Enhanced Oxidation Resistance

ROLE OF PALLADIUM IN REFRACTORY METAL ALLOYS

The refractory metals, tungsten and molybdenum, and their alloys possess excellent mechanical properties at elevated temperatures, but their propensity to rapid oxidation has precluded their industrial application. The addition of small amounts of palladium to chromium-containing tungsten alloys is known to enhance considerably their oxidation resistance (1–3), but there is little agreement on the mechanism involved.

Recently a substantial investigation on tungsten-chromium-palladium and tungsten-molybdenum-chromium-palladium alloys has been carried out at the Pennsylvania State University in order to clarify the oxidation mechanism and to characterise the oxidation behaviour in the temperature range 1000 to 1250°C. The influence of palladium coatings was also studied (4, 5).

Alloys of tungsten containing 9 to 29 weight per cent chromium and 1 weight per cent palladium, and similar alloys in which half the tungsten was substituted by molybdenum, were prepared by activated sintering of powder metallurgy compacts (6).

Cyclic oxidation tests showed unusual behaviour in that the oxidation resistance increased with increasing temperature. Isothermal oxidation curves were smooth with relatively little localised breakdown of the protective oxide scale. In general the tungsten-molybdenum-chromium-palladium alloys were more resistant. Microstructural examination showed the formation of a protective chromium oxide, Cr_2O_3, scale with a chromium-depleted alloy layer adjacent to the scale interface.

The role of palladium is to facilitate the rapid formation of these protective Cr_2O_3 scales. Palladium, segregated at grain boundaries, acts as a channel for the outward diffusion of chromium to the surface and, possibly, as a barrier to the inward diffusion of oxygen.

Further studies on (45–55) per cent molybdenum-(35–45) per cent tungsten-9 per cent chromium-1 per cent palladium alloys have shown the beneficial effect of a 7 μm electroplated palladium coating. Uncoated alloys oxidised at 1000°C showed sudden failure due to the breakdown of the protective Cr_2O_3 scale and the formation of volatile oxides of tungsten and molybdenum. Palladium coated alloys had smooth kinetic curves and a low oxidation rate. At a temperature of 1200°C, both the coated and uncoated alloys show excellent oxidation behaviour.

The observation of enhanced oxidation resistance in tungsten-chromium-palladium and also tungsten-molybdenum-chromium-palladium alloys, through the promotion by palladium of chromium diffusion to the surface, is entirely consistent with other work reviewed here earlier (6). The platinum group metals, especially palladium, have been shown to improve the sintering and secondary recrystallisation behaviour of tungsten and molybdenum, by enhancing diffusion at grain surfaces and boundaries, sites where the platinum group metals segregate preferentially.

Interestingly, research at Johnson Matthey has shown that platinum group metals—particularly platinum— as alloying additions in cast nickel-based alloys promotes enhanced oxidation and hot corrosion resistance (7) under both isothermal and cyclic conditions.

C.W.C.

References

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