Ruthenium and Refractory Carbides

TITANIUM CARBIDE COMPOSITES OF REMARKABLE STABILITY

The strong reactions that occur at high temperatures between platinum, palladium and the carbides of tungsten, niobium and tantalum were first described about nine years ago by Professor E. Raub and G. Falkenburg of the Forschungs Institut für Edelmetalle at Schwäbisch Gmünd (1). The carbides were completely decomposed, and while the metal thus released formed compounds or solid solutions with the noble metal, carbon was liberated in elemental form as graphite lamellae or spheroids. Rhodium and iridium reacted similarly with the carbides of hafnium and zirconium (2) and N. H. Krikorian of the Los Alamos Scientific Laboratory has also demonstrated that platinum and iridium decompose the lanthanide carbides (3) at temperatures as low as 1000°C. On the basis of such experimental results it seemed safe to conclude that none of the carbides were compatible with any of the platinum metals at elevated temperatures.

A recent paper, again by Raub and Falkenburg (4) highlights the danger of such premature generalisations. Although the four cubic platinum metals appear to decompose all the refractory carbides, hexagonal ruthenium is perfectly compatible with titanium, tantalum and vanadium carbides even when the two constituents are fused together in the argon-arc furnace.

Ruthenium, with titanium carbide, forms a quasi-binary eutectic containing about 40 molecular per cent of titanium carbide which melts at 1820°C. Up to this temperature nominally pure ruthenium co-exists with pure titanium carbide, the microstructure of such alloys showing a fine eutectiferous matrix surrounding primary crystals of either ruthenium or titanium carbide. The nominally pure ruthenium is in fact a dilute solid solution, which can contain up to about 4 molecular per cent of titanium carbide at 1500°C. Above this concentration finely divided carbide starts to form round the ruthenium grain boundaries.

An intermetallic compound TiRu appears when more than about 5 atomic per cent of titanium is added to these eutectiferous alloys, but the ternary system Ru-TiC-Ti is generally of great simplicity, only the phases Ru, TiRu, TiC and Ti being present. No evidence of carbide decomposition or graphite precipitation was observed within this triangular field. The ruthenium-tantalum carbide and ruthenium-vanadium carbide systems were less fully, though adequately studied, and the results obtained demonstrate the remarkably high stability of these refractory carbides with respect to ruthenium. The solubility of tantalum carbide in ruthenium was shown to be approximately 5 molecular per cent at 1850°C, and after heat treating the duplex eutectic alloys below 1650°C a complex carbide $Ru_3Ta(C)$ of unknown carbon content was precipitated.

The importance of these findings is considerable. Thermodynamically they appear to indicate that the ability of the platinum metals to decompose carbides is not greatly affected by the stability of the carbides concerned, but is largely controlled by the position of the platinum metal within its triad. In this respect it might be concluded that osmium would behave similarly to ruthenium, although experimental evidence for this is still lacking. The stability of titanium carbide in contact with ruthenium, and its instability with respect to platinum agrees with the predictions of Brewer and Engel, and is supported by the work of Gingerich and Grisby (5). These investigators showed that stable gaseous compounds are formed between titanium and platinum, and titanium and rhodium, although titanium-ruthenium molecules appeared to have a weaker bond.

From the practical viewpoint, the ability of titanium carbide to retain its identity in the presence of ruthenium at high temperatures suggests many intriguing possibilities. In view of the significance of titanium carbide as a cutting tool material, the mechanical properties of duplex noble metal alloys containing major quantities of carbide obviously require attention. Electrical contacts of ruthenium strengthened by a uniformly dispersed titanium carbide phase might have useful characteristics in the medium duty range, and such components could be produced by standard powder metallurgical techniques. One is also encouraged to consider instrument bearings, pivots and pen points which could profitably utilise the characteristics of these corrosion and abrasion resistant composite materials. The equilibrium diagram of the quasi-binary system Ru-TiC is similar to that of the Co-WC system so familiar to workers in the hard metal industry, and sintering in the presence of a small quantity of liquid phase appears to offer the possibility of high density components.

With the hexagonal close packed carbides of tungsten (6) and molybdenum (7) rhenium forms unbroken series of solid solutions which have interesting superconducting properties. Ruthenium also has a hexagonal unit cell, the parameters of which are close to those of rhenium, and it is tempting to inquire whether it behaves in a similar way to rhenium with respect to hexagonal carbides. The ability to change mechanical properties, gently and controllably without phase change or discontinuity, from those of a hard brittle carbide to those of a relatively ductile metal is a variable which has hitherto been unavailable to the practical metallurgist. In spite of the high cost of these rare hexagonal metals, the remarkable characteristics of their carbide solid solutions should, therefore, stimulate a good deal of speculative research.

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Standard Platinum Resistance Thermometers

The revision of the International Practical Temperature Scale which resulted in the publication of IPTS–68 has led to a careful reappraisal of methods of temperature measurement to take into account the slight modifications from the former scale IPTS–48. This journal has already reported on the implications of such work on the use of rhodium-platinum thermocouples.

The U.S. National Bureau of Standards has now published NBS Monograph 126: "Platinum Resistance Thermometry", which describes the methods and equipment used there for calibrating standard platinum resistance thermometers to IPTS–68. The text of the scale, the authorised English version of which is given in Appendix 1, is clarified and its characteristics are described. A number of thermometer designs are illustrated in detail, together with possible sources of error in their use.

Three classes of reader will find this Monograph valuable. Users of platinum resistance thermometers will find guidance as to their mechanical and thermal treatments and to transporting them. Calibrators will find a full guide to the techniques of calibration, including the fixed points used to establish the scale of temperature. Those wishing to submit their own instruments to N.B.S. for calibration will learn of the methods employed there.

F. J. S.

Methods are presented for the analysis of 41 refractory materials. An evaluation of the accuracy and the precision of these techniques are also given The materials studied are the borides of hafnium, molybdenum, niobiumL rhenium, tantalum, thorium, titanium, tungsten, uranium vanadium, and zirconium; the carbides of hafnium molybdenum, miobium, silicon, tantalum, thorium, titanium, tungsten, uranium, vanadium, and zircomium; the nitrides of boron, hafnium, niobium, silicon, tantalum, titanium, uranium, and zirconium; the silicides of. molybdenum, rhenium, tantalum, titanium, tungsten, vanadium, and zirconium; and mixed carbides of uranium with hafnium, niobium, tantalum, or zirconium. (auth). Authors: Kriege, O H. In chemistry, a carbide is a compound of carbon with a less electronegative element. Many carbides are important industrially; for example, calcium carbide (CaC2) is a feedstock for the chemical industry and iron carbide (Fe3C, cementite) is formed in steels to improve their properties. In general, carbides are classified according to the chemical bonding in the compounds, as follows: salt-like ionic carbides; covalent carbides; interstitial carbides... Refractory carbides and nitrides are useful materials with numerous industrial applications and a promising future, in addition to being materials of great interest to the scientific community. Although most of their applications are recent, the refractory carbides and nitrides have been known for over one hundred years. The industrial importance of the refractory carbides and nitrides is growing rapidly, not only in the traditional and well-established applications based on the strength and refractory nature of these materials such as cutting tools and abrasives, but also in new and promising fields such as electronics and optoelectronics. Readership. Production and research and development personnel in the carbides and nitrides industry. Table of Contents.