Mo-W-Cr-Pd 합금의 고온 산화

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High Temperature Oxidation of Mo-W-Cr-Pd Alloys

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The oxidation behavior of Mo-W-Cr-Pd alloys with and without Pd coatings was studied in a pure oxygen atmosphere above $1000°C$. The use of Pd as an alloying element provided the necessary oxidation resistance by accelerating the formation of protective Cr_2O_3 layers on the surface of the alloys. Additionally, the use of Pd as a coating further increased the oxidation resistance by preventing inward diffusion of oxygen from the initial oxidation stage. The oxidation mechanism of Mo-W-Cr-Pd alloys was described.

1. Introduction

Molybdenum and tungsten, two of the refractory metals, exhibit very attractive properties for many high temperature systems. These metals possess high melting points and have excellent mechanical strength at elevated temperatures. Unfortunately, they, which are the most promising of high temperature materials, oxidize very rapidly at even moderate temperatures. Thus, these metals must be protected by some means in order to utilize them at reasonably high temperatures.

Much effort has been extended to develop protective coatings on Mo or W alloys, with no positive general coating attained as yet. Also, coatings such as $MoSi_2$ or Ni-Cr have been applied

to essentially pure Mo or W[1]. Hence, breakdown in the coating leads catastrophic oxidation because the underlying metal has no self-healing properties.

Another technique employed to attain high temperature protection is alloying Mo or W with metals that form protective oxides to prevent the loss of the base metal[2,3]. The main advantage of alloying technique is that the alloy is capable of quickly forming a new protective scale even though the outer scale on the surface is disrupted.

Recently, Lee and Simkovich[4-7] have developed new alloy system of Mo-W-Cr-Pd, which had definite improvements in oxidation resistance over the commercially available Mo and W alloys[8]. The objective of this study is to explain the oxida

tion behavior and mechanism of Mo W Cr-Pd alloys from the oxidation kinetics and microstructures of the oxide scale obtained in this and other studies[6][9].

2. Theory

2-1 Oxdation of Tungsten

Tungsten is relatively oxidation resistant below 700°C showing parabolic oxidation behavior. Between 700 1200 C, tungsten oxidation is parali near, where initial parabolic oxidation becomes linear as the initial coherent oxide film transforms to the non protective porous oxide of WO_3. Above 850 C, WO_3 exhibits significant volatility. Above 1200 C, oxidation eventually becomes catastrophic because W is lost rapidly as the volatile WO_3 is formed. Thus, above 1200°C the rate of WO_3 formation is equal to its evaporation rate[10].
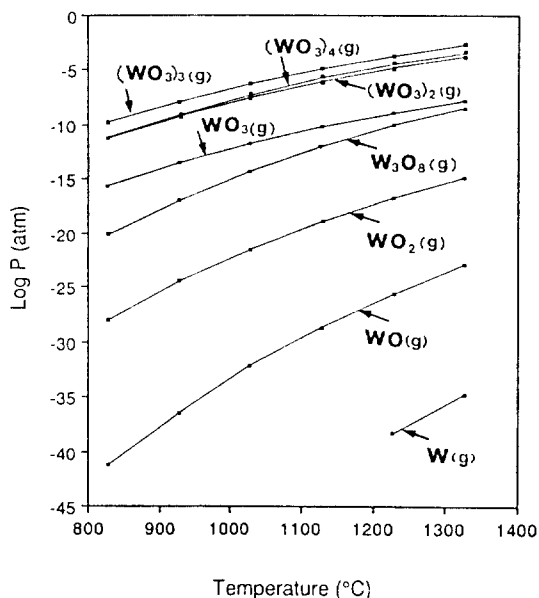
Fig 1 shows vapor pressures of tungsten oxides calculated from the thermodynamic data[1] as a function of temperature under 1 atm of pure oxygen. It was assumed that the vapor species presented are formed by direct vaporization or decomposition from $WO_3(s)$.

2-2 Oxidation of Molybdenum

The oxidation of molybdenum resembles that of tungsten but is even worse because of the higher vapor pressures of oxides formed. The main oxide is MoO_3 which melts at 800°C. MoO_3 sublimes and the vapor pressure becomes significant above 700 °C. Above the melting point of MoO_3, oxidation is accompanied by a total loss in weight.

Fig. 2 shows $(MoO_3)n$ vapor pressures as a function of temperature under 1 atm of pure oxygen. The vapor species are formed by direct
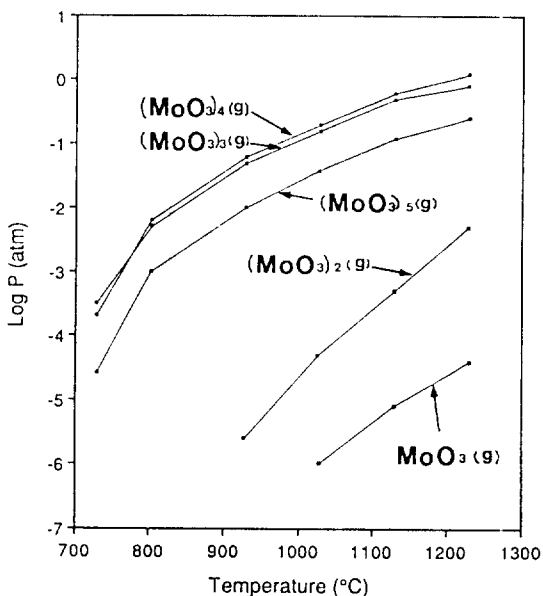

Fig. 1 Partial pressures in W-O_2 system as a function of temperature under 1 atm of pure oxygen.

Fig. 2 Partial pressures in Mo-O_2 system as a function of temperature under 1 atm of pure oxygen.

vaporization or decomposition from MoO₃ (solid
or liquid). Calculated vapor pressures of Mo(g)
and MoO₂(g) are not displayed since they are too
small. It is seen that the most prominent species
is (MoO₃)₃ (g) above 700°C and the total vapor
pressure of oxides reaches 1 atm around 1100°C.

3. Experimental

Alloys of Mo-W-Cr-Pd were prepared by an
activated sintering method[12]. The compositions
of the alloys in this paper are given in weight
percent. Each cylindrical sample, about 3㎜ thick
and 13㎜ in diameter, was sintered under H₂
atmosphere at 1370°C for 22 hr followed by 1420
°C for 2 hr. The properties of the starting powders
and sintering condition are described elsewhere
in detail[7].

Some of the sintered Mo-W-Cr-Pd alloys were
electroplated to about 7μm thickness of Pd. Palla-
dium was plated using a Pd(NH₃)₄Cl₂ containing
electrolyte, at a current density of 2 A/d㎡ and
an electrolyte temperature of 40°C[13]. After electro-
plating, the samples were heat treated for 30 min
at 1250°C under vacuum to enhance bonding of
Pd to the base alloys.

Then, each sample with or without a Pd
coating was oxidized above 1000°C in 1 atm of
flowing oxygen. The oxidized specimens were
examined by scanning electron microscopy (SEM),
energy dispersive X-ray analysis (EDXA), and
X-ray diffraction techniques.

4. Results and Discussion

4-1 Oxidation of Mo-W-Cr-Pd Alloys

Photo 1 shows the oxide scale formed on the
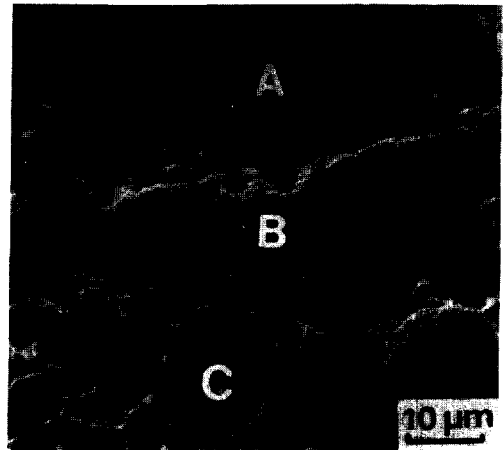45%Mo-45%W-9%Cr-1%Pd alloy oxidized at 1200

Photo 1. Scanning electron micrograph of the
cross-sectional scale formed on 45%Mo-45%W-9
%Cr-1%Pd alloy after oxidation in pure oxygen
at 1200°C for 48hr. Etched. A=mount : B=oxide
scale : C=base metal

°C for 48hr. The outer scale is porous due to the
continuous evaporation of oxides at the oxide/gas
interface and is embedded in the mounting
material[7]. The net weight gain after oxidation
was measured as 2.5㎎/㎠. This indicates that
with the addition of a minor amount of Pd, a
remarkable increase in oxidation resistance is
achieved[6-9] considering that 90%Mo-10%Cr[4] at
this temperature would display total weight loss
while 90%W-10%Cr[3] would show a rapid increase
in weight of 120 ㎎/㎠ in 1 hr without any apparent
appearance of a protective oxide growing. It is
generally accepted that in Mo or W based alloys
a small change in kinetics is enough to produce
a large change in overall oxidation behavior. The
effect of Pd can be explained as follows :

Pd, which promotes densification of base
metals during sintering, is known to segregate
at the grain boundaries and lead grain boundary
diffusion[12),14)]. Also, above 1000°C, virtually
unipolar diffusion of W and Cr into Pd occurs

in the W-Cr-Pd system[15] and preferential diffusion of Pd into Mo occurs in the Mo-Pd system[16]. Hence, Pd accumulated at the grain boundaries would act as easy diffusion channels of W and, morerver, Cr, but not of Mo. This behavior is essential in providing the necessary oxidation resistance because Cr which diffuses much faster than Mo or W would form an outer protective Cr_2O_3 scale. Fig. 3 shows that the interdiffusivity of Cr-Pd[17], D_{Cr-Pd}, is much greater than the interdiffusivities of Mo-Pd[10], D_{Mo-Pd}, or W-Pd[18], D_{W-Pd}.

Additionally, Pd, having a low oxygen diffusivity[19], protects readily oxidizable Mo and W matrix by detering inward diffusion of oxygen. From the above-mentioned beneficial roles of Pd, the oxidation mechanism of Mo-W-Cr-Pd alloys can be postulated as follows :

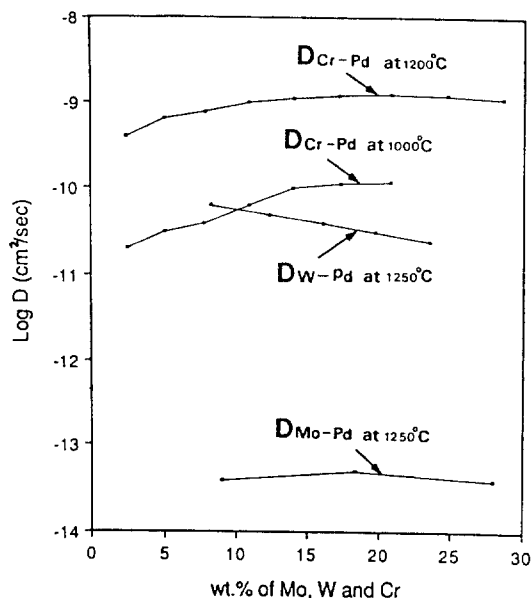When the alloy is exposed to oxygen, the

Fig. 3 Interdiffusion coefficients of Mo-Pd, W-Pd, and Cr-Pd as a function of wt.% of Mo, W, and Cr.

surface is covered with the oxides of Mo, W and Cr. Pd, being a noble metal, does not be oxdized. Oxides of Mo and W evaporate due to their high vapor pressures, leaving somewhat porous Cr_2O_3 on the surface of the alloy.

After an initial Cr_2O_3 layer is formed, a decreased effective oxygen potential beneath this oxide layer tends to favor the diffusion of Cr from the bulk alloy to the metal/oxide interface leading to the formation of a complete Cr_2O_3 layer. Mo and W diffusion from the base metal into metal /oxide interface is limited due to small concentration gradients and their low diffusion rates. As the oxide scale of primarily Cr_2O_3 gets thicker, the oxidation of the less noble element of Cr causes the enrichment of the more noble elements such as Mo, W and Pd at the metal/oxide interface. This phenomenon is similar to the sensitization of austenite stainless steel, which shows that depletion of Cr occurs adjacent to the grain boundaries where $Cr_{23}C_6$ are precipitated[20].

Since Cr diffuses much faster than Mo or W from the base alloy through the Pd-enriched zone (i.e., Cr-depleted zone) to the oxide scale, it continues to be oxidized to Cr_2O_3. At the later oxidation stage, the oxide scale and Pd-enriched zone become thicker and the oxidation rate decreases.

From the above, it is suggested that the excellent oxidation resistance of Mo-W-Cr-Pd alloys[7-8] stems from the complex roles of Pd. Under rapid oxidation conditions, impervious protective layers of Pd surrounding the readily oxidizable Mo and W based grains and Pd-enriched zone formed at the metal/oxide interface protect the alloy.

4-2 Oxidation of Mo-W-Cr-Pd Alloys with Pd Coatings.

As described elsewhere in detail[9], the oxidation lives of Mo-W-Cr Pd alloys were prolonged more than 6 times when Pd was electroplated. Photo 2 (a) shows the oxide scale formed on the Pd-coated 50%Mo-40%W-9%Cr-1%Pd alloy after oxidation in pure oxygen at 1000°C for 80 hr. The Pd-segregated grain boundaries were distorted due to the significant diffusion of W and, moreover, Cr from the base metal to the oxide scale.
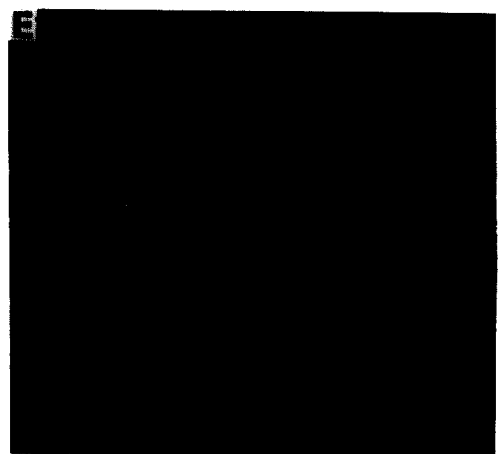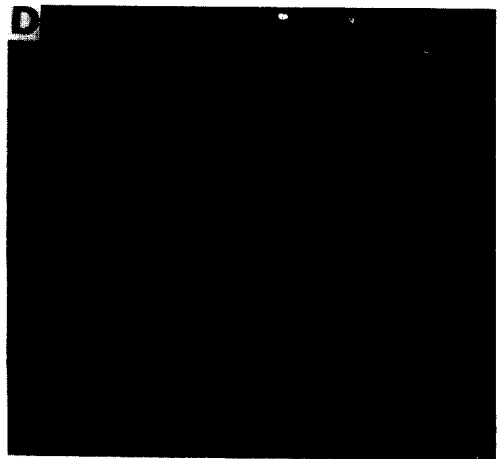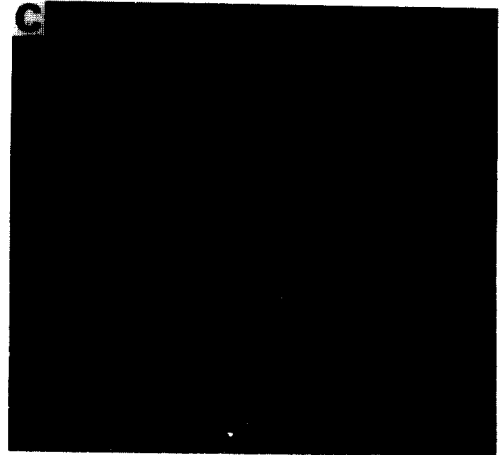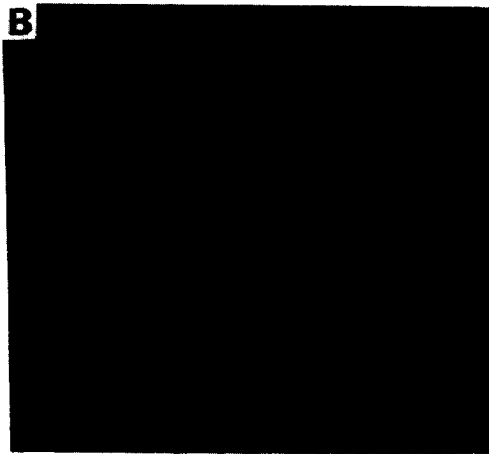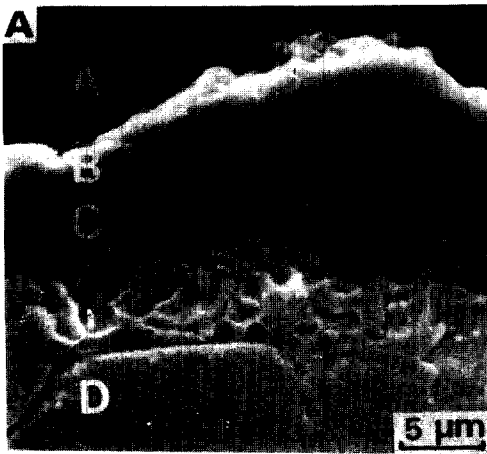

Photo 2. (a)Scanning electron micrograph of the cross-sectional scale formed on Pd-coated 50%Mo-40%W-9%Cr-1%Pd alloy after oxidation in pure oxygen at 1000°C for 80hr. Etched, A=mount, B= oxide scale, C=original Pd-coating, D=base metal, (b) Mo image, (c) W image, (d) Cr image, and (e) Pd image.

X-ray mappings of Photo 2 (a) are shown in Photo 2 (b)—(e). As shown in Photo 2 (b), Mo distribution is mainly limited to the base metal. This is consistent with the marker experiments done by Zaiss et al.[16] They found that in the Mo-Pd system at 1000°C, D_{Pd} and D_{Mo} are 8.2 $\times 10^{-14}$ and 5.5×10^{-15} cm^2/sec, respectively. Hence, diffusion in the Mo-Pd system is quite slow and Mo diffusion into the Pd coating is limited.

However, as shown in Photo 2 (c), W is present in the Pd-coated area owing to the preferential diffusion of W into Pd[15]. Photo 2 (d) shows the Cr_2O_3 scale and Cr distribution in the alloy. The outer Cr_2O_3 scale is formed by the Cr diffused from the base metal. As explained earlier, Cr diffusion occurs considerably because of the presence of easy diffusion channels such as Pd-segregated grain boundaries or the Pd coating. Photo 2 (e) shows that the original Pd-coating is somewhat smeared mainly due to the preferential diffusion of W and Cr into Pd and Pd diffusion into Mo. The effect of the Pd coating on the Mo-W-Cr-Pd alloys may be summerized as follows :

Firstly, the coating of a noble metal, Pd, provides additional oxidation resistance to the underlying alloy from the initial oxidation stage. Secondly, the coating increases the oxidation resistance by enhancing the formation of a protective Cr_2O_3 layer on the surface of the alloy.

5. Conclusion

The high temperature oxidation of Mo-W-Cr-Pd alloys with and without Pd coatings was studied. The vapor pressures of oxides of Mo or W were calculated to be significant and the total vapor pressure reaches 1 atm around 1100°C. Pd was segregated at the grain boundaries during sintering and became enriched at the Cr-depleted zone during oxidation. Since Cr diffused fast through Pd, the easiness of the outward diffusion of Cr facilitated the formation of an outer protective Cr_2O_3 scale. Also, Pd, being a noble metal, prevented the inward diffusion of oxygen. The use of Pd as a coating provided additional oxidation resistance to the underlying alloy.

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