The Refractory Noble Metals and Rhenium

ALLOYING POSSIBILITIES WITH MOLYBDENUM AND TUNGSTEN

The four scarcer platinum group metals—rhodium, ruthenium, iridium and osmium—have higher melting points than platinum and palladium, they are more resistant to acid attack (in massive form they are virtually insoluble in aqua regia) and mechanically they are stronger and much less ductile. In the past, they have thus often been referred to as the "insoluble" platinum metals. However, in a recent paper presented by R. I. Jaffee, D. J. Maykuth and R. W. Douglass at the Refractory Metal Conference of the American Institute of Metals in Detroit in May 1960, attention is drawn to the relationship between these metals and the neighbouring transition metal, rhenium. "It is apparent," write the authors, "in considering rhenium and the (above four) platinum-group metals we are really talking about one family"; and they propose that the family should be termed the "refractory noble metals".

The authors present an excellent comprehensive review of the literature dealing with the mechanical, physical and chemical properties of this group of metals, emphasising always the transition found in properties between members of the group.

Resistance to Oxidation

One feature of the group that frequently needs to be considered concerns oxidation resistance. Although the group is rightly placed among the noble metals, the oxidation resistance ranges from that of rhodium, one of the most oxidation-resistant of all metals, to that of rhenium, which is among the most readily oxidised. The authors point out, however, that "despite this vast difference in oxidation behaviour, the mechanism of oxidation of the noble metals is remarkably consistent. A volatile oxide forms at temperatures above the oxide decomposition temperature, and metal loss is due to oxide volatilisation and metal vaporisation". Nearly all other metals form stable oxides.

More than half of the review is concerned with the alloying behaviour of the refractory noble metals with each other and with other elements. Arising from this extensive review, the authors particularly note the very remarkable, and indeed spectacular, effect of additions of rhenium on the working properties of molybdenum and tungsten. This was first noted by Geach and Hughes, working in the laboratories of Associated Electrical Industries, who found that molybdenum when alloyed with 50 per cent by weight of rhenium could be cold-rolled to sheet direct from the cast condition and that tungsten alloyed with 30 per cent by weight of rhenium could be rolled at slightly elevated temperatures. The amounts of rhenium that need to be added are, it will be seen, very large, and the authors have accordingly been responsible for initiating at Battelle Memorial Institute, under the sponsorship of the Office of Naval Research, an investigation into the possibility that similar effects might be produced by adding smaller amounts of the refractory platinum-group metals.

Improving Ductility

The effects of rhenium additions in improving the ductility of molybdenum and tungsten are ascribed to three factors. First, the rhenium is said to form with oxygen a complex molybdenum-rhenium oxide which does not, like MoO_2, give rise to a eutectic that wets the grain boundaries but tends to be redistributed within the alloy grains. Secondly, the rhenium promotes twinning at room temperature and lowers the ductile-to-brittle transition temperature, thus improving low-temperature ductility. Finally, it is suggested that rhenium additions reduce the solubility of oxygen in molybdenum. This is said to be in accord with the theoretical predictions of D. A. Robins, who considers that the solubility of interstitial elements in Group VIA metals may be lowered by additions of higher group metals because of the tendency to maintain six bonding electrons. The addition of rhenium with seven electrons reduces the solubility of oxygen because the oxygen atoms tend to ionise and contribute electrons to the alloy. It is thought that the soluble oxygen atoms tend to lock dislocations, reducing low-temperature slip and influencing the yield point; so that, by reducing the oxygen content, the ductility is improved generally.

The influences of additions of the platinum group refractory metals to molybdenum, tungsten and chromium on these three factors have been examined in a very general way. The results may be summarised as follows:

(1) None of the platinum group elements appeared to have any significant effect in redistributing molybdenum oxide at the grain boundaries (osmium additions may have a very slight effect); and of other elements, those only which produced a real change in the oxide morphology were niobium and tantalum, added in amounts of 5 to 10 atomic per cent.

(2) Room temperature twinning in molybdenum, tungsten and chromium appears to be promoted by 5 to 7.5 atomic per cent of ruthenium or osmium and, to a lesser extent, by about the same amounts of the other platinum metals. The effect, for some unexplained reason, is more pronounced in cast than in annealed samples.

(3) The most interesting effect of noble metal additions was on the hardness of cast molybdenum. Small additions, of the order of 0.1 atomic per cent of ruthenium, reduced the hardness from 170 to 140 V.H.N., this being ascribed to a reduction in the oxygen solubility. Similar additions of iridium, rhodium, osmium (and platinum) reduced the hardness to 145–150 V.H.N. There are indications that about 1 per cent of osmium reduces the hardness of cast chromium. Larger additions of all the platinum metals increase the hardness of cast molybdenum, tungsten and chromium; no data are available on the effect of small additions to tungsten and chromium.

The work is by no means comprehensive or complete. An attempt to get a quick solution to the problem of finding a malleable complex molybdenum alloy was made by adding tantalum or niobium to redistribute the oxygen, together with small amounts of osmium, ruthenium, iridium or platinum to promote twinning and to reduce interstitial solubility, and small amounts of other deoxidising elements (for luck) to supplement, it was hoped, all these effects.

The most successful molybdenum alloys contained the following additions, in atomic percentages:

(*a*)		(*b*)		(*c*)		(*d*)	
Ru	1.0	Ru	1.0	Os	1.0	Os	1.0
Si	0.1	Co	0.05	Ta	1.0	Ta	1.0
				Si	0.1	Co	0.05

All these could be rolled directly to strip, but when recrystallised they were brittle on bending, indicating no marked improvement in the ductile-to-brittle transformation.

It is considered by the authors that the most significant effect of these small additions of platinum metals is the reduced solubility for oxygen (and presumably of other interstitial impurity elements) through increase in the valence electron concentration. It may well be that further studies will prove that successful methods of producing industrially important alloys with the help of the refractory noble metals can be developed.

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