

Advances in Chromium, Molybdenum and Tungsten Alloys

PLATINUM METALS ENHANCE DUCTILITY IN GROUP VIa ELEMENTS

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In the quest for higher operating temperatures in advanced turbine engines a good deal of attention has been paid to the possible use of the Group VIa metals, chromium, molybdenum, and tungsten as blade materials. A major disadvantage of these metals is that, in common with other body-centred cubic materials, they undergo a ductile-brittle transition resulting in poor mechanical properties at ambient temperatures which severely restricts their use in many applications. In a recent paper by W. D. Klopp of NASA Lewis Research Centre, Cleveland, Ohio, U.S.A. (*J. Less-Common Metals*, 1975, **42**, (3), 261) recent developments in overcoming embrittlement and other problems are reviewed with particular emphasis on high temperature strength and low temperature ductility requirements.

The remarkable effect of rhenium in enhancing the cold ductility of molybdenum and tungsten was first reported over 20 years ago and a similar effect was subsequently found in chromium-rhenium alloys. Since that time numerous other studies have been made, seeking alternatives for rhenium and attempting to explain the ductilising phenomenon. Analogous behaviour has now been found in several non-rhenium alloys, in particular in platinum metal systems such as chromium-ruthenium or molybdenum-osmium. From his examination of such systems, Klopp has been successful in identifying certain common characteristics of the solutes which promote cold ductility in the Group VIa metals:

- (a) The solute must be from Groups VIIa or VIII of the Periodic Table.
- (b) A sigma phase is formed in the system.
- (c) The solutes have relatively high solid solubilities in the Group VIa metal.
- (d) Maximum cold ductility occurs in the saturated or supersaturated solid solutions.

From these criteria certain of the platinum metals appear promising. Thus, osmium should behave similarly to ruthenium as a ductilising solute in chromium, osmium and iridium in molybdenum, and ruthenium and osmium in tungsten.

These observations do not identify the mechanism of ductility enhancement, but in view of the correlation with phase diagram considerations it is almost certainly associated with electronic characteristics. Following the Engel-Brewer theories Klopp suggests the number of (s+d) electrons in the solute as the controlling factor. If so it may be possible to combine several solutes to produce an alloy with good ductility and other desirable properties such as improved strength/density ratio at high temperatures.

In addition to ductility enhancement in relatively concentrated solid solutions, the low temperature properties of chromium, molybdenum and tungsten can also be improved at low solute contents by solution softening.

This phenomenon, first of all detected as a hardness minimum in dilute molybdenum-rhenium and tungsten-rhenium alloys, has now been observed in most body-centred cubic metals. The importance of the number of (s+d) electrons is again evident from the

results of alloying molybdenum with the 3rd Long Period elements from hafnium to platinum. Solution softening is produced only by those elements having an excess of (s+d) electrons compared to molybdenum (i.e. rhenium, osmium, iridium and platinum) while elements with a fewer or an equal number do not produce softening. A particularly good correlation was obtained by plotting hardness as a function of the square of the excess (s+d) electrons; for example, iridium with three electrons in excess was found to be nine times more effective than

rhenium with one, but the basis for this correlation remains obscure. Other factors such as atomic size or scavenging of interstitials make only a minor contribution to the hardness behaviour in these alloys.

It is perhaps significant that parallel ductility enhancement has been found in the hexagonal close-packed metal ruthenium when molybdenum is added to near the solid solubility limit. However, there has been no report as yet that osmium, the most intractable of the platinum group metals, responds similarly to alloying.

Effect of Palladium on the High Temperature Properties of Rhodium-Platinum Alloys

The only conventional metallic constructional materials currently available with sufficient strength, ductility, and resistance to oxidation to satisfy the most extreme demands of the glass industry are those based on the binary rhodium-platinum solid solutions. Between the temperature levels at which the use of these relatively costly materials becomes mandatory, however, and the lower temperature region in which nickel- and cobalt-based alloys can safely operate, a sizeable gap can now be distinguished. For many years Dr Gerhard Reinacher of Degussa has searched for cheaper alloys capable of working continuously in this intermediate temperature range. Although no materials having mechanical properties superior to those of rhodium-platinum have emerged from this survey, the possibility of certain economies can now be discerned. The object of his recent work has been to establish the extent to which cheaper and lighter palladium can be substituted for platinum without too catastrophic an effect upon high temperature properties.

In 1971 (1) and again in 1973 (2) he reported on the properties of several ternary alloys, one of which, containing 50 per cent of platinum, 40 per cent of palladium and 10 per cent of rhodium, had high temperature properties rather lower than those of the 10 per cent rhodium-platinum alloy at 1200°C, but high enough to suggest that possible applications might be found for it in the glass industry.

Since 1973 the price of platinum has increased, and significant reductions in cost are possible with even lower palladium concentrations than those Dr Reinacher originally envisaged. He has now shown (3) that at very low stress levels, of the order of 0.5 kgf/mm², the 30 per cent palladium, 60 per cent platinum and 10 per cent rhodium alloy performs almost as well in the short term as the conventional 10 per cent rhodium-platinum solid solution. At higher stresses, however, the superiority of the palladium-free alloy becomes increasingly apparent. Thus, under an applied tensile stress of 1 kgf/mm² the 30 per cent palladium alloy endures for only 25 hours at 1200°C compared to the 80 to 100 hours life of rhodium-platinum.

On a volume basis the intrinsic cost of this new alloy is approximately 25 per cent lower than that of the 10 per cent rhodium-platinum alloy which is capable of general employment at all temperatures up to 1400°C, whereas an upper temperature limit of 1200°C is imposed upon the palladium-containing material. On the other hand much of the intrinsic metal savings will be offset by the inevitably increased costs of fabrication and welding.

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References

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