89904

S/078/61/006/003/019/022
B121/B208

5.2100 , 1043 1087 1273

AUTHORS: Samsonov, G. V., Vereykina, L. L, Titkov, Yu. V.

TITLE: New method of preparing phosphides by reduction of oxides with phosphine

PERIODICAL: Zhurnal neorganicheskoy khimii, v. 6, no. 3, 1961, 749-751

TEXT: Because of their valuable and interesting properties as semiconductors, the phosphides of metals and non-metals have found wide application in pyrotechnics, in metallurgy for special coatings of steel parts, and for refining the structure of alloys. The conventional methods of preparing phosphides by direct reaction of metals with phosphorus and by reaction of metallic halides with gaseous phosphorus compounds, required a complicated equipment and were very time-consuming. A new method of preparing phosphides by the action of phosphine on oxides of metals and non-metals was devised. It bases upon the reaction $MeO + PH_3 = MeP + H_2O$, in which phosphine dissociates to phosphorus and atomic hydrogen, which promotes the reduction of oxides. The method was successfully used in the production of gallium phosphide. The gallium oxide applied is obtained by dissolving metallic

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gallium in concentrated nitric acid and by subsequent thermal decomposition of the resultant gallium nitrate at 600°C. It is then completely converted to the oxidic form at 1000°C. The resultant gallium phosphide is a yellow powder, insoluble in water, but soluble in mineral acids and alkali lyes when heated. Chemical analysis of gallium phosphide indicated 69.02% Ga, 30.78% P, corresponding to the stoichiometric composition. X-ray analysis showed a cubic lattice of the sphalerite type with a = 5.45 A which is in good agreement with the data of Ref. 9 (5.436 A) and Ref. 10 (5.4504 A). There are 1 figure and 10 references: 6 Soviet-bloc and 2 non-Soviet-bloc.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov Akademii nauk USSR
Otdel tugoplavkikh materialov (Institute of Powder Metallurgy and Special Alloys, Academy of Sciences UkrSSR, Division of High-melting Materials)

SUBMITTED: August 23, 1960

30335

S/185/61/006/005/012/019
D274/D303

24.7700 (1035, 1043, 1144)

AUTHORS: Samsonov, ~~H.~~ G.V., and Synel'nykova, V.S.

TITLE: On the width of the forbidden gap in boron carbide

PERIODICAL: Ukrayins'kyy fizychnyy zhurnal, v. 6, no. 5, 1961, 687 - 689

TEXT: The temperature dependence is investigated of the resistivity of commercial boron carbide and of relatively pure boron carbide. The specimens were prepared by hot-pressing in graphite molds. The width of the forbidden gap was calculated from the temperature dependence of the resistivity; it was found to be approximately 1.64 ev. The commercial B_4C contained Fe, Si, and Cr impurities, as well as traces of Zn, Sb, Cu and Ni. The pure boron-carbide was obtained by hot-pressing in an argon atmosphere. The temperature dependence of the resistivity of commercial B_4C was measured up to 2000°C, and of the pure B_4C up to 1600°C; the measurements were conducted by a method given in the references. The results of the measurements are shown in figures. The character of the curves is in both cases ana-

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D274/D303

On the width of the forbidden ...

logous to the curves for silicon carbide, i.e. first, the resistivity decreases owing to the excitation of the impurity electrons, then it increases due to scattering by thermal fluctuations, and then it decreases again on transition to intrinsic conductivity. The temperatures of the corresponding transitions are however different for each of the boron-carbide types, as well as for the silicon carbide. Thus, the transition to intrinsic conductivity of pure B_4C takes place at 1100-1150°C as compared to 1600°C for SiC. The activation energy of the electrons, calculated from the temperature dependence of the resistivity, is approximately 0.7 ev for pure B_4C in the temperature range 1400 - 1550°C and in the temperature range 1700 - 2000°C - approcimately 1.64 ev. In the authors' opinion, 0.7 ev. is not the width of the forbidden gap, but the transition energy of electrons. Intrinsic conductivity appears at a temperature of nearly 1700°C, and the width of the forbidden gap is approximately 1.64 ev. The energy bands of B_4C are shown in a figure, and the transition between bands is explained. The electrical conductivity in B_4C is mainly due to the flow of holes in the filled band, and of electrons - in the conduction band. There are 5 figures

30335

On the width of the forbidden ... S/185/61/006/005/012/019
D274/D303

and 6 references: 2 Soviet-bloc and 4 non-Soviet-bloc. The references to the English-language publications read as follows: R. Ridgway, Trans. Am. Electrochem. Soc., 63, 369, 1933; 66, 117, 1934; M. Yamaraki, J. Chem. Phys., 27, 3, 746-51, 1957; G. Fetterley, J. Electrochem. Soc., 24, 7, 746, 1957.

ASSOCIATION: Instytut metalokeramiky i spetsial'nykh splaviv AN URSR m. Kyyiv (Institute for Powder Metallurgy and Special Alloys AS UkrSSR, Kyyiv)

SUBMITTED: January 2, 1961

Card 3/3

26650

X-ray measurements of the thermal S/070/61/006/005/008/011
E032/E114

X

characteristic temperature Θ, the root mean square amplitude of the thermal vibrations of the complexes, and the melting temperature. Numerical results are reproduced.

The figure shows the lattice constant a of the hexaborides as a function of the atomic radii of the metals. The lattice constant a tends to increase with the atomic radius.

There are 1 figure, 2 tables and 25 references: 20 Soviet and 5 non-Soviet. The English language references read as follows:

Ref.15: E. Felten, J. Binder, B. Post. J. Amer. Chem. Soc., V.80, 3479, 1958.

Ref.17: C.F. Cline, Nature, V.181, 476, 1958.

Ref.21: H. Eick, P. Gilles. J. Amer. Chem. Soc., V.81, 5030, 1959.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M.V. Lomonosova (Moscow State University im. M.V. Lomonosov)
Institut metallokeramiki i spetsial'nykh splavov
AN USSR (Institute of Cermets and Special Alloys, AS Ukr.SSR)

SUBMITTED: March 10, 1961.

Card 2/4

27896
S/078/61/006/010/003/010
B101/B226

15.2240

AUTHORS: Samsonov, G. V., Serebryakova, T. I., Bolgar, A. S.

TITLE: Synthesis and physicochemical properties of strontium hexaboride

PERIODICAL: Zhurnal neorganicheskoy khimii, v. 6, no. 10, 1961, 2243-2248

TEXT: The authors synthesized SrB_6 by the reactions $SrO + B_4C + 2B = SrB_6 + CO$ (I) and $SrO + 7B = SrB_6 + (BO)$ (II). Initial substances were SrO obtained by heating 96.37 % $SrCO_3$ to 1250°C, B_4C, and 98.4 % B. The composition of briquetted charges corresponded to the reaction equations. They were heated to 1000-2000°C for 1 hr each. Then, their composition was analytically determined. Heating was conducted in an electric vacuum furnace. The pressure in the furnace was determined according to G. V. Samsonov (Ukr. khim. zhurn., 23, 287 (1957)). Reaction I showed a pressure increase at 1250°C caused by SrO reduction in which Sr evaporated. In the range of 1000-1200°C the reaction proceeds very slowly. In the range of 1500-1700°C, the SrB_6 yield was only 60-70 % due to evaporation

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S/078/61/006/010/003/010
B101/B226

Synthesis and physicochemical properties...

of Sr. In the range of 1800-2000°C, SrB_6 formed so rapidly that Sr did not volatilize. The yield increased to 87 %. Since reaction I yielded no carbon-free product (0.44 % C at 2000°C), reaction II was studied. Here, a minimum yield of SrB_6 (62.9 %) was observed at 1600°C due to rapid evaporation of Sr and B. Maximum yield (75.4 %) was obtained at 1800°C, the product being free from C. The following physicochemical data are mentioned: Heat of formation of $SrB_6 = 50.4$ kcal/mole; radiation coefficient $= 0.79$ at $\lambda = 0.655$ mμ between 800 and 1800°C. Between 1400 and 2100°C, vapor pressure follows the equation: $\log p_{mm} = 6.43 - 21423/T$. Therefrom, the boiling point of SrB_6 is calculated to be 5400°C. Heat of sublimation was found to be 97.2 ± 3.0 kcal/mole. For samples pressed at 2100°C and 150 kg/cm^2 (residual porosity about 10 %), the following data were found: Electrical resistivity = 191.8 μohm·cm (referred to material free from pores), microhardness = 2900 ± 90 kg/mm^2. L. Ya. Markovskiy's paper (Zh. prikl. khimii, 33, 1295 (1958)) is mentioned. There are 5 figures, 3 tables, and 14 references: 9 Soviet and 5 non-Soviet. The two references to English-language publications read as follows:

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S/078/61/006/010/003/010
B101/B226

Synthesis and physicochemical properties...

W. Dutoit, J. Chem. Phys., 24, 111 (1927); E. Jonesan, M. Becker, J. Chem. Soc., 2669 (1927).

ASSOCIATION: Otdel tugoplavkikh materialov Instituta metallokeramiki i spetsial'nykh splavov AN USSR (Division of High-melting Materials of the Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

SUBMITTED: August 5, 1960

Card 3/3

30178

S/078/61/006/012/004/011
B110/B147

15.2240

AUTHORS: Samsonov, G. V., Verkhoglyadova, T. S.

TITLE: Nitration of powdery niobium and some properties of phases formed

PERIODICAL: Zhurnal neorganicheskoy khimii, v. 6, no. 12, 1961, 2732-2737

TEXT: Nitration conditions for the formation of niobium nitrides of various compositions, and the determination of their physical characteristics were studied. Nb powder with a cubic lattice constant a = 3.29 Å and a particle size of 2 - 7 μ, sodiothermically obtained from K_2NbOF_5, was used. Nitration was carried out in a special unit (Fig. 3). According to experimental results, a solid solution of N in Nb (α-phase) forms after short nitration (15 - 30 min) at < 500°C. At 600 - 1200°C, a mixture of the nitride phases β, ε, δ', and ε is formed. After 30 - 60 min, other phases form at 900°C Nb_2N (β-phase) and 1200°C NbN (ε'-phase) without admixtures α-, β-, γ-, δ'-, and ε-phases were found radiographically. The

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lattice constant of Nb increases from 3.29 to 3.35 Å with an N concentration $\leqslant$0.7% by weight, that of Nb_2N (β-phase) (Nb = 92.0%; N = 7.1%) was: a = 3.04; c = 4.98 Å. The γ-phase only obtained in a mixture with other nitrides has the lattice constants: a = 3.22; c = 3.33 Å. The lattice constants of the δ- and ε-phases which are sufficiently constant at a high N content, were : a = 2.97; c = 5.55 Å for the δ-phase (Nb = 86.8%, N = 12.5%), and a = 2.99; c = 11.16 Å for the ε-phase (Nb = 86.95%; N = 13.1%). A study of the nitration curves (dependence of log % N - log τ; N = N content, τ = time of nitration) showed that the nitrogen saturation was linear for a time of 15 - 120 min and with formation of αNb and one-phase Nb_2N, and parabolic with formation of NbN_2. The rate of N_2 stream does not affect the composition of nitration products. The rate of furnace heating, however, has a considerable effect. On the semilogarithmical curve of temperature dependence of the rate constants, the sections of: (1) formation of the solid solution of N in Nb (α-phase); (2) β-phase, (3) ε-phase are distinguished. The activation energies are α-phase = 7260, β-phase = 7680, ε-phase = 10,000 cal/mole. This corresponds to the lower heat of formation of NbN (from elements)

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S/078/61/006/012/004/011
Nitration of powdery niobium and ... B110/B147

which is 56.8 kcal/mole (Nb_2N = 61.1 kcal/mole), and to less firm Nb-N bonds, whereas the Nb-Nb bonds of Nb_2N are firm. The microhardnesses of NbN = 1396 ± 26 and Nb_2N = 1720 ± 100 kg/mm^3 obtained by hot pressing of powdery nitration products at 1850 - 1900°C and 120 - 150 kg/cm^2 were in good agreement with the ratios of the heats of formation of the nitration reaction and coefficients of thermal expansion ($Nb_2N = 3.26 \cdot 10^{-6}$, $NbN = 10.1 \cdot 10^{-6}$ $degree^{-1}$). Measurements of the specific gravities of sintered specimens yielded extreme values on the curves of dependence of the specific gravities of the N concentration in the alloys. They correspond to the N concentration in the solid solution of Nb and in the nitride phases β and ε. The thermo-emf of NbN was 5.0 µv/degree. The thermo-emf of Nb_2N increased linearly with the temperature from 5 to 9 at 180°C and to 15.5 at 750°C. The resistivity of nitride phases increases as the N content decreases, due to the increase of Nb-Nb bonds, i. e., increase of the ion component in the bond. Thus, energy disruptions causing semiconductor properties are to be expected in N

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Nitration of powdery niobium and ... S/078/61/006/012/004/011
B110/B147

impoverishment (β-phase) and decrease of the lattice defectiveness. The temperature dependence of the vapor pressure of NbN: log p=5.1 - 20,000/T, measured according to the Langmuir method, yielded a vaporization heat of 91.5 kcal/mole, and a boiling point of ~3700°C at 1 atm. The authors thank Professor G. A. Meyerson for advice. There are 8 figures, 3 tables, and 7 references: 3 Soviet and 4 non-Soviet. The three references to English-language publications read as follows: B. Matthias, J. Phys. Rev., 92, 874 (1953); E. Gulbransen, K. Andrew. J. Metals., 2, 586 (1950); G. Brauner. J. Metals, 2, 131 (1960). X

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

SUBMITTED: October 6, 1960

Fig. 3. Diagram of nitration unit. Legend: (1) nitrogen bomb; (2) furnace with Cu filings; (3) and (6) traps; (4) absorption cylinders with Cu filings in NH_4Cl solution; (5) absorber with H_2SO_4; (7) absorbers with

Card 4/5 6

L'VOV, S.N.; NEMCHENKO, V.F.; KOSOLAPOVA, T.Ya.; SAMSONOV, G.V.

Electric properties of chromium carbides. Fiz. met. i metalloved. 11 no. 1:143-145 Ja '61. (MIRA 14:2)

1. Institut metallokeramiki i spetsial'nykh splavov AN USSR i Khersonskiy pedagogicheskiy institut im. N.K. Krupskoy.
(Chromium carbide--Electric properties)

26642
15.2630
E2c(1)/E2c(n) 6.3300
S/051/61/011/003/003/003 5
E132/E435
[illegible]
SAS(WH)
MJW(JD)
2

AUTHORS: Samsonov, G.V. and Pen'kovskiy, V.V.

TITLE: A study of the emissive power of certain refractory compounds in the infra-red region.

PERIODICAL: Optika i spektroskopiya, 1961, Vol.11, No.3, pp.410-414

TEXT: Compositions studied by the authors were limited to two types of mixtures, viz. SiC-MoSi$_2$ and SiC-Si$_3$N$_4$-MoSi$_2$. All these were found to resist oxidation when heated in air up to 1400 - 1500°C. The two-component mixtures of SiC-MoSi$_2$ were prepared with the SiC contents of 60, 80 and 85%; the three component mixtures were composed of SiC, MoSi$_2$ and Si. The amount of the latter corresponded to the stoichiometric requirement for Si$_3$N$_4$. The particle size was less than 53 μ in the case of Si and MoSi$_2$ and less than 10 μ in the case of SiC. The samples were prepared in the usual way, by compounding with a bakelite solution, pressing and squeezing out to form rods of 5 to 6 mm dia, which were subsequently dried at room temperature followed by drying at 150°C and final sintering at 500°C, in the atmosphere of hydrogen in the case of SiC-MoSi$_2$, and nitrogen in the case of SiC-Si$_3$N$_4$-MoSi$_2$. The samples were heated up to 1500°C and did not

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A study of the emissive power of ... E132/E435

show any signs of cracking after 6 hours of heating. They were mounted in water-cooled clamps, but the temperature along the rods was found to be very uniform. The emission spectra of the above samples were studied with the help of a recording infra-red spectrometer within the interval of 4 to 15 μ. The duration of emission of each spectrum was 17 minutes. The results were correlated for the general background of the dispersed light; the final intensity readings were taken on a mirror galvanometer with a scale accuracy of 1 mm. The emissivity was referred to the standard SiC globar, and plotted as relative intensity vs. wavelength for each sample. It was shown that the intensities of emission of the SiC-$MoSi_2$ and SiC-Si_3N_4-$MoSi_2$ samples were identical in the region of 4 to 14 μ. The positions of maxima in the emission spectra of SiC were not affected by the addition of 3 to 14% mol of $MoSi_2$. Additions of 6% mol of Si_3N_4 to SiC caused displacement of maxima towards the shorter wavelengths. Acknowledgments are expressed to A.F.Mal'nev and A.F.Yatsenko for assistance. There are 2 figures, 3 tables and 10 references: 4 Soviet and 6 non-Soviet. The four most recent references to English language publications read as follows: R.A.Friedel,

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26642

S/051/61/011/003/003/003

A study of the emissive power of ... E132/E435

A.G.Sharky. Rev.Sci.Instr., 18, 928, 1947;
S.Silverman, J.Opt.Soc.Amer., 38, 989, 1948;
J.E.Steward, J.C.Richmond. Science 124, 940, 1956; J.Res.Nat. Bur.Standards, 59, 605, 1957;
W.J.Spitzer, D.Kleinman, D.Walsh, Phys.Rev., 113, 127, 1959.

SUBMITTED: September 30, 1960

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[illegible]
Card 3/3

21357

S/126/61/011/004/023/023
E021/E435

9.4300 (1158, 1150, 1137)
2808, 1273, 1043, 1143
15.2220

AUTHORS: Neshpor, V.S. and Samsonov, G.V.

TITLE: Rhenium Disilicide as a New Refractory Semiconductor

PERIODICAL: Fizika metallov i metallovedeniye, 1961, Vol.11, No.4, pp.638-640

TEXT: The electrical conductivity and thermo e.m.f. of $ReSi_2$ were studied at 20 to 1000°C. The Hall-effect, the hardness and oxidation resistance in air were also investigated. Rhenium disilicide was prepared by sintering the stoichiometric mixture of powders of rhenium and silicon in a tube furnace at 1300°C for 3 hours using an argon atmosphere. X-ray studies showed that no lines other than those of $ReSi_2$ were present. The $ReSi_2$ was then ground into powder and samples were prepared by hot pressing at 1600°C and 200 kg/cm^2 in argon. They were annealed for 10 hours at 1400°C and slowly cooled to room temperature. Metallographic analysis showed only one phase which had a microhardness of 1500 ± 40 kg/mm^2. The figure shows the relation between log. electrical resistance log ρ (ρ in ohm cm) (curve 1) and thermo e.m.f. µV/deg (curve 2) with temperature °K. It can be seen

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Rhenium Disilicide ...

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that $ReSi_2$ is a semiconductor. The width of the forbidden zone is about 0.13 eV. The electrical resistance at room temperature is about 10^2 $ohm^{-1}cm^{-1}$. At this temperature the Hall coefficient has a positive sign. The conductivity is of the hole type. The concentration of admixture current carriers is about $10^{18}cm^{-3}$. The resistance to oxidation was tested at 1400°C. The change in weight during oxidation stops after 30 min oxidation, because of the protective film of silica formed on the surface. The film had a coarse grained polyhedral structure. The electrical resistance of the sample during oxidation did not change, showing that oxygen was not penetrating the sample. $ReSi_2$ has a tetragonal structure with $a = 3.131$ and $c = 7.676$ Å. There are 1 figure and 13 references: 7 Soviet and 6 non-Soviet.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN UkrSSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

SUBMITTED: July 16, 1960

Card 2/3

15 2610
25925
S/126/61/012/001/017/020
E193/E480

AUTHORS: Koval'chenko, M.S. and Samsonov, G.V.

TITLE: Relaxation processes during hot pressing of molybdenum carbide

PERIODICAL: Fizika metallov i metallovedeniye, 1961, Vol.12, No.1, pp.145-148

TEXT: The density of sintered powder compacts, prepared by the hot pressing method, depends, in addition to other factors, on the manner in which the pressure is taken off the pressed component. If the load is taken off the compact at the sintering temperature, the size of the compact gradually increases (i.e. its density decreases) after the removal of the load. The object of the present investigation was to study this after-effect ("relaxation elasticity") on hot-pressed Mo_2C. A Mo_2C powder, prepared by direct reaction between molybdenum and carbon and characterized by a particle size of 0.5 to 40 μ, was used in the hot pressing experiments carried out at 2000 to 2300°C on a manually-operated lever-actuated press. The powder, placed in a graphite die of 8 mm diameter, was sintered for 2 to 5 minutes at a given temperature under a pressure of 115 kg/cm^2, after which the load

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E193/E480

Relaxation processes during hot ...

was taken off and the compact was held at the temperature for a further 0 to 20 minutes. The compact was then rapidly cooled and its density determined by the hydrostatic weighing method. The results are reproduced in Fig.1, where the density (g/cm^3) of sintered compacts is plotted against the sintering time (minutes) at temperatures (°C) indicated by each curve, the broken parts of these curves relating to sintering under pressure. It will be seen that upon the removal of pressure from the compact its density decreased with time to approach an equilibrium or quasi-equilibrium value ρ_0 whose magnitude depends on the temperature and the density attained at the moment of removal of the pressure. Since the rate of decrease of ρ should be proportional to the relative difference $\Delta\rho/\rho_0$ between the attained and the equilibrium values, it can be shown that

$$\frac{\Delta\rho}{\rho_0} = \text{const}\ e^{-\frac{t}{\tau}} \qquad (2)$$

where t is the sintering time after the removal of pressure and

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τ is the relaxation time. Hence, the time-dependence of $\ln(\Delta\rho/\rho_0)$ should be linear, and this was confirmed by the results of the present investigation. It was shown also that

$$\tau = \tau_0 e^{\frac{U}{RT}} \qquad (4)$$

where T is the absolute temperature and U is the activation energy for the process studied. Since it was found that in the case under consideration $U = 75200$ cal/mol and $\tau_0 = 6.99$ sec, Eq. (4) becomes

$$\tau = 6.99\, e^{\frac{38850}{T}}$$

This means that an increase in the sintering temperature and the resultant increase in the plasticity of the sintered material brings about a decrease in the relaxation time. There are 3 figures and 4 Soviet references.

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Relaxation processes during hot ... S/126/61/012/001/017/020
E193/E480

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN UkrSSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

SUBMITTED: October 3, 1960

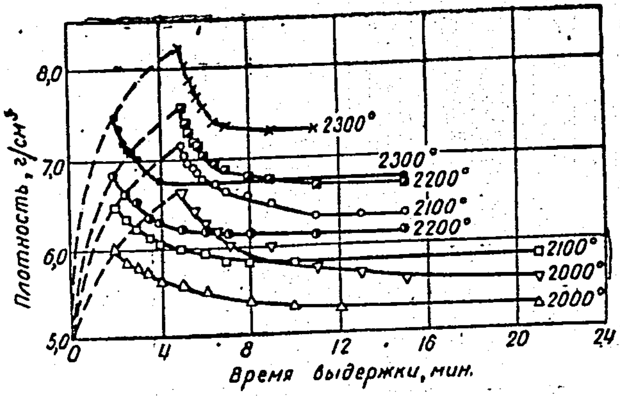

Fig.1.

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30450
S/126/61/012/003/004/021
E021/E180

15 2240

AUTHORS: Vaynshteyn, E.Ye., Verkhoglyadova, T.S., Zhurakovskiy, Ye.A., and Samsonov, G.V.

TITLE: The fine structure of X-ray absorption K-spectra of the metal in the homogeneous region of titanium nitride

PERIODICAL: Fizika metallov i metallovedeniye, v.12, no.3, 1961, 360-364

TEXT: X-ray spectrographic studies of titanium carbide were published earlier. The present work investigated the effect of concentration changes of the titanium nitrogen system in the region where only the phase TiN exists (30-50 at.% N). Samples containing 11.7, 12.8, 14.7, 15.4, 17.5, 18.1, 18.8, 20.6, 21.2 and 22.4 wt.% nitrogen were prepared by the method given by Samsonov and his team (Ref.5: Sb. Metallokeramicheskiye materialy i metody ikh issledovaniya, AN USSR, Kiyev, 1959, p.53 (Symposium: Cermets and methods of studying them, AS Ukr.SSR, Kiev, 1959, p.53). X-ray phase analysis showed that in all the specimens only one phase existed with a NaCl-type lattice having a parameter

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30450
S/126/61/012/003/004/021
E021/E180

The fine structure of X-ray ....

increasing from 4.212 to 4.235 kX with increasing nitrogen content. X-ray spectrographic studies were carried out on apparatus described earlier by I.B. Staryy, (Ref.7: Izv. AN SSSR, ser. fiz., 1958, Vol.20, 798). The crystalline structure of titanium nitride is always octahedral. Decreasing nitrogen content in the nitride phase, although maintaining the octahedral coordination, should lead to a reduction in the role of the p-functions, decreasing their contribution to the d-band and therefore decreasing the coefficient of absorption in the corresponding spectral region; this was actually observed for all compositions, except those with 21.2 and 22.4 wt.% nitrogen, which very nearly correspond to the stoichiometric composition of TiN. Another explanation of the change in the fine structure of absorption spectra is that in the nitride phase there is a considerable ionic component in the bonds which decreases with transition from the samples deficient in nitrogen to the compound with stoichiometric composition. This is confirmed by results of measurements of the electrical properties and microhardness of the samples. S.N. L'vov and V.F. Nemchenko are mentioned in the article for their contributions in this field.

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30450

S/126/61/012/003/004/021
E021/E180

The fine structure of X-ray ....

There are 2 figures and 16 references: 13 Soviet-bloc and 3 non-Soviet-bloc. The English language reference reads as follows: Ref.12: G. Kimball, J. Chem. Phys., 1940, Vol.8, 188.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys, AS Ukr.SSR)
Institut neorganicheskoy khimii Sibirskogo otdeleniya AN SSSR (Institute of Inorganic Chemistry, Siberian Department AS USSR)

SUBMITTED: January 2, 1961

X

Card 3/3

15 2640
24 7700

[illegible]
S/126/61/012/004/021/021
E073/E535

AUTHORS: Verkhoglyadova, T.S., L'vov, S.N., Nemchenko, V.F. and Samsonov, G.V.

TITLE: Electric and galvanomagnetic properties of chromium nitrides

PERIODICAL: Fizika metallov i metallovedeniye, v.12, no.4, 1961, 622-624

TEXT: In the system chromium-nitrogen two stable nitride phases are known - Cr_2N and CrN. According to one of the authors (Ref.1: Samsonov G.V. Zhurnal strukturnoy khimii, 1960, 1, 447) these are characterized by a combination of metallic and ionic bonds, whereby the latter predominate to some extent. This is due to the high ionization potential of the nitrogen atom and the low acceptor ability of the incomplete d-shell of the chromium atom. This assumption on the nature of the chemical bond in nitride phases of chromium is confirmed by the results of X-ray structural investigations, according to which the chemical bond in the higher nitride Cr_2N approaches the type of bond of the chromium oxide Cr_2O_3. In this paper the electric and galvano-

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3059

Electric and galvanomagnetic ... S/126/61/012/004/021/021
E073/E535

magnetic properties of chromium nitrides are studied. The compact specimens were produced by sintering briquettes with a porosity of 20-25% pressed from powder of electrolytic chromium. The sintering was at 950°C (for alloys with a composition approaching CrN) to 1300°C (for alloys approaching the composition of Cr_2N) for durations of 3 to 4 hours in nitrogen which was carefully purified from oxygen. The porosity of the specimens varied between 0 and 5%. This method of preparing specimens enabled avoiding changes in their phase state and the formation of carbonitride phases which are unavoidable in hot pressing of preliminarily manufactured chromium nitride powders. From thus produced specimens the specific electric resistance ρ and the absolute coefficient of thermo e.m.f. α_T, the Hall coefficient R and the thermal conductivity $\varkappa$ were determined. The results are entered in a table, which also contains data from the literature for pure chromium as published by A. Ye Vol (Ref.4: Stroyeniye i svoystva dvoynykh metallicheskikh sistem*, v.1, Fizmatgiz, M., 1959) and S. Foner (Ref.5: Phys.Rev., 1957, 107, 1513). It was found that in contrast to most of the intermediate phases (including chromium

X

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carbides), the resistance of chromium nitrides increases from the lower nitrides to the higher ones. Similarly, the Hall coefficient and the thermo e.m.f. coefficient increase with increasing nitrogen content. On the other hand, the thermal conductivity of the higher chromium nitrides is lower than of the lower chromium nitrides. This behaviour can be qualitatively explained on the basis of the electron structure of chromium proposed by Ye. S. Borovik and V. T. Volotskaya (Ref.7: ZhETF, 1959, 36, 1650) who assumed that the electric conductivity of Cr is basically due to highly mobile holes and electrons in the overlapping 4s- and 4p-bands. With some degree of approximation this enables utilizing the known expressions of the Hall coefficient and the electric conductivity for the case of two types of carriers and to determine the numerator $(n_-u_-^2 - n_+u_+^2) = \delta$ of the Hall coefficient. The appropriate values are given in the table. The chromium nitride CrN can be classified as an electron semiconductor, the use of which is promising as a negative branch of high temperature thermocouples (particularly for operation inside nitrogen) and also for producing thermoelectric transducers of heat

X

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Electric and galvanomagnetic ... S/126/61/012/004/021/021
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into electricity with an efficiency of up to 18-20% if paired for instance with MnSi. There are 1 table and 8 references: 7 Soviet-bloc and 1 non-Soviet-bloc. The English-language reference is quoted in the text.

ASSOCIATIONS: Institut metallokeramiki i spetsial'nykh splavov AN UkrSSR
(Institute for Cermets and Special Alloys AS UkrSSR)
and
Khersonskiy pedagogicheskiy imeni N.K.Krupskoy
(Kherson Pedagogic Institute imeni N.K.Krupskaya)

SUBMITTED: March 7, 1961

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SAMSONOV, G.V.; YASINSKAYA, G.A.; LAPTEVA, E.P.

Refractory products made from cerium dioxide. Ogneupory 26 no.1: 41-42 '61. (MIRA 14:2)

1. Institut metallokeramiki i spetsial'nykh splavov AN USSR.
(Refractory materials) (Cerium dioxide)

SAMSONOV, G.V.; KISLYY, P.S.; PANASYUK, A.D.; STREL'CHENKO, A.G.;
KHAVRUNYAK, I.G.; SERIKOVA, G.N.

Zirconium boride tips for thermocouples. Ogneupory 26
no. 2:72-74 '61. (MIRA 14:2)

1. Institut metallokeramiki i spetsial'nykh splavov AN USSR
(for Samsonov, Kislyy, Panasyuk). 2. Institut avtomatiki Gosplana
USSR (for Strel'chenko, Khavrunyak, Serikova).
(Thermocouples)

SAMSONOV, G.V.; YASINSKAYA, G.A.; SHILLER, E.A.

Reaction of some oxides and carbids with infusable metals at high temperatures. Ogneupory 26 no.7:335-338 '61.
(MIRA 14:7)

1. Institut metallokeramiki i spetsial'nykh splavov AN USSR.
(Metals at high temperatures)

SAMSONOV, G.V.

Conference on the manufacture and use of infusible compounds of rare elements. Ogneupory 26 no.8:385-386 '61. (MIRA 14:9)

1. Institut metallokeramiki i spetsial'nykh splavov AN USSR.
(Metals, Rare and minor--Congresses)
(Refractory materials--Congresses)

S/074/61/030/001/003/003
B013/B055

AUTHORS: Samsonov, G. V., Radzikovskaya, S. V.

TITLE: Chemistry of Sulfides of Rare-earth Elements and Actinides

PERIODICAL: Uspekhi khimii, 1961, Vol. 30, No. 1, pp. 60-91

TEXT: The present paper systematizes and generalizes the existing experimental data on sulfides of rare-earth elements and of actinides. The structure and properties of this class of compounds are dealt with in Refs. 1 to 17 (Figs. 1-3, Tables 1-5). The physicochemical properties of 76 sulfides and oxysulfides are listed in Table 6. Of the main preparation methods, the following are described briefly: 1) Direct reaction of metal and sulfur (Ref. 15), 2) Interaction between metal powder and hydrogen sulfide, 3) Action of hydrogen sulfide on metal oxides (Refs. 30, 51, and 52), 4) Thermit reduction, 5) Preparation of sulfides from hexasulfides (Refs. 24,78), 6) Interaction between metal salts and hydrogen sulfide (Refs. 53,54), 7) Thermal dissociation of higher sulfides yielding lower sulfides (Ref. 38). The preparation methods of oxysulfides are mentioned. The method described in Ref. 55 is suggested for preparing thiosulfates of

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the type $Me_2(S_2O_3)_3$, which are structurally related to oxysulfides but possess the properties of salts. Data on the following sulfides and oxysulfides are available: the only scandium sulfide described is Sc_2S_3 (Ref. 17), the yttrium sulfides and -oxysulfides described are YS, Y_5S_7, Y_2S_3, YS_2 and Y_2O_2S (Refs. 18-20, 22 and 56), lanthanum forms several sulfides, LaS, La_2S_4, La_2S_3, LaS_2 as well as La_2O_2S (Refs. 15,18,23-25, 29,56,57, and 76). The sulfides and oxysulfides of cerium, of which the following are known, have been investigated thoroughly owing to their promising possibilities of application: CeS, Ce_2S_4, Ce_2S_3 (α, β and γ modifications) and Ce_2O_2S (Refs. 2,15,18,19,22,30-32,51,52,54,56,58,60, and 61) - (Figs. 4-7, Tables 7-9). Of praseodymium, neodymium and samarium, the sulfides of composition MeS, Me_3S_4, Me_2S_3 and the oxysulfides Me_2O_2S have been described (Refs. 15,16,23,25,27,29,56 and 62). The following europium sulfides were found to exist: EuS, Eu_3S_4, $EuS_{3.81}$ and the oxysulfide Eu_2O_2S (Refs. 29 and 34). The gadolinium sulfides GdS, Gd_2S_3 (α and γ modifications), GdS_2 and Gd_2O_2S (Refs. 18,29 and 35) are known. The only sulfur compound of terbium described is the oxysulfide Tb_2O_2S (Ref. 29). Dysprosium was found to form the sulfides Dy_5S_7, Dy_2S_3 (α, γ and δ modifications) DyS_2 and the oxysulfide Dy_2O_2S (Refs. 21,29 and 56). Holmium oxysulfide Ho_2O_2S (Ref. 29) was obtained in a similar manner as Gd_2O_2S. Like dysprosium, erbium forms sulfides of the type ErS, Er_5S_7, Er_2S_3 as well as Er_2O_2S (Refs. 18,21,29,35 and 56). Thulium oxysulfide Tu_2O_2S (Ref. 29) was obtained in a similar way as the other oxysulfides. The following sulfides and oxysulfides of ytterbium are known: $YbS_{1.14}$, $YbS_{1.33}$, $YbS_{1.48}$, Yb_2S_3 and Yb_2O_2S (Refs. 18,22,36 and 56). Lu_2O_2S (Ref. 29) is the only sulfur compound described of lutetium, and the only one known of actinium is Ac_2S_3 (Ref. 57). The sulfur compounds of thorium have been

Chemistry of Sulfides of Rare-earth Elements and Actinides
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studied as thoroughly as those of cerium, i.e. ThS, Th_2S_3, Th_4S_7 (or Th_7S_{12}) and ThOS (Refs. 1,10,38,40-42 and 63-71) - (Fig. 8, Tables 10-13). The only sulfur compound known of protactinium is the oxysulfide PrOS (Ref. 43). The following sulfides and oxysulfides of uranium are known: US, U_2S_3, U_3S_5, US_2 (α, β and γ modifications) UOS_2 and UOS (Refs. 32,42, 45-48, 72 and 73). Of neptunium, the sulfide Np_2S_3 and the oxysulfide NpOS have been described (Refs. 1 and 49), and of plutonium, the sulfides PuS, Pu_2S_3, Pu_3S_4, and the oxysulfide Pu_2O_2S (Ref. 50). Similarly to plutonium, americium forms Am_2S_3 and AmSO (Ref. 75). Though most of the sulfides of the rare-earth elements and actinides have not yet been investigated thoroughly, it is possible to predict their practical applications. Foremost, cerium- and thorium sulfides can be used for the production of refractory materials. Sulfides are also used in semiconductor engineering, as catalysts, thermoelectric generators, high-resistance volumetric resistors, and for the preparation of antifriction materials and solid lubricants. Ye. S. Makarov, V. V. Serebrennikov, and N.P.Zvereva

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Chemistry of Sulfides of Rare-earth Elements and Actinides S/074/61/030/001/003/003
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are mentioned. There are 8 figures, 13 tables, and 78 references: 19 Soviet, 18 US, 1 Australian, 4 British, 26 French, 13 German, and 1 Italian.

ASSOCIATION: In-t metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

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22520

S/080/61/034/001/001/020
A057/A129

5.2400 1043, 1208, 1228
26.1632 26.2351

AUTHORS: Samsonov, G.V., Paderno, Yu.B., Kreyngol'd, S.U.

TITLE: Preparation of Lanthanum Hexaboride

PERIODICAL: Zhurnal Prikladnoy Khimii, 1961, Vol. 34, No. 1, pp. 10-15

TEXT: The preparation of lanthanum hexaboride from lanthanum oxide and boron carbide or boron was investigated and optimum conditions in vacuum were determined. Hexaborides of rare-earth metals are of interest since these borides (especially LaB_6) are used as materials for power-tube cathodes. A method is presented to establish the best conditions for obtaining also hexaborides of the other rare-earth metals. The pulverized materials La_2O_3, B_4C and B were mixed in stoichiometric compositions corresponding to the equations:

$$La_2O_3 + 3\ B_4C \longrightarrow 2\ LaB_6 + 3\ CO \quad (1) \quad \text{or}$$

$$La_2O_3 + 15\ B \longrightarrow 2\ LaB_6 + 3/2\ B_2O_2 \quad (2)$$

and then sieved and briquetted. The briquettes were fired at the tempera-

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A057/A129

Preparation of Lanthanum Hexaboride

ture investigated in a vacuum oven and the reaction rate was determined by controlling the change of pressure for different temperatures. In Fig.1 the dependence of the pressure on the holding time in the reaction of La_2O_3 with B_4C is demonstrated. The obtained products were subjected to chemical and x-ray analysis with a РКД (RKD) camera and Cu-source. The obtained experimental results are presented in Tables 1 and 2. Both reactions (1) and (2) start at 1,200-1,300°C and terminate after 1 hr at 1,500-1,600°C. Thus optimum temperature is in the range of 1,500-1,600°C. Reaction (2) gives a carbon-free product. At higher temperatures losses of lanthanum due to evaporation take place in reaction (2). Approximate heat of formation for LaB_6 was determined by tensiometric analysis with -112.3 ± 6.5 kcal/mole. Temperature dependence of the true specific heat of LaB_6 is $c_p = 21.73 + 20.4 \cdot 10^{-3} \cdot T$ cal/mole·degree. The obtained value for the heat of formation compared with the corresponding value for CeB_6 (-81 kcal/mole) confirms the theory of dependence of the thermodynamical stability on electron configuration. In connection with preparations of borides the following papers were mentioned: G.V. Samsonov, Yu.B. Paderno, SOV Patent No. 121561 (1959); G.V. Samsonov, A.Ye. Grodshteyn, ZhFKh, 30,379,1956; V.S. Neshpor, G.V. Samsonov, Elektronika 3,148 (1959); Yu.B. Paderno, T.I. Serebryakova, G.V. Samsonov, Doklady AN

SSSR, 125,317 (1959); G.V. Samsonov, N.N. Zhuravlev, Yu.B. Paderno, V.R. Melik-Adamyan, Kristallografiya, 4,538 (1959). There are 4 figures, 3 tables and 21 references: 15 Soviet-bloc and 6 non-Soviet-bloc. The references to the English-language publications read as follows: E. Felten, I. Binder, B. Post, J.Am.Chem.Soc., 80,3479 (1958); J. Lafferty, J.Appl.Phys., 22,299 (1951); A. Searcy, C. Myers, J.Phys.Chem., 61,957 (1957).

ASSOCIATION: Institut metallokeramiki i spetssplavov AN UkrSSR (Institute of Powder Metallurgy and Special Alloys of the AS UkrSSR)

SUBMITTED: April 30, 1960

27063
S/080/61/034/003/003/017
A057/A129

15.2240
11.1380

AUTHOR: Sleptsov, V. M., Samsonov, G. V.

TITLE: Preparation of boron nitride by nitration of a mixture of boron anhydride and carbon

PERIODICAL: Zhurnal prikladnoy khimii, v. 34, no. 3, 1961, 501-505

TEXT: Based on the method proposed by A. Stähler and F. Elbert [Ref. 5: Ber., 46, 2075 (1913)] the production of boron nitride by heating boron anhydride with carbon black in a flow of nitrogen at a temperature of up to 2,040°C according to the reaction $B_2O_3 + 3C + N_2 = 2BN + 3CO$ was investigated. Boron nitride, called also "white graphite", is a crystalline substance with properties (high melting point, low thermal conductivity, high resistance to different agents etc.) which make it suitable for refractory products and also as admixture for high-temperature lubricants. Several methods are known for the preparation of boron nitride and are reviewed by the present authors in a prior paper [Ref. 1: Voprosy poroshkovoy metallurgii i prochnosti materialov (Problems in powder metallurgy and material strength), Izd. AN USSR (Ed. AS UkrSSR), 5, 66 (1958)]. The most common of these methods is nitration of boron anhydride by ammonia gas, but

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considerable difficulties are encountered in the purification of the final product from the calcium oxide "carrier". An expedient development was made in Stäler's method by using carbon black simultaneously as "carrier" and as reducing agent for boron anhydride, but rather low (26%) yields were obtained and the product was contaminated with carbon. For this reason more detailed investigations of this procedure were made in the present work and attempts at improvement were centered on developing a better contact between the reacting solids, on establishing the optimum ratio of the reactants, and on finding optimum temperatures. Pure boric acid and lampblack was mixed (varying the ratio) during 1 hour, sieved (60 mesh sieve) and boric acid was dehydrated by heating according to M. S. Maksimenko and G. V. Samsonov [Ref. 6: Sb. "Kinetika i kataliz" ("Kinetics and Catalysis"), Izd. AN SSSR, 129 (1960)]. Thus a porous sinter product was obtained with a thin boric acid film on carbon black. The product was ground, sieved and finally nitrated. Preliminary tests demonstrated that with stoichiometric compositions (71% by weight H_3BO_3, and 29% by weight carbon black) a heavily carbon-contaminated product is obtained. Thus only 25, 20, 15 and 10% by weight carbon black was added, and the duration of grinding the sintered product increased correspondingly up to 8 - 10 hours. Results obtained in nitrations at 1,500 - 1,900°C show that the reduction of B_2O_3 is

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Preparation of boron nitride by nitration ...

completed above 1,600°C. Maximum nitrogen content in the product is attained with 10% carbon black in the charge and decreases for 15% and 20%, and decreases sharply at 25% carbon black content. The following mechanism of reduction is proposed by the present authors: The reaction consists of the reduction of boron anhydride with carbon black to boron and subsequent carbonization or nitration of the latter. At a low carbon content in the charge all carbon is used for reduction and the excess boron anhydride evaporizes decreasing thus the yield. Increasing carbon content in the initial mixture increases the amount of reduced boron anhydride, decreases nitration degree and increases the yield. Maximum boron nitride yield is obtained at 1,600 - 1,700°C when high volatility of B_2O_3 is depressed by reduction and nitration. Optimum conditions for the boron nitride production are: 3 hours nitration at 1,700°C and a carbon black content of 15% in the initial mixture. A further improvement is effected by two-step nitration, i.e., first to 1,500°C and then to 1,700°C. The typical chemical composition of nitride obtained in this way is: 43.1 - 43.4% B, 55.2 - 55.9% N and up to 0.1% C. Corresponding experiments demonstrated in the present work that the results obtained by Stähler were insufficient, because of the small reaction surface between the reactants by simple mechanical mixing. Thus only 3-4% yields of a highly carbon-contaminated product were obtained. There are 2 figures, 1 table

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Preparation of boron nitride by nitration ...

and 7 references: 5 Soviet-bloc and 2 non-Soviet-bloc.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys, AS UkrSSR)

SUBMITTED: June 24, 1960

Table: Results of nitration of sintered products of boron anhydride and carbon black in a flow of nitrogen

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5.2200
15.2200

27073
S/080/61/034/003/015/017
A057/A129

AUTHORS: Radzikovskaya, S. V., Samsonov, G. V.

TITLE: Vacuum-thermic method for the preparation of cerium and lanthanum monosulfides

PERIODICAL: Zhurnal prikladnoy khimii, v. 34, no. 3, 1961, 671 - 672

TEXT: A method for the production of monosulfides of rare-earth metals is described which allows for a large-scale production of these compounds used as components in refractory materials, in parts of radio- and electric engineering apparatus, as well as investigations of their physical and chemical properties. The method is based on the reaction $2Me_2S_3 + Me_2O_3 + 3C = 6MeS + 3CO$ carried out in vacuum and was tested by manufacturing cerium and lanthanum monosulfides. The sulfides Ce_2S_3 and La_2S_3 were obtained by a reaction of CeO_2 or La_2O_3 with dry hydrogen sulfide at 900 - 1,000°C. The reaction $Me_2O_3 + C = Me + CO$, $Me_2S_3 + Me = = MeS$ was proved experimentally by the reduction of CeO_2 with carbon black at temperatures from 1,000 to 1,700°C. The results show that until 1,400°C reduction occurs rather slow; the rate rises sharply at higher temperatures attaining almost the maximum at 1,600°C. Simultaneously with cerium metal, apparently cerium oxy-

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carbides and instable carbides are formed which are also converted to cerium metal. The reaction $Ce_2S_3 + CeO_2 + 2C = 3CeS + 2CO$ was carried out in vacuum (10^{-1} - 10^{-2} torr) in the temperature range 1,000 - 1,700°C with briquetted (8 x 10 mm) samples, and a holding time at each temperature for 1 hr. The obtained reaction products contained still a considerable amount of oxides and oxysulfides, as well as free carbon (up to 1%). Thus the next experiments were carried out with additional amounts of 10 - 80% Ce_2S_3 (related to the weight of Ce_2S_3). The obtained results (see Table) demonstrate that cerium monosulfide with stoichiometric composition and lowest content of impurities is obtained with a 70% admixture of Ce_2S_3. The latter can be added immediately to the initial charge and the reaction can be carried out in one step. Nevertheless, a two-step heating with intermediate grinding of the product is more effective. Corresponding experiments with lanthanum demonstrated that no additional admixture is necessary in this reaction, but two-stage heating at 1,650°C with intermediate grinding of the product. Thus lanthanum monosulfide obtained contains La_{total} 81.2%, S_{bound} 18.6% and S_{free} 0.1%. Both monosulfides are of golden-yellowish color and their X-ray structure and lattice are similar to corresponding data in the Table. There is 1 table, 1 figure and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc. The references to the Eng-

Card 2/4

27073
S/080/61/034/003/015/017
Vacuum-thermic method for the preparation of cerium and...A057/A129

lish-language publications read as follows: F. McTaggart, Austral, J. Chem., 11, 471 (1958); E Eastman, L. Brewer et al., J. Am. Chem. Soc., 72, 2248 (1950).

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys of the AS UkrSSR)

SUBMITTED: June 16, 1960

Card 3/4

24430
S/080/61/034/007/004/016
D223/D305

15 2240

AUTHORS: Samsonov, G.V., Makarenko, G.N., and Kosolapova, T.Ya.

TITLE: Preparation and properties of yttrium monocarbide

PERIODICAL: Zhurnal prikladnoy khimii, v. 34, no. 7, 1961, 1444 - 1448

TEXT: Of all yttrium carbides the highest practical interest is in yttrium monocarbide YC, whose properties in contrast to YC_2 should be closer to the chemically stable carbides of transition metals of the V period (zirconium, niobium, molybdenum). Literature does not give any data on existence of this carbide, hence the present work deals with the investigation into the possibility and conditions of its preparation and study of some properties. To prepare YC use is made of vacuum reduction of yttrium oxide, with carbon, by the following reaction:

$$Y_2O_3 + 5C = 2YC + 3CO.$$

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After explaining the preparation methodology the products of reduction-carbonization were analyzed for yttrium content, total and free carbon. The analysis was difficult, since the products of reduction decomposed in air. The results of analysis are given in Table 1 and Fig. 1.

Table 1. Results of experiments to prepare YC (change of stoichiometric composition).

Legend: 1 - temperature, °C; 2 - wt. of briquettes; 3 - initial; 4 - final, A; 5 - decrease in wt. %; 6 - calculated wt. of briquettes after heating, B (gr.); 7 - ratio A/B, %; 8 - heating time, hours; 9 - composition, %; 10 - total C; 11 - free C; 12 - C combined; 13 - C total; 14 - N.D.; 15 - N.D.; 16 - samples melted; * C combined calculated on carbide phase YC : $C_{comb} =$

$$= \frac{C_{total} - C_{free}}{100 - C_{free}} \times 100 \%.$$

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Preparation and properties ...

Table 1. (Cont'd).

A

ТАБЛИЦА 1

Результаты опытов по приготовлению монокарбида иттрия (шихта стехиометрического состава)

R ① Температура (°C)	② Вес брикета (г) начальный ③	конечный A ④	⑤ Убыль веса (%)	⑥ Расчетный вес брикета после нагрева — B (г)	⑦ Отношение A/B (%)	Время нагрева (час) ⑧	⑨ Содержание (%). ζ Y	$C_{общ}$ ⑩	$C_{своб}$ ⑪ K	$C_{связ}$ ⑫ L	$C_{общ}$ ⑬ M Σ
1000	10.20	9.90	3.0	7.20	137	2.16	62.0	24.8	24.8	не обн.	86.85
1100	10.45	10.15	2.8	8.22	124	2.00	64.1	21.3	21.2	не обн.	85.4
1200	9.90	9.82	0.8	6.99	140	2.16	63.0	20.1	20.2	не обн. ⑭	83.1
1300	10.99	10.70	2.6	7.76	138	2.16	63.0	20.4	20.4	не обн.	83.4
1400	7.99	7.65	4.2	5.64	135	2.33	62.9	20.4	20.6	не обн.	83.3
1500	9.78	9.30	4.9	6.90	135	2.00	63.2	20.4	20.1	не обн.	83.6
1550	3.12	2.85	8.6	2.46	116	2.50	64.6	18.2	10.6	8.4	82.8
1600	7.55	6.04	20.0	5.33	113	3.16	74.8	15.6	4.7	11.4	90.4
1700	9.94	7.74	22.1	7.02	110	3.16	77.4	14.1	не обн.	14.1	91.5
1800	10.22	7.65	25.1	7.21	106	3.00	81.0	14.0	не обн.	14.0	95.0
1850	11.10	8.50	23.4	8.73	97.6	2.00	83.2	14.4	не обн.	⑮ 14.4	97.6
1900	8.85	5.95	32.7	6.25	95.1	3.16	85.3	12.0	не обн.	12.0	97.3
2000	6.95	Образец расплавился ⑯				3.16	78.0	15.5	0.31	15.3	93.3

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Fig. 1. Composition of reduction products against temperature.

Legend: V - concentration (%); G - ratio A/B (see Table 1); D - temperature °C; 1 - coefficient A/B; 2 - yttrium concentration; 3 - combined C; 4 - free carbon; 5 - total C + Y; 6 - calculated concentration of Y; 7 - calculated concentration of carbon.

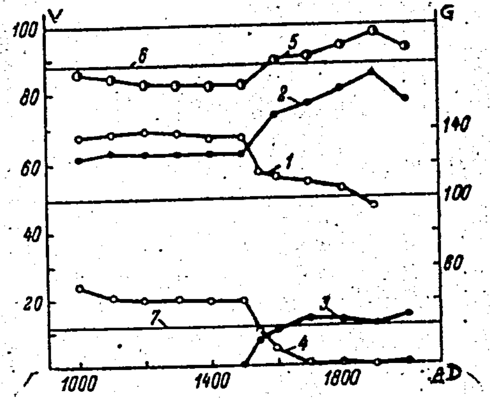

Рис. 1. Зависимость состава продуктов реакции от температуры.

В — содержание (%). Г — отношение А/В (табл.). Д — температура (°С).
1 — коэффициент А/В; 2 — содержание иттрия, 3 — то же связанного углерода, 4 — то же свободного углерода; 5 — сумма содержаний $C_{общ}$ + Y; 6 — расчетное содержание Y; 7 — то же углерода.

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Preparation and properties ...

It follows from the above data that combined carbon agrees with
the calculated value for the formation of the YC phase and free
carbon practically disappears at 1700°C; similarly the yttrium con-
centration approaches that of YC at 1900°C; at this temperature
the sum (yttrium content + total carbon) is more stable and appro-
aches an accuracy of analysis of 97-98 %. Above 1900°C the yttrium
carbide melts with a loss of yttrium by evaporation leaving a li-
quid phase rich in carbon. At temperatures of 1900°C and time of
2.5 - 3 hours a uniform product is formed, golden colored, having
a mean combined C content of 12 %, free C, equal practically to
zero which agrees with carbide YC (theoretical combined C = 11.89%).
The thermal analysis of yttrium carbide distribution for the range
from 20 to 1100° by the method of T.S. Verkhoglyadova and L.L.
Vereykina (Ref. 7: TsITEIN, M., vyp. 2, 14, 1960) using a protect-
ing atmosphere showed the absence of any transformations; the coef-
ficient of thermal expansion is small and equal to 1.36 • 10^{-1} de-
gree^{-1}. The specific resistance, determined by a probe method was
equal to 4 • 10^4 $\mu\Omega$ cm. Thermoelectric power determined for the

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couple with electrolytic copper and calculated with respect to lead was found to be 34.8 µV/degree. On the basis of this data it follows that YC possesses semiconducting properties. The melting point was equal to 1950 ± 20°C. Yttrium monocarbide rapidly oxidizes in air (in a powdered state), decomposes with water and weak acid and alkali solution; concentrated acids decomposed it slightly. Also it decomposes in air at room temperature at different rates, first rapidly (formation of oxycarbides) reaching a maximum and then gradually decreasing (decomposition of oxycarbides into Y_2O_3). After 50 hours of air oxidation, the carbon content falls to 5.1 % and after 75 hours to 2.5 %. There are 5 figures, 3 tables and 8 references: 3 Soviet-bloc and 5 non-Soviet-bloc. The reference to the English-language publication reads as follows: F. Spedding, K. Gschmider, A. Daane, J. Am. Chem. Soc., 80, 4499, 1958.

ASSOCIATION: Otdel tugoplavkikh materialov instituta metallokeramiki i spetssplavov AN USSR (Department of High Melting Materials, Institute of Metal Ceramics, AS USSR)

SUBMITTED: November 5, 1960

Card 6/6

LAKH, V.I.; PROKHORENKO, V.Ya.; TEREBUKH, L.S.; KISLYY, P.S.; PANASYUK, A.D.; SAMSONOV, G.V.

Temperature measurement of the atmosphere of an aluminum electrolysis cell. TSvet. met. 34 no.8:38-40 Ag '61. (MIRA 14:9)
(Aluminum--Electrometallurgy)

31475
S/080/61/012/034/013/017
D204/D305

18.3100 1087

AUTHORS: Samsonov, G.V., and Kosolapova, T.Ya.

TITLE: Preparation of metallic chromium by the interaction of Cr_2O_3 and Cr_3C_2

PERIODICAL: Zhurnal prikladnoy khimii, v. 34, no. 12, 1961, 2780 - 2782

TEXT: The reaction $2Cr_2O_3 + 3Cr_3C_2 = 13\ Cr + 6\ CO$ was studied to investigate the possibility of preparing pure chromium and also niobium, by an analogous method. In the present study, the reaction was followed manometrically and the products were examined both chemically and by phase analysis (the latter based on differential solubility in HCl). It was found that Cr_2O_3 and Cr_3C_2 reacted at 1200°C to give Cr_7C_3 which in turn reacted with excess chromia at 1400°C to yield metallic chromium. Heating compacted stoichiometric mixtures of the two reactants between 1000-1700°C showed that initial interaction takes place at 1200°C. With rising tem-

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S/080/61/034/012/013/017
D204/D305

Preparation of metallic chromium ...

perature the proportions of Cr_2O_3 and Cr_7C_3 in the product decreased and that of Cr increased, to 95.4 % at 1600°C. A product containing 96.0 % Cr, 0.9 % Cr_7C_3 and 2.5 % Cr_2O_3 was obtained on heating the reaction mixture from 1200° to 1600°C and maintaining the latter temperature for 1 1/2 hours. The oxide could be eliminated from the product by using only 90 % of the stoichiometric amount of Cr_2O_3 in the starting mixture, but this increased the Cr_7C_3 to $\sim$ 2 %. The best results (98 - 99 % Cr, $\sim$1 % Cr_7C_3) were obtained were obtained with 93 - 95 % of the theoretical quantity of Cr_2O_3. X-ray analysis, performed by N.N. Zhuravlev (MGU) showed the metal to be β-chromium. There are 1 figure, 2 tables and 5 Soviet-bloc references.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov, AN USSR (Institute of Metalloceramics and Special Alloys, AS USSR)

SUBMITTED: January 27, 1961

Card 2/2

S/076/61/035/002/008/015
B124/B201

AUTHORS: Kosolapova, T. Ya., and Samsonov, G. V.

TITLE: Kinetics of the oxidation of chromium carbides

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 2, 1961, 363 - 366

TEXT: A comparative study has been made of the oxidation kinetics of powder and compact chromium oxide specimens obtained in a fairly pure state by the methods described in the papers (Ref. 3 : Zh. prikl. khimii, 32, 55, 1959; Ref. 4 : Zh. prikl. khimii, 32, 1505, 1959). The average grain diameter of all carbides was 5 - 8μ ; the porosity of the sintered Cr_3C_2 specimens was 5-6 %, and that of Cr_7Cr_3 was 18 - 2o %. The specimens were burned in a Mars furnace, and the CO_2 liberated by burning was determined by a volumetric absorption procedure. Oxidation took one hour at 400 - 1000° C. The results obtained (Table 2) show that the oxidation of chromium carbides begins at 700° C, while the free carbon is burned at lower temperatures. At a ratio of the specific volume of the oxide film to the

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B124/B201

Kinetics of the oxidation .....

specific volume of the oxidized substance larger than unity, the oxidation is known to obey a parabolic relation. For chromium carbides, this relation is $v_{Cr_3C_2} = 1.62$; $v_{Cr_7C_3} = 1.77$ and $v_{Cr_{23}C_6} = 1.84$. When interpreting the data obtained in the oxidation of Cr_3C_2 at 800 - 1000° C as well as from the diagram of the dependence of the oxidation rate on time in logarithmic coordinates, equations $y^{1.9}_{800^o} = 1.091\tau$ (1); $y^{2.56}_{900^o} = 36.44\tau$ (2) and $y^{2.1}_{1000^o} = 50.23\tau$ (3) are obtained for oxidation. The oxidation of Cr_7Cr_3 carbide obeys a more complicated law which is expressed by equations: $y_{800^o} = 97 \log\tau + 4$ (4); $y_{900^o} = 196 \log\tau + 156$ (5) and $y_{1000^o} = 100 \log\tau + 672$ (6). The oxidation isotherm of $Cr_{23}C_6$ at 800° C is expressed by the parabolic equation $y^{1.84}_{800^o} = 28.4\tau$ (7) and that at 900 and 1000° C by the logarithmic equations $y_{900^o} = 100 \log\tau + 98$ (8) and $y_{1000^o} = 98 \log\tau + 165$ (9).

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It follows from the results obtained that the character of oxidation differs for different carbides and changes with temperature. For the dependence of the rate constant of the oxidation of powder carbides on temperature the following equations hold: $\log k_{Cr_3C_2} = 2.98 - 15550/T$ (10), $\log k_{Cr_7C_3} = 4.30 + 17476/T$ (11) and $\log_{Cr_{23}C_6} = 4.75 - 7903/T$ (12). The compact specimens were oxidized under continuous weight determination for four hours at 700 and 1000° C; the results are given in Table 3. The following logarithmic relations hold for the oxidation of the compact specimens of Cr_7C_3 carbide: $y_{800^\circ} = 1.5 \log \tau - 1.4$ (13), $y_{900^\circ} = 3.5 \log \tau - 3.3$ and $y_{1000^\circ} = 14 \log \tau - 17.7$ (15).
There are 3 tables and 5 references: 3 Soviet.-bloc and 2 non-Soviet-bloc; 1 reference to English language publication reads as follows: N. Pilling, R. Bedworth, J. Inst. Metals, 29, 529, 1923.

ASSOCIATION: Akademiya nauk USSR, Institut metallokeramiki i spetssplavov (Academy of Sciences UkrSSR, Institute of Powder Metallurgy and Special Alloys)

Card 3/5

22004

S/076/61/035/004/012/018
B106/B201

21.3100

AUTHORS: Samsonov, G. V. and Antonova, M. M.

TITLE: Metastable hydride phase in the niobium - hydrogen system

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 4, 1961, 900 - 904

TEXT: A study has been made of the kinetic rules governing the hydrogenation of niobium powder. The phases arising in this connection were subjected to both chemical and X-ray analysis. The niobium powder contained 99.8% Nb (the rest, tantalum). The apparatus employed for hydrogenation is schematically shown in Fig. 1. The chemical analysis of the reaction products was made in analogy to the analysis of titanium- and zirconium hydrides, as described in Ref. 5 (Sb. "Metody analiza osnovnykh materialov, primenyayemykh v elektrovakuumnoy promyshlennosti", ch. 1, 1959, str. 85). The investigation revealed that the maximum absorption of hydrogen by the niobium powder is attained in a time which is the shorter, the higher the temperature. The strongest absorption of hydrogen (~ 60 atom%) is attained at a hydrogenation temperature of 600°C after 2-4 hours. The course of absorption isothermal lines at 600 and 700°C is indicative of

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Metastable hydride phase in ...

saturation of the powder with hydrogen. X-ray analyses have shown that -hydride of niobium is formed in this connection. At 800°C, the hydrogen content begins to decrease after two hours; at 900°C it takes only 90 minutes for this decrease to begin. These results contradict data by G. Brauer (Ref. 3: Z. anorgan. Chem., 247, 11, 1953; Ref. 4: Angew. Chemie, 70, 53, 1958), who has indicated $NbH_{1.0}$ as the upper limit of the homogeneity of the β-phase, while the authors have established the composition $NbH_{1.34}$ as the upper limit. With an increase of the hydrogen content of the β-phase, the lattice parameter a changes from 3.434 kX units in the composition $NbH_{0.9}$ (in agreement with data by Brauer: a=3.44 kX units) to 3.405 kX units in the composition $NbH_{1.34}$. This phase is manifestly metastable, as it passes over to a phase resembling the $NbH_{1.0}$ phase, in case of an anomalously high hydrogen content with hydrogenation taking more time, or with a temperature rise and increasing lattice parameters. It represents the lattice of niobium, in which not all the elementary cells contain the same number of hydrogen atoms. The remaining

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hydrogen atoms occupy irregular positions, so that hydride $NbH_{1.34}$ represents no well-ordered phase. It has been established by X-ray analysis that the anomalously high hydrogen content of the $NbH_{1.34}$ phase is not due to the formation of NbH_2 dihydride. Temperature rise and longer time of hydrogenation cause the lattice to be rearranged, the positions of hydrogen atoms to be ordered, and, at the same time, the lattice parameter to rise to 3.42 kX units. The pseudocubic, rhombically distorted lattice of $NbH_{1.0}$ is formed, in which all elementary cells contain the same humber of hydrogen atoms. Excess hydrogen is given off. To bring about this stable β-phase of NbH, the hydrogenation of the niobium powder is therefore suitably performed for 4-6 hours at 700-800°C or for 1-2 hours at 900°C. The authors finally determined the activation energy of monohydride formation by diffusion. It was found to amount to 3400 cal/mol. The table compares this value with the activation energies of the formation of silicides, borides, carbides, and nitrides of niobium by diffusion. The low value in the case of hydride proves the readiness by which the 4d orbital of niobium can be occupied by the hydrogen electrons under

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formation of hybrid states. The anomalously high value of the total work function of the first electron of diffusing hydrogen is due to the absence of an interaction between hydrogen atoms in the hydrides; this interaction causes the binding of electrons with the metal to be weakened. Moreover, the very small atomic radius of hydrogen facilitates its diffusion into the metal lattice. There are 5 figures, 1 table, and 7 references: 4 Soviet-bloc and 3 non-Soviet-bloc. The reference to the English language publication reads as follows: W. Albrecht, M. Mallet, W. Goode, J. Electrochem. Soc., 109, no. 4, 1958.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys of the AS UkrSSR)

SUBMITTED: July 27, 1959

Card 4/6

21572
S/020/61/137/003/026/030
B101/B208

9.4300 (3005, 1137, 1160)
26.2531

AUTHORS: Paderno, Yu. B., and Samsonov, G. V.

TITLE: Electrical properties of hexaborides of alkaline-earth metals, rare-earth metals, and thorium

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 3, 1961, 646-647

TEXT: The electrical properties of hexaborides of alkaline-earth metals, rare-earth metals, and actinides are of practical interest because of the use of these compounds as cathodes in electronics. As the data available were obtained unsystematically and under different experimental conditions, it was the purpose of the present study to measure electrical resistance, Hall effect, thermo-emf and thermal coefficient of electrical resistance on the same samples. Parallelepipeds with the dimensions 12 × 2.5 × 0.5 mm were cut from hot-pressed borides. The porosity of the samples was 1.5-22%. To warrant satisfactory contact, electrolytic copper was applied on the ends of the samples. The Hall coefficients were measured in a field of 12,500 oe. The absolute value of the thermo-emf was calculated by taking into account the thermo-emf of copper with

X

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Electrical properties of ...

which the samples were coupled. 3-8 samples of each compound were studied so that electrical resistance and Hall constant could be extrapolated for zero porosity. Results are given in Table 1. To study the applicability of the single-zone model, the following was calculated: $\delta = R/e^2 = n_+u_+^2 - n_-u_-^2$, as well as the concentration n^* of the effective carriers and their mobility u^*. The comparatively low resistance of hexaborides of bivalent metals in spite of low concentration of free electrons is explained by the high mobility of the carriers. The low thermo-emf of Th and trivalent metals may be explained by a high concentration of free electrons. It is pointed out that a similar anomaly as that observed in the temperature dependence of the Hall effect of SmB_6 was also found in metallic samarium. There are 1 table and 8 references: 7 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: J. Lafferty, J. Appl. Phys., 22, 299 (1951).

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21572
S/020/61/137/003/026/030
B101/B208

Electrical properties of ...

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov Akademii nauk USSR (Institute of Powder Metallurgy and Special Alloys of the Academy of Sciences UkrSSR)

PRESENTED: November 18, 1960, by A. N. Frumkin, Academician

SUBMITTED: November 17, 1960

Table 1. Electrical properties of hexaborides. Legend: (1) boride; (2) specific electrical resistance ρ, μohm.cm; (3) Hall coefficient $R.10^4$, cm^3/coulomb; (4) termo-emf, μv/degr; (5) thermal coefficient of resistivity, $\alpha.10^3$ $degr^{-1}$ (0-100°C); (6) concentration n^* of carriers, electrons per atom of metal; (7) mobility u^* of carriers $(cm/sec)/(v^2/cm)$; (8) $\delta.10^{22}$, $cm/v^2.sec^2$.

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23833

S/020/61/138/002/016/024
B104/B207

18.7530, 3208, 1454, 2808 [redacted]

AUTHORS: Samsonov, G. V. and Verkhoglyadova, T. S.

TITLE: The physical properties of titanium nitride in the region of homogeneity

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 2, 1961, 342-343

TEXT: The authors investigated the microhardness and resistivity of nitrogen - titanium alloys in the region of homogeneity of the TiN phase. Microhardness was determined on powders which had been prepared by nitration of pure Ti powder (99.8 % Ti, 0.1 % Ca, 0.09 % Fe and 0.02 % H). The powders contained 35.6-49.8 % N. Briquets were sintered (pressed with 2-4 tons/cm^2, sintered at 900-1300°C for 2-4 hr) to measure the resistance. Subsequently, the samples contained 34.7-49.8 % N. Fig. 1 graphically shows the microhardness, determined with a load of 50 g, as a function of the nitrogen content. Figs. 2 and 3 show the resistance at room temperature and high temperature (up to 2000°C). The microhardness of TiN depends linearly on N in the same way as the microhardness of TiC, ZrC, Ta_2C and

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B104/B207

The physical properties of titanium...

TaC on the C content. For carbides, however, extrapolation of the microhardness to 0 % C gives approximately the microhardness of the metal. This is not the case for TiN. The authors explain this by the fact that a considerable amount of ionic bond occurs in TiN which causes the chemical bond, the electron structure, and the electron density to assume a form different from that of carbides; in the latter, electron structure, chemical bond, and electron density are similar as in metals. This is due to formation of metal-metal bonds causing a reduction of the titanium electron ratio in the bonds with nitrogen, a lesser disturbance of the nitrogen valency electrons and a corresponding increase of the energy difference between the nitrogen and titanium atoms. Therefore, the dependence of the resistance of titanium nitride differs from that of titanium carbide (Fig. 2). Fig. 3 shows that TiN with approximately stoichiometric nitrogen content (48.4 %) reveals an almost linear function between resistance and temperature. A maximum occurs at 1800°C. From these diagrams the authors conclude that in the regions of homogeneity of this compound, a reduction of the nitrogen content affects an increase of the ion bond. Finally, it is stated that the same effect may also be expected in the nitrides of other transition metals. There are 3 figures

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The physical properties of titanium...

and 9 Soviet-bloc references.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov Akademii nauk USSR (Institute of Powder Metallurgy and Special Alloys, Academy of Sciences UkrSSR)

PRESENTED: January 4, 1961, by G. V. Kurdyumov, Academician

SUBMITTED: December 29, 1960

X

Card 3/6

GAZIYEV, G.A.; KRYLOV, O.V.; ROGINSKIY, S.Z.; SAMSONOV, G.V.; FOKINA, Ye.A.;
YANOVSKIY, M.I.

Dehydrogenation of cyclohexane on certain carbides, borides, and silicides. Dokl. AN SSSR 140 no.4:863-866 O '61. (MIRA 14:9)

1. Chlen-korrespondent AN SSSR (for Roginskiy).
(Cyclohexane) (Dehydrogenation) (Catalysts)

SAMSONOV, G.V., otv. red.; KOZLOV, I.A., red. izd-va; LIBERMAN, T.R., tekhn. red.

[High-temperature ceramic metal materials]Vysokotemperaturnye metallokeramicheskie materialy. Kiev, Izd-vo Akad. nauk USSR, 1962. 149 p. (MIRA 15:9)

1. Akademiya nauk URSR, Kiev. Instytut metalokeramiky i spetsial'nykh splaviv. 2. Chlen-korrespondent Akademii nauk Ukrainskoy SSR (for Samsonov).
(Ceramic metals—Thermal properties)

PEN'KOVSKIY, Vladimir Vladimirovich; SAMSONOV, G.V., otv. red.; TRESVYATSKIY, S.G., prof., doktor tekhn. nauk, otv. red.; POKROVSKAYA, Z.S., red.; YEFIMOVA, M.I., tekhn. red.

[Effect of radiation on metals and certain high-melting materials] Deistvie oblucheniia na metally i nekotorye tugoplavkie materialy. Kiev, Izd-vo Akad.nauk USSR, 1962. 182 p. (MIRA 15:7)

1. Chlen-korrespondent Akademii nauk USSR (for Samsonov).
(Metals, Effect of radiation on)
(Materials, Effect of radiation on)

PHASE I BOOK EXPLOITATION SOV/6066

Samsonov, Grigoriy Valentinovich, and Mikhail Savvich Koval'chenko

Goryacheye pressovaniye (Hot Pressing). Kiyev, Gostekhizdat USSR, 1962. 211 p. 3000 copies printed.

Ed.: T. I. Chumachenko; Tech. Ed.: S. M. Matusevich.

PURPOSE: This book is intended for engineering personnel in the machine-building and metallurgical industries. It may also be used by students and aspirants in the machine-building and metallurgical departments of schools of higher education.

COVERAGE: Data on the hot pressing of powdered refractory metals and compounds, hard alloys, and ferrous and nonferrous metals are summarized. Presses of various designs, as well as technological processes, are described, and examples of the application of hot pressing in various branches of the industry are given. No personalities are mentioned. There are 186 references, mostly Soviet.

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Analysis of Refractory (Cont.) SOV/6030

COVERAGE: The book contains data from the literature and from laboratory research on the chemical and mechanical properties, crystalline structure, chemical analysis, production, and industrial and other applications of silicon carbide and other refractory compounds. Methods of determining the basic components of refractory compounds (carbon, boron, nitrogen, and silicon) are reviewed and detailed methods for the chemical analysis of all presently known refractory compounds given. The authors are associated with the Institut metallokeramiki i spetsial'nykh splavov, AN SSSR (Institute of Powder Metallurgy and Special Alloys, Academy of Sciences USSR). No personalities are mentioned. There are 327 references: 175 Soviet and the remainder mainly English and German.

TABLE OF CONTENTS [Abridged]:

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Analysis of Refractory (Cont.) SOV/6030

AVAILABLE: Library of Congress

SUBJECT: Metals and Metallurgy

BN/pw/bmc
10-30-62

Card 4/4

SAMSONOV, G.V.

"Activated sintering of high melting point alloys.

Paper presented at the Powder metallurgy Conference
Smolenice, Czech. 17-20 Sep 1962

S/849/62/000/000/001/016
A006/A101

AUTHOR: Samsonov, G. V.

TITLE: On the continuous-discrete nature of changes in the type of bond in refractory compounds of transition metals and principles of classifying refractory compounds

SOURCE: Vysokotemperaturnyye metallokeramicheskiye materialy. Inst. metallo-ker. i spets. spl. AN Ukr.SSR. Kiev, Izd-vo AN Ukr.SSR. 1962, 5 - 12

TEXT: For the purpose of facilitating the development of refractory alloys with prescribed properties, the author investigates the physical properties of transition metals (groups III - VIII of the periodic system) combined with non-metallic materials and attempts to establish the basic regularities in their changes with varying crystalline and electronic structures of refractory compounds. According to the concepts of several foreign authors it is assumed that the nature of bond is strongly affected by the degree of incompleteness in the d- and f-electron shells of transition metal atoms. The evaluation of this degree of incompleteness is based on the criterion 1/Nn, named the acceptor capacity of

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S/849/62/000/000/001/016
A006/A101

On the continuous-discrete nature of...

the transition metal atom, and on the ionization potential of non-metallic atoms. Depending on the number of electrons, n, in the incomplete d-level, the main quantum number of this level, N, and the ionization potential of the non-metallic atom, I, changes take place in the electronic concentration between the skeletons of atoms in the lattice, and in the nature of its distribution. An increase of criterion 1/Nn causes a shift of the relative maximum of electronic concentration toward the side of the metallic atom (if I = const); at increasing I and constant 1/Nn of the metallic atom skeleton the relative maximum of electronic concentration is shifted toward the non-metallic atom, entailing corresponding changes in the bond from a metallic to an ionic nature. At very high 1/Nn values of transition metals and in their combination with non-transition metals, characterized by low I values, intermetallic phases are formed in which the d-levels can be filled-up at the expense of outer electrons of non-transition metals. In such a manner variations of 1/Nn and I entail a multiple but not infinite number of combinations of these criteria, which in turn, predetermine the peculiar continuous-discrete nature of changes in the bond type and the physical and chemical properties of the corresponding compounds, as in the given case, of transition metals combined with non-metallic materials. The practical applica-

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On the continuous-discrete nature of... S/849/62/000/000/001/016
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tion of this theory is demonstrated by the analysis of data on the transition points to super-conductivity of various refractory compounds. As a result, ways can be indicated for the development of metals with ultrahigh transition points. On the basis of the theory developed the refractory compounds are classified into metal-like, non-metallic and inter-metallic compounds. There is 1 table.

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Thermo-emission properties of scandium and...

S/849/62/000/000/011/016
A006/A101

properties of scandium borides are mainly predetermined by the state of 4s-electrons. The dominant part of 4s-electrons in this case is confirmed. Low values of work function of gadolinium boride electrons in the boride series of rare-earth metals can be explained by the presence of one substantially free 5d-electron and a stable half-filled 4f-shell. There are 1 table and 1 figure.

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42435

S/849/62/000/000/012/016
A006/A101

24.7600

AUTHORS: Neshpor, V. S., Samsonov, G. V.

TITLE: Electric properties of molybdenum silicides

SOURCE: Vysokotemperaturnyye metallokeramicheskiye materialy, Inst. metalloker. i spets. spl. AN Ukr. SSR., Kiev. Izd-vo AN Ukr. SSR., 1962, 113 - 119

TEXT: For the purpose of studying the effect of silicon concentration and structure upon the electric properties of silicides, the authors investigated the temperature dependence of electric resistivity; thermo-emf and the Hall effect of molybdenum silicides. Molybdenum silicide powders Mo_3Si, Mo_5Si_3 and $MoSi_2$ were prepared by sintering pressed mixtures of components in argon atmosphere. Specimens, 6 mm in diameter and 15 mm high, were not pressed. Their residual porosity was 2 - 8%. The temperature dependence of electric resistivity and thermo-emf of the compounds were determined for a 250 - 1300°K temperature range. The measured differential thermo-emf was converted to an absolute value using the temperature dependence of absolute thermo-emf of a platinum comparison electrode for $MoSi_2$ and of an alumel electrode for Mo_5Si_3. The Hall constants were

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Electric properties of molybdenum silicides

measured in a constant magnetic flux of 12,000 oersted strength at about 300 amp/cm^2 current density. Hall constants and specific resistivity of Mo silicides were measured at room temperature and from these values the effective concentrations of current carriers and Hall mobilities were calculated. As a result, the metallic type of conductivity of the investigated compounds was established. The Mo_3Si and Mo_5Si_3 silicides are electronic conductors, whereas $MoSi_2$ is a hole conductor. The latter fact is in accordance with the result predicted by H. Schenk and U. Dehlinger in 1956 on the basis of the quantum-mechanical calculation of the energy spectrum for this compound. The probability of scattering of current carriers in molybdenum metal and silicides Mo_3Si, Mo_5So_3 and $MoSi_2$ are in a 1:20:20:1.5 ratio and their Hall mobilities in a 1:0.055:0.04:2.7 ratio. This indicates the high density of electronic states in the conductivity zones of lower molybdenum silicides Mo_3Si and Mo_5Si_3. It is shown that the lower molybdenum silicides are similar to σ-phases in binary systems of transition metals as regards both their crystalline properties and electronic structure. The ordered substitution of a portion of silicon atoms in molybdenum disilicide by aluminum,

Card 2/3

32665

S/131/62/000/001/002/002
B105/B110

15.2630
21.2300

AUTHORS: Samsonov, G. V., Fomenko, V. S., Paderno, Yu. B.

TITLE: Radiation coefficients of difficulty fusible compounds

PERIODICAL: Ogneupory, no. 1, 1962, 40-42

TEXT: The radiation coefficients of a number of borides, carbides, silicides, and nitrides of transition metals were measured in the temperature range of 800-2000°C, according to T. I. Serebryakova et al. (Ref. 1: Optika i spektroskopiya, 1960, 8, 410) at the Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR). Powders of the compounds investigated were applied in a paste like form to the surface of a hollow cylinder provided with an 1mm opening, and uniformly heated. The temperatures (°K) on the cylinder surface (T_{br}) and in the cylinder opening (T_{tr}) (br = brightness, tr = true) were determined with the optical pyrometer of the type ОППИР-09 (OPPIR-09) and the microoptical pyrometer of the type МП (MP), respectively. The radiation coefficients were calculated according to the formula

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32665
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B105/B110

Radiation coefficients of ...

$\ln\varepsilon_\lambda = \frac{c}{\lambda}\left(\frac{1}{T_{tr}} - \frac{1}{T_{br}}\right)$, where c = 1.438 cm degree, λ = 650 mμ. A difference of about 0.15-0.20 existed between the radiation coefficients of powders and compact bodies from beryllium oxide, graphite, and tantalum. This permits a utilization of the tabulated data for calculating the radiation coefficients of smooth surfaces of difficulty fusible materials. There are 1 table and 2 references: 1 Soviet and 1 non-Soviet.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

Card 2/2

15.2230
21.2100

32417

S/021/62/000/001/006/007
D251/D303

AUTHORS: Samsonov, G.V., Corresponding Member AS UkrSSR, and Verkhohlyadova, T.S.

TITLE: Physical properties of zirconium nitride in the homogeneity region

PERIODICAL: Akademiya nauk Ukrayins'koyi RSR. Dopovidi, no. 1, 1962, 48 - 50

TEXT: The authors investigated the properties of 99.96 % pure zirconium nitride powder, prepared by a method similar to that described for titanium nitride in T.S. Verkhohlyadova, T.V. Dubovik and G.V. Samsonov (Ref. 4: Poroshkovaya metallurgiya, 1, 4, 1961). X-ray analysis showed that the homogeneity region of zirconium nitride lies between 40 - 50 at.% of nitrogen (9.5 - 13.3 % by weight). A table is given of the physical properties of zirconium nitride in this region. By comparisons of the specific conductivity, microstrength and temperature-concentration of zirconium nitride and titanium nitride, it is shown that the role of the ionic bond in

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Physical properties of zirconium ... S/021/62/000/001/006/007
D251/D303

the zirconium nitride lattice increases in this region as the nitrogen content decreases, and that this increase is higher than in the corresponding homogeneity region of titanium nitride. It is stated that this phenomenon is due to the fact that the d-shell of electrons is less unfilled in the zirconium atom than in titanium. There is 1 table, 3 figures and 4 references: 3 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: D. Domagala, D. Pherson, and M. Hansen, J. of Metals, 8, 98, 1956.

ASSOCIATION: Institut metalokeramiki ta spetsial'nykh splaviv AN URSR (Institute of Metal Powders and Special Alloys of the AS UkrSSR)

SUBMITTED: June 28, 1961

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S/226/62/000/002/001/010
I003/I203

AUTHOR: Samsonov, G. V.

TITLE: Proposed classification of refractory compounds

PERIODICAL: Poroshkovaya metallurgiya, no. 2, 1962, 3-8

TEXT: Great theoretical and practical importance is attached to scientific data which can be obtained from investigations of the crystalline structure of refractory compounds and the nature of their chemical bonds. A classification of refractory compounds is proposed, based on the periodical regularity of change in the nature of chemical bonds with the electron-acceptance capacity of atoms in the case of transition metals, and the ionization potentials of non-metallic atoms. Based on these regularities, an explanation is given for the pyhsico-chemical properties of refractory compounds, and for the changes that occur in these properties. There are 2 tables.

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ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Power Metallurgy and Special Alloys AS UkrSSR)

SUBMITTED: June 12, 1961

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39927

S/226/62/000/003/005/014
I003/I203

1.1600

AUTHOR: Kislyy, P. S. and Samsonov, G. V.

TITLE: Extrusion die-forming of pipes and rods from refractory metal powders

PERIODICAL: Poroshkovaya metallurgiya, no. 3, 1962, 31–48

TEXT: The article deals with the problem of extrusion die-forming of mixtures of refractory compounds with plasticizers, outlines the technological process of manufacture by a method never before used for refractory metal powders. The initial conditions of the powders, the method of preparation of the mixtures, initial grain size, the type, amount, and method of introduction of the plasticizer, applied pressure and humidity of the powder and their effects on the properties of the finished products are discussed. There are 15 figures and 2 tables.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

X

SUBMITTED: January 4, 1961

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S/226/62/000/002/004/010
I003/I203

AUTHOR: Kislyy, P.S., Panasyuk, A. D. and Samsonov, G. V.

TITLE Activated sintering of niobium carbide

PERIODICAL: Poroshkovaya metallurgiya, no. 2 1962, 38–43

TEXT: Niobium carbide is used in construction of high-temperature resistance furnaces and for high temperature thermocouples. Sintering of niobium carbide should be done at temperatures up to 3000°C which are, however, difficult to attain. This work investigates the possibilities of lowering sintering temperatures of niobium carbide poweders by activating the sintering process. Since additions of nickel fail to activate the process to any substantial extent, the authors used 270 mesh niobium carbide powder containing 88.5% of Nb and 11% of C with an addition of 1% of Fe and 2% of $CoCl_2$. Physicochemical properties are given of powders sintered in resistance furnaces at temperatures ranging from 1700 to 2600°C in an atmosphere of hydrogen. Their lower porosity as compared with that of niobium carbide powders sintered without any activating additions is stressed. There are 5 figures and 3 tables.

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ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN USSR (Institute of Powder Metallurgy and Special Alloys AS UkrSSR)

SUBMITTED: June 11, 1961

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S/180/62/000/003/003/016
E202/E335

AUTHORS: Samsonov, G.V. and Shulishova, O.I. (Kiyev)

TITLE: Calculation of the crystal-lattice energies of metallic compounds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye tekhnicheskikh nauk. Metallurgiya i toplivo, no. 3, 1962, 51 - 55

TEXT: Although Sarkisov's formula for the crystalline-lattice energy of a metallic compound MX, given by:

$$E = K \frac{m^3 (A_M f_M + A_X f_X)^{7/3}}{m_M m_X (A_M F_M^{1/3} + A_X F_X^{1/3} + F_f^{1/3})} \qquad (4)$$

(where K - empirical coefficient depending on the last filled shell of M, m_M, m_X - number of M and X atoms in the molecule, respectively; m - their sum; A_M, A_X - atomic fractions of the corresponding components; $F_M F_X$ - repulsion effects of the electrons of skeleton atoms; F_f - repulsion effect between the valency electrons; f_m, f_x - valency electrons)

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S/180/62/000/003/003/016
E202/E335

Calculation of ....

permits the calculation of E, for compounds the bonds of which cannot be referred to the determined types, there are inherent difficulties in determining the multiplicity of the bond σ and the calculations are very cumbersome. The authors overcome these difficulties by relating the magnitude of the lattice period a_o (assuming $a_o = ka$, where a is the lattice parameter) of a single-type compound to the electronic structure of the components, viz:

$$a_o = \frac{A_M F_M^{1/3} + A_X F_X^{1/2} + F_f^{1/3}}{(A_M f_M + A_X f_X)^{1/3}} \qquad (5)$$

in which the repulsion effect of the shared electrons F_f is given by $(A_M f_M + A_X f_X)^{2/3}$ and is thus independent of the principal quantum number and the introduction of σ. Relation (5) substituted in Eq. (4) gives:

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E202/E335

Calculation of ....

$$E = K' \frac{a}{a_o} \left(\frac{m}{m_M m_X} \right) \left(\frac{(m_M f_M + m_X f_X)^2}{a} \right) \qquad (6')$$

which for pure metals reduces further to:

$$E = Kf^2/a \qquad (6a) .$$

Calculations of a_o and comparison with a as a/a_o, $(a/a_o)\%$, for the b.c.c. and f.c.c. metals, hexaborides and certain fluorides confirmed the suitability of the authors' assumption. The values of K', which depend on the crystalline structure of the metal, were also evaluated for the b.c.c. and f.c.c. metals and compared, using the known data of the bond energy of the metals. It was found that Sarkisov's formula is more strictly obeyed by the metallic bonds rather than ionic. [Abstractor's note: references to Kapustinski's empirical formula for the lattice energy were ignored since it is of considerably lower accuracy than the one of Sarkisov; Eq. (6) is incorrectly printed in the journal.]

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Calculation of S/180/62/000/003/003/016
E202/E335

There are 7 tables.

ASSOCIATION: Institut metallokeramiki i spetsial'nykh splavov AN UkrSSR (Institute of Powder Metallurgy and Special Alloys of the AS UkrSSR)

SUBMITTED: January 10, 1962

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35711
S/136/62/000/003/003/008
E021/E435

18.1210

AUTHORS: Samsonov, G.V., Dubovik, T.V.

TITLE: Technology for preparation of aluminium nitride and the possibilities of its commercial use

PERIODICAL: Tsvetnyye metally, no.3, 1962, 56-61

TEXT: The aim of the present work was to establish the optimum conditions for preparing aluminium nitride powder. The initial materials were aluminium powder ПА-4 (PA-4) with particle size 0.1 to 0.25 mm, aluminium powder ПАК-4 (PAK-4) with particle size less than 0.042 mm, purified nitrogen containing a trace of oxygen, and ammonia. The apparatus, described in detail previously, enabled material to be nitrided by passing nitrogen over a boat containing the material. Experiments at 700 to 1200 °C showed that after up to 240 minutes, nickel and zirconium boride did not react with the powders of aluminium nitride. The boats were therefore made from these materials. The rate of heating has to be low enough to prevent fusion of the aluminium because, if fusion occurs, the surface area of the reaction is decreased and the aluminium is more likely to react with the material of the X
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boat. The optimum rate of heating without fusion taking place was found to be 6 to 7 °C/min for the 0.1 to 0.25 mm powder and 10°C/min or lower for the 0.042 mm powder. The optimum conditions for nitriding were found by a series of experiments in a current of nitrogen for 15 to 240 minutes and in a current of ammonia for 2 hours at 500 to 1200°C. The results showed that there is relatively full nitriding of the finer powder at 700°C but the coarser powder requires a temperature of 1100 to 1200°C. From the results the following scheme for production of aluminium nitride was put forward.. PAK-4 powder is nitrided at 800°C for 1 hour with a rate of increase of temperature up to 800°C of 10°C/min. The prepared product is thoroughly mixed and a repeated nitriding is carried out at 1200°C for 30 to 60 minutes (with a temperature increase of 40°C/min). This gives a powder of accurate stoichiometric composition. A commercial powder with about 33% nitrogen content can be prepared by a single nitriding process at 1200°C (with rate of temperature increase 10°C/min). Components of aluminium nitride with 12 to 16% porosity can be prepared by sintering, after pressing, nitride powder or nitride

Technology for preparation ... S/136/62/000/003/003/008
E021/E435

powder containing 5 to 10% aluminium powder in nitrogen at 1800 to 2000°C. Components with zero porosity can be prepared by hot pressing the nitride powder at 2000 to 2100°C.
There are 5 tables.

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S/226/62/000/004/001/012
1003/I240

AUTHORS: L'vov, S.N., Nemchenko, V.F., and Samsonov, G.V.

TITLE: The influence of non-metal atoms on the electric properties of refractory compounds of transition metals

PERIODICAL: Poroshkovaya metallurgiya, no.4 (10), 1962, 3-10

TEXT: Refractory compounds of group IV-VI transition metals are becoming more widely used in modern industry. The authors investigated the Hall effect, electric resistivity and their molelectric properties of the borides, carbides, and nitrides of the above metals at various compositions and of their mutual solid solutions. The electric properties change regularly, probably as a result of a change in the electron-affinity of the d-subshells of the metal atoms and the ionizing potential of the non-metal ions. There are 4 figures and 2 tables.

ASSOCIATION: Khersonskiy gosudarstvennyy pedagogicheskiy institut im. N.K. Krupskoy i Institut metallokeramiki i spetsial'nykh splavov AN USSR (The Kherson Government Pedagogical Institute im. N.K. Krupskaya and the Institute of Metal

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I003/I240

The influence of non-metal atoms...

Ceramics and Special Alloys, AS UkrSSR)

SUBMITTED: January 15, 1962

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