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BIBLIOGRAPHY ON METALLURGY OF HIGH-PURITY TUNGSTEN, JANUARY 1911 THROUGH FEBRUARY 1959

By Earl T. Hayes and Ruth A. Pritchard

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BIBLIOGRAPHY ON METALLURGY OF HIGH-PURITY TUNGSTEN, JANUARY 1911 THROUGH FEBRUARY 1959[1]

BY

EARL T. HAYES[2] AND RUTH A. PRITCHARD[3]

Summary and Introduction

THIS BIBLIOGRAPHY has been assembled to aid research by the Bureau of Mines and others on high-purity tungsten. It appears approximately 50 years after the development of ductile tungsten—one of the first metals to be produced in a high-purity form. Requirements of the missile age are ever more demanding that engines run hotter and space vehicles fly higher and faster. Thus, it has become necessary to reexamine all conventional materials of construction as well as to investigate new combinations. At this stage of our technology we have alloys capable of operation at 1,800° F. and several possibilities of developing some that will be satisfactory up to 2,500° F. Strength-weight comparisons, detrimental to tungsten at lower temperatures, disappear at this point, and tungsten or its alloys appear to be the only metal capable of operation at truly high temperatures.

The aim of this bibliography has been to include only references that concern improving the purity of tungsten—from processing the ore to treating the finished metal. In this sense it is a selected and not a critical bibliography. The period from January 1911 through February 1959 has been covered. Because recent literature has the greatest value, most of the selected items refer to publications issued within the past 5 years.

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The indexing and abstracting services consulted were: American Society of Metals, Review of Metal Literature; ASTIA Bulletins, Battelle Technical Review, British Metallurgical Abstracts, Ceramic Abstracts, Chemical Abstracts, Crerar Metals Abstracts, Industrial Arts Index, Nuclear Science Abstracts; Office of Technical Services and Patent Office, Department of Commerce; Powder Metallurgy Bulletin; Technical Information Division, Library of Congress; and Translators' Monthly.

The authors gratefully acknowledge free use of Chemical *Abstracts* and British Metallurgical Abstracts. Many abstracts were copied verbatim; others are excerpts from the article. Although the above-mentioned abstracting services have been the major sources of information, references from current periodicals (both foreign and domestic) were used.

SELECTED BIBLIOGRAPHY[4]

(Arranged alphabetically)

1. Agte, Curt. [Sinterability of Powdered Metals, Especially Powdered Tungsten.] Výzkummý ústav pro práškovou met., Prague. Hutnické Listy, vol. 8, 1953, pp. 227–234; Chem. Abs., vol. 49, 1955, p. 2968.

Quality of products made from powdered W depends on purity, particle size, presence of small quantities of other metals, absence of blemishes, etc. Reduction of tungstic acid (WO_3) obtained from Czechoslovakian ore produces a very fine powdered W, which sinters at comparatively low temperatures, i.e at 1,300°–1,400°. The product has specific gravity 17.0–17.8 and bulk specific volume (after shaking) 31–4 cc./100 g. Tungstic acid was reduced by H at 900°; the powder obtained was subjected to a pressure of 3 tons/sq. cm. and then sintered in a H atmosphere at 1,300°–1,350° for 1 hour. Vickers hardness "10" was about 390 kg./sq. mm. However, when bulk specific volume of the powder was 52.2 and 22.4, respectively, its sinterability was bad and the product obtained had Vickers hardness of only 160 and 47, respectively. Presence of powdered Ni 0.5–2 percent decreased the sintering temperature to approximately 800°. Better results were obtained when powdered W was mixed with Ni salt and then reduced with H at 500°–700°. When W+1 percent Ni and W+2 percent Ni were sintered at 1,100°, Vickers hardness of the product was 430 and 401, respectively. Electrical contacts made from powdered W with or without addition of Ni 1 percent were nearly as good as contacts made from forged W.

2. Ames Laboratory (Ames, Iowa). Semi-Annual Summary Research Report in Physics for July Through December 1956 (ISC–833), Mar. 13, 1957; Nuclear Sci. Abs. item 8117 (Contract W–7405–eng–82), vol. 11, Aug. 15, 1957, 40 pp. (Available Office of Technical Services, Washington (25), D.C.)

Describes a new method of preparing single crystals of tungsten oxide using high-pressure tungsten oxide vapor.

Ando, Rinjiro. *See* abs. 179.

3. Andreeva, V. N. Rastvorimost' okislov metallov v rasplavlennom metafosfate i pirofosfate natriia. [Solubility of Metal Oxides in Fused Sodium Meta- and Pyro-Phosphates.] Ukrain. Khim. Zhur., vol. 24, No. 1, 1958, pp. 23–28; Battelle Tech. Rev. item 10710, vol. 7, August 1958, p. 535-a.

Investigation of the solubility of Sb_2O_3, MoO_3, PbO, Bi_2O_3, CuO, ZnO, NiO, WO_3, CdO, Fe_2O_3, and TiO_2 by the isothermic saturation method, in fused metaphosphate at 720° C. and in pyrophosphate at 1,000° C.

4. Andrieux, J. L. Preparation of Metal Powders by Igneous Electrolysis. Jour. four élec, vol. 57, No. 1, 1948, pp. 12–14; No. 2, pp. 26–27; Met. Abs., vol. 16, 1949, p. 572.

Andrieux deals first with the general principles of the method—the separation of crystals, the effect of cathodic conditions on the size of crystals, the choice of electrolysis bath, and the mechanism of electrolysis. About a score of metals, some highly refractory, can be prepared in crystal form by this method. Examples given are Be, Ti, Zr, Th, Ta, Nb, Cr, Mo, W, U, Mn, Cu, Ag, Fe, Co, Ni, metals of the platinum group, and iron-tungsten alloys.

Andrew, K. F. *See* abs. 78.

5. Andrieux, Lucien. Electrolysis of Metallic Oxides Dissolved in Fused Boric Acid and in Fused Borates: Tungsten, Molybdenum, Zinc. Masson et Cie, Paris, France (Thesis, 1929). Chem. Abs., vol. 23, 1929, p. 4893.

Andrieux found that in the electrolysis of borax, Na metal is the primary product. The Na thus liberated reacts with the B_2O_3, resulting in amorphous B at the cathode. Thus, the electrolysis of a metal borate is a means of liberating the metal of this borate. The electrolysis of K and Li borate likewise produces B. Electrolysis of borates of the alkaline earths results in a product composed of amorphous B and boride of the alkaline earth metal. The borates of Ce and Mn produce borides of these two metals. Mg borate results in a very pure B. This reaction was studied in detail. The addition of MgF_2 facilitates the reaction. A graphite crucible was used, and the charge consisted of B_2O_3, MgO, and MgF_2. The method is much better than the older method of Moissan. The electrolysis of tetraborate of Ca results in a mixed product of B and boride of Ca. With Mg, there is a tendency to form pyroborates. These borates gather around the cathode in the shape of a solid crystalline ball surrounded by the bath, which is perfectly fluid at 1,000°. This is a new and curious phenomenon. To obtain the boride of a metal, Andrieux electrolyzes a mixture of borate and fluoride of the metal. In this way 17 borides have been prepared, 10 of which are new: CaB_6, SrB_6, BaB_6, ThB_6, Zr_3B_4, Cr_3B_2, MnB, and the new borates: CeB_6, LaB_6, NdB_6, GdB_6, YB_6, ErB_6, YbB_6, TiB_2, VB_2, UB_4. Among the metals produced are Zn, W, and Mo. Zn can be obtained by the electrolysis of the oxide of Zn dissolved in a bath of B_2O_3 or of borates to which fluorides or other salts have been added to lower the fusing temperatures of the bath. W and O can be obtained by dissolving the trioxide of the metal in the bath of borate and fluoride with an addition of oxide of zinc.

6. ———. The Electrolysis of Metallic Oxides Dissolved in Fused Boric Anhydride or Borates. New Methods for the Preparation of Amorphous Boron,

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[4] Titles enclosed in brackets are translations from the language in which the item was published.

Borides and Some Metals. Ann. chim. vol. 11–12, No. 10, 1929, pp. 423–507; Chem. Abs. (thesis), vol. 23, 1929, p. 4898; vol. 24, 1930, p. 5238. A translation of this article (53F23, 58 pp.) is available at Battelle Memorial Institute.

Anikin, I. N. *See* abs. 19.

7. Arslambekov, V. A., and Gorbunova, K. M. K kinetike protsessov obrazovaniia okisnykh plenok na vol'frame i molibdene. [The Kinetics of the Formation of Oxide Films on Tungsten and Molybdenum.] Doklady, Akad. Nauk S.S.S.R., vol. 119, No. 2, 1958, pp. 284–297; Battelle Tech. Rev., item 11121, vol. 7, August 1958, p. 55–a; Nuclear Sci. Abs., item 11461, vol. 12, No. 17, Sept. 15, 1958, p. 1358.

Describes installations and method for an accurate continuous analysis of the weight changes and oxidation processes in W and Mo in a wide range of oxygen pressures and temperatures.

Asada, H. *See* abs. 95.

Asada, Kazuo. *See* abs. 60.

8. Atomic Energy Commission. Pub. IB–101, 1952, 5 pp.; Met. Abs., vol. 22, 1954, p. 10.

Compilation of 40 references to many metallurgical aspects of Mo and W. Subjects covered include the following: Analysis, cleaning, melting, surface protection, structure, production, uses, sintering, properties, etc.

9. Bauer, J. P., Bridges, D. W., and Fassell, W. M., Jr. High Pressure Oxidation of Metals—Tungsten in Oxygen. Jour. Electrochem. Soc., vol. 103, No. 5, 1956, pp. 266–272, 28 refs., 3 tables, 6 figs.

Tungsten rod and sheet were found to oxidize linearly in oxygen from 600° to 850° C. at oxygen pressures ranging from 20 to 500 p.s.i.a. Oxidation rate increased with increased oxygen pressure at temperatures of 750°–850° C. Theoretical considerations indicate that an equilibrium adsorption process occurs before the rate-determining step. The assumption of a linear change of adsorption energy with increase of surface coverage allowed observed oxidation rates to be corrected for pressure effect. The activation energy was 48 kcal. Tungsten sheet volatilization losses were appreciable above 800° C. Only tungsten rod data were free from volatilization losses at 850° C. Photographs show the effect of shearing samples at room temperature before oxidation on the final physical appearance of the oxide. Cold shearing produces exfoliated tungsten oxide.

10. Bechtold, J. H. Strain Rate Effects in Tungsten. Trans. AIME vol. 206, 1956, pp. 142–146; Chem. Abs., vol. 50, 1956, p. 4745.

The yield strength of annealed W was found to have a strain-rate exponent 12 times greater than that of low-C steel. The effects of temperature and strain rate could be correlated through the Zener-Hollomon parameter with a heat of activation associated with yielding of 32,000 cal./g.-atom. This heat of activation is independent of strain, although both the temperature and strain-rate dependence of the yield strength vary with strain.

11. Bechtold, J. H., and Shewmon, P. G. Flow and Fracture Characteristics of Annealed Tungsten. Trans. Am. Soc. Metals, vol. 46, 1954, pp. 397–408, 1 table, 10 figs., 9 refs.

Tungsten, like iron and molybdenum, has a body-centered cubic crystal structure and experiences a change from ductile to brittle behavior with decreased test temperature. When fine-grained, annealed tungsten is tested in uniaxial tension at a strain rate of 2.8 x 10^{-4} sec^{-1}, this transition in ductility occurs between 150° and 450° C. (300° and 840° F.). Except for the temperature at which brittleness occurs, the effect of temperature on the tensile properties of tungsten is similar to the effect of temperature on the tensile properties of other body-centered cubic metals.

12. Beck, A. H. W. Thermionic Valves: Their Theory and Design. Cambridge Univ. Press, London, 1953, p. 24; Office of Defense Mobilization (ODM) Materials Survey—Tungsten, December 1956.

No abstract.

13. Belkin, H. M. Investigation of the Rate of Reduction of Tungsten Ore With Hydrogen. Office of Tech. Services Tech. Rept. PB–109,834, June 1950, 83 pp., photos, diagrams., graphs, and tables. (Available Publication Board Project, Library of Congress, Washington (25), D.C. Microfilm $3.75, photostat $11.25.) Bibliography of Tech. Repts., OTS., vol. 20, No. 3, Sept. 4, 1953, p. 93.

The rate at which water was evolved was utilized as a measure of the rate of this reaction since the overall chemical reaction yields H_2O as the only gaseous product. The reaction was performed in a specially constructed reactor through which heated hydrogen was passed at a controlled flow rate over pelletized tungsten ore. Analyzed H_2O temperature-condensation data showed that the reaction rate was faster for a smaller size pellet than for a larger one. (Thesis — Rensselaer Polytechnic Institute)

14. Benesovsky, F., Sedlatschek, K., and Wirth, W. High-Vacuum Arc Melting of Refractory Metals. *Metallwerk Plansee, Reutte, Australia,* Berg-und hüttenmännische Monatshefte, Hochschule, Leoben, vol. 100, No. 7/8, 1955, pp. 219–224; Met. Abs., vol. 23, 1956, p. 1046.

An illustrated description of various types of high-vacuum arc melting furnaces—both laboratory and industrial—for Ti, Mo, Zr, Ta, and W. The advantageous effects of such procedures on the mechanical properties and the formability of the metals are noted. (13 refs.)

15. Benesovsky, Fritz. Neuentwicklungen auf dem Gebiete der hochschmelzenden und seltenen Metalle. [New Developments in the Field of High Melting-Point Metals and Rare Metals.] Planseeber. Pulvermet., 1953, vol. 1, No. 4, pp. 145–164; Stahl u. Eisen, vol. 74, No. 4, Feb. 11, 1954, pp. 210–215; Jour. Inst. Metals, vol. 21, pt. 9, May 1958, p. 758.

The commercial importance of the high-melting-point metals, Ti, Zr, Hf, V, Nb, Ta, Cr, and W, has increased considerably in recent years. The method of production is changing over from powder metallurgy to the melting of purified sponge material. The methods of obtaining the pure metals and their subsequent working are briefly described, and their applications are discussed. (Bibliography of 38 refs.)

16. Berken, Ali Riza (Univ., Istanbul.) [Conductometric and Potentiometric Study of the Displacement of Tungstic Acid by Other Acids.] Rev. faculte sci. univ., Istanbul 14–A, 1949, pp. 7–19; Chem. Abs., vol. 44, 1950, p. 7179.

The effect of several acids and pH on the formation of Na tungstates and on the precipitation of the tungstates of Pb and the alkaline earths was studied. The tungstates, obtained either by crystallization or by precipitation, varied with the different acids studied. With AcOH, the crystals corresponded to $Na_2O.2WO_3$, $Na_2O.5$–WO_3, and $Na_2O.3\ WO_3$, as the pH was decreased from 8.9 to 2.6. Formic acid caused the precipitation of the 2, 7, and 3 salts in the same pH range; with HCl only $Na_2O.2WO_3$ and $Na_2O.7\ WO_3$ were formed. In AcOH, Ba forms $BaO.$–$2WO_3$, $BaO.7WO_3$, $BaO.5WO_3$, and $BaO.3WO_3$ as the pH decreases. $BaO.7WO_3$ was not found in formic acid solutions, while in HCl and HNO_3 only the 2, 7, and 4 compounds occurred. Potentiometric titrations of Na_2WO_4 solution with various acids showed two inflection points, one corresponding to the monotungstate and the second, depending on the acid used, characterizing a different ion. With organic acids, the second inflection was not sharp. Conductometric curves show three inflection points when the titration is made with acetic or formic acid and only two with strong acid such as HNO_3 or HCl. With strong acid, the inflections correspond to the para- and metatungstates, while with weak acids from the pH and the amount of acid used some conclusions can be drawn as to the ions presents. The pH range where a certain tungstate is obtained is not the same for crystallization and precipitation.

17. Bielstein, Hans. New Process for Production of Pure Metallic Tungsten. Project KQ-242. AAF-AMC Tech. Rept. F-TR-1150-ND, August 1947, 9 pp. (On file at Hdqtrs. Material Command, Wright Field, Dayton, Ohio; also at Library of Congress, Washington (25) D.C., as PB-L 89,617, photostatic copy (in English), $1.00. Bib. 9-500; and at Bureau of Mines Library (CP-1511), College Park, Md.

Bielstein worked this out with Ing. Hueffner for Borchers Bros., Goslar, Harz, Germany, and it was put into use at once during the war. Bielstein was brought to Wright Field for a period to write this and other technical reports. The process differs from previous practice by dissolving tungstic acid in ammonia, crystallizing ammonium paratungstate, and reducing this to metal with theoretical ratio of carbon. Raw materials, wolframite, and scheelite, cleaned magnetically, and a nonmagnetic residue, mainly tin oxide, sent to a tin smelter. The magnetic concentrate contained 65–70 percent WO_3, ground to very fine size and elutriated to remove more gangue; the filtered dried mud put into an autoclave at 8–10 atmospheric steam pressure with NaOH solution for 5 hours. Poured into a thimble 1.5 meters deep and settled to decant a sodium tungstate solution containing sodium silicate. The clear leach diluted 1:3 with water and dilute HCl added to pH 8 to precipitate granular silica that can be filtered out. The filtered solution is then treated with calcium chloride solution returned from a later step of the solution to precipitate calcium tungstate and leave sodium chloride solution to be discarded.

The filtered and washed calcium tungstate precipitate is then slowly poured into hydrochloric acid solution in a stirred vessel made of Haveg (a reinforced plastic), the stirring and boiling by live stream lasting about 4 hours and the final liquor still containing 80–90 g.p.l. free HCl. The product is tungstic acid precipitate, which, if not of the proper yellow color, is treated by adding a small amount of nitric acid, but this usually is not necessary. The suspension is diluted with water and decanted to a filter, where further water washing is done; the filter cake is not allowed to crack. Sulfuric acid must be absent in this operation, as it would add a calcium sulfate precipitate to the tungstic acid. The tungstic acid is dissolved in ammonia water in a closed vessel to make a solution of ammonium paratungstate, which is passed through a filter to an evaporator and crystallizer and then to a drier. The dry $(NH_4)_2WO_4$ is mixed with theoretical carbon as low-ash pitch, put into a graphite crucible with luted lid, and heated to 1,400° C. for an unspecified time to reduce tungsten to metal with not over 0.1 percent carbon. The tungsten sponge is 99.80–99.90 percent pure, whereas the older practice gave 98–99 percent W.

The residue of the soda digestion is mixed with soda ash and calcined at 750°–800° C., leached with water to get sodium tungstate, and the residue, high in tin, sent to a tin smelter.

Suitable control tests for operators are included.

Blechta, V. *See* abs. **111.**

18. Blomberg, Birgitta, Kihlborg, Lars, and Magnell, Arne (Univ., Uppsala, Sweden). Crystal Structures of $(Mo, W)_{10}\ O_{29}$ and $(Mo, W)_{11}\ O_{32}$. Arkiv. Kemi, vol. 6, 1953, pp. 133–138. Chem. Abs. vol. 43, 1949, pp. 3261, 4072; vol. 14, 1950, p. 5176; vol. 47, 1953, p. 11872.

The oxides were prepared by heating mixtures of Mo and the trioxides of Mo and W for some days at temperatures of 700° and above. Crystals were studied by rotation and Weissenberg photographs, followed by Fourier summations. For $(Mo, W)_{10}\ O_{29}$ (I) the dimensions of monclinic unit cell $a=17.0$, $b=4.00$, $c=17.5$ A, $\beta=111°$. There were two formula units of one per unit cell. The space group was P $2/a$, for $(Mo, W)_{11}\ O_{32}$ (II); dimensions of monoclinic unit cell were $a=16.6$, $b=4.00$, $c=18.7$ A, $\beta=74°$. There were two formula units of II per unit cell. The space group was P $2/a$. Electron-d maps gave no reliable data on the position of the O atoms, so this information had to be obtained from spatial and functional considerations. The structural properties of both oxides were in agreement with those predicted for two members of the "homologous series" M_n0_{3n-1}, where M=metal atom.

Bogoraz, Yu. *See* abs. **58.**

19. Bokii, G. B. and Anikin, I. N. Determination of the Solubility of Scheelite ($CaWO_4$) in Water and in Aqueous Solutions of Sodium Chloride and Lithium Chloride by the Radiochemical Method. Zhur. Neorg. Khim., vol. 1, 1956, pp. 1926–1928; Chem. Abs., vol. 51, 1957, p. 6284.

The solubility of $CaWO_4$ was determined by use of W^{185}. The data show that equilibrium was established after 1.5 hours. The solubility was determined in H_2O, M NaCl, and M LiCl over the temperature range 20°–100°. The solubility decreases with increasing temperature. The solubilities at 20° are 13.3 mg./l. (H_2O); 25.5 mg./l. (M NaCl); and 33.5 mg./l. (M LiCl). At 90° they are 2.3 and 18 mg./l., for H_2O and M NaCl, respectively. The last determination in M LiCl was at 60° (28 mg./l.).

20. Booss, H. J. [Notes on Oxide Layer Formation on Tungsten.] Metallwirtschaft, vol. 11, June 1957, pp. 511–515, ills., figs., and 20 refs.

Conclusion: The treatment of tungsten by electrolytic and thermal oxidation is described. Emphasis was given to the influence of pretreatment of the surface on the rate of thermal oxidation. Tests with platinized surfaces show that in the oxidation of tungsten an oxygen diffusion is involved. Through prior electrolytic oxidation there is a certain protection against subsequent thermal oxidation. The protective action of the surface layer is limited with time and becomes less with rising temperatures.

21. Bosworth, R. C. L. The Formation of Mobile and Immobile Films of Oxygen on Tungsten. Proc. Roy. Soc. (New South Wales), vol. 83, pt. 1, 1949, pp. 31–38; Met. Abs., vol. 18, 1951, p. 646.

The contact p.d. has been used to study the condensation of oxygen on W at low temperature. The process follows the kinetics expected by the Roberts' theory of condensation with dissociation as an immobile film. At higher temperature the condensation (once θ, the fraction of the surface covered, has exceeded a value of $\sim$0.4) proceeds the more slowly the higher the temperature or the lower the pressure. This is interpreted as due to the activation of some of the adsorbed oxygen atoms to a mobile state, which proceeds the more rapidly the higher the temperature and the more completely the lower the pressure. Calculation of the surface diffusion coefficient at 830° K. gives a figure of 2.5×10^{-16} cm.^{2} sec.$^{-1}$ for $\theta = 0.5$, increasing with increase in θ, and an activation energy of 0.50 e V. for $\theta = 0.5$, this time decreasing with increase in θ.

Brenner, A. *See* abs. 182.

Bretschneider, Otto. *See* abs. 85.

22. Brewer, L., Bromley, L. A., Giles, P. W., and Lofgren, N. L. The Thermodynamic Properties of Molybdenum and Tungsten Halides and the Use of These Metals as Refractories: Thermodynamics. Nat. Nuclear Energy Ser., IV–19B, 1950, pp. 276–311; Met. Abs. (British), vol. 20, 1952–53, p. 208.

The free energies, heats, and entropies of formation of the Mo and W halides at 298°, 500°, 1,000°, 1,500°, and 2,000° K. are estimated from the thermodynamic data of the elements, the heats of formation at 298° K. of $MoCl_5$ and WCl_6, and a knowledge of the preparation, decomposition, and disproportionation of the Mo and W halides. Methods of estimation are described. From these estimated data the gaseous halide equilibrium pressures over solid Mo and W between 298° and 2,500° K. are estimated, using the relation $\Delta F = -RT \ln K$, and graphs showing equilibrium composition of vapour against temperature are given. Using the criterion that a metal is not attacked if the equilibrium value of the halide over the metal is $> 10^{-5}$ atmosphere, the maximum allowable halogen vapour pressure is calculated for various temperatures. Calculations are made of the maximum halogen vapour pressure which will just form the solid dihalide at various temperatures. The attack by H halide gases is considered, and the amount of H at 1 atmosphere total pressure that must be added to prevent attack is calculated. With Mo some H addition is always necessary, but in some temperature ranges W is not attacked by the pure H halide. Known and possible ways of preparing the Mo and W halides and their physical properties are described. The possibility of the existence of monohalides at high temperature is considered.

Bridges, D. W. *See* abs. 9.

Bright, H. A. *See* abs. 81.

23. Brock, G. W. Digest of the Embrittlement of Tungsten by Ammonia, by G. L. Davis, Metallurgia, vol. 54, July 1956, pp. 18–20; Metal Prog., vol. 71, March 1957, pp. 190, 192, and 194.

Tungsten oxidizes rapidly at temperatures above 1,100° F., so it is processed and used at higher temperatures either in a vacuum or in protective atmospheres of inert or reducing gases. Pure nitrogen or hydrogen atmospheres are satisfactory, but it is generally advantageous to use mixtures of the two gases. If the mixture of these gases contains traces of impurities such as oxygen, water vapor, or carbon-containing gases, the heated tungsten wire will be severely embrittled.

During an investigation into brittle wires, it was discovered that small concentrations of ammonia gas could have a disastrous effect on the toughness of tungsten wires heated in a mixture of 90 percent nitrogen and 10 percent hydrogen. In view of the prevalence of N-H mixtures obtained from dissociated ammonia, it was considered that the subject warranted some study.

Following five points in the Conclusions, it is stated: "From a practical point of view, it is imperative that traces of ammonia be excluded from atmospheres in which W is heated, although the effects can be mitigated by certain pre or post treatments.

Bromley, L. A. *See* abs. 22.

Brown, E. D. *See* abs. 81.

24. Buehler, E. Growth of Molybdenum, Tungsten, and Columbium Crystals by Foating Zone Melting in Vacuum. Jour. Metals, vol. 10, September 1958, p. 580; Crerar Metals Abs. item 636, vol. 7, No. 3, October 1958, p. 154. Presented at fall meeting, AIME Metallurgical Society, Cleveland, October 26–30, 1958.

A vacuum floating zone apparatus using r.f. heating was used to grow single molybdenum crystals. Single-pass runs improve purity markedly. Electrical and physical properties of the crystals are being studied.

25. Burgers, W. G., and Van Liempt, J. A. M. Behavior of Thorium Oxide in Annealed Tungsten Wires. Ztschr. anorg. allgem. Chem., vol. 193, 1930, pp. 144–160; Chem. Abs., vol. 25, 1931, p. 669.

X-ray investigation shows that in unannealed drawn W wire containing ThO_2 and of polycrystalline structure the oxide of Th is present as such. In single-crystal wire the ThO_2 crystallite shows no preferential orientation. By annealing the polycrystalline at high temperatures (above 2,500° absolute), part of the ThO_2 is reduced to metallic Th. At these temperatures there is also found that a lattice with varying values of parameter could be obtained by annealing superficially oxidized Th wire in vacuo for different time intervals. Accurate determinations of the lattice constants of ThO_2 and Th were made, the following values being obtained for a: ThO_2, highly ignited and prepared from the nitrate—5.585±0.001 A.U.; Th prepared by reduction of chloride with Na—5.074±0.002 A.U.; Th metal prepared by thermal decomposition of the iodide—5.081±0.002 A.O.

26. Business and Defense Service Administration. Materials Survey—Tungsten, December 1956, 100 pp. (Available Supt. of Documents, Washington (25), D.C., 75 cents.) Metals Rev., item 96-a, vol. 31, February 1958, p. 32.

Technical and economic status in relation to material requirements.

27. Campbell, I. E., (Editor-in-Chief). High-Temperature Technology. Author and subjet indices published by John Wiley and Sons, Inc., New York, N.Y., 1956, 526 pp., approximately 1,000 refs. (Sponsored by The Electrochem. Soc., Inc., New York, N.Y.)

In general, consideration is primarily given to a service at temperatures above 1,500° C. However, much of the processing of materials for service at these temperatures is done at considerably lower temperatures and, therefore, particularly in the Materials and Methods Section, much of the discussion relates to processing at moderate temperatures. . . . The book is divided into four sections: Introductory (tracing the development of modern refractories and modern high-temperature techniques), Materials, Methods, and Measurements.

See also Powell, C. F., abs. **165.**

28. Carne, I. H. The Manufacture of Tungsten Powder and Ferrosilicon at the Works of the Broken Hill Proprietary Co., Limited, Newcastle. Proc. Australasian Inst. Min. and Met., 1947, vol. 145, 1951, pp. 1–14; Chem. Abs., vol. 46, 1952, p. 7953.

In a batch process for making tungsten powder, 7½ cwt. of wolframite, crushed to 90 percent —200 mesh, is digested 5 hours with 80 gallons of NaOH (containing 3 cwt.) solution, diluted with H_2O, settled, and the clear Na_2WO_4 solution drawn off and precipitated as $CaWO_4$ with $CaCl_2$ solution. The precipitate is washed, settled, and treated with 100 gallons of commercial HCl at 75° to form bright yellow crystalline H_2WO_4 (cold dilute HCl forms a colloidal precipitate difficult to purify). The precipitate is washed five times as a slurry, filtered by suction to a cake containing 15 percent H_2O, and roasted at 1,000°; pale yellow WO_3 being formed. The WO_3 is finally reduced by a mixture of coke-oven and blast-furnace gases in a furnace (10 hours at 1,075°) to metallic W powder, 99.680 percent pure. Ferrosilicon and other ferroalloys are made by reducing oxide ores with coke and coal at the temperature of the electric arc (about 3,400°); scrap steel being added if the ore is Fe-deficient. Coal is used with coke to open up (with the volatiles given off) the upper layers of the charge and allow more uniform escape of the gases produced and to minimize atmospheric oxidation of the electrodes. Equipment consists of three 4,500-kv.-a. buried arc furnaces and one 1,500-kv.-a. Heroult-type tilting furnace; two of the furnaces have been fitted to use Soderberg self-baking electrodes, the normal current in each electrode being 29,000 a. when operating at 90 volts between phases. Ferrosilicon of 50 percent grade is the alloy produced in largest tonnage, a typical charge being; Quartzite (97 percent SiO_2), 2,000 pounds; coke, 800; coal, 200; and steel scrap, 1,000. The quartzite-carbon ratio is critical, excess C raising the electrodes in the furnace (hot fiery furnace top and cold taphole) and deficient C allowing them to go deeper, resulting in sticky, semifused, unreduced quartzite around the taphole.

29. Charlton, M. G. Hydrogen Reduction of Tungsten Trioxide. Nature, vol. 169, 1952, pp. 109–110; Chem. Abs., vol. 46, 1952, p. 6537.

Time curves for the reduction of WO_3 by H are obtained by a continuous weighing technique. They show well-defined inflections that correspond to the β-and γ-oxides intermediate in composition between WO_3 and WO_2. The average compositions for the β-and γ-oxides were $WO_{2.88}$ and $WO_{2.70}$ respectively. It is probable that the formation of these oxides by reduction will tend to give O-deficient compounds. X-ray powder photographs of partially reduced samples showed that these inflections correspond to homogeneous compounds with two-phase regions on either side. The γ-oxide inflection was never observed at about 585° and was only found at 645° when very low flow rates were used. The presence of H_2O vapor increases the induction period that occurs before one oxide is reduced to the next lower oxide. The reaction ultimately slows down at a stage beyond the point corresponding to WO_2, and this final slow reaction is due to reduction of WO_2 to W. At this stage the product contains approximately equal amounts of α- and β-tungsten when reduction is accomplished below 650°. Above 650°, only traces of β-W ever are found, together with α-W. The mechanism of formation of the β-form is discussed.

30. ———. Hydrogen Reduction of Tungsten Oxides. Nature, vol. 174, 1954, p. 703; Chem. Abs., vol. 46, 1952, p. 6537; vol. 49, 1955, p. 2924.

The first stage in the hydrogen reduction of WO_3 was always the β-oxide. This oxide was reduced directly to β-tungsten, although WO_2 was formed also in moist hydrogen. The γ-oxide was reduced directly to both β-tungsten and α-tungsten. Only WO_2 was completely reduced to α-tungsten. The removal of oxygen was not complete in those cases where β-tungsten was formed; this supports the suggestion that β-tungsten is a metallic oxide. (Hägg and Schönberg, Chem. Abs., vol. 48, 1954, p. 11143.)

31. Charlton, M. G., and Davis, G. L. Allotropes of Tungsten. Nature (London), vol. 175, No. 4446, 1955, pp. 131–132; Met. Abs., vol. 23, 1956, p. 396.

It is found that β-W can be formed by chemical processes only when certain oxides are present. This work supports the view of Hägg and Schönberg (Acta Cryst., vol. 7, 1954, p. 351; Met. Abs., vol. 22, 1954, p. 319) that β-W is really an oxide of W.

32. Chaston, J. C. Production of Metals of High Purity. Metal Prog., vol. 69, No. 1, 1956, pp. 64–67; Met. Abs., vol. 23, 1956, p. 1022.

Chemical and thermal processes, including zone melting, the van Arkel, distillation, and electrolytic processes for the production of metals containing <50 p.p.m. impurities are discussed briefly. The application and probable developments are considered.

33. ———. The Preparation and Properties of Pure Metals. Schweiz. Arch. angew. Wiss. u. Tech., vol. 21, December 1955, pp. 411–414; Met. Abs., vol. 23, 1956, p. 840.

Pure metals can be produced either by reduction from purified compounds or by refining the metal itself

Purification of compounds can be achieved by repeated precipitation of an insoluble compound, by repeated recrystallization, by precipitation of impurities, by fractional distillation, and by solvent extraction. In all chemical methods there is the danger of contamination by impurities in the reagents and from the containers. Methods of refining are by oxidation and fluxing of impurities from the molten metal, fractional distillation, the van Arkel process (selective dielation via a volatile iodide), electrolysis, zone-melting, and vacuum-melting. Recent developments in the preparation of pure metals have thrown further light on the effect of trace impurities on the properties of metals; where the metal is so pure that the impurities can no longer be detected by chemical or spectrographic methods, the effect on physical properties must be used as an indication of the presence of foreign atoms. The main properties affected are the temperature coefficient of resistivity in true metals, the specific resistance in semiconductors, the temperature of the ductile-to-brittle transition, the corrosion-resistance, and the mechanical strength, particularly the yield point.

34. Claeys, A. The Gravimetric Determination of Tungsten in Tungstate Solutions. Anal. Chim. Acta, vol. 17, No. 4, 1957, pp. 360–367; Jour. Inst. Metals, Met. Abs., vol. 25, July 1958, p. 879.

Methods of determining W by precipitation of WO_3 from tungstate solution are examined, using as refining method the precipitation of Hg_2WO_4 with $Hg_2(NO_3)_2$ in NH_4 solution. Precipitation with acids, followed by digestion, did not give quantative results. Several organic reagents were tried, cinchonine and β-naphthoquinoline being the best, with average errors of —0.09 and —0.06 percent, respectively. (32 refs.)

35. Clark, W. E., and Lietzke, M. H. The Mechanism of the Tungsten Alloy Plating Process. Jour. Electrochem. Soc., vol. 99, No. 6, 1952, pp. 245–249; Met. Abs., vol. 20, 1952, p. 183.

Absorption spectra indicate the possibility of Co tungstate complexes in the citrate Co-W plating bath. Polarographic evidence for the existence of complexes of tungstate and citrate is also presented. It is shown by calculations of energies of activation of W-Fe alloy deposition that the tungstate reaches the cathode by diffusion rather than by migration. The mechanism put forward for the plating of W alloys includes the deposition of a film of partly reduced tungstate on the cathode and the catalytic reduction of this film by H in the presence of freshly deposited Fe, Co, and Ni. (27 refs.)

36. Corson, M. G. A Proposal for Research in Metallurgy—Properties of Very Pure Metals. Metal Prog., vol. 55, No. 1, 1949, pp. 55–58; Met. Abs., vol. 16, 1949, p. 629.

Corson pleads for greatly increased expenditure on the study of the fundamental properties of metals. At least three laboratories should be established that are capable of producing very pure metals (99.99 percent$^-$), and the following properties of the metals merit investigation: Compressibility, specific volume, thermal expansion, electrical conductivity, magnetic susceptibility, work function, heat content, electrochemical and contact potentials, behavior under mono- and bi-directional stress.

37. Cox, M. Thermal and Electrical Conductivities of Tungsten and Tantalum. Phys. Rev., vol. 64, Oct. 1 and 15, 1943, pp. 241–247 (QC 1.P4); Thermal Properties of Certain Metals. II. Abs. Bull. TP-14-9, Bib. Sec., Tech. Inf. Div., Library of Congress, Washington (25), D.C.

A study was made of the variation with temperature of the resistance, thermal conductivity, and Wiedemann-Franz ratio of pure tungsten. Measurements were made of the resistance (as a function of power input) of wires suspended in vacuum and thermostated at 273.2 to 373.1° K. A method was developed for calculating the thermal conductivity from the resistance at zero power input and the slope of the resistance versus power-input curve.

38. Daunatt, C. W. Metal Refining: Physical, Electrolytic, and Chemical Methods. Metal Ind., vol. 72, No. 1, 1948, pp. 3–5; No. 2, pp. 25–27; Met. Abs., vol. 16, 1948, p. 77.

Read before the London Local Section of the Institute of Metals. Daunatt discusses the close relationship that exists between all operations of ore treatment, each in itself a refining process, and gives details of physical, electrolytic, and chemical methods of refining.

Daunt, J. G. *See* abs. **89.**

39. Davis, G. L. Recrystallization of Tungsten Wires Metallurgia, vol. 58, No. 348, October 1958, pp. 177–184; No. 349, November 1958, pp. 228–232.

From observation of mechanical properties and microstructures, it was found that tungsten wires recrystallize first by formation of a columnar structure with good retention of strength and ductility. At higher temperatures, secondary recrystallization occurs with embrittlement and lowered strength. The practically important temperature for onset of this coarsening is very sensitive to the nature of the starting material and its history. A hypothesis is advanced to explain the phenomena, and the kinetics of the processes are considered.

40. ———. Embrittlement of Tungsten by Ammonia Metallurgia, vol. 54, July 1956, pp. 18–20; Metal Prog., vol. 71, March 1957, pp. 190, 192–194.

Conclusions: 1. The embrittling action seems to be due to reaction with ammonia rather than the products of its dissociation and is associated with the presence of nitride as an insoluble phase. 2. The reaction seems to involve diffusion of some agent into the metal from the surface. 3. Either the reaction is initiated (or catalyzed) by oxide on the surface or the extent of the effect is strongly dependent on surface area. 4. The effect is not apparent with specimens that have undergone coarsening by secondary recrystallization. 5. Since the embrittlement is removed by dissolving off a disproportionately small quantity from the surface, this defective surface material must act as a source of ready initiation of cracks, which then propagate through the unaffected interior of the specimen. Tungsten is, in fact, very notch sensitive. From a practical point of view, it is imperative that traces of ammonia be excluded from atmospheres in which tungsten is heated, although the effects can be mitigated by certain pre or post treatments. (*See* abs. **23.**)

See also Charlton, M. G., abs. **31.**

41. Davis, G. L., and Gentry, C. H. R. The Electrodeposition of Tungsten. Metallurgia, vol. 53, No. 315, January 1956, pp. 3–17, 49 refs.; Met. Abs., vol. 23, 1955–1956, p. 910.

The difficulties often associated with working refractory metals could frequently be overcome by applying them as surface coatings. After reviewing previous work on the production of W coatings, Davis and Gentry consider deposition from aqueous solution, organic solvent baths, and fused-salt baths. No success was acheived with aqueous baths, and theoretical considerations lead to the conclusion that aqueous W deposition is impossible. Negative results were obtained with organic solvent baths. Thick coherent layers of W were deposited from fused-salt baths containing borates and tungstic oxide. The disadvantages of fused-salt deposition is the reactivity of the melt with the containing vessel. The theoretical aspects of the deposition process are fully treated.

42. Davis, M. (U.K.A.E.A., Ind. Group, Culcheth, England). Molybdenum and Tungsten, Possibilities in the Nuclear Field. Nuclear Eng., vol. 3, June 1958, pp. 243–246; Nuclear Sci. Abs. item 11472, vol. 12, No. 17, Sept. 15, 1958, p. 1359.

Molybdenum and tungsten have high-temepratur e and other properties that may make them attractive as canning materials for some types of advanced nuclear reactors. Exploitation in this field may first require the development of suitable alloys. The properties of the metals are discussed and tabulated.

43. Davis, R. T., Jr. The Activated Absorption of Nitrogen on a Finely Divided Tungsten Powder. Jour. Am. Chem. Soc., vol. 68, No. 8, 1946, pp. 1395–1402; Met. Abs., vol. 15, 1947, p. 139.

The adsorption of nitrogen on tungsten powder was studied in a pressure range of 10^{-6} to 35 mm. and a temperature range of 400°–750°. At saturation there was 1 molecule of nitrogen for every 4 surface atoms of tungsten. The thermodynamics of the tungsten-nitrogen system are discussed.

44. Dawihl, W. Tungstic Acid in the Form of Ammonium Paratungstate From Sodium Tungstate Solutions. Board of Trade, German Div. Doc. Unit (London). PB-102,470–S, U.S. T.I.I.D.–O.R.I. Mar. 3, 1948.

The material, which emanates from the Studiengesellschaft Hartmetall, Berlin (Hard Metal Research Association), consists of a microcopy of a report entitled "Versuche zur Abtrennung von Wolframsäure als Amoniumparawelfromat aus Matrium-Wolframstlösungen" [Experiments on the Separation of Tungsten Acid in the Form of Ammonium-Paratungstate From Sodium Tungstate Solutions], dated March 1, 1941, and signed by Dr. Dawihl.

It is stated that ammonium paratungstate is soluble in water at room temperature corresponding to about 1 percent in weight of tungstic acid. Sodium paratungstate is soluble in water at the same temperature corresponding to about 6 percent in weight tungstic acid. As sodium tungstate with up to 20 percent in weight of tungstic acid can be obtained by the extraction of roasted hard-metal scrap with soda lye or by the nitrite preparation method, it should be possible to be able to separate the tungstic acid as ammonia paratungstate with a yield of more than 90 percent in weight.

The tests are described briefly, and results tabulated. The tests show that a yield of 80 percent of fully crystallized parasalt was reacted by the addition of ammonium salts to sodium tungstate solution. The sediments were not sufficiently free of sodium as sodium pure tungstate does not dissolve easily.

The reader is referred to BIOS Final Report 925, entitled Tungsten Carbide Research in Germany, for further information.

45. ———. The State of the Tungstic Acid in Solutions of Ammonium Tungstate and the Adsorption of Tungstic Acid on Ferric Hydroxide. Ztschr. anorg. allgem. Chem., vol. 244, 1940, pp. 198–204; Chem. Abs. vol. 35, 1941, pp. 2773, 3140.

NH_4 paratungstate (I) dissolves very slowly in water and in aqueous NH_3, although its equilibrium solubility is quite high. In an attempt to account for this the precipitation of tungstic acid along with $Fe(OH)_3$ was studied. $FeCl_3$ or Cl-Free $Fe(OH)_3$ was added to an exactly neutral solution WO_3 in NaOH, and the composition of the solution in equilibrium with the precipitate was determined. An increase in the ratio Fe_2O_3/WO_3 produced a great decrease in the amount of WO_3 remaining in the solution; the precipitate was of variable composition. When a solution of I was treated in a similar way, the results were qualitatively the same. X-ray examination of three of the precipitates showed them to be amorphous. It is concluded that in the solutions studied WO_3 is present in a loosely combined, essentially colloidal form. The process of solution is then a slow peptization rather than a rapid imic reaction.

46. Delahay, Paul, and Stagg, L. J. A Polarographic Method for the Indirect Determination of Polarization Curves for Oxygen Reduction of Various Metals. III. Cr, Mo, Ta, Ti, W and Zr. Jour. Electrochem. Soc., vol. 99, 1952, pp. 546–548; vol. 97, 1950, p. 205; Met. Abs., vol. 18, 1950–51, p. 199; vol. 20, 1952–1953, p. 501.

Polarization curves were determined for these metals for the electrolytic reduction of O. The contributions of the two- and four-electron processes, namely, reduction of O to H_2O_2 and to H_2O, respectively, were determined. The electrolytic reduction of O on Cr, Ta, Ti, and W may yield appreciable quantities of H_2O_2. Very little H_2O_2 is formed on Zr and Mo. (5 refs.)

47. Drechsler, M., Paukow, G., and Vanselow, R. [Detection of Dislocations in the Reduction of Tungsten, Tantalum, and Nickel Monocrystals.] Zschr. physik. Chem. (Frankfurt), vol. 4, Nos. 5–6, July 1955, pp. 249–263; Am. Soc. Metals Rev. of Metal Literature, item 290-M, Metals Rev., vol. 28, No. 10, 1955, p. 34.

Several methods of gradually reducing monocrystal tips by field emission microscopes at elevated temperature and in the electric field. (Micrographs, diagrams, 17 refs.)

48. Druyvesteyn, M. J. The Variation of the Resistivity of Some Metals With Elastic Deformation. Physica, vol. 17, No. 8, 1951, pp. 748–760; Met. Abs., vol. 20, 1952–1953, p. 76.

The anisotropy of electrical resistance was studied. The metals used included Cu, Ag, Au, Al, Mo, Pt, Ti, W, and some alloys; and these were measured in polycrystalline form—Al as single crystals and Cu, Ag, Cu, and Al as foils with textures present. The quantities determination in the experiments are applied to the simple case of hydrostatic pressure.

Druzhinina, O. S. *See* abs. **187**.

49. **Du Pont de Nemours**, E. I., and Co., Inc., and **Rohm and Haas Co.** Tungsten, Tantalum, Columbium and Vanadium. Materials Data Sheet, vol. 37, June 1953, p. 127.

Tabulated data on physical and mechanical properties, thermal treatment, fabricating properties, corrosion resistance, and available forms and uses of tungsten.

Ebert, Fritz. *See* abs. **85**.

50. **Ehrlich, Gert, Hickmott**, T. W., and **Hudda**, F. G. Interaction of Rare Gases With a Tungsten Surface. Jour. Chem. Phys., vol. 28, May 1958, pp. 977–978; Battelle Tech. Rev., item 11783, vol. 7, September 1958, p. 589-a.

No abstract.

51. **El Shamy**, H. K. (Farouk Univ., Alexandria, Egypt). Acid Tungstate Solutions. Jour. Indian Chem. Soc., *vol. 29, 1952, pp. 667–673; Chem. Abs.*, vol. 47, 1953, p. 6796.

Dilute acid solution of low-molecular tungstate acid when cathodically reduced, gave W blue corresponding to W_2O_{11} instead of W^{6+}. A 11 *M* HCl solution gave W^{5+} with platinized Pt and W^{3+} with plain Pt as the cathode. It was not possible to determine the standard reduction potential of W^{4+} W^{5+} because of the difficulty of varying the pH and the metal-ion concentration. At 11.06 *M* HCl and 30° the potential was 0.3155 v.

52. **Espe**, W., and **Knoll**, M. Werkstoffkunde der Hochvakuumtechnik. [High-Vacuum Applications.] Springer, Berlin, 1936.

The refractory metals, tungsten, molybdenum, tantalum, and columbium, are extensively surveyed for high-vacuum applications. *See* abs. **70**, item 2352, p. 169.

Fassell, W. M. Jr. *See* abs. **9**.

53. **Fischer**, R. B. Tungsten. Paper from The Reactor Handbook, vol. 3 (Materials) Tech. Inf. Service, AEC Rept. AECD 3647, pp. 373–381, Am. Soc. Metals Review of Metal Literature, item 305–V. Metals Rev., vol. 28, No. 12, 1955, p. 44.

This paper covers the economics and physical, mechanical and metallurgical properties of tungsten. (Tables and a graph are included.)

54. **Fitzer**, E. [High-Temperature Resistant Materials by Silicizing Tungsten and Molybdenum.] Berg- u. hüttenmänn. Monatsh. montan. Hochschule Leoben, vol. 97, No. 5, 1952, pp. 81–91; Ceram. Abs., vol. 35, Sept. 1, 1952, p. 161.

By depositing a coating of a silicide on W and Mo (in the form of wires), materials were obtained that were stable up to 1,800° with Mo as a base and above 2,000° with W as a base; the coatings were completely resistant to oxidation. The coatings are 0.02 to 0.05 mm. thick (depending on the time of silicizing) and are produced with $SiCl_4$ vapor in an H_2 atmosphere at 1,000° to 1,200°; they consist mainly of the disilicides of Mo and W, according to the reaction $Mo_{metal}+2SiCl_{4\,vapor}+4H_2 \rightarrow MoSi_2+8HCl$; no volatile W or Mo chlorides are formed. Tables giving melting point, ductility, and oxidation resistance of metals, carbides, nitrides, *borides, silicides, and oxides are added for* materials used at high temperatures, and comparative hardness values are given for the coatings and the basic material. The microhardness (in kg./mm.^{2}) is 1410 for $MoSi_2$ and 1632 for WSi_2; the respective base metals show 371 and 668. The glass apparatus used *and the method of depositing the coatings are described.* (21 refs.)

55. **Fonda**, G. R. Evaporation Characteristics of Tungsten. Phys. Rev., vol. 21, 1923, pp. 343–347.

The variation with size, when gas was present, is in agreement with the Langmuir theory of heat-conducting for a hot filament, which supposes a stationary film of gas around the wire through which the atoms must diffuse. *See* abs. **70**, item 2407, p. 173.

56. **Fontana**, M. G. Corrosion of Tantalum, Niobium, Zirconium, Tungsten and Molybdenum. Ind. Eng. Chem., vol. 44, July 1952, pp. 71A–72A, 74A.; Met. Abs., vol. 20, 1953, p. 581.

Tabular data on the corrosion resistance of Ta, Nb, Zr, W, and Mo.

57. **Frankenberg**, W. G. Adsorption of Hydrogen on Tungsten Powders. Jour. Am. Chem. Soc., vol. 66, *1944, pt. 1 pp. 1827–1837 and pt. 2 pp. 1838–1847.*

Part I presents method and experimental results, preparation of tungsten powders, and general principle of the adsorption measurements; results are in tables and curves. In part II the isotherms and adsorption equilibria are studied. *See* abs. **70** item 1741, p. 120.

Freeman, L. L. *See* abs. **106**.

58. **Fridman**, Ya. D., and **Bogoraz**, Yu. [chlorination of Tungsten Ores With Liquid Sulfur Chlorides.] Jour. Appl. Chem. (U.S.S.R.) vol. 19, 1946, pp. 833–840; Chem. Abs., vol. 41, 1947, p. 4421.

Chlorination at 100° for 1 hour of a scheelite concentration with 71 percent WO_3, 1 g., with various fractions of liquid S chlorides prepared by action of dry Cl_2 gas on S at 40°–80°, gave highest yields in W chlorides with fractions b. 120°–130°, d. 1.62–1.68, Cl 56–61. Aging reduces the chlorinating ability of the reagent (from 6.22 to 1.27 percent per g. WO_3 after 37 days). Products are $CaCl_2$ and $WOCl_4$, chocolate-brown prismatic needles, b. 200°–250°; the outgoing gas contains SO_2. With a constant amount, 5.1 g. S_2Cl_2 of Cl 54, per 1 g. WO_3 containing ore or concentrate, at 100° for 1 hour, the yield *y* in W chlorides is very high material poor in W, very low with W-rich material; generally the higher, the greater the ratio Cl : WO_3, without, however, there being any direct relation; while products with 0.16 and 0.6 percent WO_3 gave *y* 94.0 and 52.0, scheelite; and wolframite concentrates with WO_3 71.0 percent (7.2 g. Cl used per g. WO_3) gave *y* 3.4 and 3.6; the yield varies considerably wih the nature of the material. On more prolonged chlorination, *y* increases somewhat (for example, to

7.6 after 5 hours with the scheelite concentrate), tending to a limit that, however, remains well below 100 percent extraction; with the wolframite, *y* reached only 5.4; with an artificial mixture $CaWO_4$ 8.1+$CaCO_3$ 81.9 (WO_3 5.2, using 98.07 g. Cl per g. WO_3), *y* reached 38.5, 46.6, 57.7, 62.5 in 1, 2, 3, 5 hours, respectively. Sulfides in the ore depress *y;* for example, the above $CaWO_4+CaCO_3$ mixture, +FeS 0, 2.88, 9.61, 19.2 g./g. WO_3, $y=38.5$, 21.6, 14.4, 12.5. Because of the slight dissociation of S_2Cl_2 at 100°, the mechanism of the process is represented as: $24\ SCl_2=12\ S_2Cl_2+12\ Cl_2$: $12\ Cl_2+4\ MeWO_4=2MeCl_2+4\ WOCl_4+12\ O$; $12\ O+3\ S_2Cl_2=6\ SO_2+3Cl_2$; $3\ Cl_2+MeWO_4=MeCl_2+WOCl_4+3\ O$, etc.; that is, the chlorination is brought about by the relatively slight admixture of SCl_2, not by the main constituent S_2Cl_2, which only serves to regenerate Cl_2 in the chain; the process is bound to stop when SCl_2 is exhausted, that is, long before completion of the extraction.

59. Fullman, B., and Richardson, F. D. (Editors). The Extraction and Refining of Metals. Ch. in Reports on the Progress of Applied Chemistry. Soc. Chem. Ind., vol. 39, pp. 129–161, 1955; Metals Rev., item 39–C, vol. 29, February 1956.

Survey of advances in inorganic systems and basic physical chemistry. Recent technological advances with the most important metals. (267 refs.)

60. Funaki, Koemon, and Asada, Kazuo. Fundamental Research on the Metallurgy of Tungsten. I. The Heterogeneous Equilibrium Among Tungsten, Its Oxides, Hydrogen, and Water Vapor. Jour. Electrochem. Soc. (Japan), vol. 18, 1950, pp. 250–253; Chem. Abs., vol. 45, 1951, p. 8423.

The reduction process on heating WO_3 in a stream of H gas was studied by measuring the weight of WO_3 by a thermobalance, and the following 7 stages of reduction were found: $WO_3 \rightarrow W_4O_{11} \rightarrow W_2O_5 \rightarrow W_4O_9 \rightarrow WO_2 \rightarrow W_2O_3 \rightarrow WO \rightarrow W$. Taking into account the equilibrium constants calculated for each stage, the experimental results so far obtained for the H reduction of WO_3 are satisfactorily explained.

61. Funk, H., Muller, C., and Tormyn, J. Separation and Preparation of Pure Metal Compounds by Chlorination of Ores and Industrial Wastes. Chem. Tech. (Berlin), vol. 5, 1953, p. 530; Chem. Abs., vol. 48, 1954, p. 5755.

The volatilization of W, Mo, and V by chlorination of ores or waste products by means of Cl and in the absence of coal proceeds readily and permits separation from other metallic compounds. Fe (III) can be volatilized at between 200° and 300° in a Cl-HCl stream. Fe also can be separated from Mn, Cr, Al, and Zr by chlorination.

62. Gaumann. A [Electrolytic High-Grade Purification by Liquid Electrodes.] Schweiz. Arch. angew. Wiss. u. Tech., vol. 21, October 1955, pp. 337–342; Metals Rev., item 32–C, vol. 29, February 1956.

Use of liquid electrodes for purification and separation of metals. Process has been applied to 10 metals so far. Indium, for example, has been obtained with a purity as high as 99.99995 percent. (Graphs and diagrams included.)

63. Geach, G. A., and Jones, F. O. An Arc Furnace for Zone-Refining Metals. Metallurgia, vol. 58, No. 348, October 1958, pp. 209–210.

The use of a furance in which the metal to be melted is held in a water-cooled copper hearth while heated by an arc from an inert electrode overcomes the difficulty of contamination from the containing vessel in zone-refining the more refractory or reactive metals.

Gentry, C. H. R. *See* abs. **41.**

Gerasimov, Ya. I. *See* abs. **207.**

64. Gerasimov, Ya. I., Rezukhina, T. N., Simanov, Yu. P. and others. The Reduction of Tungstates and Molybdates With Hydrogen and the Thermodynamic Properties of Such Salts. Vestnik Moxkov Univ., Ser. Mat. Mekh., Astron., Fiz. i Khim. vol. 12, No. 4, 1957, pp. 185–200; Chem. Abs., vol. 52, 1958, 10783.

The tungstates investigated were of Mg, Ca, Sr, Ba, Mn, Co, Fe, Ni, Cu, Zn, Cd, and Pb; and the molybdates were of Mg, Ca, Sr, and Ba. Two different apparatuses were used, depending on whether the H_2 was passed over the salts above or below 1,100°. The reductions occur in steps in a rather complicated manner. $NiWO_4$ is reduced first to a compound best written as $NiWO_{3.72}$, then to $NiWO_3$; then the reduction proceeds farther to give a final product of Ni_4W+W. An attempt is made to explain all the individual phenomena observed with the various salts, on the basis of the heats, of the isobar potentials and of the entropies of formation of the metal oxides and of the tungstates and molybdates from the metals at 1,000°; but these attempts were not quite successful, as the lattice parameters are involved. The best relation between the reduction phenomena observed and any other physical property could be established on the basis of the magnetic moments. Diamagnetic salts (at 20°), such as the tungstates of Mg, Ca, Sr, Ba, Zn, Cd, and Pb, are reduced with difficulty only; that is, the reduction does not proceed much beyond the W^{11} stage. Paramagnetic salts, such as the tungstates of Mn, Fe, Co, Ni, Cu, and Zn, reduce fairly easily. (25 refs.)

Germer, L. H. *See* abs. **116.**

Giles, P. W. *See* abs. **22.**

65. Glazunov, A., and Jolkin, V. The Electrolytic Deposition of Tungsten From Aqueous Solutions. Chem. Listy, vol. 31, 1937, pp. 309–313, 332–335; Chem. Abs., vol. 32, 1938, 1185.

From aqueous solutions of alkali tungstates metallic W deposited upon the cathode at the higher temperatures. From a bath containing Na_2CO_3 330 g., WO_3 100 g., and H_2O 1 liter Glazunov and Jolkin deposited metallic W upon the cathode at 80°–100° with a c.d. of 10 a./$dm.^2$; at 50°, 60° and 70° they deposited only the oxides of W. Better metallic W deposits were prepared at 108°, 110° and 115° from the electrolyte containing K_2CO_3 170 g., WO_3 12.5 g., and H_2O 100 cc.; metallic W began to deposit at 15 a./$dm.^2$ and deposited best at 20–35 a./$dm.^2$ With an electrolyte containing

WO_3 100 g./l. and enough NH_3 to form a clear solution Glasunov and Jolkin were able to deposit only the oxides of W and not the metal at 60°–80° and over a range of c.d. Attempts to deposit metallic W from solutions of WO_3 containing Na_3PO_4 or $(NH_4)_3PO_4$ were not successful. The use of acid electrolytes similar to those used in electroplating with Cr was not possible because the WO_3 was insoluble in acids and the alkali tungstates decomposed under the influence of strong acids to form WO_3. From weakly acid electrolytes (H_3BO_3, H_3PO_4) or from alkali tungstate electrolytes containing H_2SO_4, H_3PO_4, AcOH, or tartaric acids only, the lower oxides of W formed at the cathode. From useful electrolytes the W deposited only for a short interval of time; later, the deposition ceased, and the deposited metal began to reenter the solution. In the successful electrolytes the deposition was not influenced by large changes in the concentration of the Na_2CO_3 or of the WO_3.

66. ———. [The Electrodeposition of Tungsten.] Atti X° cong. intern. chim., vol. 4, 1939, pp. 353–355; Chem. Abs., vol. 34, 1940, p. 3184.

Metallic tungsten is deposited on Cu electrolytically only from an alkaline medium, above 80°, and if the c.d. is at least 1,500 a./sq. m. At lower temperature and current density only black oxides are deposited. Deposits free from oxides are obtained at 115° from a solution containing 1,500–1,700 g./l. K_2CO_3 and 120 g./l. WO_3. Even under the best conditions, the deposition of W stops after one-half hour of electrolysis, and the deposited W begins to redissolve. This is not due to a change in the electrolyte, as more deposit of W can be obtained on new Cu cathodes. These processes are considered due to a primary deposition of a lower oxide of W, which is then reduced to the metal by atomic H. The reaction is soon stopped by the accumulation of W ions of higher valence, which react with the deposited metal.

67. GLEMSER, OSKAR, HANSCHILD, ULRICH, AND LUTZ, GERTRUD (Rheinisch-Westfalischen Tech. Hochschule, Aachen, Germany). *Preparation of Hydroxides by the Action of Atomic Hydrogen on Oxides.* Ztschr. anorg. u. allgem. Chem., vol. 269, 1952, pp. 93–98; Chem. Abs., vol. 47, 1953, p. 438.

Atomic H, generated by electric discharge, was allowed to react directly with powdered metallic oxides. An intermediate, MnOOH, is formed in the reduction of MnO_2 to $Mn(OH)_2$. Prolonged reaction results in the formation of MnO. Atomic H reduced Na_2O_2 to NaOH. Reaction with WO_3 gives $H_{0.1}-WO_3$ and $H_{0.33}$ WO_3. Reaction with MoO_3 gives $Mo_4O_{10}-(OH)_2$, which can be reduced further to $Mo_2O_4(OH)_2$ and to $Mo_5O_7(OH)_8$ by prolonged exposure. Hydroxy compounds appear to be produced in the reductions of CrO_3, V_2O_5, Nb_2O_5, and TiO_2. Metals are obtained from AgO, Ag_2O, CuO, PbO_2, and HgO. Reduction of GeO_2 gives the hydride.

68. GLEMSER, OSKAR, SAUER, HUBERT, AND KÖNIG, PAUL. The Sulfides and Selenides of Tungsten. Ztschr. anorg. Chem., vol. 257, 1948, pp. 241–246; Chem. Abs., vol. 43, 1949, p. 5321.

Mixtures of W and S in the range $WS_{0.1}$ to $WS_{3.0}$ were heated at 900° in quartz tubes in an atmosphere of pure N. X-ray studies showed that only WS_2 is thermally stable. It forms a C_7-type lattice with interatomic distances of $a=3.18$ A., $c=12.5$ A. The calculated density is 7.55; the experimental, $d^{20}_4=7.75$. No other W sulfides could be prepared in this manner. The reaction of CS_2 with WO_3, W_4O_{11}, and WO_2 also led to WS_2 only. WS_3 was obtained as a chocolate-brown amorphous powder by the reaction of HCl on $(NH_4)_2WS_4$. At 170°, WS_3 decomposed into WS_2 and S. A crystallized WS_3 was obtained by acidifying piperazine tungsten sulfide. WSe_2 was prepared by heating the stoichiometric mixture of W and Se at 950° for 150 hours in a N atmosphere. X-ray studies gave $a=3.29$ A., $c=12.97$ A. Calculated density=9.32; experimental, $d^{20}_4=9.22$. K_2WSe_4 acidified with diluted HCl gives WSe_3, amorphous, decomposed at 220°.

69. GLEMSER, OSKAR, AND VÖLZ, HANS G. (Univ., Göttingen, Germany). Gaseous Hydroxides. I. Gaseous $WO_2(OH)_2$. Naturwissenschaften, vol. 43, 1956, p. 33; Chem. Abs., vol. 51, 1957, p. 13529.

When water vapor is passed over solid WO_3 at 1,000°, gaseous $WO_2(OH)_2$ is formed. When mixtures of H_2O and N were used, the weight loss of the WO_3 was proportional to the H_2O content of the mixture. The equilibrium constant $K_p=P/_{wo_2}(OH)/pH_2O=3.84 \times 10^{-3}$, where p is pressure. Between 1,100° and 1,200° the enthalpy of the reaction is −13 kcal./mole. The heat of sublimation of WO_3 between 1,100° and 1,200° is 42 kcal./mole.

70. GOETZEL, C. G. Treatise on Powder Metallurgy. III. Intersci. Pub., Inc., New York, N.Y. (Intersci. Pub. Ltd., London), 1952, 899 pp.

Classified and annotated bibliography.

71. GOMER, R., WORTMAN, R., AND LUNDY, R. Mobility and Adsorption of Hydrogen on Tungsten. Jour. Chem. Phys., vol. 26, May 1957, pp. 1147–1164, (45 figs. 31 refs.); Ind. Arts Index, 1957, p. 2123.

The surface diffusion of hydrogen on W field emitters has been investigated by making use of the low vapor pressure and high sticking coefficient of H_2 at liquid helium temperature to obtain unilateral contamination. Average values of the energy of desorption of H_2 also have been obtained. It is found that spreading occurs in three distinct phases. At very high initial coverages a moving boundary migration occurs below 20° K, corresponding to migration of physically adsorbed H_2 on top of the chemisorbed layer, precipitation at its edge, and further migration over the newly covered region.

See also Wortman, R. abs. **211.**

72. GOMER, ROBERT, AND HULM, J. K. Adsorption and Diffusion of Oxygen on Tungsten. Jour. Chem. Phys., vol. 27, December 1957, pp. 1363–1376; Battelle Tech. Rev., vol. 7, March 1958, p. 212-a (61 figs., 3 tables, and 14 refs.).

The surface diffusion and adsorption of oxygen on W have been studied by a field emission technique by utilizing the high sticking coefficient and negligible vapor pressure of O_2 at 4.2°–20° K. Three types of migration were noted. At ~27° K. diffusion occurs with a sharp boundary and an activation energy $E_d \approx 0.9$ kcal. This is believed to be migration of physically adsorbed O_2 over the chemisorbed layer, with precipitation on the bare surface. The distance traversed by the boundary was found to be limited by desorption above ~40° K. A study of this effect yielded an estimate of 2.3 kcal. for the heat of adsorption, H_a, in the physisorbed layer. At 400°–500° K.

and high coverages, diffusion occurs within the monolayer with activation energies of 23–25 kcal. Boundaries moving radially outward from the close-packed faces are observed and believed to result from precipitation of O atoms in trap sites on the rough regions of the surface. At low coverages boundary-free diffusion with $E_d \sim 30$ kcal. is observed and interpreted as migration from trap sites. The latter are believed to constitute ~60 percent of all sites. Activation entropies for the various diffusion processes are estimated to vary from ~7–13 eu.

It was found that 89 percent of the chemisorbed layer can be formed without appreciable activation at 27° K. The layer is stable up to 700° K., where desorption and oxidation begin. The latter is markedly dependent on the amount of oxygen on the surface. At 300° K. there is a slow oxygen uptake, probably associated with incipient oxidation.

Gonser, B. W. *See* abs. **165**.

73. Goodwin, H. B., and Greenidge, C. T. Forgeable Arc-Melted Tungsten. Metal Prog., vol. 59–60, June 1951, pp. 812–814; Battelle Mem. Inst., Columbus, Ohio, Contract AF–33 (038)–6413.

Vacuum-melting with a consumable electrode of pressed and sintered tungsten powder was practiced on a small scale, using a water-cooled copper crucible lined with a thin sheet of molybdenum, which did not seriously contaminate the tungsten. Vacuum 0.5 micron, a.-c. current, 1200 a. at 22–24 v. Carbon-reduced powder that contained enough residual carbon to remove oxygen was used. The ingot had a 1-inch-high film of W at the edge and was 0.75 inch high and about 3 inches in diameter. A 1.25-inch cylinder of sound metal cut from the ingot for forging test was heated to 2,800° F. for one-half hour, with no protective atmosphere, and was flattened to a pancake in forge.

Gorbunova, K. M. *See* abs. **7**.

74. Goucher, F. S. Strength of Single Crystal of Tungsten and Its Variation With Temperature. Phil. Mag., vol. 48, ser. 6, No. 284, 1924, pp. 229–249.

It was found that the time required for fracture of the crystal is an exponential function of the load and the temperature; for a given rate of deformation the load is proportional to the cross-sectional area. *See* abs. **70** item 2411, p. 173.

Greenidge, C. T. *See* abs. **73**.

75. Greenwood, J. N. Manufacture of Tungsten Rod and Wire in Australia. Chem. Eng. and Min. Rev., vol. 39, 1947, pp. 367–370; Chem. Abs., vol. 41, 1947, p. 6502.

Details of the plant are given for producing W from Tasmanian wolframite. Wolframite concentrate from Storey's Creek, Tasmania, contained 73.1 percent WO_3. The process produced W powder and fabricated it into rod and wire.

Gregg, C. C. *See* abs. **110**.

76. Griffs, R. C. Equilibrium Reduction of Tungsten Dioxide by Hydrogen. Jour. Electrochem. Soc. vol. 105, July 1958, pp. 398–402; Battelle Tech. Rev., item 11881, vol. 7, September 1958, p. 594–a.

A study was made of the heterogeneous equilibrium involving H_2-W-WO_2-H_2O in the temperature range 500°–1,000° C., using a static equilibrium-type of apparatus. The standard heat of formation and entropy of WO_2, as calculated from the equilibrium data, was found to be $\Delta H° = -135.0 \pm 0.3$ kcal. and 17.1 ± 1.0 e.u. The heats of formation of WO_3 and the two higher suboxides were determined by direct combustion. $\Delta H°$ of $W_{18}O_{49}$ $(WO_{2.72}) = -183 \pm 1$ kcal./mole W, $\Delta H°$ of $W_{20}O_{58}$ $(WO_{2.90}) = -193 \pm 1$ kcal./mole W, and $\Delta H°$ of $WO_2 = -137 \pm 1$ kcal./mole W.

77. Grosman, L. I., and Perlov, P. M. Separation of Scheelite-Barite Products by the Autoclave-Soda Method. Tsvetnye Metal., vol. 29, No. 5, 1956, pp. 16–18; Chem. Abs., vol. 51, 1957, p. 10853.

Flotation products containing WO_3 24.6, Mo 0.63, Ba 35.5. S 8.98, and P 0.34 percent were heated with Na_2CO_3 (Na_2CO_3:WO_3=4 and 5) for 2 hours at 225° before grinding (68.80 percent, -74μ) and at 200° after grinding (100 percent, -74μ) at 15–25 atmospheric pressure. The residue contained 0.32–0.8 percent WO_3 and the liquor 98.95 percent. WO_3 was precipitated from the liquor with a solution of $CaCl_2$; all the S remained in the liquid phase. Precipitation with iron chloride reduced the recovery by 20 percent; reduction with C and subsequent leaching out of the BaS formed was cumbersome.

Gulbransen, E. A. *See* abs. **87**.

78. Gulbransen, E. A., and Andrew, K. F. Reactions of Metals In High Vacua. Jour. Phys. and Colloid Chem., vol. 53, No. 5, 1949, pp. 690–711; Met. Abs., vol. 18, 1951, p. 756.

The nature of chemical reactions occurring in vacuum and at high temperature on various metals is considered. These reactions are grouped into three classes: (1) Those that form a gas as a result of a reaction; (2) those that react with gases in the vacuum; and (3) those that exchange one gas for another as a result of chemical reaction. Equilibria calculations are made where data are available on the reactions for the metals Zr, W, Fe, Cr, and Mg. The various reactions are discussed as sources and sinks in high-vacuum technique. An apparatus is described for studying these reactions at temperature up to 1,200° C. and at pressures of 10^{-6} mm. Hg or better. A new type of high-temperature vacuum furnace tube is described briefly; it can be sealed to Pyrex and is vacuum-tight at 1,200° C. Results are presented on the following problems: (1) The vacuum oxidation of Zr, W, Mo, and mild steel; (2) the formation of carbon monoxide by the reaction of carbon in the metal with the surface oxide for the alloy Nichrome V; (3) the volatilization of MoO_3 and WO_3; and (4) the oxidation and evaporation of magnesium.

79. **Gulbransen, E. A., and Wysong, W. S. Thin Oxide Films on Tungsten. Metals Technol., AIME Tech. Pub. 2224, vol. 14, No. 6, September 1947, 14 pp.**

The behavior of W and its surface oxides in oxidizing and reducing atmospheres and in high vacua at elevated temperatures is a question of considerable technical importance. The use of W as a metal or as an important component in alloys in high-temperature oxidizing atmospheres has been limited because of the unprotective nature of its oxide film and the volatility of its oxide. This paper presents results of a microbalance study of the following problems: (1) The oxidation behavior in the temperature range of 25° to 550° C., (2) the reduction with pure hydrogen of thin oxide films formed on W, and (3) the volatility of thin oxide films on W. Both thick and thin oxide films on W appear to be reduced at temperatures of 500° C. and higher. An analysis of the maximum rate of reduction as a function of the reciprocal of the absolute temperature indicates an energy of activation of 18,000 cal. for the reaction. The volatility of the W oxides is studied as a function of temperature and thickness. Thick films are found to evaporate at temperatures as low as 800° C.; thin films require a higher temperature.

80. **Hägg, G., and Schönberg, N.** β-Tungsten (Considered) as a Tungsten Oxide. Acta Cryst., vol. 7, No. 4, 1954, pp. 351–352; Met. Abs., vol. 22, 1958, p. 319.

The phase, hitherto considered as β–W, prepared by the electrolysis of fused mixtures, as described by Hartmann, Ebert, and Bretschneider, (Ztschr. anorg. Chem., vol. 198, No. 116, 1931; Met. Abs., vol. 50, 1932, p. 761) or by Burgers and Van Liempt (Rec. trav. chim., vol. 50, 1931, p. 1050) at temperature below 700° C., is now shown, by powder X-ray analysis, to be a metallic W oxide with the probable ideal formula W_3O. A lattice constant of a=5.036 Å. and *a d* of 15.0 g./cc. were found; this calculated value of the *d* is 20 percent too low. This low *d* and the decomposition of "β–W" into W and WO contradicts the existence of "β–W" as a modification of W. The unit cell contains 6W+2 O atoms distributed at random over the eight positions of the A 15-type crystal structure.

81. **Hague, J. L., Brown, E. D., and Bright, H. A.** Separation of Titanium, Tungsten, Molybdenum and Niobium by Anion Exchange. Nat. Bureau of Standards Jour. of Res. Paper 2542, vol. 53, No. 4, October 1954, pp. 261–262.

The results of a systematic study of the elution behavior of Ti, W, Mo, and Nb in various hydrochloric-hydrofluoric acid media are given. These data demonstrate the behavior of the anion complexes of these elements on an anion-exchange resin column. The possibility of several interesting quantitative separations is evident, and experiments are described that demonstrate that these elements can be separated from each other.

82. **Hall, R. W., and Sikora, P. F.** (Advisory Committee for Aeronautics, Lewis Flight Propulsion Laboratories). High-Temperature Tensile Properties of Molybdenum and Tungsten. Fall meeting of the Met. Soc., Cleveland, Ohio; Oct. 27–31, 1958; Jour. Metals, vol. 10, September 1958, p. 40.

No abstract.

83. **Halsey, George, and Taylor, H. S.** The Adsorption of Hydrogen on Tungsten Powders. Physica, vol. 15, September 1947, pp. 624–630; Powder Met. Bull., vol. 2, No. 5, October 1947, p. 115.

The experimental data of Frankenburg on the adsorption of hydrogen by metallic tungsten between 194° and 750° C. (Jour. Am. Chem. Soc., vol. 66, 1944, pp. 1827, 1838) are analyzed from the standpoint of statistical mechanics. It is not possible to interpret the experimental isotherms on the basis of an interaction taking place between adsorbed species on a uniform adsorbent surface (Fowler and Guggenheim. Statistical Thermodynamics. Cambridge Univ. Press, 1939). Omitting interaction, the data can be interpreted on the basis of a nonuniform surface, that is to say, by assuming a surface with variable energy differences between the lowest energy state of the gas and the lowest energy state of the adsorption complex. Specification of the surface heterogeneity in terms of an exponential distribution of sites yields expressions which are in full agreement with the results of Frankenburg.

Hanschild, Ulrich. *See* abs. 67.

84. **Hargreaves, G. B., and Peacock, R. D.** Higher Complex Fluorides of Tungsten. Jour. Chem. Soc., June 1958, pp. 2170–2175; Battelle Tech. Rev., vol. 7, October 1958, p. 659–a.

The salts K_3WF_8, K_2WF_8, $RbWF_7$, $CsWF_7$, and $CsWOF_5$ were obtained and characterized.

85. **Hartmann, Hellmuth, Ebert, Fritz, and Bretschneider, Otto.** Electrolysis in Fused Phosphates. I. Electrolytic Preparation of α and β-Tungsten. Ztschr. anorg. allgem. Chem., vol. 198, 1931, pp. 116–140; Chem. Abs., vol. 25, 1931, p. 4471.

Experiments were made in an effort to deposit W electrolytically from fused alkaline phosphate solution. Pure metaphosphate fusions were found unsuitable for the deposition of pure W, but from a mixture of pyrophosphate, metaphosphate, and WO_3; with addition of NaCl, pure W was obtained at 650° and 700°. Similar results were obtained from a solution of WO_3 in pure $Na_4P_2O_7$. Roentgenographic study of the W so obtained indicated a new substance in addition to the already known cubic, body-centered crystalline W, this new substance being identified structurally as a β-modification of W. β–W crystallizes cubically according to a characteristic type with eight building bricks; the length of the cubic edge α=5.04 A.U. Complete agreement is obtained between observed and calculated intensity of the individual lattice planes if the eight W atoms are arranged in the centers of gravity 000, ½ ½ ½, 0 ¼ 0/2, 0 ¼ 0/2, 0 ¾ ½, ½–¼, ½ 0 3/4, ¼ ½ 0, ¾ ½ 0. The new form of β–W is confirmed by quantitative chemical analysis and testing-weight constancy through thermal treatment in a high vacuum at 900°. At about 650° there is a slow irreversible transformation into the α-form. Above the transformation point W separates only in the α-form, below it in the β-form. During electrolysis in the region of the transformation point the β-form is slowly converted into the *α-form.* Density determinations show that this is dependent upon grain size.

Hegedüs, A. J. *See* abs. **147**.

Herres, S. A. *See* abs. **209**.

86. Hermann, O., and Pfisterer, H. Reduction of Tungstic Oxide. Metallwirtschaft vol. 8, 1954, pp. 759–764; Chem. Abs., vol. 50, 1956, p. 6991.

The finest grained W powder, with predominantly cubic crystals, which is superficially covered with the still finer crystalline ThO$_2$, is thoriated W powder. Moderately fine powder, also with well-defined crystal form with ball-like particles, is obtained from WO$_3$ without additives. The coarsest powder is obtained by reduction with addition of NS-additive. The residue from the additive is present in the form of thin platelets as H$_2$O-insoluble SiO$_2$ in statistically distributed clumps. In the recrystallization of W wire the thoriated powder yields a finer grain structure than that obtained without vaporized ThO$_2$ additive. Further growth is prevented by the ThO$_2$ additive. In the sintering of W wires obtained by reduction of WO$_3$ containing NS-additive, the alkali silicate influences the type and size of crystal form, depending on the conditions of preparation. (6 refs.)

87. Hickman, J. W., and Gulbransen, E. A. Electron Diffraction Study of Oxide Films Formed on Molybdenum, Tungsten, and Alloys of Molybdenum, Tungsten and Nickel. AIME Metals Technol., Tech. Pub. 2144, vol. 14, No. 3, April 1947, pp. 1–17 (22 refs., 3 tables, and 12 figs.).

This paper presents a survey of recent literature and also sets forth experimental procedure and method of interpretation for each metal treated. The results of this investigation of thin oxide films are presented as existence diagrams of the oxide on a time-temperature scale. Heating and cooling experiments also are included.

Hickmott, T. W. *See* abs. **50**.

Higasimura, S. *See* abs. **95**.

88. Holt, L. M., and Kahlenberg, Louis. The Electrodeposition of Tungsten From Aqueous Alkaline Solutions. Am. Electroplaters Soc., Quarterly Rev., vol. 19, January 1933, pp. 41–52: Metal Ind., vol. 31, March 1933, pp. 94–97 (33 refs.); Metals and Alloys, May 1934, p. 49.

An alkaline solution containing 100 g. Na$_3$PO$_4$.12H$_2$O 30 g. WO$_3$ in a total volume of 150 cc. was found to give the best results. At a temperature of 90° C. nice silver-colored deposits weighing between 0.02 and 0.03 g./dm.^{2} of cathode area were obtained in 20 minutes through a wide range in current density, the best being 10 a./dm.^{2}. Satisfactory deposits were obtained only on brass, copper, or chromium-steel cathodes.

Honda, Masatake. *See* abs. **156**.

89. Horowitz, M., and Daunt, J. G. The Electronic and Lattice Specific Heats in W, Mo and Re. AEC U–2538, 1953, 34 pp.; Nuclear Sci. Abs., vol. 7, July 31, 1953, p. 503.

Calorimetric measurements have been made in the temperature range 1° to 77° K on W, Mo, and Re. At the lowest temperatures for W and Mo the specific heat could be resolved into a lattice T^3 function together with an electric term, γ T. It was found that at the lowest temperatures for W, $\theta=250$ to 380° K. and $\gamma=1.8\pm0.7 \times 10^{-4}$ cal./mole-deg.^{2}, and for Mo, $\theta=445°$ K. and $\gamma=5.1\pm0.4 \times 10^{-4}$ cal./mole-deg.^{2} These new measurements on W indicate the need for revising previously quoted data. The measured lattice specific heat of W agreed approximately with the theoretical computations made by Fine. The measured lattice specific heat of Mo varied with temperature in the manner predicted by Fine for the b.c.c. lattice of W. The measured electronic specific heat of W was in moderate agreement with the theoretical computation of Manning and Chodorow, and the measured electronic specific heats of W and Mo were considerably less than those of most other transition elements except Cr., a result which may be approximately explained by assuming a d-band shape similar to that calculated by Slater. The question of the d-band shape is discussed in detail in the light of recent experimental results. Pure Re powder has been measured in the temperature range 68° to 77° K. At these temperatures the Debye temperature, θ, was found equal to 262° K.

Hougen, J. O. *See* abs. **130**.

90. Hougen, J. O., Reeves, R. R., and Mannella, G. G. Reduction of Tungsten Oxides With Hydrogen. Ind. Eng. Chem., vol. 48, February 1956, pp. 318–320.

An investigation of the reduction of finely divided tungsten trioxide and tungsten dioxide in pelletized form with hydrogen has been conducted in the temperature range of 500° to 800° C. The study covers the effect of pellet size, flow rate, and temperature on the rate of reduction. The tungsten dioxide was prepared from tungsten trioxide by passing hydrogen containing a known amount of water vapor over the trioxide for a given period. The identity of this oxide and of intermediate oxides formed during the reaction was established by X-ray and gravimetric analyses. No attempt is made at present to explain the mechanism of the reduction. The reaction rate was found to be temperature-dependent and sensitive to pellet size. From the latter effect it appears possible that in the temperature interval under consideration diffusional processes may be a controlling factor.

91. Hoyt, S. L. Ductile Tungsten. No. 8 in a series of case histories in metallurgical research.) Metals and Alloys, vol. 6, January 1935, pp. 11–18.

This article is an excellent testimonial to the research and patents of Dr. W. D. Coolidge, who began his work on tungsten in 1905. It gives a detailed account of the legal entanglements encountered in support of his claims to his patent for ductile tungsten and at the same time defends the position of Dr. Colin G. Fink in the case. The General Electric Co. asserted, and supported its assertion by examination of Fink, Coolidge, and experts, that the "so-called ductilization of Mo had been accomplished by an annealing treatment in hydrogen while the ductilization of tungsten was accomplished by mechanical treatment, that obviously the work on Mo did not teach the tungsten art. * * * In the court decision the patent was adjudged not invalid because issued to the wrong person." Further, the decision incorporates part of the plaintiff's brief (General Electric Co.) as follows: "The process which brings out the ductility of W destroys ductility in other metals. The condition in which tungsten is most ductile is the condition in which other metals are least ductile; the condition in which other metals are most ductile is the condition in which W is least ductile."

Hudda, F. G. *See* abs. **50.**

92. Hughes, F. L. Interaction of Thermal Atoms With Surfaces. Final Rept., Sept. 1, 1958. Syracuse Univ. Res. Inst., New York, N.Y. (Contract DA. 30-115-ORD-815) (Unclassified Rept. ASTIA AD-201, 153), Div. 4, ASTIA Bull. U58-17, Nov. 1, 1958, p. 3132.

This report includes: 1. Mean Adsorption Lifetime of Rb on Etched Tungsten Single Crystals. I. Ions, by F. L. Hughes and H. Levinstein (Sept. 1, 1958, 28 pp, including illus.). 2. Mean Adsorption Lifetime Rb on Etched Tungsten Single Crystals. II. Neutrals, by F. L. Hughes (Sept. 1, 1958, 13 pp. including illus.). 3. Surface Properties of Etched Tungsten-Single Crystals, by F. L. Hughes, H. Levinstein, and R. Kaplan (Sept. 1, 1958, 22 pp, including illus.).

Hughes, J. R. *See* abs. **152.**

Hulm, J. K. *See* abs. **72.**

93. Hulme, K. F. The Distribution of Impurity in Crystals Grown From Impure Unstirred Melts. Proc. Phys. Soc. (London), vol. 68B, 1955, pp. 393-399; Chem. Abs., vol. 49, 1955, p. 13725.

When growing crystals by controlled solidification from impure melts, it is of interest to know how the impurity will be distributed in the resultant solid. Unless the melt is stirred vigorously, the impurity concentration is not uniform, and a diffusion-controlled boundary layer of different impurity concentration is formed on the solid-melt interface; this boundary layer can, under certain circumstances, cause "constitutional supercooling." If constitutional supercooling exists, the solid-melt interface loses its flatness. The results derived are valid only so long as the interface retains its flatness, although they may represent approximations to the truth when the interface becomes corrugated.

94. Institute of Mining and Metallurgy. The Refining of Non-Ferrous Metals: Proceedings of a Symposium, London, July 1949. Author and subject indices, Growther and Goodman, London, E.C. 4, 1950, 534 p.

The objectives before the organizing committee were: (a) To stimulate interest in extraction metallurgy in Great Britain and the British Commonwealth; (b) to widen the knowledge of British metallurgists in the subject of refining; (c) to make more generally known the amount and important nature of the work being done in Great Britain in the field of extraction metallurgy; and (d) to reassert the Institution's function to act as a platform for the discussion of metallurgical subjects.

Irion, C. E. *See* abs **210.**

95. Isada, S., Asada, H., and Higasimura, S. Influence of Chromium on Oxide Resistance of Tungsten at High Temperatures. Aeronautical Res. Inst. Rept., Tokyo Imp. Univ., vol. 13, 1938, pp. 195-202; Iron and Steel Inst. (Japan), vol. 25, 1939, pp. 106-114; Met. Abs., vol. 5, 1938, p. 265.

Mainly from X-ray analysis a tentative equilibrium diagram is advanced for the W end of the W-Cr system, which indicated a solid solubility of chromium. Tungsten is rendered appreciably more resistant to oxidation above 13 percent Cr. Alloys prepared from powders. *See* abs. **70,** item 5423, p. 379.

Ishimori, Tatsujiro. *See* abs. **156.**

Ito, Koichi. *See* abs. **181.**

Iwata, Shigeo. *See* abs. **107.**

96. Jaffee, R. I., and Sims, C. T. The Effect of Rhenium on the Fabricability and Ductility of Molybdenum and Tungsten. Battele Mem. Inst. Tech. Rept. to Dept. of the Navy, Office of Naval Res., Contract Nonr-1512(00), Apr. 1, 1958, 40 pp. 7 tables, 24 figs., 15 refs.

Summary: The results obtained by Geach and Hughes on the effects of rhenium in improving the working properties of Mo and W have been confirmed. The ability of a Mo-Re alloy to be directly hot-worked, even with high oxygen present, is the result of the formation of a new phase containing oxygen, which does not wet the grain boundaries so readily as the oxide of the base metal. The same mechanism probably holds also for the W-Re alloy. The temperatures of transition from ductile to brittle behavior of both Mo and W are lowered drastically by the presence of Re as a result of the ability of these alloys to deform at low stresses through mechanical twinning. Deformation by slip occurs at later stages, apparently with much less dislocation pinning than for the parent metal. Yield-point behavior was not observed under conditions of testing. The elevated-temperature strengths and the recrystallization temperatures of Mo and W are raised considerably by rhenium.

97. Jahnke, L. P. The Future of High-Temperature Metallurgy. Metal Prog., vol. 72, No. 4, October 1957, pp. 113-118, 6 figs.

Future advances must be conceivable, feasible, and desirable. On this basis the author considers the effect of purity (both chemical and structural), especially of alloys based upon columbium, molybdenum, or tungsten, and predicts that by A.D. 2000 we will have alloys of useful strength up to 5,500° F.

98. Jander, Gerhart, and Krüerke, Ulrich. Paratungstic Acids and Paratungstates. Ztschr. anorg. u. allgem. Chem., vol. 265, 1951, pp. 244-254; Chem. Abs., vol. 46, 1952, 3440.

By progressive acidification of H_2O solutions of simple tungstates such as Na_2WO_4 by means of strong mineral acids, hexameric "paratungstic acids" and "paratungstates" are formed. Solutions of alkali tungstates were studied in relation to H^+ concentration and age by conductometric and potentiometric measurements, and by light absorption. Light-absorption measurements confirm the existence of $[HW_6O_{21}.xaq.]^{5-}$ (A) and $[HW_6O_{21}.(x\text{-}y)aq.]^{5-}$ (B). Conductivity measurements of the acidified alkali tungstate solutions in relation to age indicate that in the transition from "paratungstate A" into the "χ-metatungstate" an intermediate product "metatungstate A," $[H_3(HW_6O_{21}.xaq.)]^{2-}$ exists. It is unstable and in a strongly acid solution yields the same hexatungstic acid from which the paratungstate A is derived. Only from this is the χ-metatungstate, $[H_3W_6O_{21}.(x\text{-}z)aq.]^{3-}$ formed, probably by splitting off H_2O. (11 refs.)

99. Jeffery, P. G. Photometric Determination of Mo in W Ores. Analyst, vol. 82, August 1957, pp. 558–563; Battelle Tech. Rev., item 17, 302, vol. 6, December 1957, p. 810–a.

The suppression by citric acid of the formation and subsequent extraction of the complex of W with toluene-3 : 4-dithiol is used to permit the determination of molybdenum.

Jolkin, V. See abs. **65, 66.**

Jones, F. O. *See* abs. **63.**

Kahlenberg, Louis. *See* abs. **88.**

100. Kashima, Jiro (Waseda Univ., Tokyo). Tungsten Plating. II. Effect of an Addition Agent. Appl. Chem. Soc. Bull. (Japan), vol. 19, 1942, pp. 69–74; Chem. Abs., vol. 44, 1950, pp. 6746.

Under the optimum plating conditions found previously (at 85° for 30 minutes with NaOH 120 and WO_3 120 g./l., Pt anode, Cu plate cathode, and c.d. 25 a./dm.^{2}), an addition of 90 g./l. H_3PO_4 increased the W deposition several times. With longer time, however, the plated surface became dull, and precipitation velocity decreased, although the WO_3 concentration did not decrease appreciably, indicating that under these conditions thick plating of W seems impossible.

101. Kawane, Makoto (Kyoto Univ.). Electrolysis of Aqueous Tungstate Solutions. I. Prolonged Electrolysis. Jour. Electrochem. Soc. (Japan), vol. 17, 1949, pp. 172–174; Chem. Abs., vol. 44, 1950, p. 6304; vol. 48, 1954, p. 13481.

To obtain an electrodeposited film of tungsten, the effects of Fe^{++}, Ni^{++}, and Co^{++} ions on the electrolysis were studied in the carbonate bath. The findings were: (1) Fe^{++} ion was the most effective; (2) when the concentration of Fe^{++} ion was held constant, the current efficiency was unaffected by the character of the base metal after a certain period of electrolysis; (3) the current efficiency was best during the first hour, then it gradually decreased, becoming constant after 3 hours, during which the efficiency was two-thirds that of the first hour.

102. ———. (Kyoto Univ.). Electrolysis of Aqueous Tungstate Solutions. II. Prolonged Electrolysis. Jour. Electrochem. Soc. (Japan), vol. 17, 1949, pp. 206–208 (*see* abs. **101**); Chem. Abs., vol. 48, 1954, p. 13482.

It was concluded that prolonged electrolysis of the Fink and Jones carbonate bath, with Fe as the second ion, was too inefficient for practical W plating.

Kawazu, Shigeo. *See* abs. **149.**

103. Keil, Albert, and Meyer, Carl-Ludwig. [Non-Destructive Tests of Cracks of Tungsten Rods by the Eddy-Current Method.] Ztschr. Metallkunde, vol. 45, April 1954, pp. 194–196; Am. Soc. Metals Rev. of Metal Literature, item 267–S, Metals Rev., vol. 27, No. 8, 1954, p. 51.

Practical experiences with the testing of rods of 2- to 8-mm. diameter. Typical defects, causes, and possibilities of recognition. (Micrographs, 8 refs.).

104. Kenty, Carl, and Turner, L. A. Surface Layers on Tungsten Produced by Active Nitrogen. Nature, vol. 120, No. 3018, Sept. 3, 1927, p. 332; Phys. Rev., vol. 32, No. 5, November 1928, pp. 799–811.

Conclusions: A clean tungsten surface at a dull-red heat, if placed in an atmosphere of nitrogen, activated either by a condensed discharge or by an electron bombardment at more than 22 volts, becomes covered with a nitrogen layer of the order of 1 atom deep. The effect of this layer, at this comparatively low temperature, is to cool the surface. It seems probable that it does this by allowing the surface to conduct more heat to the gas, that is by increasing the accommodation coefficient. At relatively high temperatures, the same layer is probably so unstable that only a small fraction of the surface can be covered at any one time, but it acts to increase the work function. The flashing of a filament covered with such a layer in the neighborhood of a clean filament causes the production of a layer upon the latter. Apparently the layer evaporated by flashing comes off in an active form. These experiments suggest that active nitrogen can be produced by bombardment of nitrogen gas with 22-volt electrons, but further work is necessary to establish this conclusion. The experiments are being extended and completed, and will be described in detail later (*see* abs. **105**).

105. ———. Surface Layers on Tungsten and the Activation of Nitrogen by Electron Impact. Phys. Rev., vol. 32, No. 5, November 1928, pp. 799–811; Phys. Rev., vol. 37, Apr. 15, 1931, p. 1006.

(*See* abs. **104** for preliminary account.)

A fine W filament at 400° C. in active nitrogen is quickly covered with a layer, which produces a lowering of the resistance of the filament. This lowering of the resistance is apparently the result of a lowering of the temperature of the filament, which occurs because heat is more readily conducted away from the coated filament by the gas than from the clean filament. At a given temperature, 15–20 percent more heat is conducted away by the gas with the layer present. The same effect is produced by activating the nitrogen by bombardment with electrons. In a tube with a large nickel anode the production of the active agent could be detected down to 10.8±0.5 volts. In a tube with a hot tungsten spiral anode of small area the effect could be detected down to the ionizing potential (16.3 volts). Traces of oxygen cause the spontaneous formation of a layer, which renders the filament insensitive to active nitrogan. Traces of hydrogen prevent the formation of the nitrogen layer and remove it if already present. Experiments with a tube of small volume containing W disks of large area show that the amount of nitrogen adsorbed is of the order of magnitude of the quantity necessary to produce a layer of single atoms. Activation of a stream of nitrogen reduces the thermionic emission from a tungsten filament in the stream. Similarly, the striking of an arc in nitrogen under suitable conditions gives a momentary slight increase of current followed by a great decrease, the emission apparently being cut down by the active form of nitrogen produced in the arc. Upon subsequent breaking of the same arc by reducing the anode voltage the current drops and then quickly rises to its much higher former value at that voltage. With an interrupted arc in pure nitrogen, and in argon containing a small percentage of nitrogen, an emission of the D lines persists for several hundredths of a second after the extinction of the arc. The sodium is evaporated from an oxide-coated filament and excited by some active form of nitrogen produced in the arc, presumably atomic nitrogen.

106. Kenworthy, H., Starliper, A. G., and Freeman, L. L. Recovery of Tin and Tungsten From Tin-Smelter Slags. Bureau of Mines Rept. of Investigations 5327, 1957, 12 pp.; Chem. Abs., vol. 51, 1957, p. 7983.

Laboratory studies were made to determine the possibility of recovering several million pounds of Sn plus W contained in stockpiled and currently rejected slags from the Longhorn Sn smelter at Texas City, Tex. Of the several methods of attack investigated, best results were attained from fusion reduction and chlorination and sulfidization treatments, each in conjunction with a reductant to break up the Sn-W-slag complexes. Fusion reduction experiments showed that a large portion of the Sn and W, along with the Fe content of the slag, could be collected in a metal layer by fusing the slag with coke or other suitable reductant. Stripped slags contained less than 0.1 percent Sn and smaller amounts of W. The metal layer content consisted of a total of 20 percent Sn plus W, with the balance largely Fe. Chlorination of fused slags was carried on at 1,450° by using gaseous Cl or NaCl as source material to volitilize Sn, W, and Fe as chlorides. The addition of coke produced treated slags lean in Sn and W. The use of Cl, coke, and S gave slightly better results and increased Fe retention in the slag.

Khalitov, R. Sh. *See* abs. 137.

Khavskii, N. N. *See* abs. 134.

Kihlborg, Lars. *See* abs. 18.

107. Kinjyo, Kisei, and Iwata, Shigeo. Preparation of Highly Pure Tungsten. I. Reduction of Tungsten Trioxide in a Current of Hydrogen. Jour. Soc. Chem. Ind. (Japan), vol. 54, 1951, pp. 573–575; Chem. Abs., vol. 47, 1953, p. 6321.

The reduction of WO_3 calcined at various temperatures by H_2 gas was studied by means of a thermobalance. The reduction into metallic W takes place through various lower oxides according to the calcination temperatrue of WO_3. The reduction temperature is 550° for the WO_3 calcined at 300°–800° and 670° for 1,000°.

Knoll, M. *See* abs. 52.

108. Kobakhidze, L. P. (Sbornik Nauch. Trudov Moskov). Ways of Increasing the Effectiveness of Utilization of Tungsten Ores Mined in U.S.S.R. Inst. Tsvetnykh Metal. i Zolota 25, 1955, pp. 300–303; Chem. Abs., vol. 50, 1956, p. 15366.

Wider use of flotation methods of enrichment is proposed for skarnitic scheelite ores; in some instances, as in enrichment of complex scheelite-molybdenum ores, where Mo is present in the form of powellite, to use with flotation, hydrometallurgical methods of treatment; for coarsely crystalline ores to combine gravity with flotation and hydometallurgy, which would to a marked degree warrant utilization of W ores.

109. Koerner, W. E. The Electrolytic Behavior of Tungsten. Trans. Electrochem. Soc. vol. 31, 1917, pp. 221–225 (discussion, 18 tables, 43 refs.).

The single potentials of tungsten in normal solutions of acids, alkalies, and neutral salts were calculated from e.m.f. measurements, and the results discussed. The occurrence of tungsten as cation or anion, in different solutions, was investigated. The passivity of W in various solutions and under various conditions was studied. The electrochemical equivalent was experimently determined. The use of W in battery and storage cells was experimented with. The tungsten storage cell is particularly interesting.

Koizumi, Tadayoshi. *See* abs. 144.

Konig, Paul. *See* abs. 68.

110. Kopelman, Bernard, and Gregg, C. C. Particle Agglomeration in Tungsten Metal Powder. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 557–563; Trans. Am. Soc. Metals, vol. 41, 1949, p. 293; Chem. Abs., vol. 45, 1951, p. 6010.

Particle-size distribution of W powder in 11 liquids of different dielectric constants as determined by turbidimetric analysis showed the apparent average particle size (μ) to decrease with increasing dielectric constant (D) up to a maximum at $D=25$. Over this range, $\mu=(\text{const.})/D^{0.28}$. The surface bonds in the metal powder resulting from electric attraction are completely broken in associated liquids for which D exceeds 25. Essentially complete agglomeration of the powder occurs in liquids for which D is less than 2. The W powder would be expected to behave in air or vacuum as though it were a powder with an average particle size corresponding to that observed in the liquids of low dielectric constant, even though the true particle size was much smaller.

111. Kordik, E., and Blechta, V. Production of Technical Tungstic Acid From Tin-Tungsten Concentrates. Chem. Průmysl, vol. 5, No. 1, 1955, pp. 1–7; Chem. Abs., vol. 49, 1955, p. 11968.

A procedure on a pilot-plant scale for the isolation of tungstic acid was worked out, consisting of the following steps: Pulverization of the concentrate, decomposition by NaOH to obtain Na_2WO_4, purification of Na_2WO_4 by HCl, precipitation of $CaWO_4$ by the addition of $CaCl_2$ and NaOH, conversion of

$CaWO_4$ by HCl on a suction filter to obtain H_2WO_4, and drying of the acid at 100°–110°. A diagram of a setup for 100-kg. charges is given. Total loss of WO_3 was 3.79 percent. The tungstic acid obtained was very pure and can meet the requirements for the electric-bulb filament.

112. KOREF, F. Crystal Recovery, Observations on the Softening of Hardened Tungsten Crystals. Ztschr. Metallkunde, vol. 17, 1925, pp. 213–220; Chem. Abs., vol. 19, 1925, p. 2893.

Deformation of single crystals of W causes an increase of tenacity. Heating brings the crystal back to its original softness. This process is called crystal recovery (Kristallvergütung or Kristallerholung). Measurements on the tenacity of single crystals of W, hardened by tension, show the relation between softening and heat treatment. Crystal wires of about 0.1-mm. diameter showed crystal recovery at 2,100°. Pure crystal recovery is distinguished from recrystallization by the fact that no change can be detected microscopically in the crystal during crystal recovery, while new crystals become visible after recrystallization. There is a critical value of the deformation to which a crystal may be subjected, after which heat treatment produces only recrystallization, not crystal recovery. The location of this "recrystallization threshold" depends on the diameter of the crystal sample. Recrystallization sets in after very slight deformation in the larger crystals. Conglomerates of small crystals of W, after hardening, are subject to a partial crystal recovery between 700° and 1,500°. Above 1,500°, recrystallization sets in. Drawn single crystals of W, which have an abnormally small density in the region of crystal recovery. Koref's conclusions are in agreement with those advanced by R. Gross.

113. ———. Formation of Tungsten Crystals. Ztschr. Elektrochem., vol. 28, 1922, pp. 511–517.

Tests of the growing of a tungsten crystal are made by producing a built-up deposit. *See* abs. 70 item 2403, p. 172.

114. KÖSTER, VON WERNER, AND SCHÜLE, WOLFGANG. Leitfähigkeit und Hallkonstante. VII. Verformung und Rekristallisation reiner Mettalle. [Conductivity and Hall Constant. VII. Deformation and Recrystallization of Pure Metals.] Ztschr. Metallkunde, vol. 48, December 1957, pp. 634–636, 2 figs., 1 table, 6 refs.; Metals Rev., item 158–P, vol. 31, April 1958, p. 46.

Summary: The effect of deformation and recrystallization on the electrical conductivity and the Hall constant of eight pure metals has been investigated. The resistivity increases with deformations, the mobility decreases. Since the relative changes of both are about equal, the perturbation of the lattice periodicity is considered to be the main reason for the resistivity increase. Resistivity and Hall constant of deformed Mo and W specimen anneal out in separate stages preceding recrystallization. The electrical resistivity of recrystallized Ag and Au specimens increases with temperature of quenching due to frozen-in vacancies. On annealing the resistivity recovers in two stages. The Hall constant does not change here.

KRÜERKE, ULRICH. *See* abs. 98.

115. KUCZYNSKI, G. C. Fundamentals of Powder Metallurgy. Proc., 13th Ann. Meeting, Metal Powder Assoc., vol. 1, 1957, pp. 125–130; Battelle Tech. Rev., vol. 7, July 1958, p. 494-a.

Surveys recent additions to the knowledge of sintering phenomena. The thermodynamical motivation of sintering is the excess surface energy contained in a mass of powder. This energy excess is not large, but its existence insures a tendency toward coalescence of the particles, provided sufficiently efficient mechanisms of sintering are available. Most observations of the progress of sintering of powder compacts suggest two largely overlapping stages of this process. The first early stage, manifesting itself by a rapid decrease of electrical resistivity and increase of cohesion with no appreciable change in density is attributed to the formation of bridges or necks between the adjacent particles. The second stage, during which densification of the compact occur, is due to the elimination of the voids remaining in the compact.

KURIHARA, ICHIRO. *See* abs. **143**.

116. LANDER, J. J., AND GERMER, L. H. Plating Molybdenum, Tungsten and Chromium by Thermal Decomposition of Their Carbonyls. Metals Technol., AIME Tech. Pub. 2259, vol. 14, No. 6, 1947, 42 pp.; Summary, Metal Ind., vol. 71, No. 23, 1947, pp. 459–461; No. 24, 1947, pp. 487–489; Met. Abs., vol. 15, 1948, p. 284.

Neither pure W nor pure Mo can be electroplated successfully; the carbonyl method gives a very hard protective coating. It is not required that the base metal should have good electrical conductivity (as in the electrochemical processes) nor need it have the temperature stability necessary in plating from a halide. The properties of Mo, W, and Cr carbonyls are reviewed. The type of coating obtained depends on the method of plating; it can be carried out with various pressures of carbonyl and hydrogen, or with carbonyl, hydrogen, and water; this latter method can prevent the deposition of carbon, and the coating is therefore softer. The bond between the coating and the base metal was tested by compression and by quantitative shear tests. The bond strength varies with the plating technique; the carbonyl concentration must be the same all over the area to be plated to ensure even distribution of the coating. Gaseous decomposition products must be removed continuously.

117. LANGMUIR, I. Surface Chemistry. Chem. Rev., vol. 12–13, No. 2, 1933, pp. 147–191 (from bibliography on article by Bauer, J. P., Bridges, D. W., and Fassell, W. M., Jr., *see* abs. **9**); Jour. Electrochem. Soc., vol. 103, May 1956, pp. 266–272.

This paper was presented as the Nobel Lecture in Chemistry in Stockholm on December 14, 1932. It is designed to summarize the author's contributions and present views in this field but does not adequately describe the work of others.

118. LEBER, SAM. X-Ray Metallographic Study of Arc-Cast Tungsten. Trans. Am. Soc. Metals, Preprint 103, 1958, 12 pp.; Chem. Abs., vol. 52, 1958, p. 19807.

Double-crystal X-ray diffraction camera techniques are described, which can be used to provide a complete analysis of the distortions of the lattice planes within crystals. Data for two arc-cast W grains are used to describe the modes of distortion, mis-orientations across sub-boundaries, and character of sub-boundaries. An X-ray micrographic technique is presented as an aid in determining the spatial and orientation relations between subgrains.

119. Lee, J. A. Tungsten and Tantalum. Chem. Eng., vol. 55, 1948, pp. 110–112, 152–155.

Production processes such as filtration, crystallization, precipitation, and reduction to the metal powder in the plant of Fansteel Metallurgical Corp. are described. *See* abs. **70**, item 1136, p. 79.

120. Leo, Shoo-Tze, and Shen, Tsing-Nang. Electrolytic Production of W Metal From a Fused-Phosphate Bath. Trans. Electrochem. Soc., vol. 66, 1934, (preprint) 9 pp.; Chem. Abs., vol. 28, 1934, p. 6067.

In the electrolytic production of W in a fused-phosphate bath, the current efficiency and energy efficiency can be much improved by using high temperature and higher current density than those suggested by Hartmann (*see* abs. **237**). A temperature of 900° and a current density of 35 a./dm.^{2} seem to give the best result. The best composition of the electrolyte with respect to current efficiency was found to be that selected by Hartmann. The best current efficiency was 88.08 percent. On the basis of energy efficiency an electrolyte containing 7 mols. $Na_4P_2O_7$, 3 mols. $NaPO_3$, 4 mols. WO_3, and 15 mols NaCl seems to be most favorable. A yield of 469.9 g. of W per kw.-hr. was obtained.

121. Li, K. C., and Wang, Chung Yu. Tungsten: Its History, Geology, Ore-Dressing, Metallurgy, Chemistry, Analysis, Applications and Economics. Third edition. Am. Chem. Soc. Mon. 94, 1955, 506 pp.; Reinhold Pub. Corp., New York, N.Y., and Chapman and Hall, Ltd., London; Met. Abs., vol. 23, 1956, p. 506.

This volume includes bibliographies, illustrations, and maps (24 cm.).

122. Liddell, D. M., (Editor-in-Chief). Handbook of Nonferrous Metallurgy. Vol. II. Recovery of the Metals. Staff of specialists, McGraw-Hill Book Co., Inc., New York, N.Y., and London, 1st ed., 1945, 721 pp.

Extract from preface: There is much that is elementary. The book is designed for the student as well as for the engineer and consultant, yet it is hoped that there is enough advanced material to make the book useful to the metallurgist of experience, particularly if he is confronted with problems somewhat outside his own specialty. There is no attempt to give extensive tables of basic data—for these the seeker is referred to International Critical Tables, the tables of the International Congress of Applied Chemistry, or to Landolt, or to the editor's metallurgists' and Chemists' Handbook. Note: The titles of data in the chapter on Tungsten are as follows: Occurrence, Extraction from the Ores, Concentration Methods, Metallic Tungsten, Ferrotungsten, Tungsten Carbide, Uses of Tungsten, and Analytical Methods for Tungsten (pp. 623–632). The Davis, Shapely, and Fansteel processes for producing metallic tungsten are described (pp. 626–628).

Lietzke, M. H. *See* abs. **35**.

123. Linde Air Products Co. Synthetic Calcium Tungstate Crystals. Chem. Eng. News, vol. 27, Jan. 3, 1949, p. 48.

Successful production of water-white single crystals of pure calcium tungstate in research quantities has been announced by Linde Air Products Co. Among the applications indicated for this fluorescent material are its use in scintillation counters in the detection and measurement of radioactivity, and as screens in X-ray fluoroscopy. Single crystals of pure calcium tungstate are at the present time being grown in rods, about ⅛-inch-square section and up to 2 inches in length. Representative samples of these calcium tungstate crystals are colorless, and clarity varies from a transparent to a slightly cloudy crystal. Work is being done on growing uniformly clear crystals and producing other forms and sizes.

124. Lindqvist, Ingvar (Univ. Uppsala). The Structure of the Paratungstate Ion. Acta Cryst., vol. 5, 1952, pp. 667–670; Chem. Abs., vol. 46, 1952, p. 10996.

The structure of the complex ion in 5 $Na_2O.12 WO_3.28H_2O$ was determined by use of a new vector-algebraic method. The formula of the ion, $W_{12}O_{46}^{20-}$ has no direct relation to the analytical formula, which would require a $W_{12}O_{41}^{10-}$ ion for the paratungstate to be a neutral salt.

Lofgren, N. L. *See* abs. **22**.

125. Long, C. Examples of Reactions in the Solid State Applied to Industry. Chim. et ind., vol. 69, 1953, pp. 635–645; Chem. Abs., vol. 47, 1953, p. 8329.

Discussion of solid-state reactions involved in the production of metal carbonates, tungstic acid, sodium vanadate, and sodium dichromate.

Lundy, R. *See* abs. **71**, **211**.

Lutz, Gertrud. *See* abs. **67**.

126. Ma, Chuk-Ching. Crystal Size Distribution of Electrolytic Metal Powders. Ind. Eng. Chem., vol. 44, February 1952, pp. 342–346.

The generalized relationships between crystal size distributions, temperature, current density, and impurities in the bath have been established by a careful study of the crystalline powders of various metals obtained from different fused electrolyte baths. In general, within the range of the conditions specified herein, raising the temperature tends to yield larger metal crystals, while raising the current density tends to yield smaller crystals. Partially fusible impurities, such as ferric oxide, also affect the crystal size, an increased concentration of such impurities tending to decrease the size of crystals.

A new theory is developed based on the polarization effect of alkali metal vapor film deposited on the cathode surface. This theory readily accounts for the many phenomena—sometimes very perplexing—observed in the behavior of the various fused electrolyte baths, as well as the phenomena relative to the size and size distribution of the various metal crystals deposited at the cathode. As there are no contradictory results brought forth by quite a number of runs in many fused-salt baths of widely distinct physical and chemical properties, this new theory may be extended to include all electrolytic metal powders obtained from fused alkali salt baths.

Finally, the terms "metal powder" and "metal crystal" may be used interchangeably, since all the electrolytic metal powders are polycrystalline powders or crystals.

127. **Magnéli, Arne** (Univ., Uppsala, Sweden). Crystal Structure of Tetragonal Potassium Tungsten Bronze. Arkiv Kemi, vol. 1, 1949, pp. 213–221; Chem. Abs., vol. 44, 1950, p. 1775.

A pure product of composition K_xWO_3, with x between 0.475 and 0.57, was prepared by reducing acid K tungstates with H_2 at 600° and purifying successively by repeated boilings with concentrated K_2CO_3, concentrated HCl, and aqua regia. Powder photographs of K_xWO_3 with x=0.57 gave the cell dimensions: a=12.317, c=3.841 A., and V=582.7 cu. A. A small dependence of a and c on x was observed. Rotation and Weissenberg photographs about a and c revealed the extinction (Okl) when k is odd, permitting three possible space groups. A Patterson projection $p(z)$ permitted the assignment of the W and K atoms to positions of the most symmetrical space group, D^5_{4h}–$P^4/m\ b\ m$. The unit cell contains 10 mols. K_xWO_3, and when x=0.60 the W and K parameters are: 2W in 2(c), $8W_2$ in 8(j) with x=0.078 and y=0.209; 2K in 2(a), 4 K_2 in 4(g) with x=0.175. Reasonable positions for the 30 O atoms were determined on considerations of space and coordination. The structure is built of WO_6 octaheda sharing corners in an intricate way and with the K atoms inserted in the larger interstices. The arrangement in part is a deformed perovskite structure, but no K analog was found for the cubic Na tungsten bronze, which possesses the actual perovskite structure.

128. ———. Crystal Structure Studies on Molybdenum and Tungsten Oxides and Related Compounds. Nova Acta Regiae Soc. Sci., Upsaliensis, vol. 14, No. 8, 1950, 20 pp.; Chem. Abs., vol. 44, 1950, p. 1776–5176.

The general structural aspects of the various Mo and W oxides, and the Li, Na, and K tungsten bronzes (for example Li_xWO_3) are given, omitting crystallographic details. The fundamental structural units are MO_6 octahedra, joined by sharing corners or edges.

See also Blomberg, Birgitta, abs. 18.

129. **Mamykin, P. S.** High-Temperature Refractory Materials in Modern Metallurgy. Khim. Nauka i. Prom., vol. 3, 1958, pp. 27–34; Chem. Abs., vol. 52, 1958, p. 10833 (Review, 48 refs.).

No abstract.

130. **Mannella, G. G. and Hougen, J. O.** Tungsten Oxide Reduction. Ind. Eng. Chem., vol. 49, 1957, p. 897; vol. 48, 1956, p. 318; Chem. Abs., vol. 50, 1956, p. 7642; vol. 51, 1957, p. 10289.

Mixtures of 25 percent H with 75 percent N, He, or A were used to reduce pellets of WO_3 and WO_2 temperatures between 700° and 850°. A particlewise diffusion process seems to take place at lower temperatures; at higher temperatures, diffusion in the pellet becomes the controlling step.

See also Hougen, J. O., abs. 90.

Marshokov, I. A. *See* abs. 183.

131. **Marx, Peter.** Eber die Filtration von Molybdün- und Wolframsäure. [Filtration of Molybdic and Tungstic Acid.] I. G. Farbenindustrie, A. G., Bitterfeld, Res. Rept. 654, Jan. 4, 1943, reel and frame 73487.

Microscopic investigations show that PC-filter cloth cannot be used for filtering molybdic acid but can be used for filtering tungstic acid, because several pores of the filter are larger than the smallest particles of molybdic acid.

Masal'tseva, M. M. *See* abs. 187.

132. **Massachusetts Institute of Technology** (Cambridge). The Adaptation of New Research Techniques to Mineral Engineering Problems. Dept. of Metallurgy Prog. Rept. (NYO–7708) Contract AT (30–1)–956 (MITS–36), July 31, 1957, 46 pp. (Available Office of Tech. Services, Washington 25, D.C., $1.25); Nuclear Sci. Abs. item 247, vol. 12, Jan. 15, 1958, p. 28.

Report of studies on adsorption of organic and inorganic ions on quartz, flotation of quartz with hexylamine, slime coating, ion exchange properties of muscovite, solvent extraction of W, solvent extraction of transition metals from thiocyanate solutions, intergranular comminution, energy-size reduction, and electrical concentration of minerals. (*See* NYO–7707 for preceding period.)

133. **McIntosh, A. B.** The Use of Chlorine in the Extraction of Metals for the Atomic Energy Programme. Ind. Chem., vol. 32, May–June, 1956, pp. 195–199; Metals Rev., vol. 29, September 1956, p. 14.

A demand recently has arisen for a number of metals, previously little used, for the atomic-energy program. After outlining the properties and history of the chlorides of these metals, the author describes modern extraction methods in which the chlorides are used.

During the period in which interest in atomic energy has widened, attention has been directed to metals such as uranium and thorium, suitable as nuclear fuels, and to others which by their properties can be used to protect the fuel from corrosion or oxidation. These metals must be inert to the fuel and coolant, have a low capacity for absorbing neutrons, and have adequate mechanical properties at elevated temperatures. Be, Mg, Al, Ti, Zr, Va, Nb, Ta, Mo, and W have potentialities for such application. Many of the metals have only recently been available in significant quantities in the ductile form, and much of the research effort which has been expended in the study of the extraction and fabrication of these metals has been stimulated by their possible use in the production of atomic energy. In the course of this study the ways in which the properties of chlorides could be utilized in extraction have been examined.

134. Meerson, G. A., and Khavskii, N. N. Acid Treatment of Scheelite. Tsvetnye Metal. vol. 30, No. 3, 1957, pp. 41–47; Chem. Abs., vol. 51, 1957, p. 10332.

In a closed revolving ball mill maintained at 100° scheelite concentrates containing 47.1 and 42.32 percent WO$_3$ were treated at a liquid-solid ratio of 1:1 with 21 and 26 percent HCl; this corresponded to 110 and 120 percent of the theoretical. The amount of HCl remaining as a function of the duration of the reaction decreased abruptly during the first 2 hours, then slowly. The degree of decomposition of scheelite increased rapidly during the first 2 hours, then at slow rate approached a value of 100 percent in 6 hours. The acid left unreacted was 1.6 percent against the theoretical 1.3 percent. Increasing the excess of the initial HCl increased the degree of recovery from 98.1 to 99.45 percent after 6 hours, from 92 to 93.4 percent after 2 hours, and from 80.4 to 85.05 percent after 1 hour. To remove the adhering flotation reagents the concentrate was roasted for 3 hours at 600° and then treated with 126.1 percent HCl: the recovery of scheelite after 1, 2, 4, and 6 hours of digestion in the ball mill was 92.4, 97.4 99.2, and 100 percent, respectively.

135. Mennicke, Hans. Die Metallurgie des Wolframs. M. Krayn., Berlin, 1911, 416 pp., 39 figs.

Powder metallurgy of W and production of powders from the ore. *See* abs. 70, item 2370, p. 170.

Meyer, Carl-Ludwig. *See* abs. **103.**

136. Meyer, R. New Developments in Powder Metallurgy in the Field of High-Temperature Resistant Materials. Metaux, vol. 369, 1956, pp. 219–232; Translators' Monthly, item 57–3281, vol. 3, December 1957, p. 541.

No abstract.

137. Mikhailova, G. V., Turovtseva, Z. M., and Khalitov, R. Sh. [Determination of Oxygen, Hydrogen, and Nitrogen in Molybdenum, Tungsten and Niobium.] Zhur. Analit. Khim., vol. 12, May–June, 1957, pp. 338–341. Nuclear Sci. Abs., item 10445, vol. 11, Oct. 15, 1957, pp. 1148.

The vacuum-fusion method with an iron bath was used for the determination of O$_2$, H$_2$, and N$_2$ in Mo, W, and Nb. The experiments were made in a specially constructed apparatus.

Miyamoto, Masatoshi. *See* abs. **155.**

138. Morden, J. F. C. Powder Metallurgy. IX. Metal Ind., vol. 92, Jan. 17, 1958, pp. 43–46; Battelle Tech. Rev., item 5843, vol. 7, April 1958, p. 292–a.

Briefly discusses broad aspects of a number of metallurgical methods and equipment including sintering in salt baths and vacuum resistance and induction furnaces, liquid phase and effect of powder characteristics and compacting pressure on properties. Salt baths can be used up to 1,300° C.; they provide quick and uniform heat out of contact with air but after sintering require tedious washing or other treatment to remove the salt from the pores of the piece. Describes an electric resistance furnace for sintering W rods, and a G.E. furnace for vacuum sintering in which the charge is heated by radiation from a triangular-shaped assembly of graphite bars, which surrounds the charge space.

139. Mullard, Limited. The Production of Fine Tungsten Wire—Methods Used by Mullard, Limited. Engineering, vol. 178, No. 4619, Aug. 6, 1954, pp. 174–178; Ind. Arts Index, 1956, p. 2083.

This article covers all phases of tungsten metallurgy from the chemical treatment of ore to drawing of wire. The various operations involved in this process, as carried out at the Blackburn factory of the Mullard organization are described in some detail and illustrated by nine figures.

Muller, C. *See* abs. **61.**

140. Müller, E. W. Surface Migration of Tungsten on Its Own Crystal Lattice. Ztschr. Physik, vol. 126, 1949, pp. 642–665.

Tungsten atoms were deposited from vapor phase on a very fine tungsten point, and the surface migration of the condensed atoms was followed by means of the field emission electron microscope. *See* abs. **70,** item 5028, p. 350.

141. Murphy, J. Production of Tungsten Metal Powder. Western Mach. and Steel World, vol. 30, October 1939, pp. 318–319; Met. Eng. Digest (Metals and Alloys), vol. 11, No. 2, 1940, p. 72; Chem. Abs., vol. 34, 1940, p. 3631.

Scheelite or wolframite with ¾ to 1 percent W is commercially profitable. The concentrate containing 60–77 percent WO$_3$ is ground and digested in acid to give 99.5 percent WO$_3$, which is dried and calcined. The oxide is then reduced to W in a special gas-fired furnace using natural gas. In the furnace are a number of 4-inch Ni-Cr steel tubes with cross rods of the same material; welded onto the heat-resisting tubes are lengths of ordinary steel pipe, which form the cold zone. The brick floor is so designed as to prevent the flames from impinging on the tubes. The WO$_3$ is charged in special-alloy trays, which just fit into the tubes. After the charge is held in an H atmosphere at 1,800–1,900° F. for 15 hours, it is pushed into the cold zone and allowed to cool to room temperature before it is brought in to contact with the air. A condenser removes the moisture from the H and recirculates the latter

142. Nacktigall, Eduard. (Metallwerk Plansee G.m.b.H. Reutte, Tirol, Austria). Properties of Tungsten and Molybdenum at Low and Medium Temperatures. Ztschr. Metallkunde, vol. 43, 1952, pp. 23–36; Chem. Abs., vol. 46, 1952, 3929.

Measurements were carried out on 2-mm. sheets of Mo and W alloys having the compositions (*a*) Fe 0.03, W 0.05, SiO$_2$ 0.05, balance Mo; (*b*) Fe 0.02, Mo 0.05, SiO$_2$ 0.03, Ca 0.01 percent balance W, on their hardness between —78° and 800°, tensile strength, elongation, and temperature coefficient of electrical conductivity. Unexpected hardness and strength changes are noted at 200° and 300°, respectively. In case (*a*) an additional change in expansion is found upon heating between 0 and 200°. These phenomena can be utilized in the forming and working of these materials.

143. Nakao, Tomosakuro, and Kurihara, Ichiro. The Effect of Impurities on the Refining of WO_3. Jour. Min. Inst. (Japan), vol. 69, 1953, pp. 353–357; Chem. Abs., vol. 48, 1954, p. 12000.

The separate effects of P, As, S, and CO_2 on the refining of WO_3 from wolframite were examined by preparing wolframite from pure WO_3 and impurities. P and As greatly affected the yield of WO_3. P was dissolved in Na_2WO_4 solution in the form of $P_2O_5.24WO_3.nH_2O$, and As was dissolved as either $As_2O_5.24WO_3.nH_2O$ or $As_2O_5.6\text{–}12WO_3.\text{–}nH_2O$, depending on whether AsO_4^{3-} or AsO_3^{3-} or AsO_3^{3-} was involved. S and CO_2 had little effect on the yield. The amount of NaCl that remained in WO_3 depended on the state of the precipitate. A cooperative effect was observed for As plus S, P plus CO_2, and P plus As.

Nakazawa, Genichi. *See* abs. **181.**

144. Nakazawa, Genichi, Koizumi, Tadayoshi, and Terunuma, Kiyoshi. The Dearsenizing Roasting of Tungsten Ore. Jour. Min. Inst. (Japan), vol. 72, 1956, pp. 75–80; Chem. Abs., vol. 50, 1956, p. 16597.

Roasting scheelite in an oxidizing atmosphere to volatilize As_2O_3 was not very successful because nonvolatile arsenate was formed; 50–70 percent was removed at 700°–1,000° in 1 hour. Roasting in N_2, CO_2, and SO_2 almost completely volatilized As_2O_3 at 900°–1,000° in 1 hour. The fluidized-bed technique was used. Flotation concentrate of —325-mesh was stably fluidized together with 60–100-mesh pyrrhotite.

145. Nakazawa, Y., and Okada, T. Preparation of Pure Tungsten. Electrical Rev. (Japan), vol. 17, 1928, p. 89; Jour. Inst. Metals, vol. 42, 1928, p. 411.

The degree of the hydration of tungstic acid for the preparation of pure tungsten powder is determined with concentrated hydrochloric acid solution by different methods. *See* abs. **70**, item 966, p. 67.

146. Nasu, Jôji (Awamura Mining Co.). The Treatment of Low Grade Scheelite Ore. Nippon Kogyo Kaishi, vol. 72, 1956, pp. 511–515; Chem. Abs., vol. 51, 1957, p. 8600.

The impurities S and As could be removed from a low-grade scheelite (WO_3 46.43 percent, SiO_2 7.34, As 2.43, P 0.17, S 4.75, Cu 0.11, Mn 1.51, Fe 11.54, Sn 5.40, Mo 0.005, and CaO 8.92) by oxidizing roasting; the removal was complete to 99.6 percent and 80.1 percent, respectively, for S and As by 850° roasting for 2 hours. Sulfurizing roasting by adding S 10 percent at 850° was as effective for removal of As as oxidizing roasting at 1,000° (97.1 percent). The decomposition of a lower grade scheelite (WO_3 18.12 percent and CaO 41.02 percent in an autoclave at pressures of 13–16 kg./sq. cm. in the presence of 20 percent Na_2CO_3 aqueous solution resulted in the leaching of as much as 99.9 percent of the WO_3 at 200°. The effects of additions of $KClO_3$, active C, SiO_2, and CaO on the autoclave decomposition were examined. $CaWO_4$ prepared from the leached solution contained As and P, which were removed by treating it with 4 equivalents of magnesia mixture. Soluble SiO_2 was precipitated by controlling pH of the leached solution to 8.4. Mo could be controlled by precipitating ammonium paratungstate after purifying it by acid precipitation (HCl and HNO_3). Metallic W thus obtained was of comparable uses to that from wolframite.

147. Neugebauer, J., Hegedüs, A. J., and Millner, T. [The Problem of β-Tungsten—H Reduction of WO_3 Containing H_3PO_4.] Nachrichtentech. Ind. u Ver Glühlampen-u. Elektrizitäts A. G., Tungsram, Budapest. Ztchr. anorg. u allgem. Chem., vol. 293, 1957, pp. 241–250; Chem. Abs., vol. 52, 1958, 10784.

At temperatures up to 560° $PdCl_4$ and especially KCl catalyze the reduction of WO_2 by H, but the amount of β-W in the product increases with decreasing temperature at which the WO_2 was prepared from WO_3. Reduction of WO_2 containing KCl with wet H gives only β-W. The β→α-W transition temperature varies from 520° to 820°; small amounts of Si $(OEt)_4$, H_3BO_3, $Th(NO_3)_4$, Ce $(NO_3)_4$, or $H_3—PO_4$ favor the higher temperatures. A gravimetric study of the H reduction of WO_3 containing H_3PO_4 (P/W=0.5 percent) shows only the β-W forms at 790°; the β→α-W conversion temperature is approximately 810° and at 900° only the α-form is present. No α→β-W conversion by O or H_2O at normal pressures is found. A study of the O content of pure β-W indicates that the last traces of O cannot be removed without simultaneous change to α-W. β-W is regarded as a metal with disturbed structure rather than as a definite oxide or an allotropic form of W, the disturbances, which may be other than O, stabilize the structure.

See also Millner, Tivadár, abs. **246.**

148. Nikitina, E. A. (I. V. Stalin 2d Med. Inst., Moscow). Preparation and Properties of Sodium Metatungstate and Metatungstic Acid. Sbornik Statei Obshchei Khim., Akad. Nauk, S.S.S.R., vol. 1, 1953, pp. 44–52; Chem. Abs., vol. 49, 1955, p. 15586.

Na metatungstate was prepared by two methods: (1) To a solution of Na paratungstate (40 g. in 600 ml. of warm H_2O) tungstic acid was added drop by drop and the mixture boiled for 1.0–1.5 hours until 0.3 ml. HCl (d. 1.12) failed to precipitate H WO. The solution was concentrated on a H_2O bath and finally over H_2SO_4; yield 70 percent. (2) Moistened tungstic acid was added to a saturated solution of Na paratungstate (1 g. to 1 ml. H_2O) and the salt crystallized out over H_2SO_4; yield 87–88 percent (Leontovich, J., Russian Physicochem. Soc., vol. 37, 1905, p. 130). Metatungstic acid was prepared from the Na salt (100 g./100 ml. H_2O) to which 100 ml. Et_2O and 40 ml. HCl (d. 1.19) were added at 0°. The heavy, oily etherate of metatungstic acid was separated in a separatory funnel and evaporated on a watch glass. Excellent needlelike crystals were obtained; the metatungstic acid decomposed after 12–16 hours to the yellow tungstic acid. The solubility of Na metatungstate in the range 0°–55° indicates three solid phases with 23.94, 22.56, and 21.64 mol. H_2O; at 60° a vitreous solid is formed. The K salt in the range 0°–86° gives four solid phases with 23.33, 22.40, 13.72, and 12.71 mols. H_2O. The solubility of the Na salt at 55° and that of the K salt at 80° are 81.5 and 84.80 g./100-g. solution. The formula of these salts is considered to be that of Pffeifer (Chem. Abs., vol. 14, 1920, p. 241), but tentatively that of Rosenheim and others (Chem. Abs., vol. 25, 1931, p. 468) is given, $Na_6H_4[H_2(W_2O_7)_6].xH_2O$.

149. Nishikawa, Kunio, Yamaguchi, Noboru, and Kawasu, Shigeo. Calcium Tungstate Phosphor. II. Evaluation of Several Purification Methods of Tungstates by Means of Chemical Spectroscopic Analysis. Jour. Chem. Soc. (Japan), Ind. Chem. Sec., vol. 57, 1954, pp. 531–533; Chem. Abs., vol. 49, 1955, p. 6732.

The spectroscopic examinations were worked out for raw and purified Na_2WO_4, I, H_2WO_4, $(NH_4)_2WO_4$, etc., to detect the minute impurities. Al, As, Cu, Fe, Mg, Si, etc., have been detected in each compound, irrespective of the purification procedures used.

150. Nishikawa, Kunio, Yamaguchi, Noboru, and Yamamoto, Masayuki (Shimazu Mfg. Co., Ltd., Kyoto). Calcium Tungstate Phosphor. III. Comparison of Several Purification Methods of Tungstates by Means of Spectroscopic Analysis. Jour. Chem. Soc. (Japan), Ind. Chem. Sec., vol. 57, 1954, pp. 617–618; Chem. Abs., vol. 49, 1955, pp. 6732, 8703.

As, Ca, Cu, Fe, Mg, Mn, Mo, Si, Sn, etc., were recognized spectroscopically in para-ammonium wolframate (I) prepared from purified Na_2WO_4. The repeated purification of I with H_2O did not reduce the impurities. It appeared that the presence of As does not necessarily control the duration of afterglow of the phosphor. The effect of Ti also was discussed.

151. Nobel, J. de. Thermal and Electrical Resistance of a Tungsten Single Crystal at Low Temperatures and in High Magnetic Fields. Physica, vol. 15, No. 5/6, 1949, pp. 532–540; Met. Abs., vol. 17, 1950, p. 329.

The tungsten single crystal used in previous experiments (Physica, vol. 5, 1938, p. 449; Met. Abss., vol. 5, 1938, p. 762) has been examined in stronger magnetic fields, up to 36,000 gauss, by methods similar to those used previously but apparatus on a reduced scale. The electrical and thermal resistivities continue to increase in stronger magnetic fields. The increase in electrical resistance may be represented by the equation $R=a(t)H^{1-9}$. The Wildemann-Franz law is not valid in these stronger fields nor does it seem possible to separate the thermal conductivity into a lattice and an electronic conductivity.

152. Noesen, S. J., Hughes, J. R., and others (General Electric Co.). Arc Melting and Fabrication of Tungsten. Fall meeting of the Met. Soc., Cleveland, Ohio, Oct. 27–31, 1958; Jour. Metals, vol. 10, September 1958, p. 28.

No abstract.

Nomura, Shoichiro. *See* abs. **179.**

153. Novikov, G. I., and Shchukarev, S. A. (Uchenye Zapiski, Leningrad, Gosudarst Univ. im. A. A. Zhdanova.) Gravimetric Method for Measuring the Pressure of a Saturated Vapor. Ser. Khim. Nau, vol. 163, No. 12, 1953, pp. 37–40; Chem. Abs., vol. 49, 1955, p. 5908.

A static gravimetric method is described for measuring the pressure of a saturated vapor, which is useful in the case of high-boiling and chemically active substances. The method was applied to the vapors of WCl_6 over the temperature range 156°–383°. The data appear to be a good continuation of those obtained by Vernon (Chem. Abs., vol. 31, 1937, p. 8285) at low temperatures. The heat of vaporization was calculated and found to be equal to 13.7 kcal./g. mole.

See also Shchukarev, S. A., abs. **184.**

154. Office of Technical Services. Bibliography of Reports on Molybdenum and Tungsten, 1952, 5 pp. Lists of informal bibliographies and selected bibliographies of PB reports IB–101; also CTR–101 (1954).

No abstract.

155. Oka, Yoshinaga, and Miyamoto, Masatoshi (Tohoku Univ., Sendai). Extraction of Tantalum and Niobium Oxides From Niobite. II. Removal of Ti From Ta and Nb. Jour. Electrochem. Soc. (Japan), vol. 17, 1949, pp. 114–118; Chem. Abs., vol. 48, 1954, pp. 7857, 14136, 14137.

The tartaric acid hydrolysis method and peracid method are studied for the removal of Ti from Ta and Nb. In the case of the tartaric acid hydrolysis method, the effect of concentration of tartaric and HCl on the precipitation of pentoxide and upon the adsorption of Ti are examined. In dilute solution the content of TiO_2 can be reduced to 0.6 percent from 10.9 percent. When W is present alone, it does not precipitate by tartaric acid hydrolysis, but in the presence of Ta and Nb it precipitates completely. With regard to the peracid method solution of Ta and Nb peroxide are unstable and when the solution is boiled they are easily precipitated, although Ti peroxide is stable. By utilizing these properties about half of the Ti contained can be removed. Removal of Ti from Ta is easier than from Nb, and 0.7 percent of TiO_2 contained in Ta oxide can be reduced 0.05 percent by fusion. Yield of Ta is good. In the case of Nb oxide good results cannot be obtained.

Okada, T. *See* abs. **145.**

156. Okuno, Hisateur, Honda, Masatake, and Ishimori, tatsujiro (Rikkyo Univ., Tokyo). Ion-Exchange Separation of Tungsten and Rhenium. Japan Analyst, vol. 4, 1955, pp. 386–387; Chem. Abs., vol. 50, 1956, 16551.

The sample solution containing $KReO_4$ (800–100γ as Re) and Na_2WO_4 (1–0.1 g. as W) was made alkaline to 0.05N NaOH and was passed through a column of Amberlite IRA–400 (Chloride form, 65–100 mesh, 2 ml. of column with 4 cm. height). After washing with H_2O, WO_4- was eluted with 100–125 ml. 0.5N NaOH–O.5N NaCl. Then the column was turned upside down, and this ReO_4- eluted with 150 ml. 8N HCl. Purity of each component in each fraction was checked by a spectrographic method. Recovery of Re was almost 100 percent.

157. Opinsky, A. J., and Orehotsky, J. L. (Sylvania Electric Products, Inc.). Orientation of Large Grains in Annealed Tungsten Wire. Fall meeting of the Met. Soc., Cleveland, Ohio, Oct. 27–31, 1958; Jour. Metals, vol. 10, September 1958, p. 28.

No abstract.

Orehotsky, J. L. *See* abs. **157.**

Ozasa, Minoru. *See* abs. **178.**

Paukow, G. *See* abs. **47.**

Peacock, R. D. *See* abs. **84.**

158. **Percival, G. A.** Manufacture of Pure Tungsten. World Power, vol. 4, 1925, pp. 11–19.

By wet treatment of sodium tungstate a pure oxide is obtained in a mechanical form suitable for reduction to metallic powder. *See also* abs. **70,** item 957, p. 67.

Percy, A. L. *See* abs. **214.**

Perlov, P. M. *See* abs. **77.**

159. **Pfann, W. G.** Zone-Melting. A Fresh Outlook for Fractional Crystallization—1955 Review. Chem. Eng. News, vol. 34, Mar. 26, 1956, pp. 1440–1443.

Zone-melting, -refining, -remelting, -leveling are all explained simply. The distribution coefficient K, which is the ratio of solute concentration in the freezing solid to the solute concentration in the liquid (solidus concentration) liquidus concentration approaches an equilibrium value with time and can be derived from the phase diagram for either the end components or the compounds between them. C_0 in the mixture yields C_0/K by drawing a horizontal line from intersection of C_0 with solidus out to liquidus and KC_0 by a similar line from C_0 liquidus to the solidus. Used largely as a batch process now, but the way to make it continuous is pointed out. The more passes, the more perfect the separation. The process was applied originally to germanium, later to silicon, but it has been applied to InSb, GaAs, AlSb, Sb, and As and favorable results for Bi, Zn, Fe, Cu, Al, Ga, Zr, and Cr; also $NaCl\text{-}H_2O$, anthranaphthalene. Heavy water from H_2O appears to have merit. Zone-leveling is a way of introducing activator elements unformly.

Pfisterer, H. *See* abs. **86.**

160. **Phillips, M. A.** Preparation of Phosphotungstic Acid and of Sodium and Barium Phosphotungstates. Jour. Soc. Chem. Ind. (London), vol. 69, 1950, pp. 282–284.

Na phosphotungstate (I) is prepared by adding 200 cc. concentrated HCl to a boiling solution of 250 g. Na tungstate (II) and 37.5 g. Na_2HPO_4 in 300 cc. H_2O. After chilling, the precipitate is filtered and dried. The air-dried crude product (180 g). is recrystallized from H_2O (80 cc.); yield 135 g. of a product having a variable amount of water of crystallization. The mother liquor from the recrystallization can be reused. All mother liquors in the process can be treated with $BaCl_2$ crystals to obtain Be phosphotungstate (III). III is prepared by adding 250 g. $BaCl_2.2H_2O$ in 800 cc. boiling H_2O 330 g. Na tungstate in 1 liter boiling H_2O. After cooling, the precipitate is filtered, washed with hot H_2O, and dried at 90°; yield 398 g. of Ba tungstate (IV), sparingly soluble in H_2O. 3.5 cc. of 86° H_3PO_4 is added to 160 g. IV suspended in 250 cc. boiling H_2O. Concentrated HCl (100 cc.) is added and the mixture boiled for 2 hours. Completion of the reaction can be determined microscopically since the crystallized form of the suspension changes. The yield of filtered, washed, and air-dried III is 120 g. To prepare III from I, a solution of I (130 g.) in boiling water (300 cc.) is added to a solution of $BaCl_2.2H_2O$ (40 g.) in boiling water. Upon concentration to 350 cc. and cooling, III crystallizes out. The yield of washed and air-dried product is 127 g. To prepare phosphotungstic (V) acid from IV, 240 g. IV is suspended in 200 cc. boiling water and treated with 5 cc. 86 percent H_3PO_4, then with a mixture of 33.5 cc. concentrated H_2SO_4 and 100 cc. water with agitation and boiling. After 2 hours the $BaSO_4$ is filtered off while hot. The filtrate is concentrated to dryness under reduced pressure. The yield of V is 160 g. It can be purified with charcoal. The solubility in water at 20° is approximately 5 g. per cc. To prepare V from III, 200 g. of the Ba salt is suspended in a liter of boiling water and a mixture of concentrated 5.4 cc. H_2SO_4 and 50 cc. water is slowly added with agitation and boiling. The boiling is continued for 1 hour, charcoal is added, the $BaSO_4$ is filtered off, and the filtrate evaporated to dryness at reduced pressure. The yield is 180 g.

Pitkin, W. R. *See* abs. **192.**

161. **Pogodin-Aleksayev, G. I.** (Editor, Moscow, Mashgiz, 1958. (Vyssheye tekhniches koye uchilishche. Termicheskaya obrabotka i prochnost' metallov i splavov; sbornik statey.) [Heat-Treatment and Strength of Metals (Collection of Articles).] Accession List of AF Material Received, No. 8, 1958 (May 19–30), 177 pp., illus., bib. (Available Library of Congress, Air Information Division (Project, Treasure Island), item 136.)

No abstract.

162. **Pokorny, E. A.** Preparation of Technical Carbon-Free Tungsten by Chlorinating Wolframite. Bitterfeld Sci. Lab. Rept. 273, Sept. 29, 1930 (PB L 73557), FIAT Reel BB–187, from 1808–1825 (Bib. 6–9–756). Photostat $2, microfilm 50 cents, available Office of Tech. Services and Publications Board Project, Library of Congress, Washington 25, D.C.; also on file, Bureau of Mines Library, College Park, Md.

Pilot-planting of a process worked out and reported May 15, 1928. A horizontal rotating tube furnace with 2,340-mm. length heated of electrode graphite 120-mm. inside diameter, heated [illegible] first by Cr-Ni-Fe strip heaters but later by Mo wire wound on tube. The ore flowed countercurrent to a stream of 8.5 parts H_2 and 1 part Cl at 950° C. to chlorinate and remove most of the impurities to leave a product 80–90 percent W with Fe and Mn as main impurities suitable for preparation of ferrotungsten for the steel industry. Analysis of the product said to be with the specifications but the latter not listed.

Main work done on a wolframite concentrate ground to 125-mesh per linear inch (2,400 mesh per sq. cm.), containing 66.2 percent WO_3, 12.9 percent Fe, 4.78 percent Mn, 0.46 percent Sn, 0.33 percent As, 0.04 percent P, 0.23 percent Cu,and 0.52 percent Si. The final product contained 85 percent W, 2.5–4 percent Fe, 0.3–0.5 percent Mn, 0.002–014 percent Sn, Tr–0.02 percent As, 0.05–0.08 percent Cu, 0.02–0.07 percent Si. Yield of W 88–90 percent, the losses being partly vaporized chloride and part as dust. Power consumed 32 kw.-hr./kg. W. The tungsten lost as chloride formed at the cold end of the tube and was swept out.

Tests on ore held on shallow trays showed that not over 10-mm. deep layer could be treated in a countercurrent stationary muffle through which the trays could be pushed. Costs were calculated:

Per kilogram tungsten metal obtained:

	Reichsmark
WO_3 in ore, 1.40 kg. at 2.00 RM	2.80
Hydrogen, 9.5 cu. m. at .01 RM	.095
Chlorine, 3.6 kg. at .08 RM	.029
Power, 37 kw.-hr. at .013 RM	.48
	3.67

The commercial design would be a long muffle heated by silicon carbide strip heaters with chammotte and kieselguhr insulation through which is pushed a string of shallow trays (ceramic) at a rate allowing at least 2.5 hours of residence in the heated part of the furnace. With the usual size muffles available, the capacity would be about 1 metric ton of finished tungsten per month.

163. ———. Studies in the Chlorination of Some Complex Ores—Wolframite, Vanadinite and Chromite. Ch. in Extraction and Refining of the Rarer Metals—A Symposium on Extraction Metallurgy of Some of the Less Common Metals. Proc. Roy. Soc. of Arts, (London), Inst. Min. and Met., Mar. 22–23, 1956, pp. 34–48.

Discussion: The chlorination of wolframite, by using the method described, allowed technically for the utilization of low-grade ores with high arsenic and tin contents for the production of tungsten metal of sufficient purity for steelmaking purposes and, if desired, for the manufacture of chemical compounds of W for satisfactory purity simply by continuing the treatment with chlorine only, after having terminated the separation by using a mixture of chlorine with excess hydrogen. The process, when carried out in a continuous run on a small scale, required, for 1 kg. W of about 80 percent W and about 8 percent Fe, 1.35 kg. WO_3 in the ore, 6 cu. mH and 3.5 kg. Cl. . . . Economically the process described could not compete with those now used industrially for the production of tungsten and vanadium metals or compounds except in times and at places where chlorine and hydrogen were available as surplus products.

164. Poltorak, O. M. (M. V. Lomonosov State Univ., Moscow). The Active Forms of the Cathodic Hydrogen and the Stationary State of the Polarized Cathode. Zhur. Fiz. Khim., vol. 27, 1953, pp. 599–606; Chem. Abs., vol. 47, 1953, p. 11049.

When amalgamated Cu or amalgamated Pb was cathodically polarized on a microscope stage, WO_3 crystals 0.5μ distant from the cathode surface turned blue, that is, were reduced to W_2O_5. Hg, cathodically polarized in a solution (not specified) saturated with H, when dropped on a WO_3 plate rapidly reduced the WO_3 up to 0.3-mm, distance. When Pb was cathodically polarized by 0.1 a./sq. cm. (the composition of the solution was not stated) and the current interrupted, followed by touching t sec. later with a WO_3 crystal, reduction occurred as long as t was <120 sec. Other cathodes (Ni, amalgamated Pb, or amalgamated Cu) were "active" for shorter time. This reduction of WO_3 proved that cathodes emitted active H, in agreement with Kobozev (Chem. Abs., vol. 47, 1953, p. 4766). Frumkin's criticism (Chem. Abs., vol. 46, 1952, p. 6527) of Kobozev's views was incorrect, because Frumkin applied equilibrium equations to a steady state.

165. Powell, C. F., Campbell, L. E., and Gonser, B. W. Vapor-Plating—The Formation of Coatings by Vapor-Deposition Techniques. (Sponsored by the Electrochem. Soc., Inc., New York, N.Y., 1955, 158 pp. (Author and subject indices, 14 refs., 17 tables, and 407 refs.)

A portion of the preface is quoted as follows: It is the aim of this book to present a unified picture of the art of vapor-plating, as tempered by the authors' experience in many applications for which coatings of special characteristics have been required. The general techniques employed in vapor-plating are described and critically reviewed. Discussions are given of the conditions required for the deposition of pure metals, carbides, nitrides, borides, silicides, and oxides from gaseous mixtures of their vaporized compounds.

166. Price, G. H. S. Powder Metallurgy: An Indexed Bibliography of the Literature. Metal Treatment, 1947, vol. 14, No. 49, pp. 42–65; No. 50, pp. 113–130 (bib., 934 refs.); Met. Abs., vol. 18, 1950–1951, p. 185.

Some articles of the more popular type have been intentionally omitted, although many have been retained. This also applies to many of the early references to tungsten, and although this bibliography does not claim to be exhaustive, it is hoped that very few references of any real value have been omitted. * * * In order to arrive at certain limits to the subject, the following general definition of Powder Metallurgy has been adopted: The preparation of metal powders and their subsequent fabrication (either alone, or mixed with other metals or nonmetals) either into substantially dense bodies or into materials with intentional and controlled porosity.

167. Pugh, J. W. Refractory Metals: Tungsten, Tantalum, Columbium, and Rhenium. Jour. Metals, vol. 10, May 1958, pp. 335–339 (1 table, 6 figs., and 35 refs.).

All four metals can be arc-melted, sintered, forged, swaged, and rolled. * * * The properties that determine the attitude of a refractory metal for high-temperature structural applications are summarized in table 1. The metals are arranged from left to right in diminishing order of their melting points. Figure 2 gives the tensile parameters for W as a function of temperature. * * * The high-temperature scaling of W has also received some attention. Scale growth is determined by two processes: The diffusion of oxygen and the volatility of the scale. Up to about 1,350° C. the oxygen diffusion is said to be more important. * * * The refractory alloy designer of today has an advantage over those who designed current commercial high-temperature materials, because he can approach the task with more knowledge about the fundamental nature of alloying. He has new theories on dispersion hardening by Mott, and by Fisher, Hart, and Pry to guide him. Moreover, the ideas of Fisher and of Cottrell on solution-hardening should prove helpful. Also of considerable importance are the recent experiments relating polyonization and subgrain growth to mechanical strength. Substructure hardening is particularly well suited to refractory metals because, in general, their recrystallization temperatures are high relative to application temperatures. Perhaps the assistance available from these new basic concepts will compensate in some measure for the additional problems of brittleness and oxidation attack that face the designer of refractory alloys.

168. ———. Tensile and Creep Properties of Tungsten at Elevated Temperatures. Proc. ASTM, vol. 57, 1957, pp. 906–916 (discussion, 13 figs., 3 tables, and 9 refs.).

Summary: Tungsten has been shown to be stronger than other representative refractory metals in short-time tension tests from room temperature to 2,000° F. The margin of its superiority in this respect is proportional to its higher melting point. Tungsten's creep-rupture properties are more remarkable by comparison with commercial austenitic alloys and molybdenum in the range 1,600° to 2,200° F. Many high-temperature applications depend on strength-to-weight ratio, and in this respect tungsten is less outstanding. However, tungsten is slightly superior to molybdenum even in strength-weight ratio at 2,000° F. Furthermore, it is highly probable that tungsten's advantage above 2,000° F. would increase rapidly with temperature. These considerations indicate that tungsten's future as an ultrahigh-temperature metal is somewhat brighter than anticipated.

Ray, J. P. *See* abs. **209.**

169. Reed, E. L. Tungsten. AEC Pub. AECD–2700, 1947, 54 pp.

A complete summary of the known data on W, with 111 references. The report includes data on the physical properties, stability in various media, fabrication and casting, methods of preparation of the solid metal and its powder, chemical analysis, microscopical examination, nuclear properties, behavior on irradiation, and alloying characteristics.

Reeves, R. R. *See* **abs. 90.**

Rezukhina, T. N. *See* abs. **64.**

170. Richards, C. E. C., and Smith, M. L. Preparation of Anhydrous Tungsten Hexachloride. Atomic Energy Res. Estab. (Harwell, Berks, England), AERE–GP/M–167, Feb. 17, 1954, 7 pp. Nuclear Sci. Abs., vol. 8, No. 10A Sept. 30, 1954, p. 658.

A method is described for preparing 500-gram batches of anhydrous tungsten hexachloride suitable as source material in ion arcs. The process involves the direct chlorination of tungsten freshly reduced from tungsten trioxide and the collection of the product in such a way as to minimize hydrolysis by atmospheric water vapor. The material obtained by this process was 100 percent volatile in vacuo at 150° C.

Richardson, F. D. *See* abs. **59.**

171. Rideal, E. K., and Trapnell, B. M. W. The Adsorption of Hydrogen by Tungsten, and the Mechanism of the Parahydrogen Conversion at Tungsten Surfaces. Jour. Chem. Phys., vol. 47, No. 1/2, 1950, pp. 126–138; discussion (in English), p. 138; Met. Abs., vol. 18, 1950, p. 150.

The adsorption of hydrogen by tungsten was studied experimentally between 0° and —183° C. The main conclusions reached are: (1) The order of reaction of evaporation of chemisorbed hydrogen and of the conversion are both unity; (2) the activation energy of evaporation is much less than the heat of adsorption and is between 2,200 and —2,200 cal.; the activation energy of the conversion is ~2,000 cal.; (3) characteristics of the conversion are interpretable in terms of a uniform surface activity rather than on the basis of a few sites of special activity as suggested by Farkos (Trans. Faraday Soc., vol. 35, 1939, p. 943). (21 refs.)

172. ———. (The Davy Faraday Foundation. The Royal Institution). Adsorption on Evaporated Tungsten Films. I. Oxygen and Carbon Monoxide Chemisorption and the Determination of Film Surface Areas. Proc. Roy. Soc. (London), ser. A., vol. 205, No. 1082, 1951, pp. 409–421, 15 refs., 7 tables, 4 figs.

The chemisorption of oxygen and of carbon monoxide by evaporated W films has been studied between 20 and —195° C. and at pressures up to 10^{-3} mm., with the primary aim of measuring the surface areas of the films. The two methods give results that agree, and the film areas have been determined to an accuracy of about 5 percent.

Chemisorption of oxygen is followed by a second process, probably an oxidation, which shows very rapidly as gas is taken up, and for which an activation energy of 7,000 cal. has been evaluated. The heat of carbon monoxide chemisorption is so low in densely packed layers that measurable equilibrium gas pressures are required even at liquid-air temperatures for completion of chemisorption. Values for the fraction of the surface atoms covered at various temperatures and pressures have been obtained, together with isothermal heats at various coverages. At the lowest temperatures, onset of second-layer formations do not form a stepwise process.

173. Robbins, D. Solution of Tungsten in Mixtures of Hydrofluoric and Nitric Acids. Metallurgia, vol. 55, 1957, pp. 257–259; Chem. Abs., vol. 51, 1957, p. 10195.

W is most readily dissolved by a mixture of approximately 40 percent by volume of concentrated HNO_3 and approximately 60 percent by volume of concentrated HF. The metal surface is oxidized by NO_2; the oxide thus produced is soluble in HF but insoluble in other mineral acids (8 refs.)

Rohm and Haas Co. *See* abs. **49.**

Rooksby, H. P. *See* abs. **192.**

174. Rovinskii, B. M. Structure of Crystallites and Structural Changes in Metals Upon Action on Them of Mechanical Stresses. Izvest. Akad. Nauk S.S.S.R., ser. fiz. 17, 1953, pp. 333–341; Chem. Abs., vol. 48, 1954, p. 1801.

It follows from metallographic and X-ray dispersion data that in polycrystalline material crystallites should contain a great number of blocks. However by X-ray diffraction micromethods it can be shown that the crystallites are composed of one or a few blocks in recrystallized Al or W. This discrepancy is attributed to an absorption effect, falsifying X-ray pictures decreases in Al samples with relaxation time at constant load in the elastic range. Upon removal of the load the number of spots increased to the original value. The half-width of interference lines of steel 15 heated to 870° and held in vacuo at 700° and stressed in steps to 20 percent is plotted vs. the remaining deformation for planes (310) and (211); the average block size ϵ and the relative inhomogeneity η of the interplane distance d are also plotted as functions of remaining deformations. $\epsilon\eta$ is a linear function of deformation between 8 and 20 percent deformation. To investigate the orientation of microcracks in a plastically deformed metal, a narrow X-ray beam was used, collimated by two 0.014-mm. apertures 60 mm. apart. The sample was 170 cm. away from the photographic plate. Samples of pure Cu and Al sheet, nonstressed, cold-rolled, and recrystallized were examined parallel and perpendicular to the direction for rolling. It can be seen that in all conditions the X-ray line appears diffused but that the amount of diffusion increased in the cold-rolled samples and depends on the direction of rolling; this is attributed to an orientation of submicrocracks on rolling.

175. Sagamore Ordnance Materials Research Conference (Fourth) on High Temperature Materials, Their Strength Potentials and Limitations. Sagamore Conf. Center, Raquette Lake, N.Y., Aug. 21–23, 1957. Cosponsored by The Ord. Mat. Res. Office and The Office of Ord. Res., U.S. Army, 1957, 353 pp. (13 papers).

Volume contains discussion, abstracts of some papers, a list of attendees, 150 ref., 157 figs., and 6 tables. Conference arranged by Syracuse University Research Institute, Syracuse 10, N.Y.

176. Sasaki, Nobuji, and Ueda, Ryûzô. The Precipitates of Tungstic Acid. Inst. Chem. Res. Bull., Kyoto Univ., vol. 25, 1951, p. 67; Chem. Abs., vol. 46, 1952, p. 4408.

A turbid solution obtained by adding 0.5 cc. 0.1 M Na_2WO_4 to 10 cc. 0.05 M HCl at room temperature was centrifuged to give a precipitate (a) of thin crystals of various forms (0.2–2.0μ). These crystals, if left in solution, slowly formed aggregates which dispersed with difficulty on addition of water. The supernatant solution contained fine needles (0.1μ) and small granules (0.2μ), which on standing tended to form a network and threads, respectively. When Na_2WO_4 solution was poured into hot HCl, a precipitate (b) of very fine angular plates (0.05μ) was obtained. The dehydration curves of "a" are continuous; those of "b", whose composition is WO_3-H_2O at 85°–185°, are discontinuous. A strong electron beam or heating decomposed thin crystals of H_2WO_4 to small granules of the original forms.

177. ———. Reduction of Tungsten Oxide With Hydrogen. III. Reduction Velocity of Tungsten Oxide and Oxidation Velocity of Reduced Powder Measured by a Spring Balance. Inst. Chem. Res., Bull., Kyoto Univ., vol. 20, 1950, pp. 49–50; Chem. Abs., vol. 47, 1953, p. 10321.

The reduction velocities of variously prepared W oxides by flowing H_2 at various temperatures and the oxidation temperatures and the oxidation velocities of metallic powders thus formed by air at room temperature were measured with a sensitive quartz-fiber spring balance placed in the reaction tube. The higher the reduction temperature and the finer the oxide, the more rapidly was the trioxide reduced, not below 400°. Ammonium paratungstate was not reduced by H_2 but was completely decomposed to trioxide without being reduced at all at 400°. The finer oxide (particle size 0.01μ) was reduced 100 percent in 3 hours at as low as 480°, but the coarse oxide (3μ) 40 percent in 3 hours at 500°. When reduced below 700° the products were subject to oxidation by air at room temperature. The velocity and the extent of reoxidation were greater with finer oxide and lower reduction temperature. The product could even be pyrophoric. Primary particles or single crystals of W produced by atomic sintering in the course of reduction of W trioxide crystals with H_2 were small when the reduction was effected at low temperatures, because the mobility of W atoms or W oxide molecules was then small. The presence of very small primary particles is the cause of the reoxidability of the W powder.

178. Sasaki, Nobuji, Ueda, Ryûzô, and Ozasa, Minoru. Physiochemical Properties of Tungsten Metal Powder. Inst. Chem. Research Bull., Kyoto Univ., vol. 25, 1951, pp. 66–67; Sci. Powder, vol. 3, 1949, p. 1; Chem. Abs., vol. 46, 1952, p. 8463.

The effect of pressing on the structure of W powder produced from two different sorts of oxide, one obtained by decomposition of Na_2WO_4 with HCl and the other by roasting $(NH_4)_{10}W_{12}O_{41}$, was studied. The powder was pressed to a briquet under hydraulic pressure, 11 tons per square inch. In water the briquet disintegrated at once and on slight stirring dispersed to fine particles. On the original and pressed powder were measured: (*a*) specific gravity calculated from the sedimentation volume. (*b*) surface area per gram and mean particle diameter calculated therefrom, (*c*) particle-size distribution. Electron microscopic observations were made. The pressing greatly decreased the particle size of the original powder and halved the sedimentation volume, but the surface area or the mean particle diameter remained almost unchanged: this indicates that presssing disintegrated almost completely the secondary and tertiary particles to the primary ones without producing any fresh surface by deforming or crushing the primary particles themselves.

Sauer, Hubert. *See* abs. **68.**

179. Sawasa, Shozo, Ando, Rinjiro, and Nomura, Shoichiro. Thermal Expansion and Specific Heat of Tungsten Oxide at High Temperatures. Phys. Rev., vol. 84, 1951, pp. 1054–1055; Chem. Abs., vol. 45, 1951, p. 8308; vol. 46, 1952, p. 3844.

The thermal expansion coefficient is plotted against temperature, 20°–850°. There is a contraction of 0.0012 at 755° (heating) or 725° (cooling). The isobaric specific heat is plotted against temperature, 690°–790°. There is a sharp maximum at 728°.

180. Schneider, K. Preparation of Molybdenum-Free Tungstic Acid. I. G. Farben industric, A. G., Bitterfeld Sci. Lab. Rept. 241, Mar. 19, 1930 (PB L 73557), FIAT reel BB-187, frames 2025–2037, bib. 6-9-757. (Photostat, $1.50, available Photo Duplicating Service, Publications Board Project, Library of Congress, Washington 25, D.C.; on file, Bureau of Mines Library (CP-309), College Park, Md.)

In precipitating tungstic acid from sodium tungstate solutions with H_2SO_4 in the impure solutions of an operating plant there is a loss of 10–20 g./l. of tungstic acid under optimum conditions. The sodium tungstate is poured into 60 percent H_2SO_4 at 130° C. for acid and 90° C. for solution and the mixture boiled 15 minutes. It was found that the impurities in the solution and the acid form a colloidal bluish tungstic acid that does not settle. This is thought to be partly reduced. Additions of electrolytes did not coagulate it, but oxidizing agents like HNO_3, $KClO_3$ or air gave some improvement, and the best results were given when chlorine gas was absorbed in both the Na_2WO_4 solution and the H_2SO_4. This brought the loss down to 1–2 g./l. and the precipitate also contained only 0.003–0.010 percent MoO_3. Use of HCl usually gives losses of only 2–3 g./l, but is more expensive. Use of 9 liters HNO_3 in 200 liters Na_2WO_4 and 9 liters HNO_3 to 360 liters H_2SO_4 solution is the optimum method of operation.

Schönberg, N. *See* abs. **80.**

Schüle, Wolfgang. *See* abs. **114.**

Sedlatschek, K. *See* abs. **14.**

181. Sei, Rempel, Nakazawa, Genichi, and Ito, Koichi. Extraction of Tungsten From Scheelite. II. (No subtitle given.) Jour. Min. Inst. (Japan), vol. 70, 1954, pp. 513–517; Chem. Abs., vol. 48, 1954, p. 12000, vol. 49, 1955, p. 6062.

The solubilities of the ternary system Na_2WO_4–Na_2CO_3–H_2O were measured at 19° and 29°. A graph is given. These data were then used for recovery of excess Na_2CO_3 in the leach liquor obtained by the autoclave-soda process. Addition of NaOH was very effective for the extraction of W from rich ores. The W in the leach liquor was reduced partly by impurities in the ore, and the yield of $CaWO_4$ from the leach liquor was 70–80 percent around pH 7. For the complete recovery, it was necessary to oxidize W to the sexivalent state with a suitable oxidizing agent such as NaClO.

182. Senderoff, S., and Brenner, A. Platting Experiments With Aqueous Solutions at High Temperatures. Jour. Electrochem. Soc., vol. 97, 1950, pp. 361–366; Chem. Abs., vol. 48, 1954, p. 3167.

Aqueous solutions of salts of Cr, Cu, Mo, Ni, Ti, W, V, and Zr were electrolyzed under pressure at temperatures up to 300°. Under these conditions, intermediate reduction steps were favored over reduction to metal. Instability of the solutions was frequently encountered, but anodic processes were improved in some instances.

183. Shatalov, A. Ya., and Marshokov, I. A. [Electrode Potentials and Corrosion of Molybdenum and Tungsten.] Zhur. Fiz. Khim., vol. 28, January 1954, pp. 42–50. Met. Abs., vol. 21, 1954, p. 1065.

Measurements of electrode potentials of Mo and W in buffer solution containing different amounts of Cl^- have shown that the change of electrode potentials with pH can be represented by the following relations: $E_{Mo}=0.35$ to 0.40–0.045 pH; $E_W=0.28$ to 0.33–0.045 pH. The potentials of Mo and W assume intermediate values between the equilibrium potential of the metallic oxide electrode $E_{M/M_0/OH^-}$ and that the O electrode E_{O_2/OH^-}. Behavior of Mo and W in 20 different electrolytes has been studied, and the influence of anions in solution investigated. A substantial lowering of anodic polarization has been observed in alkaline solution (pH>11), accompanied by a marked decrease in corrosion-resistance. The loss of weight due to corrosion agrees with losses of weight, calculated from O-absorption measurements, assuming formation of Mo_2O_3 and WO_2.

184. Shchukarev, S. A., and Novikov, G. I. Thermodynamic Study of Some Chlorine Derivatives of Tungsten. I. Saturated Vapor Pressure of the Hexa-penta-, and Oxytetrachlorides of Tungsten. Zhur. Neorg. Khim., vol. 1, No. 3, 1956, pp. 357–361; Chem. Abs., vol. 50, 1956, p. 13588.

The vapor pressure of WCl_6 increases from 43 mm. at 215° to 752 mm. at 341°; of $WOCl_4$ from 36 mm. at 158° to 755 mm. at 223°; of WCl_5 from 4 mm. at 140° to 760 mm. at 286°. The heat of vaporization (kcal.) for WCl_6, WCl_5, and $WOCl_4$ from solid and liquid phases are, respectively, 14.6, 12.6; 16.7, 15.7; 18.9, 16.2; with an uncertainty of ±0.5. The corresponding entropies of vaporization (entropy units) are 24.2, 20.4; 30.3, 28.3; 38.0, 32.6; with an uncertainty of ±1.0. The m.p. and b.p. are, respectively, WCl_6 275°, 348°; WCl_5 230°, 286°; $WOCl_4$ 204°, 224°. The uncertainty in the m.p. is ±10°, in the b.p. ±2°.

See also Novikov, G. I., abs. **153.**

Shen, Tsing-Nang. *See* abs. **120.**

Shewmon, P. G. *See* abs. **11.**

Sikora, P. F. *See* abs. **82.**

Simanov, Yu. P. *See* abs. **64, 207.**

185. Simnad, M., and Smoluchowski, R. Effect of Proton Irradiation Upon the Electrode Potential of Tungsten. Phys. Rev., vol. 99 (2d ser.), No. 6, Sept. 15, 1955, pp. 1891–1892.

The experiments show that irradiation alters significantly the electrochemical properties of metals and that such measurements may be used to study the nature and extent of the effects produced. The tables give electrode potentials of Proton irradiated tungsten.

Sims, C. T. *See* abs. **96.**

186. Skaupy, Franz. Principles of Powder Metallurgy. Phil. Library, New York, N.Y., 1944, 80 pp., 69 refs.

Introduction: The metallic materials from which our apparatus, tools, and objects of daily life are formed consist either—which seldom happens—of a single crystal or in the majority of cases of an aggregate of tiny crystals of most diverse sizes. The size and manner of arrangement of these crystals differ in the same substance according to their origin and production, and it has long been known that numerous chemical and physical properties and accordingly their applicability for various useful purposes depend not unessentially on the size and arrangement of these small crystals. I shall here group together some especially instructive examples of the influence of the sizes of grains and also how, what up to now has seldom been considered, how in some cases the position and form of the grain boundaries among the crystallites is of decisive influence on the properties of the substance.

For purposes of comparison let us consider a drawn wire of wolfram and so-called unicrystal filament (Pintsch). Both can be bent and wound easily without breaking if they are not too thick. But if heated to about 2,000° C., then the wolfram becomes brittle, while the Pintsch wire has retained its flexibility unchanged. We find the explanation if we make lengthwise sections of the wires before and after heating, etched with suitable solvents. The drawn wire then shows before heating a fibrous structure (drawing structure); after heating, it is finely crystalline. The Pintsch wire shows before and after heating the same structure consisting of few crystallites, whose length amounts to a number (often very many) of fibre diameters. The unglowing wolfram wire evidently consists of a large number of crystallites parallel to the axis of the wire, developed by the drawing-out process. On heating, these crystal fibres disintegrate into very small crystals, while at the same time the flexibility of the wire disappears. Thus we reach the conclusion that a certain length of crystallites is essential for flexibility, since this length is common to the crystallites of the Pintsch wire and to the fibres of the drawn wire. To be sure, of importance for the flexibility of the drawn wire is the circumstance that the single fibres are very thin and can be shifted against each other lengthwise and are elastically flexible, just as a thick bundle of wires can be bent much more easily than a massive wire of the thickness of the bundle. To complete our explanation, one more observation will be useful. Pintsch wires also show a certain inclination to breaking, and this is all the greater, the shorter are the crystallites and it turns out that the break almost always takes place at the point of impact (grain boundary) between two crystallites. Now the brittleness of the heated crystalling wolfram wire is also comprehensible; it is evidently conditioned by the numerous breaking spots between the crystallites.

187. Skljarenko, S. I., Druzhinina, O. S., and Masal'tseva, M. M. [Electrodeposition of Tungsten and Its Practical Utilization.] Jour. Appl. Chem. (U.S.S.R.), vol. 13, 1940, pp. 1326–1331; Chem. Abs., vol. 35, 1941, p. 2422; Battelle Mem. Inst. translation 45R2.

A review. Periodic addition of $NiSO_4$ and WO_3 to keep the ratio W: Ni=3:1 constant, to the bath used by Gol'ts and Kharlamov (Chem. Abs., vol. 31, 1937 p. 1299), enabled preparation of a deposit 0.2 mm. and more thick. The deposits were not stable with respect to thermal treatment and corrosion and were mechanically weak. (57 refs.)

188. Smeaton, T. F. Tungsten: Its Preparation for Use in Electronics and Carbide Products, From the Refining of Non-Ferrous Metals. Proceedings of a Symposium held in London in July 1949. Book published by Inst. Min. and Met. (London) 1950, p. 367–386; discussion, pp. 387–390.

Conclusion: To answer the question How do you refine tungsten? is obviously difficult. It is, however, prepared in a very high state of purity by refining one or other of the intermediate products from which it is derived. For example, if a sample of "heavy oxide" which has been brought through process B is immediately reduced in one state at a top temperature of 925° C. a metal P is obtained, which should be nearly spectrographically pure and could at the worst only exhibit the most feeble indications of the presence of molybdenum and aluminum.

The production of pure tungsten is a simple matter. While this metal has presented manufacturers with many intricate problems, those concerning its purification have been by far the least abstruse.

189. Smith, G. F. Thermionic and Surface Properties of Tungsten Crystals. Phys. Rev., vol. 94, ser. 2, Apr. 15, 1954, pp. 295–308; Am. Soc. Metals Rev. of Metal Literature, item 211–M, Metals Rev., vol. 11, 1954, p. 369.

Plateaulike surface structure found. Shingle structure observed superimposed upon plateaus. Photograph, micrographs, tables, graphs, diagrams, 40 refs.

Smith, M. L. *See* abs. 170.

190. Smithells, C. J. Tungsten—Its Metallurgy, Properties, and Applications. 3d Ed., 1953. Chem. Pub. Co., Inc., 212 Fifth Avenue, New York (10), N.Y. Price $8.50. Am. ed. of book published by Chapman and Hall, Ltd. (London), 1952; Am. Soc. Metals Rev. of Metal Literature, item 87–V, Metals Rev., vol. 11, 1954, p. 647.

In a long review of this book by N. P. Allen, he states that—In the chapters dealing with the preparation and reduction of tungstic oxide and the production of ductile tungsten, the manufacturing processes are described in an intimate and detailed way, which adds interest to the reading. It is apparent that since the last edition (1936), the scale of operations in the industry has increased. Numerous additions to the section dealing with the measurement of the properties of metallic powders suggest that the methods of technical control have at the same time been refined.

191. ———. Creep Resistance of Tungsten Filament. Engineer, Feb. 15, 1946, pp. 148–149; Powder Met. Bull., vol. 1, No. 4, July 1946, p. 65.

C. J. Smithells points out that tungsten filament when converted to a single crystal, i.e., in the absence of grain boundaries, is completely stable against creep. Such tungsten single crystals show no sign of deformation after 4,000 hours. It is concluded that undoubtedly the presence of impurities affects creep and that in practice, particularly at high temperatures, it is necessary to take account of the material in the grain boundaries.

192. Smithells, C. J., Rooksby, H. P., and Pitkin, W. R. The Deformation of Tungsten Crystals. Jour. Inst. Metals, vol. 36, 1926, pp. 107–120.

Description of the change in the microstructure of sintered W bars, which takes place during swaging and wire-drawing of tungsten wires. *See* abs. 70 item 5190, p. 362.

Smoluchowski, R. *See* abs. 185.

193. Spier, H. L., and Wanmaker, W. L. (Philips Research Laboratories, Eindhoven, Netherlands). Influence of Additives on Particle Size of Tungsten Powder Prepared by Reduction With Hydrogen From Tungsten Trioxide. Philips Res. Repts., vol. 13, 1958, pp. 149–156; Chem. Abs., vol. 52, 1958, p. 11690.

The reduction with H of H_2WO_4 and of WO_3, prepared from H_2WO_4 by firing at 800°, was investigated. The addition of K silicate and K silicotungstates to

WO_3 resulted in a marked growth of W particles, whereas other additives, Ca $(NO_3)_2$, $Al(NO_3)_3$, $MgSo_4$, and KCl tend to give small particle size. Thermobalance measurements on pure $K_2H_2SiW_{12}O_{40}$, $K_4SiW_{12}O_{40}$, and $K_8SiW_{11}O_{39}$ indicate that reduction takes place between 500° and 800°. Total weight loss corresponds to reduction to *a*-W, K_2WO_4, and SiO_2.

194. Spitsyn, V. I., and Torchenkova, E. A. (M. V. Lomonosov State Univ., Moscow). An Application of the Isotope Exchange Method to the Structure Study of Aquapoly and Heteropoly Compounds. Doklady Akad. Nauk S.S.S.R., vol. 95, 1954, pp. 289–292; Chem. Abs., vol. 49, 1955, p. 15591.

The W^{185} isotope (designated W*) was used in the study of the relative stability of tungstate anions in solution. The purity of the isotope compounds was tested by the half-life determination and the measurement of the maximum energy of the β-radiation. Silico- and phosphotungstic acids were prepared from the ordinary and W* para- and metatungstates. The double-exchange reaction between the para- and metatungstates did not proceed instantaneously (contrary to Sonchay, Chem. Abs., vol. 38, 1944 p. 6224; vol. 40, 1946 p. 4310). The ordinary tungstate anion did not enter into double-exchange reactions with the heteropoly anions, while the hexatungstate anion of the paratungstate did, which might indicate it to be the structural unit of heteropoly anions. Na phosphotungstate and the acidified Na_2W^*O solution interact very rapidly, while the crystals of $Na_2W^*O_4$ react much more slowly than does the freshly formed paratungstate. Two heteropoly compounds, the radioactive silicophosphotungstic acid and the phosphotungstic acid, interact to an extent of only 20 percent at pH 1.8 in any length of time between 5 minutes and 240 hours. At higher pH, the reaction is more rapid. The bondings of the added ions in the inner reaction is more rapid. The bondings of the added ions in the inner spheres in metatungstate anions and the phosphotungstate anions appear to be quite different.

Stagg, L. J. *See* abs. 46.

Starliper, A. G. *See* abs. 106.

1954. Stranski, I. N. Forms of Equilibrium of Crystals. Discussions, Faraday Soc., vol. 5, 1949, pp. 13–21; discussion, pp. 66–79; Met. Abs., vol. 17, 1950, p. 497.

Recent theories and experiments on the equilibrium shapes of crystals grown from supersaturated vapours are reviewed, including, of metallurgical importance, the growth of zinc, cadmium, and tungsten crystals. The growth form of crystals and the mechanism by which they may subsequently change to the equilibrium form also are discussed. Growth from fused liquids is mentioned with reference to cadmium crystals.

196. Stranski, I. N., and Suhrmann, R. Electron Emission From Crystalline Metal (Tungsten) Surfaces and its Relation to the Laws of Crystal Structure. I. Pure Surfaces of Single Crystals. II. Surfaces of Single Crystals With Adsorbed Foreign Atoms. Ann. Physik, (VI), vol. 1, 1947, (4/5), pp. 153–168, pp. 169–180; Met. Abs., vol. 17, 1950, p. 420.

I. The work function of emitted electrons, as reported elsewhere, is related to the atomic structure of the corresponding planes of a tungsten single crystal. It is concluded that the work function is closely connected with the work of separation of the most weakly bound atom of the surface, with the special surface energy of the crystal plane, and with the smallest distance between atoms on the surface, but it is impossible to say which of these is the predominant factor.

II. The crystallographic and energy laws of the adsorption of foreign atoms at different crystal planes is discussed on the basis of the experimental evidence of electron emission of tungsten crystals contaminated with caesium and barium atoms. It is possible to deduce which kind of atoms can be adsorbed on particular crystal planes. The close agreement with the experimental results shows that caesium and barium are adsorbed as atoms and not as ions. The diffusion of the adsorbed atoms proceeds along hollow edges of the crystal surface, while the measured energy of activation corresponds to the energy of separation of atoms in hollow corners.

Suhrmann, R. *See* abs. 196.

Taylor, H. S. *See* abs. 83.

Terunuma, Kiyoshi. *See* abs. 144.

197. Tesen, D. E. Tungsten and Molybdenum Wire. FIAT Final Rept. 413, Dec. 19, 1945, 17 pp., diagrams. (PB–18785) (Photocopy, \$2, microfilm, 50 cents, available Photo Duplicating Service, Publications Board Project, Library of Congress, Washington 25, D.C.; also on file, Bureau of Mines Library, College Park, Md.

A summary of German practices is given. A review, by plants, on tungsten includes A. G. Starck (Gebruder Borches), Osram Glühlampenfabrik, Radium Electric Co., Metallwerke Plansee, and Others. A similar review of molybdenum plants is the same list with the exception of Starck. Three tungsten-extraction flowsheets are given. In all cases the metal trioxide is obtained in pure condition ready for reduction by hydrogen, except that when carbide is to be made, the oxide is mixed with C and other oxides like TiO_2. Hydrogen-reduction schedule for production of 860-gram. and 650-gram. ingots are given temperatures beginning at 550°C. and ending at 820°–1,000° C., depending on stage of reduction. Two grades of tungsten wire are made, one for rough service, the other for general lighting. Reduction tubes of chrome steel. Sintering is done with 90–92 percent of the amperes that would cause fusion. Swaging dies are of solid hard metal for small sizes and with hard-metal inserts for large sizes. Hard metal is 86 percent WC and 14 percent Co, or it is 85 percent WC, 2 percent TiC, and 13 percent Co.

Drawing was done with hard metal dies down to 0.25 mm., using reduction of only about 10 percent per pass and annealing in hydrogen. For wire smaller than 0.25 mm., diamond dies are used.

In sheet rolling the ingots were first forged to 50 percent reduction in thickness before starting rolling. Osram includes three cleaning and grinding operations during rolling to keep a cleaner smoother surface.

Sketeches of the Metallwerke Plansee reduction furnace are given, showing molybdenum rod resistors, protected by hydrogen, used for heating; the rods being 2.5 mm. diameter resting on alundum tube.

A sketch of Metallwerke's MoO_3 sublimation furnace and fume filter is given; MoO_3 calcine from roasting MoS_2 ore concentrate being heated in a crucible with electric resistors and a current of air blown over it.

198. Thomson, B. Embrittlement of Tungsten Wire. Nature, vol. 176, No. 4477, 1955, p. 360; Met. Abs., vol. 23, 1955, p. 271.

Very slight traces of nickel on the surface of tungsten can cause embrittlement. Contamination can occur from contact with nickel formers or rollers. When contaminated wire is heated, there is rapid diffusion of the nickel into the tungsten, and the wire becomes brittle at temperature above 1,200° C.

199. Ting, C. W., and Ting, H. H. Purification of Tungstic Oxide Extracted From Tai-Ho-Shan Wolframite. Chinese Cehm. Ind. Eng., vol. 1, No. 1/2, 1950, pp. 37–48. (English summary); Chem. Abs., vol. 47, 1953, p. 1344.

Various methods of purification have been studied. The following yields WO_3 99.99 percent pure, containing only 0.007 percent Fe_2O_3 and 0.003 percent SiO_2: (1) Precipitation of crude WO_3 from Na_2WO_4 solution, followed by solution in NH_4OH; (2) crystallization of ammonium paratungstate from the solution, followed by decomposition with NaOH; (3) repetition of step (1), followed by crystallization of ammonium paratungstate, which, when acidified, yields WO_3 of high purity.

Ting, H. H. *See* abs. **199.**

200. Tomoashov, N. D. Electrochemical Theory of Corrosion and Means for Increasing the Corrosion Resistance of Metal Alloys. Uspekhi Khim., vol. 24, 1955, pp. 453–470; Translators' Monthly, item ATS–RT–342, December 1957.

No abstract.

Torchenkova, E. A. *See* abs. **194.**

Tormyn, J. *See* abs. **61.**

Trapnell, B. M. W. *See* abs. **171, 172.**

201. Troitskii, K. V. The Extraction of Tungsten Thiocyanate Complex by Organic Solvents With Radioactive W^{185} as Indicator. Primenenie Mechenykh Atomov v Anal. Khim., Akad. Nauk S.S.S.R., Inst. Geokhim. i Anal. Khim. 1955, pp. 133–47; Chem. Abs., vol. 50, 1956, p. 3940.

Tungsten was extended by Et_2O from solutions containing varying amounts of Na_2WO_4, NaOH, KSCN, $SnCl_2$, and HCl. At 0.25–1.2γ of W per ml., the extraction was 58–60 percent; at 2.5–6.0γ ml., 98–99 percent; and at 12–90 γ/ml., 80 percent. The ratio of W in the original solution to that in the ether layer on a log scale gives a straight line. In the absence of KSCN the extraction of W by Et_2O was 6.2 percent; at 0.245-mole KSCN/l., the extraction of W was 93 percent; on heating this solution, the extraction was 99.9 percent. The optimum quantity of KSCN was 0.15 mol./l. NaOH had little effect on the extraction. When $SnCl_2$ dissolved in concentrated HCl was added after the addition of HCl, the solution did not color, and varying the cencentration of $SnCl_2$ had no pronounced effect; the extraction was 66–67 percent. When $SnCl_2$ was added before the HCl, the solution became green-yellow. In W solutions containing 0.0–6.0 mole/l. HCl, 0.0–1.6 percent W was extracted; with 9 mole/l. HCl 6 percent W was extracted. In the presence of KSCN, at small HCl concentrations, only little W was extracted; at 4.5–5.5 mole/l. HCl the W extracted was 75–85 percent; the optimum HCl concentration was 6–7 mole/l. CH_3Cl and CCl_4 did not extract W. Other organic solvents extracted the following percentages: isopropyl ether 45.8, Et_2O 72.7, Et acetate 76.5, amylacetate 77.3, amyl formate 77.5, BuOH 8.13, isoamyl alcohol 82.5, methyl butyl ketone 94.3, and cyclohexanone 99.2 percent. Of the complex-forming substances tested Na_2HPO_4 and Na ascorbate had little effect on the extraction of W; Na citrate, Na oxalate, and Na tartrate lowered the amount of W extracted.

Turner, L. A. *See* abs. **104, 105.**

Turovtseva, Z. M. *See* abs. **137.**

Ueda, Ryûzô. *See* abs. **176–178.**

202. Van Arkel, A. E. Reine Metalle. [Pure Metals.] Julius Springer, Berlin, 1939.

Methods of reduction; methods for purification; purifying tests. Special part for the individual metals. Includes refractory and rare metals. *See* abs. 70, item 1913, p. 135.

203. ———. Uni-Crystalline Tungsten. Physica, vol. 3, 1923, pp. 76–87; Chem. Abs., vol. 17, 1923, p. 2068.

Tungsten crystals are produced by heating a W wire consisting of one crystallite in an atmosphere of supersaturated WCl_6. The W thus obtained is very soft and can be worked without any special treatment. By that treatment the single-crystal structure is lost, as proved by X-ray analysis, as well as by the fact that no single crystal could be found under conditions favoring growth after mechanical treatment. At the same time, the X-ray analysis proved rigidly the single-crystal structure before the working. As the plane of cleavage proved to be the (100) plane, it is possible to explain why the mechanical properties depend on the orientation of the crystal axes.

204. Van Liempt, J. A. M. Diffusion in Metals in the Solid State. Metallwirtschaft, vol. 7, 1928, pp. 558–559. A review covering the diffusion of molybdenum in tungsten and carbon in tungsten; refs. *See* abs. **70**, item 4859, p. 337.

205. ———. The Binary Systems Na_2WO_4–Li_2WO_4, K_2WO_4–Li_2WO_4, Li_2WO_4–WO_3, Na_2WO_4–WO_3, and K_2WO_4–WO_3. Ztschr. anorg. Allgem. Chem., vol. 143, 1925, pp. 285–292; Chem. Abs., vol. 19, 1925, p. 1826.

No abstract.

206. ———. The Electrolytic Deposition of Tungsten. Ztschr. Elektrochem., vol. 31, 1925, pp. 249–255.

Description of production of tungsten powder by fusion-electrolysis of alkali tungstates (for example, lithium tungstate) at 900° C. (1,650° F.) and higher temperatures through formation of so-called "tungsten-bronzes." *See* abs. **70**, item 958, p. 67.

See also Burger, W. G., abs. **25.**

Vanselow, R. *See* abs. **47.**

207. **Vasil'eva, I. A., Gerasimov, Ya. I., and Simanov, Yu. P.** (M. V. Lomonosov State Univ., Moscow). The Equilibrium of Tungsten Oxides With Hydrogen. Zhur Fiz. Khim., vol. 31, 1957, pp. 682–691; Chem. Abs., vol. 52, 1958, p. 35.

Two modifications of WO_3 were obtained. WO_3 I was obtained by the ignition of WO_3 for 10 to 12 hours at 800° and slow heating in the furnace to room temperature, and WO_3 II by heating to 900°–1,100° for 5 to 6 hours and rapid cooling. The structure of WO_3 II was similar to Glemser and Sauer's rhombic structure (Chem. Abs., vol. 38, 1944, p. 1967), whereas WO_3 I was monoclinic, and the parameters agreed closely with the results of Magneli, and others (Chem. Abs., vol. 47, 1953, p. 2693). The structure of the intermediate W oxides depended on the structure of the WO_3 reduced. The interplanar distances of $WO_{2.90}$, $WO_{2.72}$, and WO_2 obtained from WO_3 II were measured; its reduction at 600°–791° proceeded in four stages, whereas below 584° the intermediate oxide $WO_{2.72}$ disappeared, and the reduction proceeded in three stages. The thermodynamic properties of WO_3 II were: $\Delta H^\circ_{298}=-205.3$; $\Delta Z^\circ_{298}=-186.2$ kcal./mol.; $\Delta S^\circ_{298}=-63.90$; and $S^\circ_{298}=17.4$ cal./mol.

208. **Venturini, Jean.** Thermodynamic Study of Reduction of Tungstic Oxide With Hydrogen and With Carbon Monoxide. Cong. Matériaux Résistants à Chaud. AERA, 1951, pp. 307–331; Chem. Abs., vol. 48, 1954, p. 3767.

Preparatory theoretical work for experimental research on direct reduction of metal oxides at elevated temperature is beset with uncertainties, anomalies, and missing data on physical constants and of equilibria. This is especially the case for the oxides of tungsten, WO_3, WO_2, and W_2O_5. Of the two latter compounds, neither the standard entropy nor the specific heats are known. In order to determine the entropy of these substances, different methods were applied that can mutually confirm the underlying assumptions and that are based upon earlier work referring to dissociation tensions, reaction heats, etc. For extrapolating the phenomena beyond 1,800°–1,900° K., computation must take into account important dissociations, neglected by former investigators, which are particularly pronounced from 2,200° K. on, namely, dissociation of water vapor into its elements, of H_2 into atomic H, and of O; last but not least, the vapor pressure of W must be considered, too, at temperatures above 3,000° K. The various reactions and equilibria that take place in certain temperature ranges are calculated and demonstrated with numerous graphs. Above 2,000, K. there is direct reduction of WO_3 into metal, without going through the stages of lower oxides.

Völz, Hans G. *See* abs. **69.**

Wang, Chung Yu. *See* abs. **121.**

Wanmaker, W. L. *See* abs. **193.**

209. **Ward, J. J., Ray, J. P., and Herres, S. A.** Calculations for Reactions of Cr, Mo, Ti, and W With Oxygen, Nitrogen, Hydrogen, Carbon, Sulfur, and Refractory Oxides. Douglas Aircraft Co. Rept. R-108, 1948, 97 pp.; Chem. Abs., vol. 47, 1953, p. 4822.

Practical considerations, including availability and cost, indicate that primary emphasis should be laid on Cr, Mo, Ti, and W as bases for alloys with good strength at elevated temperature. The high reactivities of these metals with O, N, H, C, and refractory oxides normally used as furnace linings for containing other molten metals lead to serious problems in producing the alloys and using them for high-temperature service. Conditions under which reactions could occur are calculated from physiochemical principles.

210. **Wendt, G. L., and Irion, C. E.** Experimental Attempts to Decompose Tungsten at High Temperature. Jour. Am. Chem. Soc., vol. 44, 1922, pp. 1887–1893.

Apparatus and method for attaining a temperature above 20,000° F. (11,000° C.) are described. When fine W wires are exploded in vacuo by electric arc of high voltage at such temperature, the spectrum of helium appears in the produced gases. *See* abs. **70,** item 2406, p. 172.

Wirth, W. *See* abs. **14.**

211. **Wortman, R., Gomer, R., and Lundy, R.** (Univ. of Chicago. Surface Diffusion of Hydrogen and Oxygen on Tungsten. Jour. Chem. Phys., vol. 24, January 1956, pp. 161–162.

Field emission studies of the surface migration of hydrogen and oxygen on tungsten at low and very high coverages have been reported previously. Slow activated diffusion occurs in the former case, while spreading with a sharp boundary, moving almost uniformly over the tip, occurs for very high averages with both gases.

This article describes the behavior observed when one monolayer is initially deposited on the covered portion of a 011 oriented tungsten tip. Under these conditions migration sets in at 205° K. with hydrogen and 500° K. with oxygen.

The findings on these studies show that two types of surface heterogeneity are active in decreasing heats of adsorption with increasing coverage on metal surfaces: (1) Crystallographic anisotropy and (2) the existence of inherently different adsorption sites on a given face.

See also Gomes, R., abs. **71.**

212. **Wright, S. J.** The Elasticity of Pintsch Crystals of Tungsten. Proc. Roy. Soc. (?), vol. 126, 1930, pp. 613–629.

In tungsten wires of large diameter, it was found that a large percentage of them consisted of two or three crystals, and that the modulus of elasticity was higher than in true single crystal wire. *See* abs. **70,** item 5382, p. 376.

Wysong, W. S. *See* abs. **79.**

Yamaguchi, Noboru. *See* abs. **149, 150.**

Yamamoto, Masayuki. *See* abs. **150.**

213. Yntema, L. F. Electrodeposition of Chromium, Molybdenum and Tungsten. Jour. Am. Chem. Soc., vol. 54, 1932, pp. 3775–3776; Chem. Abs., vol. 26, 1932, p. 5262.

Tungsten has been deposited from aqueous media (Fink and Jones, Trans. Am. Electrochem. Soc., vol. 59, 1931, p. 461) of alkaline nature. It also may be deposited from acid solutions in bright coherent form. Two grams of tungstic acid is dissolved in potassium hydroxide, 5 cc. of 2.5 M citric acid. The solution is diluted to 20 cc. A platinum foil (5 sq. cm.) is the anode, and a copper sheet is used as the cathode. Similar results may be obtained if sodium hydroxide and tartaric acid are substituted for potassium hydroxide and citric acid, respectively. Tungsten also may be obtained from solutions containing acetic acid and glycerol or glucose.

214. Yntema, L. F., and Percy, A. L. Tungsten, Ch. in Rare Metals Handbook. Reinhold Pub. Corp., New York, N.Y., 1956, pp. 483–500.

Ores, metallurgy, working properties, fabrication, and applications. (Photographs, tables, and 9 refs.)

215. Zambrano, Egberto (General Elecric, S.A., Rio de Janeiro, Brazil). Tungsten Production in the Mazda Plant of General Electric, S.A. Rio de Janeiro. A.B.M. (Bol. assoc. brasil, metais) (Sao Paulo), vol. 10, 1954, pp. 293–301; Chem. Abs., vol. 50, 1956, p. 745.

The operation of the first Brazilian plant producing metallic W, an addition to the filament factory of General Electric in Rio de Janeiro, is described and illustrated by eight photographs. Domestic raw materials are used. Scheelite exists in 200 deposits in northeastern Brazil and in the States of Sao Paulo and Rio Grande do Sul, wolframite in Santa Catarina. Successive caustic and acid digestions of concentrated ores produce pure NH_4 paratungstate, which is then reduced to the powdered metal. Ductile W is made by the Coolidge process (U.S. patent 1,082,933, Chem. Abs., vol. 8, 1914, p. 633).

SELECTED PATENTS

(Arranged alphabetically)

216. Alexander, P. P. (Assigned to Metal Hydrides, Inc.) Reduction of Refractory Oxides. U.S. Patent 2,584,411, Feb. 5, 1952; Chem. Abs., vol. 46, 1952, p. 5276.

An oxide of Zr, Ti, Cr., W, Mn, or Th is heated with an alkaline-earth metal in an atmosphere of H to about 500°. The heat of formation of the hydride of the alkaline-earth metal raises the temperature to 800°-900° and reduces the oxide.

217. Andrieux, J. L. Electrolytic Production of Metals, Metalloids or Compounds. French Patent 638,345, Dec. 1, 1926; Chem. Abs., vol. 23, 1929, p. 46.

A fusion bath composed of boric acid or borax with the addition of fluorides, chlorides, or phosphates is used to dissolve oxides of metals or metalloids or other O compounds from which the elements or their borides, or compounds of metals and metalloids may be obtained by electrolysis.

218. ———. Electrolytic Processes. French Patent 34,495, Oct. 17, 1927 (addition to French Patent 638,345); Chem. Abs., vol. 23, 1929, pp. 46, 5120.

In all electrolytic operations, particularly fractionated electrolysis, refining of metals, gabanic deposition, electrolytic cementation, fusion baths composed of boric anhydride, borax, or other B compounds, along with one or more other substances are used.

219. Armstrong, H. H., and Menefee, A. B. Electrodeposition of Tungsten and Its Alloys. British Patent 478,640, Jan. 18, 1938; Chem. Abs., vol. 32, 1938, p. 4445.

In the electrodeposition of W from an aqueous flouride bath, soluble anodes are used that consist of discrete W and (or) W carbide particles packed into a perforated acid-resistant container or formed into a compact mass; the mass may include a cementing agent, preferably carbonaceous, and be compacted by heat and (or) pressure. W oxide may be incorporated as an additional constituent in either form of electrode. Other metals, for example, Fe, Ni, Co, Sb, Cd, Cr, may be incorporated as powders in the anodes for the electrodeposition of W alloys. An alternative form of anode for the electrodeposition of W alloys comprises a core of C or metal with an electrodeposited coating of the constituent metals. (Chem. Abs., vol. 31, 1937, p. 4605.)

220. Bates, C. F. W. (Assigned to Ohio Instrument Manufacturing Co.) Purification of Tungsten. U.S. Patent 1,896,606, July 2, 1933, British Chem. Abs., vol. 53, 1934, p. 24.

Metallic tungsten (reduced by H_2) to be freed from included oxide is mixed with silver compacted, the silver volatilized out, and the mass forged.

221. Bederlunger, Hans. Removing Arsenic From Tungsten Ores. Austrian Patent 167,832, Mar. 10, 1951; Chem. Abs., vol. 46, 1952, p. 6580.

The ores are melted in an arc furnace or in a resistance furnace at such temperatures that As and (or) its oxides sublime. The melting capacity is approximately 1,000 kg. per hour and the current consumption approximately 600 kw.-hr. per ton. The method is applicable too for other ores having low vapor pressures at high temperatures.

Brennan, J. H. *See* abs. **222.**

222. Burwell, Blair, and Brennan, J. H. (Assigned to United States Vanadium Corp.) Recovering Tungsten From Low-Grade Ores. U.S. Patent 2,459,868, Jan. 25, 1949; Chem. Abs., vol. 43, 1949, p. 3768.

Low-grade flotation and table concentrates are digested with about 570 percent of the theoretically necessary Na_2CO_3 to convert the W in the ore to Na tungstate. The digester uses steam at 200 p.s.i. pressure. Operation is countercurrent; final solution is neutralized with acid and the W precipitated by lime addition.

223. Carosella, M. C. (Assigned to Union Carbide and Carbon Corp.) Tungstate Solutions Containing as Impurities Antimony, Arsenic, or Molybdenum. U.S. Patent 2,556,255, June 12, 1951; Chem. Abs., vol. 45, 1951, p. 9861.

Alkaline earth-metal tungstates, free from Sb, As, or Mo, are prepared by treating an aqueous solution containing soluble sulfide, preferably NaHS. The initial pH of the solution is adjusted to between 5 and 8, and during the sulfiding to between 8 and 11. The sulfide is added in excess of the stoichiometric proportion sufficient to react with all the impurities. The solution is maintained at a temperature between 65° and its b.p., and a soluble alkaline earth-metal compound, such as $CaCl_2$, is added to precipitate a pure alkaline earth-metal tung-state.

224. Claude-Paz and Silva Etablissements. [Purifying Tungstic Acid] Société anon. pour les applications de l'electricite et des gaz rares. French Patent 963,796, July 20, 1950; Chem. Abs., vol. 46, 1952, p. 3227.

Freshly precipitated and washed $WO_3.H_2O$ (100 g.) is boiled in aqueous NH_3, third commercial strength, and filtered warm. The solution is concentrated to give 70 g. crystallized $(NH_4)_6W_7O_{24}$. This is washed and boiled with 700 cc. water, the solution is filtered, reboiled, and 80 cc. HNO_3, 1.3 sp. gr., is added. The steps may be repeated to give a very pure $WO_3.H_2O$. If only 20 percent of the HNO_3 is added, molybdic acid is precipitated first, and this may be filtered off; the rest of the HNO_3 is then added.

225. Davis, Michael, and Lever, R. F. (Assigned to National Research Development Corp.) Zone Melting and Refining of Metals. U.S. Patent 2,809,905, Oct. 15, 1957; Chem. Abs., vol. 52, 1959, p. 2722.

A solid rod of the material to be treated is mounted in a metallurgical apparatus and then is heated by electron bombardment to affect melting and refining by the floating-zone method. The apparatus consists of a rigid, vacuum-tight chamber with accessories to draw the rod longitudinally through the electron source and its focus shields so that a molten zone traverses the length of the rod. Single crystals of W, Ta, Re, Mo, V, Pt, Ni, Si and Ru have been prepared in this way. (Chem. Abs., vol. 50, p. 9187; and U.S. Patent 2,792,317, Chem. Abs., vol. 51, p. 11896.

226. Deutsche Gold und Silber-Scheideanstalt (Formerly Roessler). Production of Metals by Reduction of Their Halides. British Patent 741,630, Dec. 7, 1955; Chem. Abs., vol. 50, 1956, p. 9991.

Ti, Zr, Si, V, W, or Mo is produced continuously as a compact solid metal from a molten mass, without contamination, by the reduction of a metal halide (I) (heat of formation not over 70 cal. per gram-atom of halogen present) with an alkali metal, such as Na, or Mg. Both I and Na are directed as separate, preheated vapor streams into a reaction chamber, containing an inert atmosphere. They are burned in a flame, which is impinged on a condensing surface, made concave to the flame. The condenser is held at a temperature below the melting point of the metal as a compact mass. For the continuous operation the temperature of the collecting surface is adjusted to yield a thin molten layer of metal on the surface of the deposited metal layer, and it is gradually drawn from the reaction chamber.

Dice, C. M. *See* abs. **243.**

227. Edelmann, Kurt. (Assigned to Chemische Fabrik von Heyden Akt.-Ges.) Dry, Colloidal, Soluble Tungstic and Molybdic Acids. German Patent 710.224, July 31, 1941; Chem. Abs., vol. 37, 1943, p. 3888.

The dry acids are obtained by dialyzing the respective colloidal acids, which are produced by adding HCl to alkali tungstate or molybdate. The colloidal solution is matured, but not flocculated, and dialyzed. The dialysis is interrupted before appreciable quantities of the sol pass the membrane. The sol is aged, whereupon the dialysis is finished and the sol evaporated.

228. Egyesült Izzólámpa es Villamossági R.-T. Tungsten Filaments. British Patent 468,449, July 6, 1937; Chem. Abs., vol. 32, 1938, p. 436.

In manufacturing double or multiple helical W incandescent bodies for use in gas-filled vessels containing N by subjecting to at least one heating a W wire wound on at least two cores made of metal of high metling point and subsequently removing the cores, the incandescent body, before being mounted in the vessel that receives the gas filling, is heated to such a temperature between 1,450° and the recrystallization temperature of W and for such time that not only are the internal stresses eliminated but, under continued heating or reheating, the content in the incandescent body of the material taken up from the core is less than 0.4 percent. At least one core wire is made of Mo, Ta, or Zr. In an example a W wire that assumes a macrocrystallized structure during heat treatment is wound on primary and secondary cores of Mo and drawn for a few seconds through a H atmosphere in a furnace at 1,500°, the secondary helix is then cut into pieces of the required length, which are caused to incandesce for 1 minute at 1,600° in a W tube furnace through which a mixture of H 25 percent and N 75 percent is passed, the cores are then dissolved out of the helices with a mixture of H_2SO_4 and HNO_3 to which a few drops of Hg are added. The Mo content of the resultant W bodies is about 0.04 p.

229. ———. (Tivador Millner and Jenö Neugebauer, inventors). Sintered Tungsten Articles. Austrian Patent 198,531, July 10, 1958; Chem. Abs., vol. 52, 1958, p. 14509.

Tungsten articles are made from W powder by pressing, sintering, hammering, and drawing, the pressed rods being purified between the presintering and the final sintering to remove excess addition agents and contaminants by evaporation and/or chemically The heating is preferably conducted electrically with 40–50 percent of the current strength required for melting the metal. Preferably, a 20–60 percent, especially a 40 percent HF solution, is used for dissolving the impurities.

230. Fink, C. G., and Jones, F. L. Treatment of Tungstate. U.S. Patents 1,885,701 and 1,885,702, Nov. 1, 1932.

Sodium tungstate or ammonium paratungstate is electrolyzed with a Pt anode and brass cathode; the W plating can proceed only up to a certain thickness and then stops, but if solution contains $NiCO_3$ the plating process continues. *See* abs. **70**, item 720, p. 440.

231. Fink, C. G., and Ma, Chuk Ching. Electrolytic Production of Tungsten. U.S. Patent 2,554,527, May 29, 1951.

A good prior literature review of electrolytic extraction of tungsten precedes the disclosure that tungsten minerals can readily be dissolved in fused alkali phosphates like sodium pyrophosphate or metaphosphate and that these fusions can be electrolyzed to yield substantially pure tungsten metal grains.

Graphite is the preferred anode, and for cathode, graphite or iron could be used; but the preferable metal is molybdenum or tungsten. Best temperature of cell is 1,050°–1,250° C. and current density 2.5–3.5 a./sq. in. of cathode. Current efficiency rises sharply as temperature is raised from 950° to 1,025° C., then rises more slowly to maximum at 1,050°–1,150°. Efficiency is also maximum with 3 a./sq. in. Greatest purity of product is at 2.5 a./sq. in. Good current efficiency is 80 percent with yields of 1.12 pound of W per kw.-hr. The product analyzes 99.7 percent W.

232. ———. Method of Producing Tungsten. U.S. Patent 2,463,367, Mar. 1, 1949. Chem. abs. vol. 43, 1949, p. 4964.

Pure crystalline grains of W are produced directly from oxidic W-ores and their concentrates by mixing the W-containing material with molten NaB_4 and maintaining the solution so obtained at a temperature between 950° and 1,300° C. (1,740° and 2,370° F.) *See* abs. **70**, item 766, p. 443.

Fleck, Gustav. *See* abs. **240.**

233. FOULKE, TED, MAYFIELD, O., AND HOLTAN, H. M., (Assigned to General Electric Co.). Tungstic Acid. U.S. 2,366,250, Jan. 2, 1945.

A method of producing anhydrous tungstic acid in bulky loose, finely divided form, by reaction between a tungstate solution and a solution of another acid, which comprises introducing the tungstate solution into a hot agitated body of the acid solution in the form of hot discrete droplets of a size and degree of dispersion approximately the same as is produced by dropping the tungstate solution from a capillary tube into the acid at a rate that corresponds to the equation $R=9.1\times(1.083)^x$, where R is the rate of flow in cc./min. and x is the height in inches of the orifice of the capillary above the surface of the acid.

The drawing shows a reservoir of Na_3WO_4 (?) solution descending through a manifold to multiple capillary tips of jets and dropping into a solution of HCl or HNO_3 heated by live steam.

234. FREDENBURGH, M. N. (Assigned to Radio Corp. of America.) Processing Tungsten and Molybdenum Powders. U.S. Patent 2,666,696, Jan. 19, 1954; Chem. Abs., vol. 48, 1954, p. 6948.

To increase the apparent density of W and Mo powders and to obtain a narrow particle size range (0.1–8μ) with a controlled particle size distribution peaking at 1–2μ the powders are slugged by presintering and then reground. Commercial powders supplied to a specification of 0.10μ particle-size range are presintered for one-half hour in an atmosphere of dry H at 1,500° for Mo, 1,600° for Mo plus W, and 1,700° for W. The slugs are crushed to pass through a No. 8 sieve, and the product is then ball-milled.

235. GRASSO, D. J. B. Reducing Metallic Oxides. French Patent 979,503, Apr. 27, 1951; Chem. Abs., vol. 47, 1953, p. 7426.

Metallic oxides, such as those of Fe, Mo, and W, are mixed with an oxide that absorbs CO_2, for example, BaO or CaO. A mixture of H and CO_2 is passed over the heated oxides. Exothermic absorption of the CO_2 maintains the temperature high enough for reduction to take place.

236. HALL, R. D. (Assigned to Westinghouse Electric Corp.) Consolidation of Metal Powder. U.S. Patent 2,675,310, Apr. 13, 1954.

The metal powders, W, Mo, Ta, Ti, or Zr, all of which melt at or above 1,800° C. are difficult to sinter after pressing on account of the type of heating equipment needed at the temperatures required. Nine claims apply to tungsten, five to molybdenum, and four to the group.

Green pressed shapes can be consolidated chemically by heating the tender presslings between 1,000° C. and 1,500° C. where such a reaction as $W+3Cl_2=WCl_6$ is reversible and goes to the right below 1,000° C. and to the left above 2,000° C. In the reversible range in an inert atmosphere containing preferably 0.0066 to 0.0132 percent by volume (permissibly up to 1 percent) of Cl_2, Br_2 or I_2 *metal halide is repeatedly formed* and decomposed until the mass is consolidated to a point where it can be worked and deformed as a sintered mass can.

In the case of Mo the temperature range is 750°–1,150° C. and about 2 hours is needed. For some of the metals, nitrogen is an inert gas, and H_2 can be used for Mo, W, and Ta. Vacuum can be used for any. Action of gas can take place as a first step at a lower *temperature, just long enough to strengthen the shape,* after which the temperature is raised to the appropriate operating range.

237. HARTMANN, HELLMUTH. Electrolytic Manufacture of Tungsten. German Patent 514,365, Sept. 11, 1928; Chem. Abs., vol. 25, 1931, p. 1448.

Tungsten is manufactured by electrolyzing a solution of WO_3 in fused alkali phosphate, with or without H_3PO_4 or other phosphates. An example is given. Other heavy metals, for example, Mo, Ta, V, and Nb, may be extracted similarly.

HOFFMANN, H. *See* abs. **241.**

HOLTAN, H. M. *See* abs. **233.**

238. HURD, D. T. (Assigned to General Electric Co.) Tungsten and Molybdenum Carbonyls. U.S. Patent 2,557,744, June 19, 1951; Chem. Abs., vol. 45, 1951, p. 8728.

W and Mo carbonyls can be prepared by treating CO with an oxychloride of the metal in the presence of granular Al and a small amount of carbonyl of Fe, Ni, or Co. The oxychloride is allowed to react with Al in anhydrous Et_2O containing a small amount of $Fe(CO)_5$ at a pressure of 1,500 p.s.i. CO and a temperature of 100°. Yields up to 75 percent of the theoretical can be obtained, depending on the reaction time. (Chem. Abs., vol. 45, 1951 p. 7341.)

JONES, F. L. *See* abs. **230.**

239. KASEY, J. B. Tungstic Oxide. U.S. Patent, 2,801,152, July 30, 1957; Chem. Abs., vol. 51, 1957, p. 17122.

Clean WO_3, free of Mo compounds, is produced from all fine W ores (100–200 mesh) by dissolving the W in concentrated HCl at 65°–70°. It is very important that the temperature limits are closely observed and that for each gram of W at least 20 cc. of concentrated HCl is present. Under the specified conditions the dissolving is complete after 30 minutes maximum. After separating the solution from the insoluble gang, the W is precipitated as WO_3 by heating the solution to 95°. After renewed filtration and thorough washing with dilute HCl, a product is obtained. A representative spectrographic analysis is Ti 0.04, Si 0.02, Na 0.008, Mg 0.002, B 0.002, Ca 0.0007, Fe 0.006, Al 0.002, Bi 0.0005, Mn 0.0003, Cr 0.0003, and Cu 0.0001 percent. For economical production the gaseous HCl losses must be kept to a minimum, and the HCl combined with impurities must be recovered by distillation with H_2SO_4.

240. KÖLBL, FRANZ, MESSMER, KARL, AND FLECK, GUSTAV. (Assigned to Metallwerk Plansee G.m.b.H.) Metal Powders of Fine Particle Size. Austrian Patent 166,923, Oct. 10, 1950; Chem. Abs., vol. 46, 1952, p. 7510.

Finely divided metal oxides or metal oxide hydrates are placed on supporting sieves in a furnace so that the reducing gas (H, optionally mixed with 5–25 volume percent NH_3) flows from underneath, also through the oxide material. When the reduction is performed in a tubular revolving furnace, the sieves may be in the form of concentric tubes. The process may proceed in several steps and is useful for obtain-

ing W, Mo, Fe, Ni, Co powder, especially for obtaining W powder from WO_3, tungstic acid, and $(NH_4)_2WO_4$.

241. Koref, F., and Hoffmann, H. Single-Crystal Wire of Tungsten or Similar Metal. U.S. Patent 1,617,161, Feb. 8, 1927; Chem. Abs., vol. 21, 1927, p. 888.

A single crystal is built up to larger size by deposition of the same kind of metal from a gaseous atmosphere at such limited rate as to avoid formation of small crystals. For the deposition of W an atmosphere of WCl_6 and H may be used at a temperature of about 1,000°.

242. Kurtz, Jacob. (Assigned to Callite Tungsten Corp.) Porous Metallic Bodies. U.S. Patent 2,461,517, Mar. 15, 1949; Chem. Abs., vol. 43, 1949, p. 3769.

An ingot of W is heated at 2,800° to form coarse crystals and is later crushed to form small crystallized particles, which are screened and separated according to size. The fragments are then mixed in predetermined amounts according to the degree of porosity desired, thoroughly wetted with an aqueous solution of $AgNO_3$, and heated until a coating Ag oxide is formed. These particles are mixed with a solution of paraffin in CCl_4 and shaped in a die under pressure. The mass is heated to volatilize the paraffin without leaving a residue, to reduce the oxide coating to metallic Ag, and to sinter the Ag-coated W particles into a strong porous body.

Labrie, R. J. *See* abs. **254**.

Lever, R. F. *See* abs. **225**.

243. Li, Kuo Ching, and Dice, C. M. (Assigned to Wah Chang Trading Corp.) Tungsten Separation. U.S. Patent 2,535,217, Dec. 26, 1950; Chem. Abs., vol. 45, 1951, p. 1943.

W can be separated from Sn, Cu, As, S, P, Pb, Bi, and Sb by heating their oxides above 2,500° with C in the presence of at least 10 percent of Fe-Sn alloy. This reduced W to WC or FeW_2C, depending on C and Fe concentration, the rest of the elements dissolving in the Fe-Sn alloy. No Sn need be added to W ore, because it usually carries enough Sn to provide the alloy. A mixture of 100 parts of W ore containing 2.5 percent Sn mixed with 10 parts of Fe and 10 parts of bituminous coal heated 2 hours at 2,750° reduced 95 percent of available W producing FeW containing about 14 percent Fe. With 20 parts of C, the same treatment reduced 93.43 percent of W to a mixture of WFe and WC. With 20 parts of coal and no Fe, 85.61 percent W was converted to WC. The FeW produced and contained C 0.03, Sn 0.02, As 0.02, Cu 0.01 percent and WC carried traces of As and Cu, Sn 0.03, Fe 0.01 percent.

244. Lilliendahl, W. C. (Assigned to Westinghouse Electric Corp.) Tungsten Compounds. U.S. Patent 2,414,601, Jan. 21, 1947; Chem. Abs., vol. 41, 1947, p. 1983.

Tungsten compounds of such purity that they have high fluorescent response may be prepared from WO_3, which has been essentially freed of metal impurities by a process that employs 8-hydroxyquinolin. WO_3 containing less than 0.001 percent each of Fe, Mn, Cu, Co, Ni, Al, and Mg results when these metals are **removed as organometallic compounds from a solution of an alkali metal tungstate.**

Ma, Chuk Ching, See abs. **231, 232**

Mayfield, O. *See* abs. **233**.

245. McKnight, R. Compounds of Tungsten or Other Rare Metals. U.S. Patent 1,306,070, June 10, 1919; Chem. Abs., vol. 13, 1919, p. 2008.

An ore or concentrate containing WO_3 or other rare-metal compound is heated with NaCl and the product is placed in H_2O to extract the soluble chloride of the rare metal formed. Upon evaporation the chloride is obtained as a powder, which may be used in the formation of a cake or ingot. The latter may then be used for incorporation with other metals such as steel, for example, in making W steel for high-speed tools. Compounds of Mo, U, V, and Te, singly or collectively, may be similarly prepared and incorporated with steel or other common metals. The compound produced by melting the salts of the rare metal compounds with NaCl fuses at a temperature below that required for its formation so that incorporation with common metals having relatively low melting point without overheating is readily accomplished.

Menefee, A. B. *See* abs. **219**.

Messmer, Karl. *See* abs. **240**.

246. Millner, Tivadar, and Neugebauer, Jeno. (Assigned to Egyesült Izzólámpa es Villamossági Részvenytársaság.) U.S. Patent 2,806,774, Sept. 17, 1957.

When W powders are reduced normally by H_2 from WO_3, its hydrates or ammonium tungstates, these powders pressed into bars and sintered give metal with large crystals outside and small crystals inside and on pulling into wire give weak spots in places. Present process is to reduce the WO_3 to about WO_2 with hydrogen, then intimately intermix the partly reduced product and complete the reduction at about 820° C. The powder pressed into bars give metal of uniform crystal size, and wires drawn suffer fewer breaks. It is thought the useful additives (traces of alkali and SiO_2, Al, etc.) originally on the faces of the WO_3 particles normally concentrate on the surface of the W metal particles nonuniformly. Partial reduction and remixing before completion of reduction gives a more homogeneous metal.

See also Neugebauer, J., abs. **147**.

247. Nakao, Tomosaburo. (Assigned to Sumitomo Electro-Industries Co.) Tungstic Acid From Wolframite Containing Sulfur, Arsenic, and Phosphorus. Japanese Patent 4757, Aug. 3, 1954; Chem. Abs., vol. 49, 1955, p. 11,970.

Calcined ore containing sulfur, phosphorous, and arsenic is heated with HNO_3 (density 1.1 to convert them into soluble H_2SO_4, H_3PO_4, and H_3AsO_4. The solution is decanted off, and the residue washed with water, treated with NaOH to obtain Na_2WO_4, and reprecipitated, as usual by an acid to obtain H_2WO_4.

248. ———. (Assigned to Sumitomo Electro-Industries Co.) Refining of Tungsten Oxide From Tungsten Ore Containing Much Arsenic and Phosphorus. Japanese Patent 2408, May 4, 1954; Chem. Abs., vol. 49, 1955, p. 2690.

A crude $NaWO_4.2H_2O$ (200 kg.) containing WO_3 68.2, As 0.07, and P 0.08 percent in 600 liters of water is neutralized with 250 liters of waste liquor from decomposition of the parasalt, $5(NH_4)_2O.\text{-}12WO_3.5H_2O$, and containing HCl 115 gr. and NH_4Cl 280 gr./l. The solution is treated with 50 liters NH_4OH (d. 0.94) and 20 liters $MgCl_2$ (d. 1.08), the precipitates of $Mg_2As_2O_7$ and $Mg_2P_2O_7$ are removed by filtration, and the filtrate is refined by the usual method to yield 92.5 percent WO_3 with purity 99.7 percent.

249. ———. (Assigned to Sumitomo Electro-Industries Co.) Recovery of Tungsten From Tungsten Ore Containing Tin. Japanese Patent 5302, Oct. 16, 1953; Chem. Abs., vol. 48, 1954, 10,521.

NaOH-extracted W ore containing 20 kg. $Na_2WO_4.2H_2O$ and 0.08 percent Sn impurity is treated with 30 liters HCl (d. 1.13) and 20 grams 10 percent $KMnO_4$ in 60 liters H_2O. The $SnCl_4$ is removed by filtration and the residue treated with 24 liters NH_4OH (d. 0.94). The solution of $(NH_4)_2WO_4$ is concentrated, reprecipitated with 10 liters HCl, washed with water, and heated at 500° to give 99.50 percent WO_3 in 76.8 percent yield. The treatment without $KMnO_4$ yielded 99.30 percent WO_4 in 68.2 percent yield.

250. ———. (Assigned to Sumitomo Electro-Industries Co.) A Method of Decomposition of Ammonium Paratungstate in the Refining Process of Tungsten. Japanese Patent 2453, May 19, 1951; Chem. Abs., vol. 47, 1953, p. 1906.

$5(NH_4)_2O.12WO_3.5H_2O$ (15 kg.) in 6 liters water is heated by steam. Then 4 liters HCl (d. 1.13) is added dropwise; the mixture is boiled with agitation and then boiled for 30 minutes with 10 liters HCl (d. 1.13) and 1 liter HNO_3 (d. 1.30). The decomposition product is washed 3 or 4 times with water and dried to obtain WO_3 (NaCl content 0.05 percent).

251. NAKAZAWA, GENICHI. (Assigned to Agency of Industrial Science and Technology). Dearsenizing Roasting of Tungsten Ores. Japanese Patent 7905, Sept. 13, 1956; Chem. Abs., vol. 52, 1958, p. 9932.

Arsenic is removed from scheelite by roasting the ore in a nonoxidizing atmosphere. In an example, 1.19 percent. As in scheelite containing 17.49 percent tungsten (as WO_3) and 8.33 percent S was completely removed by roasting in a CO_2, SO_2, or N atmosphere at 1,000°. Under a pressure of 20 mm., 85.7 percent removal was achieved; in air only 63.1 percent.

OGATA, NARITO. *See* abs. 255.

252. OHKAGE, HITOSHI. Tungsten From Scheelite. Japanese Patent 7,560, Nov. 18, 1954; Chem. Abs., vol. 50, 1956, p. 4760.

Scheelite (75 kg.) of —150-mesh and containing WO_3 65.51, CaO 16.38, SiO_2 15.78, and Fe_2O_3 0.32 percent and 35 kg. $(CO_2H)_2.2H_2O$ in 170 liters water are heated for 3 hours at 90°–95°. The precipitate is filtered and washed with 0.3–0.5 percent HNO_3 to obtain 165 kg. residue (I) composed of WO_3 and Ca oxalate, I in 50 liters water is added portionwise to 50 liters of 28 percent NH_4OH in 200 liters water at 80° and allowed to stand overnight. The precipitate is filtered, and washed with 5 liters of 28 percent NH_4OH in 120 liters water. The filtrate and washings are combined and evaporated to dryness to obtain NH_4 paratungstate (equivalent to 47.92 kg. WO_3 or 97.5 percent recovery).

253. OKAGE, SUSUMU, AND OTHERS. Tungstic Acid From Scheelite. Japanese Patent 172,961, June 22, 1946; Chem. Abs., vol. 46, 1952, p. 2247.

Scheelite (I) or ore containing I is treated with oxalic or tartaric acid to obtain a solution of H_2WO_4 (II), $CuCl_2$ is added to precipitate the organic acid as the Ca salt, and II is purified from the filtrate, or II is precipitated by the addition of a mineral acid.

254. SENEDROFF, SEYMOUR, AND LABRIE, R. J. (Assigned to United States of America, as represented by the Secretary of Commerce.) The Lower Chlorides of Molybdenum and Tungsten. U.S. Patent 2,715,058, Aug. 9, 1955; Chem. Abs., vol. 49, 1955, p. 16372.

Reduction of the higher chlorides is effected by heating with saturated aliphatic hydrocarbons containing 10 to 50 C atoms per molecule. In an example, 40 g. of $MoCl_5$ was added to 200 ml. of cetane in an inert atmosphere. The mixture was heated with continuous stirring to 160°. The product had an atomic ratio of Mo : Cl of about 1 : 4 and when heated in an inert atmosphere at 275° produced $MoCl_3$.

255. SHIRAISHI, TAKESHI, AND OGATA, NARITO. (Assigned to Nippon Electric Co.) A Pure Tungsten Oxide From Scheelite. Japanese Patent 176,352, June 9, 1948; Chem. Abs., vol. 45, 1951, p. 5889.

A solution prepared by extraction of scheelite with mineral acids by heating and filtration is dried by heating at 110°–210° to give $SiO_2.0.2\text{–}0.6H_2O$ and $WO_3.0.5H_2O$. The residue is then extracted with aqueous NH_4OH or $(NH_4)_2CO_3$ to obtain a product containing no SiO_2.

256. SIEMENS AND HALSKE, A.-G. (Berlin 2). Refractory Metals (Method of Melting Refractory Metals, Especially Ta, W, Th and Their Alloys in a Water-Cooled Container). German Patent 518,499, Feb. 16, 1921; Chem. Abs., vol. 25, 1931, p. 2408.

Metals such as Ta, W, Th or their alloys are completely fused in strongly cooled crucibles made of materials of lower melting point than the said metals, for example, of quartz, Cu, or Ag. The metal to be fused may be heated by high-frequency electric current, and the crucible, if electrically conductive, may be made in a number of insulated segments. (Battelle Mem. Inst. translation 51G8.)

257. SUPIRO, L. D. Pure Tungsten Sponge or Powder. U.S. Patent 2,829,962, Apr. 8, 1958; Chem. Abs., vol. 52, 1958, p. 10,855.

Pure W powder or sponge is obtained by treating alkali or alkaline earth tungstates with H_3BO_3 in the presence of H as the reducing agent at 1,200° in a tube furnace in a ratio of 10 parts $CaWO_4$ to 2 parts H_3BO_3 (minus-100-mesh) to 10 parts Na_2WO_4 8.25 parts H_2CO_3, and at a 0.5-hour reaction time to yield up to 96 percent recovery.

258. ———. Method of Producing Tungsten Sponge or Powder of High Purity. U.S. Patent 2,829,962, Apr. 8, 1958.

The method of producing tungsten of high purity comprising reacting material selected from the group consisting of alkaline earth tungstates, alkali metal tungstates, mixtures thereof, with boric acid in the presence of a reducing agent at approximately 1,200° C.

259. TECHNISCHEN HOCHSCHULER, ZÜRICH (Schweiz). Gesellschaft Zur Förschung an der Eidgenössischen. [Process for Making Tungsten Ductile—Electrolytic.] Swiss Patent 271,659, Feb. 1, 1951; Chem. Abs., vol. 45, 1951, p. 8380.

To confer ductility to tungsten wires and similar articles that have become brittle during drawing or working, they are made to act as temporary electrodes in the electrolysis of an aqueous system. In an example a brittle tungsten wire, 0.6 mm. in diameter, is made ductile by electrolysis of a $NaNO_3$ solution (counterelectrode nickel) at 2.5a. and 6 v. for 2 minutes.

260. THOMPSON-HOUSTON (COMPAGNIE FRANÇAISE). Purifying Tungstic Acid. French Patent 976,591, Mar. 20, 1951; Chem. Abs., vol. 47, 1953, 2946.

A warm aqueous solution of Na tungstate, prepared by adding Na_2CO_3 to a crude solution of H_2WO_4, is slowly fed, in a finely divided state, into a boiling mixture of HCl and HNO_3 to give a finely divided precipitate of H_2WO_4. Distance of the capillary feed tube in inches above the surface of the acid, χ, and flow of tungstate in cubic centimeters per minute, R, may be correlated by the equation $R=9.1\times1.1.083^x$ in the example, a tube, having a capillary of 2 mm., is 686 mm. above the surface of the acid. Na_2WO_4 solution (1,300 cc.) specific gravity 1.2 is run into 732 cc. of HCl solution containing 2 percent HNO_3, specific gravity of the mixture being 1.2 at a rate of 60–70 cc. per minute. The acid is kept hot by passing in steam. After decanting, the acid is washed with boiling dilute HCl, then boiling dilute HNO_3, and finally with boiling distilled H_2O. The dried acid yields tungstates of enhanced phosphorescence.

261. WILLIAMS, T. J. Beneficiation of Tungsten Sulfide Ore Concentrates. British Patent 579,743, Aug. 14, 1946; Chem. Abs., vol. 41, 1947, p. 1983.

The 50 percent WO_3 concentration is ground to approximately 60-mesh, mixed with pyrolusite and $NaNO_3$ ground to the same size, then leached with a nonoxidizing acid. Bi is recovered from this solution. Analyses up to 72 percent WO_3, with Bi 0.08 and Cu 0.17 percent, were obtained.

262. ———. Purifying Sulfide Tungsten Ore Concentrates. U.S. Patent 2,437,870, Mar. 16, 1948; Chem. Abs., vol. 42, 1948, p. 4120.

See abs. **261**.

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