794):1194, 16 Sep 1961.

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

40. Dolloff, R. T. and R. V. Sara
RESEARCH STUDY TO DETERMINE THE PHASE EQUILIBRIUM RELATIONS OF SELECTED METAL CARBIDES AT HIGH TEMPERATURES.
National Carbon Co., Cleveland, Ohio. May 1961.
25p. [Contract AF 33(616)-6286] (WADD-TR-60-143, Pt. II). NASA N62-12524.

The work here reported is the result of an investigation of phase equilibria in the binary system, tungsten-carbon. A tentative phase diagram is presented which differs significantly from the one proposed by Sykes in 1930 and which is generally accepted today. The data were obtained by high-temperature differential thermal analysis and classical quenching procedures, both supplemented by metallographic, x-ray, and chemical techiniques. Results for the tungsten-carbon binary system indicate a eutectic between W and W_2C at 2735°C, and a eutectic between W_5C_3 and C at 2765°C. The W_2C lattice accommodates 72 and 74 atomic percent W at 2475° and 2735°C, respectively. Carbon solubility is evident only at 2540°C, the eutectoid temperature. A new phase, W_5C_3, has been discovered which is stable only above 2540°C. WC decomposes at 2730°C into W_5C_3 and C.

41. Elliott, R. P.
The Cb-C system. AMERICAN SOCIETY
FOR METALS. TRANSACTIONS 53:13–28, 1961.

The columbium-carbon system has been determined by x-ray and metallographic examination of sintered and arc-cast alloys. Two carbides exist: hexagonal Cb_2C with a limited range of homogeneity, and cubic CbC with a solubility range from 8.25 to 10.25 wt %C. Dilute alloys freeze by eutectic reaction at 2230°C. The solubility of carbon in columbium is 0.80 at the eutectic temperature, but this decreases rapidly with temperature. Metallographic evidence indicates a peritectic reaction between melt, Cb_2C, and CbC; alloys richer in carbon than CbC freeze by eutectic reaction.

42. Elliott, R. P.
NIOBIUM PHASE DIAGRAMS – MANUSCRIPT
REPORT ON NIOBIUM CARBON SYSTEM.
Armour Research Foundation, Chicago, Ill.
Rept. no. ARF-2120-4. 6 May 1959. 29p.
(Contract At(11-1)-515). (Available from
Office of Technical Services, Washington 25,
D. C.)

The niobium-carbon system has been determined by x-ray and metallographic examination of sintered and arc-cast alloys. Two carbides exist: hexagonal Nb_2C with a limited range of homogeneity, and cubic NbC with a solubility range from 8.25 to 10.25 weight percent carbon. Dilute alloys freeze by eutectic reaction at 2230°C. The solubility of carbon in niobium is 0.80 at the eutectic temperature, but this decreases rapidly with temperature. Metallographic evidence indicates a peritectic reaction between melt, Nb_2C, and NbC; alloys richer in carbon than NbC freeze by eutectic reaction.

43. Elliott, R. P. and C. P. Kempter
Thermal expansion of some transition metal carbides. JOURNAL OF PHYSICAL CHEMISTRY 62:630−631, May 1958.

The physical and chemical properties of some transition metal carbides were determined, and it is concluded that for a given temperature range, the linear thermal expansion of titanium carbide, zirconium carbide, niobium carbide, and tantalum carbide decreases with increasing weight, and for a given temperature range the melting point is almost constant.

44. Feisel, D. H.
Some metallurgical observations of the transition metal borides. JOURNAL OF METALS 14:21, Sep 1962.

The unusual combination of properties possessed by the transition metal diborides and the borides Mo B and W B make them potentially useful in high-temperature structural applications. These properties include high melting point, high strength and hardness, a resistance to oxidation, chemical stability at high temperatures, and high thermal and electrical conductivity. Since these compounds have many properties typical of metals, observations were made on their response to various metallurgical handling and processing procedures.

Commercially available powders of the compounds were consolidated by arc melting and by sintering. Each of the borides and many binary combinations of the borides were successfully arc melted as 10 g buttons. Specimens with no cracks were produced from HfB_2, ZrB_2, CrB_2, Mo_2B_5, and W_2B_5. Decomposition during melting was indicated for TaB_2, CbB_2, VB_2, and especially CrB_2. Sintering of powder compacts was done in vacuum at temperatures ranging from 1600° to 2500°C depending on the compound involved; specimens of about 80 percent of theoretical density were produced. A ZrB_2 compact: (1) reacted with a graphite container at 2500°C to produce a liquid phase; (2) reacted extensively with tantalum at 2300°C, and (3) did not react with tungsten at 2300°C.

Because of the high hardness and brittle nature of the compounds, special shaping methods were investigated. Consolidated specimens produced by arc melting or sintering were successfully shaped by diamond wheel grinding, by diamond saw cutting, and by spark machining.

Information was obtained on metallography, X-ray examination, hardness, density, and alloying behavior of consolidated specimens. Results of an examination of the ZrB_2-HfB_2 system are reported in detail as an example of typical data. Complete solid solubility was indicated in this system. The lattice parameters, hardness, density, and microstructure are given as a function of composition.

45. Few, W. E. and G. K. Manning
Solubility of carbon and oxygen in molybdenum.
JOURNAL OF METALS 4:271–274, Mar 1952.

It has been known for some time that both intergranular carbide and intergranular oxide phases cause brittleness in Mo. Hence experiments were made on their solubility at temperatures up to 4000° F., following heat treatments in various atmospheres. Results are tabulated, charted, and illustrated by photomicrographs.

46. Few, W. E. and G. K. Manning
Solubility of carbon and oxygen in molybdenum.
JOURNAL OF METALS 5:746–747, Mar 1953.

A discussion.

47. Fitzer, E. and J. Schwab
The chemical stability of molybdenum disilicide as a construction material. (<u>Die chemische Beständigkeit von Molybdaendisilized als Werkstoff</u>)
METALL 9(23/24):1062–1066, Dec 1955.
(In German)

The chemical stability of $MoSi_2$ samples, cold pressed and sintered at 1750°C and having a pore volume of about 10%, was tested against metallic melts, gases at high temperatures and aqueous acid solutions. In general, $MoSi_2$ is resistant against such fused metals as do not form intermetallic compounds with silicon; e.g., lead and tin. Aluminum destroys $MoSi_2$ by the formation of molybdenum aluminides. Copper, iron, chromium and platinum also react with $MoSi_2$. Particularly important is the stability of $MoSi_2$ against oxygen at very high temperatures; it is also resistant to sulfur-containing gases at 1000°C, but not against chlorine. Aqueous mineral acid solutions do not, or only very slightly, attack $MoSi_2$.

48. Fitzer, E.
CONSTRUCTION PARTS CONTAINING MOLYBDENUM DISILICIDE FOR HIGH TEMPERATUE USE, PARTICULARLY ELECTRIC HEATING ELEMENTS.
(Assigned to Siemens-Planiawerke Aktiengesellschaft fuer Kohlefabrikate, Meitingen, near Augsberg, Germany).
German Patent 1,080,313. 21 Apr 1960.

$MoSi_2$ construction parts intended for high temperature use are coated, in those portions which are subjected continuously to temperatures between 300° –700°C, with a protective gas-tight layer, either produced from the $MoSi_2$ itself, an electrolytically produced chromium layer, or a sintered $TiSi_2$ layer.

49. Fitzer, E. and O. Rubisch
Heating conductors of molybdenum disilicide for temperatures up to 1700°C. INTERCERAM 7:39–40, 1958.

The ignition-resistant $MoSi_2$ has a smaller specific electrical resistance than many materials used as heating conductors, and requires special shaping or transformers when thus used. Because of the high fusion point of $MoSi_2$, shaped pieces are made by powder metallurgy techniques (vertical press, extrusion press or slip-casting). The U-shape is best because it is easier to insulate than the rod shape. The $MoSi_2$ heating conductors permit calcining up to 1650°C by indirect electrical resistance heating in an oxidizing atmosphere. Concentrated sulfur-containing gases or those with fluorides and chlorides are destructive. Photographs and a graph of comparative electrical properties are shown.

50. Fitzer, E., O. Rubisch and F. Selka
Heating elements from molybdenum disilicide.
ELEKTROWAERME 16(7):253–259, Jul 1958.
(In German)

A review of $MoSi_2$ heating elements covers the electrical characteristics of the material and of elements produced therefrom, the various types of elements produced from $MoSi_2$, and the most suitable methods for their installation and use.

51. Fitzer, E. and O. Rubisch
Molybdenum disilicide as a heating element material. ELEKTROWAERME 16(5):163–169, May 1958. (In German)

A survey based on the published literature, covers the properties of the Mo-Si system, and, in particular, the physical, chemical and mechanical properties of $MoSi_2$. When heated above 1300°C in air, $MoSi_2$ forms a strongly adherent, pore-free SiO_2 layer which is scale resistant up to about 1700°C. This property renders the disilicide useful for electric heating elements in high temperature applications and in oxidizing atmospheres.

52. Fitzer, E.
Molybdenum disilicide as a refractory material. (Molybdaen disilizid als Hochtemperaturewerkstoff) PLANSEE SEMINAR "DE RE METALLICA" 2:56–79, 1956. (In German)

The high resistance of $MoSi_2$ against oxidation at high temperatures (up to 1700°C) is described and attributed to the formation of protective vitreous coatings in which free SiO_2 and solutions of molybdenum oxides in SiO_2 play the main part. A surprising fact is the exceedingly low resistance to oxidation in the interval 450° –600°C, when the sample crumbles into a powder of oxidation products. The impact strength of molybdenum disilicide materials is low; preliminary tests with various metallic and non-metallic binding substances point to possibilities of correcting this defect. A special pressure-free method of molding sintered $MoSi_2$ is suggested.

53. Fitzer, E.
PROCEDURE FOR THE PRODUCTION OF EASILY GRINDABIE MOLYBDENUM-SILICON HARD ALLOYS. (Assigned to Siemens-Planiawerke Aktiengesellschaft fuer Kohlefabrikate, Meitingen bei Augsburg, Germany). German Patent Application 40b, 2. S 51006. 21 Aug 1958. (In German)

A procedure for the production of easily grindable Mo-Si hard alloys for the pulverized components is described. The reaction mixture is heated from 1100°C to 1400° –1500°C in a time no longer than six minutes, and is kept, during the completion of the spontaneous exothermic reaction, at a temperature between 1500° and 1800°C. The reaction product is then allowed to cool.

54. Fitzer, E.
Production of materials resistant to high temperature by siliconizing of W and Mo.
BERG- UND HUTTENMANNISCH MONATSHEFTE DER MONTANISTISHEN HOCHSCHULE IN LEOBEN 97:81–90, 1952. (In German)

The siliconizing of W and Mo wire and their properties. Production of Mo-Si alloys by means of powder metallurgy. Practical applications. Tables, micrographs, diagrams, and graphs.

55. Fitzer, E.
SINTERED PRODUCT, PARTICULARLY HEATING ELEMENT, OF MOLYBDENUM SILICIDE. (Assigned to Siemens-Planiawereke Aktiengesellschaft fuer Kohlefabrikate, Meitingen bei Augsburg, Germany). German Patent Application 40b, 17. S 52269. 16 Oct 1958.

Sintered molybdenum silicide heating elements are described whose various parts are exposed simultaneously to temperatures above 1600° C and between 300° –700° C, respectively. The molybdenum silicide in the high-temperature part contains 3-35.5 wt-% Si, while that in the part exposed to temperatures in the 300° –700° C range contains 36–37 wt.% Si.

56. Fitzer, E.
WORKPIECES FOR HIGH TEMPERATURE OPERATION AND METHOD OF MAKING THEM. (Assigned to Siemens-Planiawerke Aktiengesellschaft fuer Kohlefabrikate, Meitingen, near Augsberg, Germany). U.S. Patent 2,902,392. 1 Sep 1959.

A heating rod of $MoSi_2$ for an electric resistance furnace is exposed to an oxidizing atmosphere and 1000° –1700° C at the hot end. Oxidation resistance is provided at the hot end by the SiO_2 coating which forms, and at the terminal end (300° –700° C) by coating with chromium, $TiSi_2$ or silver-silicon alloy.

57. Freundlich, W., F. A. Josien and A. Erb
Reductions and solid-state exchange reactions with tungsten monocarbide. SOCIÉTÉ CHIMIQUE DE FRANCE. BULLETIN 2:281–283. 1960.

The reductions of Fe_2O_3, TiO_2, B_2O_3, and SiO_2 by WC were studied by following the loss of weight caused by loss of CO, by radiocrystallographic studies, and by chemical analysis. The initial reduction by WC gives CO, W_2C, and the element present in the initial oxide. The W_2C also participates in the reduction, but to a degree dependent on the oxide and on the conditions. The final products of the reductions are mixtures of W, W_2C, and compounds formed by reaction of the free element with WC and W_2C. These include FeWC, TiC, W_2B, and a mixture of W silicides, for Fe_2O_3, TiO_2, B_2O_3, and SiO_2, respectively.

58. Fries, R. J. and C. P. Kempter
Crystallographic data: dimolybdenum carbide.
ANALYTICAL CHEMISTRY 32:1898, 1960.

59. Fries, R. J.
Vaporization behavior of niobium carbide.
JOURNAL OF CHEMICAL PHYSICS 37:320–327, 15 Jul 1962.

The vaporization behavior of niobium carbide was studied over the temperature range from 2260 to 2940°K utilizing the Langmuir method. NbC was observed to lose carbon preferentially down to a composition of $NbC_{0.75}$, at which composition the vaporization proceeds congruently at a temperature of 2940°K. The vapor pressure of carbon above nearly stoichiometric NbC could be represented by the equation log P (atm) = 5.296 5.296 - $3.276 \times 10^4/T$ with a corresponding second law heat of vaporization of 150 kcal/mole of C vaporized. However, third law calculations and heat of formation data indicate a ΔH^0_{298} of from 180 to 189 kcal/mole. Several possible explanations of this disagreement are discussed. The total rate of evaporation from NbC_x was found to increase by a factor of two as the value of x decreased from 0.97 to 0.80. Finally, a semi-quantitative evaluation of the diffusion constant of C in NbC was made, resulting in a value of $D \cong 8 \times 10^{-7}$ cm^2/sec at 2940°K.

60. Fujishiro, S.
On molybdenum silicides. SCIENCE OF POWDER 4(1):18–24, 1956. (In Japanese)

A review on metal silicides, mainly on $MoSi_2$, covers published information on preparation methods, anti-oxidative property, mechanical properties, resistance to chemical corrosion, structure, hardness and industrial potentialities.

61. Geach, G. A. and F. O. Jones
Interactions in mixtures of hard materials at very high temperatures. In SECOND PLANSEE SEMINAR. PROCEEDINGS. Reutte/Tyrol, Austria, Metallwerk Plansee, 1955 and New York, Pergamon, 1960. p.80–91.

Solid state reactions of refractory materials at high temperatures were studied from the powder metallurgy point of view. TiC was mixed with proportions of borides of titanium, zirconium and molybdenum and with $MoSi_2$; the evenness of melting points suggested that no compounds were formed. TaC reacts with $MoSi_2$. $MoSi_2$ and Mo_2B are generally sensitive to other refractory compounds but do not interact. Much data are tabulated and micrographs are shown.

62. Gilles, P. W. and B. D. Pollock
The molybdenum-boron system. JOURNAL OF METALS 5:1537–1539, Nov 1953.

Studies in the phase diagram at high temperatures. Diagram, table.

63. Gilles, P. W. and B. D. Pollock
THE THERMODYNAMIC PROPERTIES AND EQUILIBRIUM PRESSURES IN THE MOLYBDENUM-BORON SYSTEM. Kansas Univ., Lawrence. Rept. no. AECU-2894. 1953. 29p. [Contract AT(11-1)-83].

In the molybdenum-boron system there are four compounds, or homogeneity ranges, and six crystal stuctures, Mo_2B, Mo_3B_2, alpha $MoB_{1\pm x}$, beta MoB_{1+x}, alpha $MoB_{2.25\pm y}$, and beta $MoB_{2.25\pm y}$. From a study of the vapor pressures of these compounds and their mixtures by the Langmuir technique, their stabilities, heats of formation, and the partial pressures of the elements in equilibrium with the solid phases were determined. Values of ΔH^0_{298}, the heats of formation of the compounds, were calculated from the vapor pressures on the assumption that ΔS and ΔC_p for solid reactions are both zero. These values, with the heats of sublimation of Mo and B of ΔH^0_{298} = 155.94 and 140.9, the published free energy functions of Mo and B, and the above assumption, may be used to calculate the high-temperature behavior of this system. The partial pressures of the monatomic elements at 2200°K in equilibrium with one or two solid phases having the over-all composition indicated are given. It is shown that solid compositions having more B than Mo_2B rapidly lose B preferentially. Furthermore, in Langmuir or Knudsen experiments, Mo_2B loses B more rapidly than one-half the rate of Mo loss, so that in such experiments Mo(s) appears, and there is no constant subliming composition. In a closed system, however, Mo_2B would evaporate to give a gas having the same composition. It is demonstrated that there are no gaseous molecules of any importance in the Mo-B system at high temperature.

64. Gladyshevskii, E. I. and Kuz'ma, Yu. B.
Crystal structure of ternary phases in the systems Mo (W) - Fe (Co, Ni) - Si.
JOURNAL OF STRUCTURAL CHEMISTRY
1(1):57–62, May–Jun 1960.

The existence of the ternary phases MoFeSi, MoCoSi, MoNiSi, WFeSi, WCoSi, and WNiSi has been established and their crystal structures determined.

65. Glaser, F. W.
Contribution to the metal-carbon-boron systems.
AIME. TRANSACTIONS 194:391–396, 1952.

Metal-carbon-boron powder mixtures were hot pressed and the resulting specimens studied by x-ray diffraction. It was found that, regardless of the starting composition, a metal boride phase was always the major component in these samples. Two new phases of the system Ti-B were found: Ti_2B and Ti_2B_5. The existence of a controversial face-centered cubic phase of formula TiB was confirmed. Electrical resistivities were measured for various boride phases. Tabular data.

66. Gleiser, M. and J. Chipman
Free energy of formation of molybdenum oxide and carbide. JOURNAL OF PHYSICAL CHEMISTRY 66(8):1539–1540, Aug 1962.

Determination of equilibrium pressure, calorimetric entropy and energy of formation of Mo, MoO_2 and Mo_2C at 926–1068°C.

67. Glushko, P. I., V. I. Dorokhov, and E. P. Nechiporenko
The problem of the oxidation kinetics of molybdenum disilicide. FIZIKA METALLOV I METALLOVEDENIE 13(6):923–924, Jun 1962. (In Russian)

Measuring the oxidation of $MoSi_2$ as a function of time at several temperatures between 900° and 1200°C showed that on log-log scales the function is expressed by straight lines. Furthermore, the coefficient of the rate of oxidation characterizing each of the above lines is an exponential function of the temperature. From these data, the activation energy of the process is found to be 82 ± 2.5 kcal/mol.

68. Goldschmidt, H. G.
The phase constitutions of some niobium-bearing and associated transition metal systems. JOURNAL OF THE LESS-COMMON METALS 2(2-4):138–153, Apr–Aug 1960.

A constitutional survey of niobium-base ternary systems cites work on previously determined systems, i.e., NB-Mo-Ta, Nb-Mo-W, Nb-Mo-Ti, Nb-Zr-Ta and numerous systems involving Si, B, C, and N, discusses present work on Nb-Mo-Cr, and speculates on numerous others. The occurrence of miscibility bays is stressed, since their evolution in solid solutions permits age-hardening by sensitive compositional and heat treatment control. Evolving bays are associated with incipient precipitation of b.c.c. isomorphs or Laves or 6 phases.

69. Gorelik, S. S., et al.
Recrystallization of It, Zr, and Mo borides and Ti and W carbides. VYSSHIKH UCHEBNYKH ZAVEDENII. IZVESTIIA. TSVETNAYA METALLURGIIA 4:143−148, 1962. (In Russian)

The recrystallization of TiB_2 (66.7% Ti, 30.2% B, 0.87% C), ZrB (80.5% Zr, 19% B), MoB (89% Mo, 10.8% B, 0.09% C), TiC, WC, and metallic Mo has been studied by the x-ray diffraction method at the Moscow Steel Institute. Specimens were prepared by powder metallurgy methods, some with and some without cementing metals, under conditions that insured approximately the same grain size of the refractory base (4 to 8 μ). The specimens were work hardened by grinding and annealed in a vacuum of 10^{-3} to 10^{-4} mm Hg. X-ray diffraction patterns revealed a slight solubility of Fe in ZrB_2 and of Co in MoB and TiC, but no solubility of Co in TiB_2. The ratio of the temperature at the beginning of recrystallization T_r to melting temperature T_m for refractory borides and carbides was found to be about 0.5, as against 0.3 to 0.4 for metals. This higher factor is apparently due to the relatively higher bond energy of the refractory compounds, and also to a different character of structural changes caused by work hardening. The MoB-base and WC-base alloys cemented by Co have a lower T_r than pure hot-compacted MoB and WC. The T_r of TiB_2, TiC, and WC decreases with an increased content of the cementing metal. The relative recrystallization temperatures of TiB_2 and TiC sintered with Co are practically the same, although the absolute T_r of TiC is higher than that of TiB_2. A detailed analysis of the data obtained indicates that the recrystallization of borides and carbides apparently proceeds not through the diffusion of individual atoms but through shifting of groups of atoms.

70. Greenwood, H. W.
Powder metallurgy and heat-resisting alloys.
ENGINEER 187(4862):349−351, 1 Apr 1949.

Survey of mainlines of development of heat resistant alloys, nature of problems that have arisen, means by which they have been solved and pointers provided for further progress; what powder metallurgy can do and what possibilities it offers. Melting points are given for ... SiC 2500°, MoC 2687°, W_2C 2857° ... W boride 2882°, ...

71. Grinthal, R. D.
Effect of some metal additions on molybdenum disilicide. POWDER METALLURGY BULLETIN 8(1–2):18–22, Jun 1957.

Electrical resistivity, modulus of traverse, hardness, impact strength and oxidation resistance effects on $MoSi_2$ from adding copper, titanium and chromium were studied. The $MoSi_2$ was prepared by a solid-state reaction at 1900°F in the presence of an alloying metal (5–7%). Copper can not exist in equilibrium with $MoSi_2$, as the silicide is formed. The brittle copper silicide matrix is detrimental to oxidation resistance and all physical properties are decreased. Up to 24 percent Cr may be added without losing the $MoSi_2$ structure, but further additions displace molybdenum metal. Neither these mixtures nor those with titanium have any advantages. Titanium above 4 percent causes a structure intermediate between tetragonal $MoSi_2$ and orthorhombic $TiSi_2$, and at 25 percent Ti a hexagonal phase appears.

72. Gurevich, M. A. and B. F. Ormont
X-ray investigation of binary vanadium-tungsten carbides. METALLOVEDENIE I OBRABOTKA METALLOV 1:7–10, 1958. (In Russian)

Vanadium carbide (I) is used in addition to and replacement of tungsten carbide (II). At 1700–1800° the cubic I dissolved approximately 10 mole % II, at 2150–2200° I dissolves 50 mole % II. On the basis of I a continuous series of solid solutions is formed. The method of sample preparation and x-ray data are given.

73. Hahn, G. T., A. Gilbert and R. I. Jaffee
THE EFFECTS OF SOLUTES ON THE DUCTILE-TO-BRITTLE TRANSITION IN REFRACTORY METALS. Battelle Memorial Institute, Defense Information Center, Columbus, Ohio. Paper no. 155. 28 Jun 1962. 51p.

Influence of interstitial solutes, alloying addition and non-metallic dispersions on the ductile-brittle transition temperature, bend ductility and tensile properties of ... Cb ... Mo and W.

74. Ham, J. L.
ARC-CAST MOLYBDENUM-BASE ALLOYS.
Climax Molybdenum Co. of Michigan, Detroit.
First annual report. 1 Apr 1950. 166p.
(Proj. NR 031-331).

Seventeen potential binary Mo-base alloy systems have been examined by studying materials prepared by the arc-cast process. Some of the 17 elements were found to serve as deoxidizers only, some were effective as alloying elements only, and some were effective both as deoxidants and alloying elements. A classification of the elements according to their solid solubility in molybdenum has been made. In systems of limited solubility, excess phases have been recognized and in some cases identified on the basis of existing equilibrium diagrams, which for the most part have been developed from alloys prepared by powder metallurgy processes. The effects of the elements on the hardness of molybdenum at room temperature and at elevated temperatures are reported. An appraisal of the possiblity of hot working the alloys was gained from a simple forge hammer test at 2500°F. The susceptibility to control the hardness by annealing and/or precipitation hardening was examined.

75. Ham, J. L.
An introduction to arc-cast molybdenum and its alloys. ASME TRANSACTIONS 73:723–731, 1951: see also STEEL 128(3):106–108, 15 Jan 1951.

Merits of arc casting for producing metallic molybdenum and its alloys; properties of unalloyed cast molybdenum; curves showing room temperature tensile properties, hardness, and notched bar values after annealing at various temperatures, effect of testing temperature on hardness, and transition temperatures for various impact tests.

76. Iwase, K., K. Ogawa and S. Fujishiro
Study on the formation of $MoSi_2$. I. NIHON KINZOKU GAKKAISHI 20(7):371–375, Jul 1956. (In Japanese)

High-purity $MoSi_2$ was subject to x-ray and chemical analysis. Effects of particle size, duration of mixing time, atmosphere, reaction temperature and ratio of components on reaction kinetics were studied. It was found that silicon in excess speeds the reaction. Pure samples of $MoSi_2$ are difficult to prepare, owing to the difference in vapor pressure of molybdenum and silicon. Micrographs and diffraction diagrams are shown.

77. Johnson, W. R. and M. Hanson
RESEARCH ON THE ELEMENT SILICON AND SILICON ALLOYS. Armour Research Foundation, Chicago, Ill. Rept. no. AF-TR-6383. Jun 1951. 133p.

A survey of the literation on the preparation and properties of Si is followed by a report of experimental studies of Si and its alloys. The covalent diamond-type crystal lattice of Si is stable up to at least 1317°C which is within 110° of its melting point. Si lacks any appreciable degree of ductility, although extremely slight deformation may occur, apparently exclusively by twinning, before cleavage takes place. Phase relationships in binary alloys of Si with the following elements have been studied metallographically: ... Nb, Mo ... W. In most cases, the alloys consist of a mixture of Si and the disilicide of the alloying element. There appears to be no possibility of obtaining a ductile metallic lattice structure in a high-Si alloy, either by high-temperature allotropic transformation or by alloying.

78. Kempter, C. P. and M. R. Nadler
Thermal decomposition of niobium and tantalum monocarbides. JOURNAL OF CHEMICAL PHYSICS 32(5):1477–1481, May 1960.

The thermal decomposition of polycrystalline NbC was investigated from 2000° to 3200°C, and TaC from 1890° to 3320°C in the presence of one atmosphere of helium. It was found that both compounds lose carbon preferentially, and that the final carbon/metal molar ratio obtained may be represented by an equation of the form $C/M = A-B \exp(\lambda t)$, where t is the maximum temperature of heating for a constant time (30 min in both cases). Similarly the resultant lattice constant may be expressed as $a = A'-B'(\lambda' t)$, were a_0 is in A at 25°C. For a maximum temperature of 3000°C and heating times of 30 min to 12 hrs, $a_0 = 4.459084 + 0.0093071 \exp(-0.18916\tau)$ for NbC, where τ is the time in hours. It was found that $a_0 = 4.414712 + 0.056862$ (C/Nb) for the C/Nb range 0.885 to 0.981 and that $a_0 = 4.385779 + 0.070204$ (C/Ta) for the C/Ta range 0.906 to 0.996. By extrapolation, the lattice constants of stoichuometric NbC and TaC should be 4.47157 ± 0.00012 A at 25°C and 4.45598 ± 0.00038 A at 25°C, respectively.

79. Kibler, G. M., T. F. Lyon and V. J. DeSantis
CARBONIZATION OF PLASTICS AND REFRACTORY MATERIALS RESEARCH PROGRAM. VOL. II. REFRACTORY MATERIALS RESEARCH. General Electric Co., Flight Propulsion Laboratory Department, Cincinnati, Ohio. Seventh Quarterly Progress Report, 1 Jan–31 Mar 1962. 31 Mar 1962. 32p. [Contract AF 33(616)-6841; ARPA Order 24-61]. N62-11254.

Equilibrium nitrogen pressures over the ZrN single phase have been measured by determining the rate of nitrogen effusion from a Knudsen cell. The measurements span a range of temperatures from 1424 to 2360°K, a range of composition from 13% down to 9.79% nitrogen by weight and a range of nitrogen pressures from 2×10^{-8} to 3×10^{-5} atm. These data are presented graphically. In matrix isolation experiments, both infra red and visible spectra have been obtained from the matrix isolated species effusion from a Knudsen orifice in a cell containing ThO_2. The observed bands are tabulated, though the analysis of the spectra are not complete. Results of efforts to measure the resonance line absorption by boron atoms over pure boron have indicated serious interaction of the boron with all container materials thus far investigated. The six compounds, NbB, TiB, TaN, ZrN and HfN for which emissivities are being measured, have now been characterized by chemical analysis, density measurement, crystallographic structure, electron micrographic examination and x-ray diffraction measurements. In addition, normal spectral emissivities of ZrB, and NbB_2 have been measured between 1536° and 2289°K. Results of NbB_2 emissivity measurements only are given, since ZrB_2 data thus far are somewhat erratic and irreproducible.

80. Kieffer, R., F. Benesovsky and H. Schmid
Contribution to the formation of systems vanadium-silicon and niobium-silicon. (Beitrag zum Aufbau der Systeme Vanadin-Silicium und Niob-Silicium) ZEITSCHRIFT FUER METALLKUNDE 47(4):247–253, Apr 1956. (In German)

V-Si and Nb-Si alloys were prepared by several methods, viz. powder sintering under pressure, solid-state reaction of powders in the atmosphere of argon, and arc melting. The phase diagrams show the existence of intermediate compounds VSi_2, V_5Si_3 and

and V_3Si, and $NbSi_2$, alpha-Nb_5Si_3 and beta-Nb_5Si_3. The products are not hard and are not scale-resistant.

81. Kieffer, R., F. Benesovsky and E. Gallistl
Contribution to the tunsten-silicon system, and the scale resistance of some silicides. (Beitrag zum System Wolfram-Silizium und Über die Zunderbeständigkeit einiger silizide.) ZEITSCHRIFT FUER METALLKUNDE 43:284–291, 1952. (In German)

A review on the basis of the literature. New investigations on the pressure-sintering of tungsten silicides. Proposes a phase diagram of the system on the basis of thermal, microscopic, and radiographic investigations. Mechanism of scaling. Data are tabulated and charted.

82. Kieffer, R. and F. Benesovsky
High-temperature and scale-resistant sintered materials. (Warm-und Zunderfeste Sinterwerkstoffe). ZEITSCHRIFT FUER METALLKUNDE 42:97–106, Apr 1951. (In German)

Review of literature shows that powder metallurgy is an increasingly used method of producing high-temperature-resistant metallic, semi-metallic, and nonmetallic materials and castings. Advances in the field of high-temperature materials.

83. Kieffer, R., et al.
Investigation of ternary systems Cr-W-Si and Mo-W-Si. MONATSHEFTE FUER CHEMIE 93(2):517–521, 20 Apr 1962. (In German)

While the structure and the field of the Mo_3 Si phase are well established, the existence of W_3Si remains doubtful. This follows also from the present investigation of the Mo_3Si-W_3Si and Mo_5Si_3-W_5Si_3 sections of the Mo-W-Si diagram at 1500° and 1900°C. Whereas Mo_5Si_3-W_5Si_3 form a continuous series of mixed crystals, Mo_3Si, even at 1900°C, dissolves practically no W_3Si.

84. Kieffer, R. and E. Cerwenka

The molybdenum-silicon system.

(Beitrag zum System Mo-Si). ZEITSCHRIFT

FUER METALLKUNDE 43:101–105, 1952.

(In German)

Production of alloys in above system by powder metallurgy and determination of phase relationships, hardness and scaling resistance. Micrographs, macrographs, tables and graphs.

85. Kieffer, R., F. Benesovsky and E. R. Honak

A new method for production of metallic borides of the transition metals, especially of titanium and zirconium borides. (Über ein neues Verfahren zur Herstellung von Metallboriden der Übergangsmetalle, insbesondere von Titan - und Zirkonborid).

ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE 268:191–200, 1952.

(In German)

Low-carbon TiB_2 and ZrB_2 were prepared by the reaction of metallic Ti or Zr with B_4C, B_2O_3, and/or Ti O_2 or Zr O_2. The process is satisfactory for the technical production of metal borides. The density, hardness, melting point, and crystal-structure type of hot pressed compacts of TiB_2 and ZrB_2 were determined, as were those of other borides of groups IV, V, and VI, namely: BB_2, NbB_2, TaB_2, CrB, CrB_2, Mo_2B, MoB , W_2B, and WB. The hardness of TiB_2 (3400 kg/mm) exceeds that of any metal boride so far known.

86. Kiessling, R.

The crystal structures of molybdenum and tungsten borides. ACTA CHEMICA SCANDINAVICA 1:893–916, 1947. (In English)

Systems of Mo-B and W-B, prepared by heating weighed quantities of B and metal in evacuated quartz tubes for forty-eight hours at about 1200°, were studied by x-ray methods. The phases of the two systems were found to be isomorphous to a large extent. The solubility of B in the metallic lattice is apparently very low, since the

the interferences in the powder photographs always occurred at fixed angles within experimental error. Three intermediate phases (γ, δ, and ϵ) were found in each system. The γ-phases are isomorphous and have the formulas Mo_2B and W_2B. Both of these were hard enough to scratch an agate mortar. The powder photographs (Cr K and Cu K radiation) showed the phases to give tetragonal cells having four molecules of M_2B per cell, with the dimensions: Mo_2B: a = 5.543, c = 4.735 Å., c/a = 0.854, V = 145.5 cu. A.; W B: a = 5.564, c = 4.740 A., c/a = 0.852, V = 146.7 cu. A. The γ-phases are found to crystallize in space group D_{4h}^{18}. At compositions of about 50 at .% B a hard metallic δ-phase occurred in each system. The powder photographs showed the phases to be isomorphous and to give tetragonal cells having 8MB molecules per cell, with the dimensions: MoB: a = 3.105, c = 16.97 A., V = 163.9 cu. A.; WB: a = 3.115, c = 16.93A., V = 164.6 cu. A., crystallizing in the space group D_{4h}^{19} − I 4/amd. Both systems exhibit a third intermediate phase, ϵ, at a composition of about 70% B which, though not isomorphous, are very similar. The Mo-B phase is characterized by rhombohedral lattice with the constants: r = 7.190A., a = 24°10', whereas the W-B phase is characterized by a hexagonal cell: a = 2.982, c = 13.87 A., V = 107.0 cu. A. The formula of these ϵ-phases approximates M_2B_5. The radius of the B atom was found to be 0.87 A. The B atoms have a marked tendency to form first chains and then rings or sheets as the B content of the system increases. All of the known metal borides may be classified according to the distribution of the B atoms. The structures are discussed in terms of the ratio of the metallic radius to that of B.

87. Kiessling, R. and Y. H. Liu
Thermal stability of the chromium, iron and tungsten borides in streaming ammonia and the existence of a new tungsten nitride.
JOURNAL OF METALS 3:639−642, Aug 1951.

The Cr, Fe and W borides were treated with ammonia at different temperatures. They are attacked, forming metal nitride and boron nitride. Results are summarized in tables. In the W-N system a new phase was observed, closely related to the known beta-phase.

88. Kiffer, A. D.
RESEARCH INVESTIGATION TO DETERMINE THE OPTIMUM CONDITIONS FOR GROWING SINGLE CRYSTALS OF SELECTED BORIDES, SILICIDES AND CARBIDES. Linde Co., Indianapolis, Ind. Report for Mar 1959—Feb 1960 on Ceramic and Cermet Materials. Apr 1960. 31p. [Contract AF 33(616)6326]. (WADD TR-60-52) PB161-792. (Available from Office of Technical Services, Washington 25, D. C.)

This work was undertaken to produce selected crystals in the refractory hard metals class for mechanical and other property determinations. A Verneuil-type process using an arc heat source and argon shield gas was employed. Single crystal boules of titanium diboride and tungsten disilicide, 1/4-inch diameter and up to 4-1/2 inches long, were made. Most of them cracked upon cooling. The largest single crystal pieces recovered were 1/4-inch diameter and over 1/2-inch long. Dimolybdenum carbide boules had large sections of a "single crystal Mo_2C matrix containing about 10 percent by volume of another phase distributed uniformly through it. No Mo_2C single crystal pieces free from this phase were made. In very limited work with ditungsten pentaboride only polycrystalline boules were produced. A major problem was encountered in getting powders suitable for Verneuil-type crystal growth. Best results were obtained from compounds prepared by fusing together commercially available pure elements and crushing the lumps into a suitable particle size fraction. Process improvements and purer powders are required to produce better quality TiB_2 and WSi_2 crystals. More experimental information is required on the molybdenum-carbon and the tungsten-boron systems.

89. Kimura, H. and Y. Sasaki
The niobium-carbon system. NATIONAL RESEARCH INSTITUTE OF METALS (Tokyo). TRANSACTIONS 3:111—119, 1961.

The phase diagram of the Nb-C systems shows four phases: solid solution Nb (δ) phase, Nb C (β), phase, NbC (γ) phase, and graphite. The maximum solubility of C is at 5 at. % at the eutectic temperature 2300 ± 20°.

90. King, E. G. and A. U. Christensen, Jr.
Low temperature heat capacity, entropy at 298.15°K., and high temperature heat content of Mo_3Si. JOURNAL OF PHYSICAL CHEMISTRY 62:499–500, Apr 1958.

The present paper reports heat capacity measurements between 51 and 298°K., the entropy at 298.15°K., and high temperature heat content measurements to 1451°K. of another molybdenum silicide (Mo_3Si).

91. Knapton, A. G.
The system niobium-silicon and the effect of carbon on the structures of certain silicides.
NATURE 175:730, 23 Apr 1955.

Phase diagram of the niobium-silicon system determined by melting-point determinations. X-ray examination and metallography.

92. Kolomoets, N. V., et al.
Thermoelectrical properties of some metal-like compounds. SOVIET PHYSICS – TECHNICAL PHYSICS 3:2186–2193, 1958.

All the investigated borides and carbides are, with regard to their thermoelectrical properties, typical metals with small quantities of dissolved impurities. All nitrides and silicides show some properties which are different from those of metals, which is indicated by the nonlinearity of the variations of the resistivity with the temperature. Such nonlinearity, and in the case of $FeSi_2$ and TaN even a decrease of the resistivity with the increasing temperature, can be explained only by the structural changes or the changes in the character of conductivity. If the latter is the case then these materials are semimetals, containing large quantities of dissolved impurities which cause a considerable degeneration of the electron gas.

93. Komar, A. P. and G. N. Talanin
The formation of carbides on the surface of W and Mo single crystals. PHYSIKALISCHE VERHANDLUNGEN 9(10):149, 1958. (In German)

Carbon contamination of molybdenum single crystals from a hydrocarbon source was studied with a field emission electron microscope. Hexagonal symmetry was due to absorption of carbon. The formation of MoC begins at the regions of the Mo_2C faces (0001). Surfaces overgrown with carbides were observed. This paper was presented before the 4th International Congress for Microscopy in Berlin, 10–17 September 1958.

94. Komar, A. P. and G. N. Talanin
The formation of carbides on the surface of Mo and W single crystals. In INTERNATIONAL CONFERENCE ON ELECTRON MICROSCOPY, 4TH, BERLIN. VERHANDLUNGEN 1:817–819. Berlin, Springer, 1960.

Carbide formation on the surface of single molybdenum crystals was studied by field emission electron microscopy, and different phases of growth were identified. Hemispherically rounded microcrystals grew into the intermediate edged crystals but orientation remained the same. When benzene was used as the source of carbon, hexagonal patterns of carbide were obtained more easily. They were attributed to Mo_2C. Crystals of Mo_2C and MoC can be represented only the sequence of faces were determined, and conclusions were drawn as to the activation energy of the crystal formation. MoC faces form on the region (0001). Micrographic images are shown.

95. Kosolapova, T. Ya. and E. E. Kotlyar
The resistance of some silicides of molybdenum to acids. ZHURNAL NEORGANICHESKOI KHIMII 3(5):250–254. May 1958. (In Russian). (AEC-TR-4453). 1961. Available from Office of Technical Services, Washington 25, D. C.)

With a view to applications in the chemical analysis of phases occurring in system Mo-Si and of alloys derived from this system, a study was made of the relative solubility of $MoSi_2$, Mo_2Si_2 and Mo_4CSi_3 in the following acids: hydrochloric, sulfuric, hydrofluoric, hydroiodic, HF + FI, HF + HCl, HF + HNO_3 and HF + H_2SO_4.

96. Koval'chenko, M. S. and G. V. Samsonov
Relaxation phenomena during the hot compacting of molybdenum carbide. PHYSICS OF METALS AND METALLOGRAPHY 12(1):126–128, Jul 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, decrease 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 decrease. 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.

97. Koval'skii, A. E. and S. V. Semenovskaya
On the structure of molybdenum monocarbide. SOVIET PHYSICS – CRYSTALLOGRAPHY 4(6):878–880. Nov–Dec 1959.

A hexagonal phase of MoC was prepared and studied by x-ray diffraction. Higher pressures favor formation of hexagonal MoC but instability is considerable, Mo_2C forming readily. Data are tabulated.

98. Koval'skii, A. E. and Ya. S. Umanskii
X-ray investigation of pseudobinary systems: TaC-TiC, NbC-TiC, TaC-ZrC, NbC-ZrC. ZHURNAL FIZICHESKOI KHIMII 20:769–772, 1946. (In Russian) (AEC-TR-2512. 1956. 8p.)

TaC-TiC, TaC-ZrC, NbC-Tic, NbC-ZrC formed a continuous series of solid solutions among themselves. At a component ratio of 1:1 the interference lines were very diffuse. Additional calcination for 12 hr did not alter the character of the lines, which indicates that the cause of the diffuseness of the lines is not the absence of equilibrium but a strong distortion of the lattice structure. The lattice spacing results obtained by x-ray analysis for the initial carbides and solid solutions did not agree with the data published by Becker.

99. Kreimer, G. S., L. D. Efros and E. A. Voronova
Reactive diffusion of carbon in tungsten. ZHURNAL TEKHNICHESKOI FIZIKI 22:858–873, 1952.
(In Russian)

Heating of polycrystalline W with C black in a stream of H at 1500–1800° produces first the WC phase from which C diffuses into W with formation of W_2C. In the relation of isothermal growth of W_2C layers with time it is shown that (a) the concentration of C in the layer drops linearly, (b) the difference between the terminal concentrations is constant, and (c) the coefficient of diffusion is practically independent of concentration. The most probable value of $D(C_1-C_2)$ at 1840° is 76×10^{-10} g./cm. sec. and $D(C_1-C_2) = D_0 e^{-Q/RT}$, where D is coefficient of diffusion, (C_1-C_2) = difference in terminal concentration, D_0 = parameter independent of the temperature, and Q = the heat of diffusion or disorganization of the lattice. The value of Q was 112,000 ± 3000 cal./g. atom and D_0 = 2750. The process of carburization of W proceeds basically by interaction (chemical reaction) of W surface with gaseous medium independent of presence or absence of solid C and further diffusion of C through layers of WC, W_2C, and W. Experimental data show that C does not diffuse along grain boundaries but preferentially through the free surface of the grains.

100. Krikorian, O. H.
HIGH-TEMPERATURE STUDIES: I. REACTIONS OF THE REFRACTORY SILICIDES WITH CARBON AND WITH NITROGEN. II, THERMODYNAMIC PROPERTIES OF THE CARBIDES. III, HEAT OF FORMATION OF THE $^3\pi_\mu$ STATE OF C_2 FROM GRAPHITE (thesis). California Univ., Berkeley. Radiation Laboratory. Rept. no. UCRL-2888. Apr 1955. 150p. (Contract W-7504-Eng-48).

The reactions of silicides of Ti, Zr, Ce, Nb, Ta, Mo, and W with carbon and with nitrogen were studied at temperatures around 2000°K. The data were used to establish ternary phase diagrams and to set upper and lower limits on the heats of formation of the silicides. Methods are suggested for estimating absolute entropies of carbides. The heat of formation of the $^3\pi_\mu$ state of C_2 has been determined as 191.4-5 kcal at 0°K.

101. Kudielka, H., H. Novotny and G. Findeisen
Studies of systems V-B, Nb-B, V-B-Si and Ta-B-Si. MONATSHEFTE FUER CHEMIE 88(6):1048–1055, Jan 1958. (In German)

As a part of a study of high melting silicoborides, the above systems were examined roentgenographically. In the V-B system a new phase of the approximate composition V_2B was identified. Its crystal structure is isotypic with the corresponding phase in the Nb-B system. In the system V-B-Si a ternary phase $V_5(Si_{1/3}, B_{2/3})_3$ was detected, analogous to a phase in the similar system Mo-B-Si.

102. Kuo, K. and G. Hagg
A new molybdenum carbide. NATURE 170:245–246, 9 Aug 1952.

Studies of products formed by carburizing Mo with CO confirmed existence of Mo_2C (beta phase) and MoC (gamma phase), the latter having the WC structure. In addition, a new carbide was found. Describes its transformations and lattice parameters.

103. Kusenko, F. G. and P. V. Gel'd
The heat of formation of oxides and carbides of niobium. IZVESTIIA SIBIRSKOGO OTDELENIIA AKADEMIIA NAUK SSSR. 2:46–52, 1960. (In Russian)

A series of heats of formation (kcal./mole) of Nb compounds at 298.16°K. were determined for Nb_2O_5, NbO_2 NbO, and NbC, respectively: -458.6 ± 5.0, -191.7 ± 2.6, -97.7 ± 2.6, and -34.8 ± 2.6. For lower carbides, NbC_x) the heat of formation (kcal./mol.) lies between those given by the respective expressions $-(48.1x \pm 15.9x^2)$ and $-(63.98x \pm 26.58x^2)$, where $x < 1$. The heat of formation of $NbH_{0.761}$ at 298.16°K. is -20.2 ± 2.6 kcal./g. atom.

104. Leciejewicz, J.
A note on the structure of tungsten carbide. ACTA CRYSTALLOGRAPHICA 14:200, 1961.

Neutron-diffraction data, obtained from WC powder (2μ particle size), showed that the space group for the B type of structure is P6m2 with 1W in 1(a) 0, 0, 0; 1C in 1(f) 2/3, 1/3, 1/2. A photograph of the neutron diffraction pattern of WC is included.

105. Leitnaker, J. M., M. G. Bowman and P. W. Gilles
Thermodynamic properties of the tantalum and tungsten borides. ELECTROCHEMICAL SOCIETY.JOURNAL 109:441–443, 1962.

Borides of Ta, Ta and ZrB_2, or W and ZrB_2 were heated in high vacuum and the reaction products were identified by x-ray diffraction. The results lead to limits for the values of heats of formation for the phases: $Ta_{2.4}B$, $Ta_{1.6}B$, TaB, TaB_2, and W_2B. Ternary phase diagrams at 1500° are also given for the systems Ta-Zr-B and W-Zr-B.

106. Lersmacher, B., E. Roeder and S. Scholz
Grain growth of TaC and NbC under the effect of small additions of Mn, Fe, Co, and Ni. NATURWISSENSCHAFTEN 49:35, 1962.
(In German)

The increase in average grain size area with increasing pressing time at 1800° measured for TaC and NbC powders containing 1% Mn, Fe, Co, or Ni. The activation energy for grain boundary migration under the effect of each additive was determined from the average grain area after 56 minutes pressing at different temperatures. The observed rate of grain growth for each carbide and additive combination was 2–4 orders of magnitude less than that predicted from the activation energy. The difference was attributed to the presence of residual pores, particles of a second phase, and dissolved additive metal atoms in the pressed bodies.

107. Lorenz, R. and A. B. Michael
Oxidation resistant silicide coatings for columbium and tantalum. ELECTROCHEMICAL SOCIETY.JOURNAL 107(8):188C, Aug 1960.
(Abstract)

A molybdenum layer is formed on niobium or tantalum subtrates by vapor deposition, and then converted to $MoSi_2$, by vapor phase reaction with $SiCl_4$ and hydrogen. Techniques, oxidation resistances, mechanical properties and structures are discussed. This paper was presented before the 118th meeting of the Electrochemical Society in Houston, October 9–13, 1960.

108. McGraw, L. D., H. Seltz and P. E. Snyder
Heat of combusion of tungsten carbide.
AMERICAN CHEMICAL SOCIETY JOURNAL
69:329–331, 1947.

The heat of combustion was determined in a calorimeter. The heat of combusion of WC under standard conditions to give CO_2 and WO is $\Delta H_{298.16}$= -285.80 ± 0.07 kg. cal./mole. The heat of formation from the elements, $\Delta H_{298.16}$ is -3.92 - 0.90 kg. -cal/mole. The larger uncertainty for the second figure is due to the lower precision of the value available for the heat of combustion of W.

109. Mah, A. D. and B. J. Boyle
Heats of formation of niobium carbide and zirconium carbide from combustion calorimetry.
AMERICAN CHEMICAL SOCIETY JOURNAL
77:6512–6513, 20 Dec 1955.

This note presents the results of combustion calorimetric investigations of two substances, niobium carbide (columbium carbide) (NbC) and zirconium carbide (ZrC). Although the purity of the substances available for study leaves much to be desired, it is believed that useful heat of formation data have been obtained. The literature contains no previous directly measured values for these substances.

110. Markovskii, L. Ya. and Vekshina, N. V.
Preparation of molybdenum disilicide by the carbon reduction of oxides. RUSSIAN JOURNAL OF INORGANIC CHEMISTRY 2(7):385–390, Jul 1957. (AEC-TR-4057. 1960. Available from Office of Technical Services, Washington 25, D. C.)

It is shown that, at stoichiometric proportions of the components, the reaction $MoO_3 + 2SiO_2 + 7C\ MoSi_2 + 7CO$ leads to the formation of side products like Mo_5Si_3 and SiC, while some carbon remains unused. However, it was possible to develop a satisfactory procedure for preparing $MoSi_2$ by introducing an excess of SiO_2 and heating to 1900°C.

111. Mathews, B. E. and Sias, F. R., Jr.
Testing space craft with inauction. ELECTRONICS
35(34):38–41, 24 Aug 1962.

A full-size prototype section of a coated Mo alloy wing leading edge is heated to 3000°F. in a simulation re-entry flight lasting two hours.

112. Matkovich, V. I. and H. H. Rogers
The formation of chromium or molybdenum
stabilized tungsten silicon carbide. ELECTRO-
CHEMICAL SOCIETY. JOURNAL 108(3):261–262,
Mar 1961.

An attempt to form W_4Si_3C is structural 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 or 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.

113. Maxwell, W. A.
METHOD FOR IMPROVING THE HIGH-
TEMPERATURE STRENGTH AND OTHER
PROPERTIES OF MOLYBDENUM DISILICIDE AND
OTHER INTERMETALLIC COMPOUNDS.
U.S. Patent 2,898,600. 11 Aug 1959.

A refractory workpiece is made by mixing $MoSi_2$ powder (less than 9μ) with 0.5% carbon powder, placing in a die, and sintering under high temperature and pressure. The final composition contains 0.15 –0.29%C.

114. Maxwell, W. A.
Some stress-rupture and creep properties of
molybdenum disilicide in the range 1600° to
2000°F. PRODUCT ENGINEERING 26(4):296–297.
Apr 1955.

The long-time strength of $MoSi_2$ was surveyed in the 1600° –2000°F range to give stress-rupture curves and creep data for evaluating high-temperature use. Creep rate may be the limiting factor above 1800° F; at this temperature the 110-hr strength is better than in comparison materials (TiC and superalloys). Metallography shows several aspects of damage after prolonged stress; failed specimens are difficult to polish. Data are tabulated.

115. Maxwell, W. A.
A study of molybdenum disilicide for elevated temperature applications. In Oak Ridge National Laboratory, Tenn. PROCEEDINGS OF THE METALLURGY AND MATERIALS INFORMATION MEETING, APR 16–18, 1951, HELD AT OAK RIDGE, TENNESSEE, SPONSORED BY OAK RIDGE NATIONAL LABORATORY. VOL. I. 7 Mar 1957. p.561–569. (Decl. with deletions) (Available from U.S. Office of Technical Services, Washington 25, D. C.)

$MoSi_2$ has high strength and oxidation resistance and low capture cross section. Studies were made of preparing $MoSi_2$. It was obtained in the fine grain-cold-pressed form, the fine grain hot pressed form, and the coarse grain hot pressed form. Procedures are described and micrographs are shown of the samples. The oxidation resistance is the result of a thin coat of silica. Simple forming methods appear promising for $MoSi_2$. Graphs are shown.

116. May, C. E. and P. D. Hoekstra
STABILITY OF REFRACTORY COMPOUNDS IN HYDROGEN BETWEEN 4500° AND 5000° F, AND THEIR COMPATIBILITY WITH TUNGSTEN. U.S. National Aeronautics and Space Administration. Lewis Research Center, Cleveland, Ohio. NASA Technical Note D-844. May 1961. 12p. N-62-71343.

The extent of reaction of various borides, carbides, nitrides, and oxides are studied in a state hydrogen system. HfC, TaC, TiC, ZrC, HfN, TaN, TiN, and ZrN showed considerable reaction. The reaction of ZrO_2 was slight. Any reaction occurring for NbC, TaB_2, and WB was less than the minimum detectable amount. Except for the nitrides, most of the refractory compounds were incompatible with the tungsten container material at these temperatures. Because of this incompatibility, the degrees of stability of HfB_2, NbB_2, TiB_2, and Mo_2C in hydrogen could not be determined.

117. Meerson, G. A., et al.
Properties of boride systems with transition group high-melting-point metals. ZHURNAL NEORGANISCHESKOI KHIMII 3:898–903, Apr 1958. (In Russian)

Phase compositions, structure of diffusion interaction products, microstructure, and heat resistance of TiB_2-CrB_2, TiB_2-W_2B_5, and ZrB_2-CrB_2 systems were studied. Constitution diagrams for each system are presented, and tables of the initial boride powders and the data obtained on properties of chromium, titanium, tungsten, and zirconium borides are included.

118. Meyerson, G. A., et al.
Some properties of alloys of the borides of the refractory metals of the transition groups. ZHURNAL NEORGANICHESKOI KHIMII 3:94–103, Apr 1958. (In Russian) (NP-TR-312. 1960. 11p.) (Available from Office of Technical Services, Washington 25, D. C.)

The systems of CrB_2-TiB_2, TiB_2-W_2B_5, and CrB_2-ZrB_2 are investigated. The phase composition of the starting boride diffusion interaction products, phase microhardness, and the heat resistance and structure of various compositions series of these systems are examined. CrB_2-TiB_2 was found to form a continuous series of solid solutions, while solubility in the systems TiB_2-W_2B_5, and CrB_2-ZrB_2 is limited. The solubility of TiB_2 in W_2B_5 in TiB_2 does not exceed 10 and 5 mole %, respectively. The solubility of ZrB_2 in CrB_2 is about 20 mole %. The solubility of CrB_2 in ZrB_2 is apparently slight.

119. Mitsuhashi, T. and K. Tamura
Study of $MoSi_2$ cermet. NIHON KINZOKU GAKKAISHI 22(8):416–420, Aug 1958. (In Japanese)

Vacuum-hot-pressing or -sintering after cold-pressing was used to prepare $MoSi_2$ cermet containing 5–10% binder metals. Tests showed that the optimum sintering or hot pressing temperature is lower than the binder melting point, i.e., 1300°–1400°C for nickel and cobalt, 1360°–1400°C for iron, and 1300°–1380°C for stainless steel. Increasing the amount of binder decreases the hardness. Hot-pressing gave better hardness and density than sintering with cold-pressing. Increasing the amount of binder improves thermal shock resistance and decreases hot hardness and 1100°C oxidation resistance. Corrosion resistance against 10% HCl and 10% H_2SO_4 was good, but that against 15% HNO_3 was poorer. Micrographs are shown.

120. Modylevskaya, K. D. and G. V. Samsonov
Stability of borides of transition metals to acids and bases. UKRAINSKII KHIMICHESKII ZHURNAL 25:55–61, 1959. (In Russian)

Tables are of the percentage not dissolved from 0.2-g samples of the borides of Ti, Zr, V, Nb, Ta, Cr, Mo, and W in concentrated HF, and in concentrated and dilute HCl, HNO_3, and H_2SO_4, H_3PO_4, $HClO_4$, $H_2C_2O_4$, aqua regia, and NaOH, and in the following mixtures $H_2C_2O_4$-H_2O_2-HN_3, $H_2C_2O_4$-H_2SO_4, HCl-Br water, HCl-$HClO_4$, H_2SO_4-H_3PO_4-H_2O, H_2SO_4-K_2SO_4, H_2SO_4-$K_2S_2O_8$, H_2SO_4-HNO_3, and HNO_3-Hf. CrB_2 and VB_2 are, in general, the most soluble and TaB_2 and NbB_2 the least soluble in pure acids. TaB_2 resists mixtures best and Mo_2V_5 poorest. The samples are almost completely dissolved by a 2-hr boil with a mixture of 50 ml. H_2SO_4 and 5 g. $K_2S_2O_8$ or 35 ml. H_2SO_4-HNO_3 mixture. Fusion with NaOH dissolves all of them.

121. Molybdenum boride braze.
STEEL 138(21):109, 21 May 1956.

Molybdenum boride is being used as a high-temperature braze for molybdenum, tungsten, tantalum and niobium, especially in electronic parts. While the boride melts at 3450°F, the joint withstands higher temperatures.

122. Molybdenum disilicide.
MECHANICAL WORLD 136(3443):264,
Jun 1956.

Studies show that engineering problems in service above 2000° F are solved by using $MoSi_2$. $MoSi_2$ resists oxidation and has moderate shock resistance with good high-temperature strength. Heating elements of $MoSi_2$ serve up to 3000° F but 70° F brittleness and high electrical conductivity are drawbacks. A 25% alumina composition is applicable to jet engine and gas engine parts, sand blast nozzles, hot dies and kiln fitments. Properties depend partly on the powder fabrication method. Silicide coatings may be vapor-deposited on molybdenum at 1830° –3300° F.

123. Molybdenum disilicide for high temperature
service. METALLURGIA 53(318):175, Apr 1956.

$MoSi_2$ has good high-temperature strength and resistance to oxidation and corrosion. Advantage in its use for gas turbine blades, nozzles and other jet parts is indicated. Tests show that $MoSi_2$-coated molybdenum filaments have operated at 1800° F for thousands of hours without decomposition. $MoSi_2$-$25Al_2O_3$ resists thermal shock and oxidation well up to 2700° F. Fabrication methods, on which physical and mechanical properties largely depend, include hot pressing and cold pressing with sintering. Poor thermal shock resistance is the main problem.

124. Molybdenum disilicide holds up at 3002° F.
MATERIALS AND METHODS 45(6):190, 192,
Jun 1957.

$MoSi_2$ heating elements perform well up to 3000° F, are hard, brittle and of high compressive strength and good electrical conductivity. Fansteel supplies the material as a powder or in dense shapes. Molybdenum and silicon powders are used in the synthesis at high temperatures. The reaction product is pulverized and compacted prior to sintering.

125. Nadler, M. R. and C. P. Kempter
Some solidus temperatures in several metal-
carbon systems. JOURNAL OF PHYSICAL
CHEMISTRY 64(10):1468–1471, Oct 1960.

Minimum eutectic temperatures were determined for metal-carbon systems. The solidus temperature for Mo-C is 2210°C. Mo_2C melts at 2410°C. Data are tabulated.

126. Nazarchuk, T. N. and L. E. Pechentkovskaya
Colorimetric determination of free carbon in molybdenum and tungsten carbides. INDUSTRIAL LABORATORY 27(3):258–261, Mar 1961.

The colorimetric determination of free carbon in WC was achieved by adsorption of bromothymol blue, methyl orange and methyl violet, and in Mo_2C by adsorption 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.

127. Neshpor, V. A. and G. V. Samsonov
Investigation of oxidation resistance of titanium and niobium borides. ZHURNAL PRIKLADNOI KHIMII 30:1584–1588, 1957. (In Russian)

Oxidation resistance of TiB_2 and NbB_2 and their alloys forming a continuous series of solid solutions was studied with borides of roentgenographic density TiB_2 = 4.53 and NbB_2 = 7.08 g/cm^3 and the lattice parameters of titanium and niobium borides a = 3.028 A, c = 3.224 A and a = 3.082 A, c = 3.278 A, respectively.

128. Norton, J. T. and R. K. Lewis
PROPERTIES OF NON-STOICHIOMETRIC METALLIC CARBIDES. Advanced Metals Research Corp., Somerville, Mass. Quarterly Progress Report 1. 11 May 1962. 10p. (NASA Contract NASr-98). N-62 12444.

A program is underway to investigate the carbide systems of the transition elements, titanium, zirconium, hafnium, and columbium, in the fourth and fifth Periodic Groups. Since conventional methods of carbide preparation make it extremely difficult to obtain carbides of sufficient purity to permit really significant property measurements, the first phase of the program concerns the preparation of suitable specimens. Two techniques will be tried and compared. The first is a modification of standard powder metallurgy practice, involving electron beam zone sintering in high vacuum, and finishing at a temperature as close to the melting point as possible. The second technique involves carburization of relatively thin metal wires or strips in purified gaseous atmospheres. The second phase of the program will be the measurement of specimen strength, oxidation rate in air, precision lattice constant, thermal expansion, electrical resistivity, Hall constant, thermoelectric power, and magnetic susceptibility. Of special interest will be the dependence of these properties upon carbon content at the nonstoichiometric compositions. Work accomplished to date includes literature research on carbide properties and preparation and experiments to redetermine homogeneity ranges of the carbide phases.

129. Norton, J. T. and A. L. Mowry
Solubility relationships of refractory monocarbides. JOURNAL OF METALS
1(2):133–136, Feb 1949.

Purpose was to examine solubility of several pairs of carbides by heating them together until equilibrium was established and then examining product by x-rays; raw materials used were monocarbides of titanium, zirconium, vanadium, columbium and tantalum, purest readily obtained commercially; results show limit placed on solubility by size factor; quantitative expression of size factor depends upon method of defining atom size.

130. Nowotny, H., et al.
Crystal chemistry of high-melting carbides, silicides, and borides. ACTA CHIMICA ACADEMIAE SCIENTIARUM HUNGARICAE
18:35–44, 1959. (In German)

... Nb, Ta, Cr, Mo, and W form silicides of the W_5Si_3 type, with tetragonal symmetry D_{2d}^{11}. All of these silicides ... form ternary phases with C that have hexagonal, Mn_5Si_3, symmetry. Similarly, silicides of ... Nb ... form ternary phases with boron, which have hexagonal, Mn_5Si_3, symmetry. ... Nb_3B_2 has the U_3Si_2 structure.

131. Nowotny, H. and C. Brukl
Contribution to the ternary system molybdenum-aluminum-silicon. MONATSHEFTE FUER CHEMIE 91(2):312–319, 29 Apr 1960.
(In German)

X-ray investigation of the Mo-Al-Si system demonstrated the existence of a continuous series of solid solutions between Mo_3Al and Mo_3Si. On the other hand, in the Mo_5Si_3 phase up to 1/3 of the silicon can be replaced by aluminum, while in the $MoSi_2$ phase only small amounts can be so exchanged. The ternary phase is $Mo(Si,Al)_2$, a base of solid solutions extending on the diagram to the composition MoSiAl.

132. Nowotny, H., E. Dimakopulou and H. Kudielka
Investigations of the three-component systems molybdenum-silicon-boron, tungsten-silicon-boron and in the system VSi_2-$TaSi_2$. MONATSHEFTE FUER CHEMIE 88(2):180–192, 1957. (In German)

The phase diagram of the three-component system Mo-Si-B at 1600°C shows mainly a ternary phase $Mo_5(Si, B)_3$ with T2 structure and in equilibrium with molybdenum, Mo_3Si, Mo_5Si_3(Type Tl), Mo_2B and MoB. The microhardness of the ternary phase is higher than that of the pure molybdenum silicides and seems even higher than that of the pure molybdenum borides. An isotype crystal structure exists also in the three-component system W-Si-B. Continuous mixed crystals were found in the quasi-binary system VSi_2-$TaSi_2$.

133. Nowotny, H. and R. Kieffer
Remarks on the existence of molybdenum carbide. (Eine Bemerkung zur Existenz des kubischen Molybdäncarbides). ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE 267:261–264, 1952. (In German)

Investigation of C-rich Mo carbides reveals, not the cubic phase-centered Mo_2C, but a phase that corresponds more to MoC with slight carbon deficiency.

134. Nowotny, H. and R. Kieffer
X-ray investigations of carbide systems. (Röntgenographische Untersuchung von Karbid-systemen). METALLFORSCHUNG 2(9):257–265, Sep 1947. (In German)

The lattice constants of TiC, ZrC, VC, CbC, TaC, WC and Mo_2C were redetermined and compared with previous values. Results indicate that the systems TiC, -VC, TiC-CbC, ZrC-CbC, CbC-TaC, (Ta, Cb) C-VC, VC-TaC, and TiC-TaC are miscible in all proportions, probably also TiC-ZrC.

135. Nowotny, H., R. Kieffer and F. Benesovsky
Silicoborides of transition metals vanadium, niobium, tantalum, molybdenum and tungsten.
PLANSEEBERICHTE FUER PULVER-METALLURGIE 5(3):86–93, Dec 1957.
(In German)

The crystal structure of the above silicoborides presents, with some exceptions, the following regularities. There exist two ternary phases of which the first, of the approximate composition M_5SiB_2, crystallizes according to the T_2 structure and is, in the diagram, on the line which starts with the binary phase M_5Si_3. The boron content increased with increasing group number and decreasing period number in the periodic table. The second ternary phase, crystallizing in the $D8_8$ structure, also leads from the binary M_5Si_3. The boron content increases with increasing group and period numbers.

136. Nowotny, H. and A. Wittmann
The structure of the metal-rich boride phase with V, Nb and Ta. MONATSHEFTE FUER CHEMIE 89(2):220–224, 1958. (In German)

The lattice constants of compounds in the systems V-B, Nb-B and Ta-B, forming at about 30 at-% B, were determined, assuming a tetragonal unit cell for all three systems. Based on the T_2 grating and theoretical density determinations, the structure Me_3B_2 is suggested. If a boron atom were to replace a boron couple the binary phase would have the composition Me_3B.

137. Nowotny, H., et al.
The ternary system molybdenum-silicon-carbon.
(Das Dreistoffsystem: Molybdan-Silizium-Kohlenstoff). MONATSCHEFTE FUER CHEMIE 85:255–272, 15 Feb 1954. (In German)

As a preliminary to the investigations on the ternary system Mo-Si-C, the systems Mo-Si and Mo-C were examined. In continuation of earlier work on Mo-Si it was found that the reaction for the preparation of Mo_3Si is probably solid solution $Mo_3Si_2 \rightleftharpoons Mo_3Si$. The system Mo-C with 50 at-%C was identified as belonging to the hexagonal system, with the indices a = 3.00kX, c = 14.58 kX and c/a = 486. The ternary system was prepared by hot pressing from the powdered constituent elements, or from pure Mo_2C, $MoSi_2$ and SiC. All samples were annealed for 12 hours at 1600°C in a tungsten vacuum oven, then analysis for carbon. The samples were then x-rayed, and the density and melting point were determined by methods described earlier. It was found that the system crystallizes in the $D^8{}_8$ lattice as Mo_3Si_3. The parameters in the molybdenum rich region are a = 7.27 kX, c = 5.05 kX and c/a = 0.695, and in the region poor in molybdenum are a = 7.27 kX, c = 4.99 kX and c/a = 0.687. The change in carbon content does not influence the parameters. The ternary alloy has a density of 8.0 g/cm, a microhardness of 1460 kg/mm and a metallic appearance.

138. Nowotny, H., et al
The three-component system titanium-tungsten-carbon. (Das Dreistoffsystem Titan-Wolfram-Kohlenstoff). ZEITSCHRIFT FUER METALLKUNDE 45:97–101, 1954. (In German)

Structure explained by x-ray diffraction and determination of melting points.

139. Ohlinger, L. A.
STABILITY OF MOLYBDENUM CARBIDE IN HYDROGEN AT ELEVATED TEMPERATURES.
Northrop Aircraft, Inc., Hawthorne, Calif.
Rept. no. NRR-155. 25 Nov 1957. 17p.
(Contract NEPA 675-NOR-43).
ASTIA AD-146 567.

Below 2000°C, Mo_2C is a good and stable refractory for either long- or short-term service in hydrogen, and short-term service in hydrogen up to 2200°C. With limitations, long-term service up to 2100°C is possible.

140. Parthe, E. and V. Sadagopan
THE STRUCTURE OF DIMOLYBDENUM CARBIDE BY NEUTRON DIFFRACTION TECHNIQUES.
Pennsylvania Univ., Philadelphia. 1962. 11p.
[Contract AF 49(638)-1027 and NSF Grant].
N62-12585.

It is generally believed that Mo_2C has either the hexagonal C6 Cadmium iodide antitype structure or the related hexagonal L'3 structure. A neutron diffraction study showed that this is not the case. Mo_2C crystallizes with an orthorhombic unit cell with a = 4.72_4Å, b = 6.00_4Å, and c = 5.19_4Å. The atomic arrangement of Mo_2C presents a new structure type. The space group is D_{2h}^{14}-Pbcn. The carbon atoms is Mo_2C arrange themselves in such a way that each molybdenum atom has three nearly planar carbon neighbors.

141. Pfau, H. and W. Rix
Crystalline form of tungsten carbide and the distribution of carbon atoms in the lattice.
(Über die Kristallform des Wolframkarbides WC und die Verteilung der Kohlenstoffatome in seinem Gitter). ZEITSCHRIFT FUER METALLKUNDE 45:116–118, 1954.
(In German)

Investigation indicated probable location of carbon atoms.

142. Philips Gloeilampenfabrieken, N. V. Forschungs-Laboratorium, Eindhoven, Netherlands.
PROCEDURE FOR SOLDERING MOLYBDENUM FOILS BY MEANS OF MOLYBDENUM CARBIDE.
French Patent 1,205,761. 17 Sep 1959.
(In French)

A procedure for soldering foil of a high melting metal to an object of a high melting metal is described. The solder consists of a mixture of the metal foil and of the carbide of the metal in approximately equal weights. The metal foil may be molybdenum and the solder a mixture of 45–55 wt-% Mo and the rest MoC. The procedure may be used in the manufacture of electron tubes.

143. Pinsker, Z. G. and S. V. Kaverin
Electron diffraction study of nitrides and carbides of transition metals. SOVIET PHYSICS-CRYSTALLOGRAPHY 2(3):380–387, May–Jun 1957.

Electron diffraction studies of Fe, Cr, Mo, W and some carbides of Fe have been in progress. Structureal data concerning the phases Fe_4N, Fe_2N, Fe_2N, CrN, MoN, Mo_2N, WN, W_2N, Fe_3C, Fe_4C and other have been obtained. In the course of studying nitridation processes, the phenomenon of nondiffusional rearrangement for Fe-, Cr- and Mo-nitrides has been discovered and investigated.

144. Pochon, M. L., et al.
The solubility of carbon and structure of carbon phases in tantalum and columbium. In Clough, W. R., ed. REACTIVE METALS. PROCEEDINGS OF THE THIRD ANNUAL CONFERENCE, BUFFALO, NEW YORK, 27–29 MAY 1958. New York, Interscience, 1959. p. 327–347. (Metallurgical Society Conferences, v. 2).

The nature and distribution of carbide phases were studied in arc-melted tantalum and niobium alloys containing up to 3.6 and 6.5% carbon, respectively. Improved metallographic and phase isolation techniques were developed to enhance identification of the minor phases. The solid solubility of carbon is quite limited in both tantalum and niobium, and in each case, the first stable intermediate phase is of the M_2C type. X-ray data are reported for Ta_2C, Cb_2C, and a metastable transition carbide which has been discovered in low-carbon niobium alloys. The existing tantalum-carbon and niobim-carbon constitution diagrams have been modified in accordance with the present results.

145. Post, B.
Borides of some transition metals. JOURNAL OF CHEMICAL PHYSICS 20:1050–1051, Jun 1952.

Several unreported transition metal borides were prepared in a high-temperature investigation of several metal-C-b systems. Some structural characteristics of these new phases were determined by means of an x-ray diffraction investigation of powdered samples.

146. Post, B., F. W. Glaser and D. Moskowitz
Transition metal diborides. ACTA METALLURGICA 2:20–25, 1954.

Structural characteristics of eight transition metal diborides. Extent of solid solubility appeared to depend mainly on size factors. Tables, diagrams.

147. Preller, H.
Molybdenum disilicide, heat resisting and chemically highly stable material. VEREIN DEUTSCHER INGENIEURE. ZEITSCHRIFT 98(27):1611–1612, 21 Sep 1956. (In German)

Properties of $MoSi_2$, one of the new hard, nonscaling, corrosion resistant and refractory materials, are described. Its melting temperature exceeds 2000°C and it can easily resist working temperatures around 1700°C, since at those temperatures it is not attacked by gases such as oxygen, oxygen-containing gases (e.g., SO_2, CO_2, etc.), nitrogen containing gases, or hydrocarbons. Similarly, it is stable against the action of those molten metals that do not form compounds with silicon (sodium, silver, mercury, tin, lead, zinc). A further advantage is the continuous formation of a surface coating of silica glass which protects the material against gases and water solutions.

148. PROCEDURE FOR PREPARING CARBIDES OF METALLIC TUNGSTEN, MOLYBDENUM, VANADIUM, TITANIUM, TANTALUM, NIOBIUM, CHROMIUM AND BORON. (SATT ATT FRAMSTALLA KARBIDER AV METALLERNA VOLFRAM, MOLYBDEN, VANADIN, TITAN, TANTAL, NIOB, KROM OCH BOR). (Assigned to Deutsche Edelstahlwerke A. G., Krefeld, und Gesellschaft fuer Elektrometallurgie m.b.H., Duesseldorf, Germany). Swedish Patent 148, 553. 25 Jan 1955. 2p. (In Swedish)

Unlike the existing methods requiring the use of pure metals or pure oxides as initial materials for the manufacturing of carbides of the above metals. The procedure proposed here permits the use of ores (preferably oxides). The latter are treated with a mixture of carbon and one or several of such agents as aluminum, silicon, calcium or magnesium; a heat-supplying compound such as potassium perchlorate can also be added. The reduction of the ore and the formation of the carbide are performed in a single operation, and the metallic impurities (e.g., Fe, Ni or Co) can be subsequently removed with HCl. In some cases, however, the latter metals will be left in the product to form the cementing material for the carbide crystals.

149. Renner, H., G. Brauer and A. Faessler
Bonding in the carbides of the transition metals.
ZEITSCHRIFT FUER NATURFORSCHUNG
10a:171–172, 1955. (In German)

Bonding in NbC and Nb_2C was studied by comparing the Nb L $beta_2$ emission line, excited with cathode rays, with the spectrum of Nb and Nb_2O_5. The bonding in Nb_2C is closer to the metal whereas in NbC it is similar to Nb_2O_5. This agrees with the crystal structure for the two carbides.

150. Reynolds, H. L.
Materials for nuclear ramjets. METALS
ENGINEERING QUARTERLY
2(3):1–4, Aug 1962.

Material requirements for the airframe are similar to those of any supersonic airframe. The reactor is made of a homogeneous misture of beryllium oxide and uranium oxide. These ceramic pieces operating above 2000°F are held together by Ni-base alloys and cooled refractory metals such as Mo and Cb.

151. Robertshaw, T. L.
POWDER METALLURGY OF COLUMBIUM.
General Electric Co., Evendale, Ohio.
Jan 1962. 86p. [Contract AF 33(616)-7254;
proj. 7350). (ASD-TR-61-559) N62-11161.

Powder metallurgy production of four-inch wide, 0.040 inch thick sheet of F-48, a complex columbium base alloy, was the major achievement of this program. The yield of material from billet to sheet was two to three times higher than that experienced by others in processing arc cast material. Two powder metallurgy techniques were successful in the production of billets; vacuum hotpressing and hydropressing and sintering, with hot-pressing achieving a greater degree of development. A third method of consolidation, arc-plasma spraying, proved unfeasible. The mechanical properties of the hot-pressed sheet product were about 90 percent as strong as the arc cast material and quite as ductile. Despite the fact that the oxygen content was about five times higher than the arc cast material, the sheet was workable; also, preliminary conclusions are: it is formable and weldable comparable to arc cast sheet. Only limited evaluation was made of the hydropressed sheet product, yet mechanical properties were encouragingly good. Low oxygen prealloyed powders were produced on a laboratory scale but not evaluated.

152. Rudy, Erwin, F. Benesovsky and Elizabeth Rudy
Investigation of the system vanadium-tungsten-carbon. MONATSHEFTE FUER CHEMIE 93(3):693—707, 22 Jun 1962. (In German)

In the V-W-C system vanadium and tungsten as well as carbides V_2C and W_2C form unlimited series of solid solution phases, while VC dissolves up to 43 mol-% WC and WC does not form a VC-substitutedphase. A thermodynamic examination of the equilibria in the two-phase regions (V, W) + $(V, W)_2C$ and (V, W)C + WC leads to the determination of activation energies of formation of the phases.

153. Rudy, Erwin, F. Benesovsky and K. Sedlatschek
Investigations on the system niobium-molybdenum-carbon. MONATSHEFTE FUER CHEMIE 92(4):841—855, 22 Sep 1961. (In German)

In the Mo-C boundary system of the ternary Nb-Mo-C system the existence of the γ' phase is confirmed, but is should be assigned the composition Mo_3C_2 rather than the previously given MoC. The range of homogeneity of the B_1 phase reaches from NbC to about 70 mol-% Mo_3C_2. Mo C dissolves up to about 30 mol-% Nb_2C, whereas Nb_2C aoes not dissolve Mo_2C.

154. Rudy, Erwin, Elizabeth Rudy and F. Benesovsky
Investigations in the system vanadium-molybdenum-carbon. Stabilization of the cubic molybdenum carbide. PLANSEEBERICHTE FUER PULVERMETALLURGIE 10:42—64, 1962.

Previous investigations of the ternary system Nb-Mo-C were now extended to the V-Mo-C system. A total of 48 ternary alloys was prepared from Mo metal.

(purity 99.97%), soot, and V hydride (made by hydriding 99.5% pure V) by sintering (1600−2000°) the components under pressure. The products obtained were homogenized in a tungsten arc furnace under vacuum. The alloys were investigated by x-ray and micrographs. The binary border systems V-Mo, V-C, and Mo-C are briefly discussed. In the binary Mo-C system, the existence of the two carbides Mo_2C and MoC could be confirmed in addition to the cubic B_1 Mo carbide of the formula Mo_2C recently stabilized under high pressure. In this investigation, the stabilization of the cubic Mo-C phase was accomplished through the admixture of foreign atoms such as B, U, and Th. Thermodynamic considerations indicate that the hexagonal form of Mo_3C_2 transforms at high temperature to the cubic B_1 form. Under extreme quenching conditions the cubic form of Mo_3C_2 could be obtained in a pure state. The composition was found to lie between 40.0 and 40.8 atom % C. The two-phase equilibrium (V, Mo)-(V, $Mo)_2C$ and (V, $Mo)_2C$-(V, $Mo)C_{1-x}$ are thermodynamically analyzed.

155. Rüdiger, O.
CRYSTALLINE CARBON-TUNGSTEN COMPOUND.
(Assigned to Aktiengesellschaft fuer Unternehmungen der Eisen und Stahlindustrie, Germany). German Patent 1, 006, 838.
25 Apr 1957.

An electric arc is passed between two electrodes, one consisting of W, or hexagonal crystalline WC or W C, or W-Co hard metal, the other WC in an O-free medium. Cubic face-centered crystalline C-W powder is obtained.

156. Samsonov, G. V., V. S. Sinel'nikova, and P. O. Kislin
Alloys of the system boron-carbide-molybdenum disilicide. AKADEMIIA NAUK UKRAINS'KOI R.S.R. DOPOVIDI (8): 866-868, 1959
(In Ukrainian)

B_4C-$MoSi_2$ alloys combine heat resistance with high values of thermoelectromotive force, a combination which makes these materials suitable for high-temperature thermocouples. However, at some proportions of the components, the material is readily oxidizable, and, since its thermoelectric properties are also a function of the composition, the necessity of a closer study was recognized. The authors observed the formation of a very hard phase (Mo_x(Si, B, $S)_y$ of a wide homogeneity range, which becomes the material of a monophase state at 1:1 ration of the components. At this point the oxidizing effect is at a minimum and practically zero. On the other hand, the thermoelectromotive force decreases with the increase of MoS_2 content from 10 to 50 percent.

157. Samsonov, G. V. and V. P. Latysheva
Boron, carbon, and nitrogen diffusion into the transition elements of the fourth, fifth, and sixth groups of the periodic system. AKADEMIIA NAUK SSSR. DOKLADY 109:582–585, 1956. (In Russian)

Diffusion of B and C into Ti, Zr, Nb, Ta, Mo, and W was studied by measuring the layer thickness photomicrographically, and by machining off brittle shavings thinner than the layer thickness, grinding them and analyzing the powder chemically and by x-rays. Layers of Ti C, ZrC, Ta_2C, Nb_2C, W_2C, Mo_2C, TiB_2, TaB_2, NbB_2, MoB_2, and WB_2 were identified by both methods. The B, C, and N diffusion activation energies of the metals listed are tabulated, and although the larger atomic radius of B, C, and N (0.91, 0.77, and 0.71 A., respectively) lead to the expectation of greater diffusion activation for B, the reverse is true, which is attributed to a chemical reaction during diffusion.

158. Samsonov, G. V.
Heats of formation of borides of some transition metals. ZHURNAL FIZICHESKOI KHIMII 30:2057–2060, 1956. (In Russian)

The calculated numerical values of heats of formation of TiB_2, ZrB_2, VB_2, NbB_2, TaB_2, CrB_2, MoB_2, and W_2B_5 were compared with the experimental values found tensiometrically and by an investigation of the interaction products of the borides with N and C. The heats of formation of the metal-like borides, carbides, and nitrides are determined principally by the electron concentration in their crystal lattices.

159. Samsonov, G. V., V. S. Neshpor and V. A. Ermakova
Properties of niobium-silicon alloys. ZHURNAL NEORGANICHESKOI KHIMII 3:868–878, Apr 1958. (In Russian)

Metallographic and x-ray diffraction investigations of niobium-silicon systems with 0 to 100 at.%Si showed the existence of three intermediate complexes: the Nb_4Si with hexagonal lattice with constants a = 3.59 and c = 4.46 A; the Nb_5Si_2 in three modifications alpha and beta (a = 6.56, c = 11.86 A, and a = 10.00, c = 5.07 A, respectively) and hexagonal gamma modification with constants a = 7.52 and c = 5.24 A; and the hexagonal silicides $NbSi_2$ with lattice constants a = 4.78 and c = 6.56 A. The melting points and the electric conductivity of the alloys were determined, and hypothetical phase diagrams were plotted on the basis of the data. The corrosion resistance was tested at 1000°C in the air; the systems did not exhibit strong corrosion resistance.

160. Samsonov, G. V., V. S. Neshpor and V. A. Yermakova
Study of the properties of alloys of the columbium-silicon system. ZHURNAL NEORGANICHESKOI KHIMII 3(4):46–62, 1958. (In Russian). (AEC-tr-312. 1960. 17p.) (Available from Office of Technical Services, Washington 25, D. C.)

Phase studies of the Nb-Si system at 0 to 100 at.%Si are reported. X-ray-diffraction and metallographic methods were used. Structures and formulas of intermediate silicides are listed and the melting point of various alloys was established. Electric conductivity data are given and the phase diagram is represented in preliminary form. Oxidation resistance of these alloys was studied. They are not corrosion-resistant.

161. Samsonov, G. V. and P. S. Kislyi
Technology of making tubes and stoppers from molybdenum disilicide. OGNEUPORY 24(6): 276–278, 1959. (In Russian)

A mold for making nozzles from $MoSi_2$ powder by friction pressing is shown. The plasticizer recommended for this type of pressing is starch paste in amounts of 2% (dry weight). Tubes are dried slowly for 1 to 2 days, sintered in graphite-tube furnaces in a H_2 atmosphere, and then set in Al_2O_3 or BeO powder. They are fired in "boats" to 600° to 700°, held there for 30 min., then taken to the end temperature of 1950°, and held for 5 to 10 min. The kiln and tubes are then cooled to 900° to 1000°. Shrinkage is 12 to 20%, and porosity is 5 to 12%. Variation in porosity does not exceed 1% with tubes 400 to 500 mm. long. To increase the electrical conductivity of tubes and stoppers made from $MoSi_2$, tests were made with mixtures containing SiO_2, Al_2O_3, and ZrO_2. The relation between the log specific conductivity expressed in microhms per centimeter and the molecular percentage of SiO_2 in the body is linear. $MoSi_2$ tubes may be used for making the electrodes of semiconducting thermocouples. These are $MoSi_2$ tubes containing a rod of boron carbide or graphite saturated in boron.

162. Sara, R. V. and R. T. Dolloff
RESEARCH STUDY TO DETERMINE THE PHASE EQUILIBRIUM RELATIONS OF SELECTED METAL CARBIDES AT HIGH TEMPERATURES. National Carbon Co., Parma, Ohio. Summary report, covering work for the 10-month period through 28 Feb 1962. Apr 1962. 38p. [Contract AF 33(616)-6286]. (WADD-TR-60-143, Part III). N62-17210.

Results are presented of investigations of phase equilibria in the binary systems, tungsten-carbon and zirconium-carbon. A completed phase diagram for the tungsten-carbon system is presented which differs significantly from the one proposed by Sykes in 1930 and which is generally accepted today. A tentative phase diagram for the zirconium-carbon system is included which, in general, resembles several versions published in the literature. The data were obtained by high-temperature differential thermal analysis and classical quenching procedures, both supplemented by metallographic, x-ray, and chemical techniques. Results for the tungsten-carbon binary system indicate eutectics between W and W_2C at 2710°C and between W_2C and beta-WC at 2765°C. The zirconium-carbon system is characterized by eutectic temperatures of 1860° and 2850°C on the zirconium-rich and carbon-rich sides of ZrC, respectively.

163. Schachner, H., E. Cerwenka and H. Nowotny
New silicides of the M_5Si_3 type with $D^8{}_8$ structure. MONATSHEFTE FUER CHEMIE 85:245—254, 1954. (In German)

V_5Si_3 and Nb_5Si_3 were prepared from very pure vanadium and niobium and a silicon of 99.7% purity and annealed at 1500° and 1700°C, respectively. Powder photographs of these systems show that they belonged to the $D^8{}_8$ series with the parameters a = 7.2 kX, c = 4.83 kX and c/a = 0.678 for V_5Si_3 and a = 7.52 kx, c = 5.23 kX and c/a = 0.696 for Nb_5Si_3. Mo_5Si_3 containing about 1.8%C also exhibited a $D^8{}_8$ structure, with the parameters a = 7.27 kX, c = 4.99 kX and c/a = 0.686. The system Ti_5Si_3-Zr_5Si_3 is presumable miscible in all ratios and thus only the alloy containing 60 mol-% of Ti_5Si_3 was x-rayed. Its parameters lie unambiguously between those of the constituents. The investigation of the systems Ti_5Si_3-Mo_5Si_3 and Ti_5Si_3-"W_5Si_3" showed that titanium can be replaced by molybdenum up to about 50 mol-% but only by less than 25-mol-% of tungsten.

164. Schenk, H. and U. Dehlinger
Lattice bonding and bands of valency electrons in gallium and molybdenum disilicide. (Ueber die Gitterbindung und die Baender der Valenzelektronen bei Gallium und Molybdaendisilized). ACTA METALLURGICA 4(1):7–14, Jan 1956. (In German)

The contribution of bands of valence electrons to lattice bonding was studied using an extension of the Bloch method. In $MoSi_2$ the atom function of silicon produces bands similar to gallium but are more occupied. The effective electron mass is highly anisotropic; $MoSi_2$ is a metallic conductor. Hall effect and susceptibility are discussed.

165. Schönberg, N.
The tungsten carbide and nickel arsenide structures. ACTA METALLURGICA 2:427–432, 1954. (In English)

Studies on four ternary nitrides of the tungsten carbide structure, and two new sulfides of nickel arsenide structure. Niobium sulfide phase of nickel arsenide type is stable with an excess of sulfur, but transforms to the tungsten carbide type at low sulfur content.

166. Schrewelius, N. G.
ELECTRIC RESISTANCE ELEMENTS AND THEIR MANUFACTURE. (Assigned to Aktiebolaget Kanthal, Hallstahammer, Sweden). U.S. Patent 3, 027, 331, 27 Mar 1962.

A shaped body of refractory oxidation-resistant material is based mainly on a solid continuous matrix of $MoSi_2$ with extensive intergrain portions bonded directly without any interposition of the second 0.2–20.0% montmorillonite clay phase which fills up the pores.

167. Schrewelius, N. G. and K. H. J. Medin
HEAT RESISTING MATERIALS AND METHODS FOR THEIR MANUFACTURE. (Assigned to Aktiebolaget Kanthal, Hallstahammer, Sweden). U.S. Patent 3, 027, 300. 27 Mar 1962.

A refractory oxidation-resistant and electrically conductive material consists of at least 50% $MoSi_2$ sintered from powder, and also contains silica, alumina and at least 1% quartz glass. The sintering atmosphere consists of noble gases or hydrogen either alone with a little oxygen-containing gas. Porosity of the sintered matter is less than 10 percent.

168. Schrewelius, N. G.
PRODUCTION OF SHAPED BODIES FROM HEAT RESISTANT OXIDATION PROOF MATERIALS. (Assigned to Aktiebolaget Kanthal, Hallstahammer, Sweden). U.S. Patent 2, 992, 959, 18 Jul 1961.

A body is shaped from refractory, oxidation-resistant material, e.g., $MoSi_2$, by sintering at least two separate parts together to form a nonporous body surrounded by a quartz glass film. The body is composed of $MoSi_2$ and SiO_2 powders. A diagram is shown.

169. Schultink, L. and P. M. Verpoorte
METHOD OF PRODUCING PURE CARBIDES OF THE METALS TUNGSTEN, CHROMIUM AND MOLYBDENUM. (Assigned to N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands). Canadian Patent 545, 494. 27 Aug 1957.

Pure Mo_2C is formed by passing hydrogen and hydrocarbon gas over the hot metal or its compounds. The ratio of the hydrocarbon : hydrogen concentrations must be kept lower than the ratio of the methane : hydrogen concentrations at decomposition equilibrium divided by the number of carbon atoms per molecule of hydrocarbon.

170. Schultink, L. and P. M. Verpoorte
PROCEDURE FOR THE PREPARATION OF CARBIDES OF THE METALS TUNGSTEN, CHROMIUM AND MOLYBDENUM. (VERFAHREN ZUR HERSTELLUNG VON CARBIDEN DER METALLE WOLFRAM, CHROM UND MOLYBDAEN). (Assigned to N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands). German Patent Application 12i, 37. N 10709. 14 Jun 1956. (In German)

Molybdenum carbides containing only small quantities of free carbon are prepared by passing a mixture of hydrocarbon and of hydrogen over the metal or its oxide at a high temperature and a pressure of 1 atm. The ratio of hydrocarbon to hydrogen is small than q_M/n, where q_M is the ratio of CH_4 to H in the decomposition the number of carbon atoms in one hydrocarbon molecule.

171. Schwartzkopf, P. and R. Kieffer
REFRACTORY HARD METALS. New York, MacMillan, 1953. 40p.

Covers the high-melting carbides, borides, nitrides, and silicides, which are expected to play a predominant part in future metallurgical developments. Methods of preparation and properties of these substances as well as their applications in high-temperature materials. Includes for comparison, recent high-temperature developments in superalloys and ceramics.

172. Searcy, A. W. and A. G. Tharp.
Dissociation pressures and the heats of formation of the molybdenum silicides. JOURNAL OF PHYSICAL CHEMISTRY 64(10):1539–1542, Oct 1960.

Silicon partial pressures for dissociation of Mo_3Si, Mo_5Si_3 and $MoSi_2$ were measured by the Knudsen effusion method. Heats of dissociation at 298°K were calculated as 131.9, 131.1 and 117.2 kcal, respectively, and heats of formation as -23.5, -22.6 and -13.0 kcal. Data are tabulated.

173. Sibert, M. E. and M. A. Steinberg
PRELIMINARY STUDY OF THE EQUILIBRIUM OF CARBON AND OXYGEN IN COLUMBIUM WITH CARBON MONOXIDE ABOVE 1600°C.
Horizons, Inc., Cleveland, Ohio. 1958. 19p.
[Contract AT(30-1)-1894]. (AECU-4023).
(Available from Office of Technical Services, Washington 25, D.C.)

The linearity obtained for K^1 and ΔF^1 values appears to demonstrate the validity of the assumptions made in regard to solution of C and O in niobium metal. Free energy values obtained are roughly what would be expected, the reaction becoming favorable at just under 1700°C. In order to obtain low oxygen values on a Nb product, it would be necessary to heat to an excess of 2000°C. This is borne out experimentally.

174. Simnad, M. T.
METHOD FOR FORMING A COATING OF MOLYBDENUM CARBIDE ON A CARBON BODY.
(Assigned to U.S. Atomic Energy Commission, Washington 25, D.C.) U.S. Patent 3, 028, 256.
3 Apr 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.

175. Speiser, R., et al.
Influence of carbon on the lattice parameter of molybdenum. JOURNAL OF METALS 4:275–277, 1952.

Investigation was undertaken because of the known fact that interstitial carbon may cause intergranular brittleness in Mo. Various heat treatments, C analyses, and x-ray measurements were conducted. Results show that C dissolves interstitially in Mo resulting in linear expansion of lattice parameter with increase of C in solid solution. Geometrical consideration of the relationship of C-atom size to size of interstice approximately predicts the observed volume expansion.

176. Steinitz, R.
BRAZING OF MOLYBDENUM AND TUNGSTEN AND BRAZED STRUCTURES PRODUCED THEREBY. (Assigned to Borolite Corp., Pittsburgh, Pa.). U.S. Patent 2, 775, 809. 1 Jan 1957.

Parts made from molybdenum and tungsten may be brazed by applying a Mo_2B powder to the surfaces to be joined, holding together and heating to 1900°−2100°C in a non-oxidizing atmosphere.

177. Steinitz, R.
HARD REFRACTORY METAL BORIDE COMPOSITIONS AND THEIR PRODUCTION. (Assigned to Borolite Corp., Niagara Falls, N.Y.). Canadian Patent 559, 575. 1 Jul 1958.

A strong, hard (87−90 Rockwell A hardness) material, suitable for cutting tool tips, and comprises 75−95% of a mixture of Mo_2B and the ternary compound Mo_2MeB_2 (Me = Ni or Co), the balance being Mo-Me alloy. The material is produced by forming a particulate mixture containing 30−70 at-% Mo, 15−60 at-% B and 1−40 at-% Me, compacting and sintering at an elevated temperature to cause the three elements to combine in part into Mo_2B and in part into the ternary boride.

178. Steinitz, R., I. Binder and D. Moskowitz
System molybdenum-boron and some properties of the molybdenum borides. JOURNAL OF METALS 4:983−987, Sep 1952.

Discussed in relation to raw materials and preparation, experimental procedures, room-temperature phases, and structures and properties of Mo borides. The system was studied from 0 to 25% B. Structural, physical, mechanical and oxidation-resistant properties were determined. Diagrams, graphs, and tables.

179. Steinitz, R., I. Binder, and D. Moskowitz
System molybdenum-boron and some properties of the molybdenum-borides. JOURNAL OF METALS 5:747, May 1953.

A discussion.

180. Steinitz, R.
TERNARY METAL BORIDE COMPOSITIONS.
(Assigned to Borolite Corp., Pittsburgh, Pa.).
U.S. Patent 2, 776, 468. 8 Jan 1957.

A cemented boride suitable for cutting tool tips is composed 75−95% of the compounds Mo_2B and Mo_2MoB_2, where Mo is cobalt or nickel, and a remainder of metallic alloy. Carbon is absent. A ternary diagram is shown.

181. Stolarz, S.
Siliciding of molybdenum wire and strip.
PRACE INSTITUTOW HUTNICZYCH
12(6):313−320, Dec 1960. (In Polish)

Wires and strips manufactured from molybdenum rods that were prepared by powder metallurgy were submitted to the action of SiC_4 vapors with a view to obtaining protective silicide coatings. X-ray analysis of the films so formed showed that they consisted primarily of $MoSi_2$. Depending on the temperature and the duration of the siliciding procedure, the microhardness of H_v of the coating between 829−1103 kg/mm^2, while that of the molybdenum core was 193−230 kg/mm^2. Films on wires and strips which were silicided at temperatures above 1200°C, and for periods longer than 1 hr, were the most heat resisting.

182. Storms, E. K. and N. H. Krikorian
The niobium-niobium carbide system.
JOURNAL OF PHYSICAL CHEMISTRY
64:1471−1477, 1960.

The solid portion of the Nb-NbC phase diagram has been determined. The following characteristic temperatures were measured: a eutectic temperature between $NbC_{0.08}$

and $NbC_{0.39}$ of 2335 ± 20°, a peritectic temperature between $NbC_{0.52}$ and $NbC_{0.56}$ of 3090 ± 50° and a melting point maximum at about $NbC_{0.86}$ of 3500 ± 75°. Congruent vaporization in vacuo takes place at a composition near $NbC_{0.71}$ 2800°. Below 2000° Nb_2C has a very narrow range of homogeneity. Lattice parameters for the NbC phase in equilibrium at the base boundary were found to be a_o = 3.126 ± 0.001, c = 4.965 ± 0.001 when the Nb phase was detected. In both cases c/a = 1.59. The narrowness of the homogeniety range seems to preclude the possiblity of obtaining a reliable relationship between composition and lattice parameter in this region.

183. Storms, E. K. and N. H. Krikorian
The variation of lattice parameter with carbon content of niobium carbide. JOURNAL OF PHYSICAL CHEMISTRY 63:1747–1749, Oct 1959.

A lattice constant of a_o = 4.4702 ± 0.0001 A. has been determined for $NbC_{0.994}$ ± 0.002 at 25°. The equation $a_o = 4.4704 - 0.0239\,(1\text{-}C/Nb) - 0.3586\,(1\text{-}C/Nb)^2$ has been calculated relating composition to lattice parameter of NbC. Solution of this equation for $NbC_{1.000}$ gives a lattice-parameter of 4.4704 ± 0.0005 Å.

184. Sykes, W. P., K. R. Van Horn and C. M. Tucker
A study of the molybdenum-carbon system.
AIME. TRANSACTIONS 117:173–189, 1935.

Exploration of system, by technique previously applied to tungsten-carbon series, confirmed, in part, results of one earlier investigator; more thorough examination of molybdenum-carbon constitution was initiated in effort to correlate data supplied by microstructures, diffraction patterns and chemical analyses; details of procedure.

185. Takagi, R. and K. Tamura
Vacuum hot pressing of $MoSi_2$. NIHON KINZOKU GAKKAISHI 21(3):169–172, Mar 1957.
(In Japanese)

An experimental vacuum hot press for refractory materials is described and results of tests with $MoSi_2$ are noted. The density, electrical resistivity, hot hardness, corrosion resistance, oxidation and thermal shock as well as hot modulus of rupture of the pressed specimen were measured. The temperature used was 1430°C. The properties measured were better than those produced from cold-pressing and vacuum-sintering. Micrographs are shown.

186. Tarasevich, N. I., K. A. Semenenko and K. N. Semenenko
X-ray study of the products of the chemical reactions occurring during the spectral determination of niobium. NAUCHNYE DOKLADY VYSSHEI SHKOLY, KHIMIIA I KHIMICHESKAYA TEKHNOLOGIIA p. 700–705, 1958. (In Russian)

It was shown by x-ray analysis that Nb_2O_5 and a mixture of Nb_2O_5 and SiO_2 are subjected to a series of complex chemical changes in the crater of a C electrode in the presence of the electrical arc. The only product of the interaction between metallic Nb and C is a cubic phase (apparently NbC), characterized by a lattice with a lattice constant $a = 4.38 \pm 0.1$ A. The sole product of the interaction of elementary Si with C is SiC. The interaction of the mixture Nb-Si with C is more complex, consisting of a cubic phase (i.e., NbC) and a tetragonal phase with $a = 10.00 \pm 0.01$ and $c = 5.07 \pm 0.01$ A., corresponding, apparently, to beta-Nb_5Si_3. In the interaction between Nb_2O_5 with the C of the electrode, no Nb oxide lower than NbO_2 was observed, and more NbO_2 is formed in the presence of elementary Si, which is a better reducing agent than C. In practice the most important combination is $Nb_2O_5 + SiO_2 + C$. The interaction products of this combination is NbO_2 in a mixture of two modifications of unchanged Nb_2O_5.

187. Taylor, R. E. and M. M. Nakata
STUDY OF THERMAL PROPERTIES OF REFRACTORIES. Atomics International, Canoga Park, Calif. Third Quarterly Progress Report. Rept. no. A1-7321. Apr 1962. 15p. [Contract AF 33(657)-7136; proj. 002; ARPA Order 24-61]. N62-11981.

188. Tharp, A. G.

A STUDY OF SOME REFRACTORY SILICIDES AND GERMANIDES. Ph.D. dissertation, Purdue University, Lafayette, Ind., 1957. 135p.

Heats of formation of $MoSi_2$, Mo_5Si_3 and Mo_3Si were determined by measuring the equilibrium decomposition pressures. Logarithmic plots of pressure vs. the reciprocal temperature (°K) gave a smooth curve for Mo_5Si_3, but data were scattered for the other two due to the escape of silicon vapor. Heats of formation for these silicides were estimated from free energies of dissociation. The representative heats of formation are -11.2 ± 4.0 kcal, -21.0 ± 3.5 kcal and -21.4 ± 3.0 kcal.

189. Todd, H. H.

PROCESS FOR THE MANUFACTURE OF METALLIC CARBIDES. (Assigned to Western Carbide Corp., North Hollywood, Calif.) U.S. Patent 2, 886, 454. 12 May 1959.

A carbide composition is formed exothermically by mixing comminuted carbon and aluminum with the oxide of one or more of molybdenum, vanadium, tungsten and chromium, and igniting. The carbon is 5–20 percent of the weight of the metals in the oxides.

190. Tomonari, T.

Borides, carbides, silicides and nitrides. KŌGYŌ KAGAKU ZASSHI 59(11):1272–1278, Nov 1956. (In Japanese)

Rare element compounds of boron, carbon, silicon and nitrogen which are stable and which form solid solutes are listed, and their crystalline classifications are given. Preparation methods, properties and uses are reviewed.

191. Try molybdenum disilicide.

MATERIALS AND METHODS 43(1):131–133, Jan 1956.

The engineering properties of $MoSi_2$ are being explored; strength in the 1600° – 2000° F range indicates use for turbine blades, nozzles, and similar parts. Moderate thermal shock resistance will permit many high-temperature applications. Oxidation resistance of MoSi heating elements persists up to 3000°F. A composition of 75% $MoSi_2$-25% Al_2O_3 has shown good oxidation and thermal shock resistance to 2700°F. Mechanical properties depend partly on the fabrication method. Extrusion, molding or rolling as a ceramic clay appear faesible.

192. Ueltz, H. F. G.
ELECTROLYTIC EXTRACTION OF REFRACTORY METALS OF GROUPS IV, V, AND VI FROM THEIR CARBIDES. (Assigned to Norton, Co., Worcester, Mass.) U.S. Patent 2, 910, 021. 5 Jan 1960.

A refractory metal of one of the group of Ti, V, Cr, Zr, Nb, Mo, Hf, Ta or W is electrolytically extracted from its carbide with the carbide as the anode in contact with a fused salt bath of a halide of metal from the alkali or alkaline earth groups and using a suitable conductor as the cathode. An inert atmosphere is constantly maintained. Anodes are formed by bonding the carbide with C to the desired shapes and dimensions. Thus, C-bonded rings of 8 in. inside diameter were prepared by mixing 61.5 lb. of 100 mesh TiC and 10.9 lb. powdered hard pitch and blending at room temperature. Four rings, 9-3/4 in. outside diameter by 7-3/4 in. inside diameter by 5-1/2 in. high were pressed in a mold at 3 tons/sq. in. These rings were stacked in a graphite crucible and given an Ar atmosphere. The crucible and rings were baked and volatiles distilled off by raising the temperature to 1000°. The heating period was 6 hours.

193. Verkhorobin, L. F., et al.
Reaction diffusion in systems Mo-Si, W-Si and Ta-Si. PHYSICS OF METALS AND METALLOGRAPHY 13(1):67–71, Jan 1962.

In the vacuum method of diffusion annealing of molybdenum in powdered silicon, the vapor phase of silicon plays the main role in the interaction. The silicide phases ($MoSi_x$, x = 0.33, 0.60, 2.00) form as separate layers, the diffusion being directed toward the higher silicides, and $MoSi_2$ becoming the predominant phase on prolonged annealing.

194. Vogel, R. and R. Gerhardt
The iron-molybdenum-silicon system.
ARCHIV FUER DAS EISENHUETTEN-
WESEN 32(1):47–56, Jan 1961.
(In German)

Thermal and metallographic investigations made it possible to construct for the first time the phase diagram of the Fe-Mo-Si system. An equilibrium line was found between FeSi and MoSi. Nine crystal phases were found in the system: ... Mo Si, Mo Si and MoSi. Reactions observed include six transition equilibria (of the type melt + A (solid) $\rightleftarrows$ B (solid) + C(solid), two eutectic and one eutectoid reaction. The investigations revealed also three ternary phases: Fe_2MoSi_2, Fe_3Mo_2Si and Fe_2Mo_2Si. Phase diagrams and micrographs are shown.

195. Wachtell, R. L.
A new silicide base coating for molybdenum.
AMERICAN CERAMIC SOCIETY. BULLETIN
41(8):536, Aug 1962.

A continuing effort in the development of silicide base coatings for molybdenum has resulted in the W-3 coating. Like its predecessors it derives its protective ability from the formation of silicides of molybdenum. It differs in its ability to provide complete protection even with relatively thin cases, it is glaze forming characteristics, and in much superior oxidation resistance in the 2000–3000°F range. The thinner level of case depth generally employed also makes edge preparation less critical by reducing corner build-up. Initial tests conducted under Air Force test program at General Electric have thus far been most encouraging. (Abstract)

196. Weber, W. P., et al.
PROPERTIES OF BERYLLIUM OXIDE AND
CARBIDES OF BERYLLIUM, MOLYBDENUM,
NIOBIUM, TANTALUM, AND TITANIUM.
Battelle Memorial Institute, Columbus, Ohio.
Rept. no. BMK-1165. 11 Feb 1957. 36p.
(Contract W-7405-eng-92). (Available from
Office of Technical Services, Washington 25,
D.C.)

The available data on the chemical, physical-chemical, and physical properties of several refractory materials are summarized and evaluated. The compilation covers beryllium oxide and the carbides of beryllium, niobium, molybdenum, tantalum, and titanium. A summary table of properties and a complete reference bibliography are included.

197. Woelfel, E. and E. Lassner
Contribution to the determination of oxygen in molybdenum, tungsten, tantalum and niobium, as well as in hard carbides and hard metals by hot extraction. PLANSEEBERICHTE FUER PULVERMETALLURGIE 9(3):162–169, Dec 1961. (In German)

The authors tested the possibilities of using the vacuum hot-extraction apparatus of Feichtinger and Stroehlein for determining the oxygen content in sintered molybdenum and in carbide materials (e.g., TiC-TaC-NbC). Satisfactory results were obtained, demonstrating the possibility of systematic control of the materials during production, such as oxygen contents in initial molybdenum powder, in the powder after reduction operations, in the sintered material after sintering in hydrogen or in vacuum, and in deformed materials (bar, sheet, wire).

198. Yelinson, M. I. and G. A. Kudintseva
Autoelectric-emission cathodes based on metal-like refractory compounds. RADIOTEKHNIKA I ELEKTRONICA 7(9):1511–1518, Sep 1962.

The physical properties of metallike refractory compounds, such as LaB_6, ZrC, TiC, W_2C, and W_2B_5, and particularly the first two, have been investigated under various operating conditions, and a production technology for cathodes based on these compounds has been developed. Experimental diodes under pulse and static operating conditions (pulse duration, 1.0 to 5.0 μsec; repetition frequency, 100–150 cps) were used to investigate the autoelectric properties of the cathodes. The anode, usually in the form of a cap, was made from sheet molybdenum or tungsten. The diode vacuum at the beginning of the tests was usually 1×10^{-7} to 1×10^{-8} mm hg. Tests were conducted at room temperature and constant heating up to $\sim 600°C$. An investigation of emission characteristics under static and pulse operating conditions and of the effects of vacuum and of stability under ionic bombardment, together with tests of useful life, showed that autoelectric-emission cathodes based on ZrC and LaB_6 greatly surpass tungsten cathodes. The rate of cathode sputtering was lower by four orders (ZrC) and one order (LaB_6) as compared with that exhibited by tungsten. The maximum densities of steady-state autoelectric currents were $\sim 10^6$ amp/cm^2 under static and $\sim 10^8$ amp/cm^2 under pulse operating conditions. A thermoautoelectric-emission cathode of planar structure with a current density of 10^4 amp/cm^2, based on LaB_6, has been developed.

AUTHOR INDEX

SUBJECT INDEX

III SILICIDES