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Approaches to oxidation-resistant refractory metal alloys

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Abstract. — The focus of the research reported here was on the design of high-temperature alloys which would form protective SiO_2 and Al_2O_3 scales on exposure to high-temperature, oxidizing environments. One way to promote the growth of such scales is to incorporate sufficient amounts of Si or Al in the alloy substrate; typically, additions of approximately 35 to 45 weight percent (all alloy compositions are given in weight percent unless explicitly stated otherwise) of Si or Al would be required to form the respective scales, in the absence of additional protective-scale-forming elements. At such levels of alloying additions, the formation of inter-metallic phases is likely, which may have undesirable features such as low melting temperatures or poor mechanical properties. The research described was an attempt to address these problems from a fundamentally different point of view, for Mo- and Nb-based alloys, through the use of a dispersed reservoir phase.

1. Introduction.

The Wagner criterion [1] for the formation of an external oxide scale on alloy AB requires the mole fraction of B (N_B^*) needed in the alloy to allow external scale formation to be reduced to its lowest possible value. This can be achieved by minimizing the oxygen permeability of the alloy, or by increasing the diffusivity of the desired element (D_B). The dispersed reservoir phase approach [2-4] is an attempt to effectively increase D_B by introducing local sources of B, and physically reducing the area to be covered by the BO_m oxide. This approach is based on previous research [5] with a binary Co-25Cr and ternary Co-25Cr-C alloys, which contained sufficient C to precipitate virtually all the Cr in the alloy as carbides. In the ternary alloy, the chromium carbides acted as local reservoirs of Cr, and effectively concentrated the desired element (Cr) in the location required for scale formation, and reduced the distance that the Cr must diffuse to the required site. The use of a dispersed reservoir was further demonstrated using SiC in Ni to allow the formation of a protective silica scale [2,4].

A generalized application of this approach to the design of oxidation-resistant alloys requires the selection of reservoir phases which are thermodynamically stable in the alloy, but are unstable in the presence of oxygen. Therefore, a detailed thermodynamic analysis of all the possible reactions between the reservoir phase and the constituents of the matrix alloy is a prerequisite.

2. Experimental procedures.

The composition of the Mo-based alloy was chosen from the results of prior experimentation [3] that indicated the possibility of forming a continuous SiO_2 scale if Mo contained 15 Si_3N_4 (30 volume percent) and 6Si. The size range of the starting powders was: Mo – 2 to 4 μm ,

$\text{Si}_3\text{N}_4 - 0.3 \mu\text{m}$, and Si-approximately $10 \mu\text{m}$. These powders were milled in a very high energy ball mill to obtain the desired microstructures, and compacted by vacuum-hot-pressing. A series of Nb-Al alloys, using AlN as the dispersed reservoir, and with additional Al added as NbAl_3 up to a total Al content of approximately 50 weight percent (NbAl_3 -20AlN), was prepared by high-energy ball-milling of Nb, AlN, and NbAl_3 powders, which had an average particle size of 3.5 and $10 \mu\text{m}$, respectively. The powders were milled using a modified technique which involved the use of powder handling in a Ti-gettered environment to minimize oxygen pickup and loss of AlN through reaction with moisture. The milled powders were consolidated by vacuum-hot-pressing.

The oxidation exposures were carried out in a horizontal tube furnace equipped with an alumina reaction tube, and the specimens were contained in alumina or zirconia boats. Weight change data were generated by periodically withdrawing the specimens from the furnace.

3. Results and discussion.

Mo- Si_3N_4 -Si ALLOY. — The weight change data of specimens of the Mo-15 Si_3N_4 -6Si alloy, oxidized in air at 1000, 1200 and 1400 °C are shown in figure 1. All the specimens initially lost weight due to the formation of volatile MoO_3 , the rate of loss increasing rapidly with increasing temperature. However, after a few hours, the rate of weight loss abruptly stopped, indicating that formation of the volatile MoO_3 had been suppressed due to the formation of a protective, solid scale. Figure 2 shows a cross section of a specimen oxidized for 111 hours at 1000 °C. The secondary electron image and X-ray maps for Si and O indicate that the solid oxide layer consists of Si and O, and is presumably silica.

Fig. 1. — Oxidation kinetics of Mo- Si- Si_3N_4 alloy in air.

A suggested mechanism for the formation of a protective SiO_2 scale on this Mo alloy is shown schematically in figure 3. The sequence of events that might occur is as follows: at time $t = 1$ Mo oxidizes and forms the volatile MoO_3 . Simultaneously, oxygen dissolves in the Mo and diffuses inward, and Si and Si_3N_4 particles at the surface oxidize to form SiO_2 . Also, Si from the alloy diffuses toward the surface and, where the Si and O activities are sufficiently high,

Fig. 2. — Secondary electron image and X-ray maps for silicon and oxygen from a cross section of Mo-Si-Si₃N₄ alloy after oxidation for 111 hours in air at 1000 °C.

Fig. 3. — Schematic diagram of suggested mechanism of protective scale formation on Mo-Si-Si₃N₄ alloy.

oxidizes to form SiO_2 . Decomposition of Si_3N_4 is suppressed by the presence of Si in the alloy. At time $t = 2$, volatilization of MoO_3 has caused recession of the alloy surface, which in turn causes the oxidized Si_3N_4 particles to accumulate, possibly sintering together. This increasingly dense, blocking layer reduces O ingress to the alloy so that, at $t = 3$, Si in the alloy can diffuse to this layer, where it oxidizes and seals the gaps that exist between the agglomerated Si_3N_4 particles. At $t = 4$, an essentially continuous SiO_2 -based layer has been formed, and the specimen is protected from further oxidation and suffers little weight loss.

Nb-Al-N-Al ALLOYS. — The data collected for the Nb-Al-N-Al alloys at 1000 and 1200 °C, plotted as weight gain per unit area as a function of the square root of time, are shown in figure 4. In agreement with the previous experience of a number of workers, all of the alloys except NbAl_3 -20AlN exhibited rapid rates of oxidation at both temperatures.

Metallographic examination of the scales formed indicated voluminous oxides of apparently uniform composition, with no obvious subscale that might be expected to control the oxidation rate.

Further oxidation of the NbAl_3 -20AlN alloy at 900 and 1400 °C showed protective behavior at all the temperatures investigated, although the oxidation rate measured at 900 °C was somewhat faster than that observed at 1200 °C, as is shown in figure 5. It is not clear whether this change in behavior is inherent in the way this dispersion-containing alloy forms protective scales, but it does not appear to be due to the onset of a pest mechanism. The oxidation rates for this alloy are plotted in a Arrhenius plot, as is shown in figure 6a, which also contains data from the literature [6, 7]. The best straight line through the experimental points from this work for 1000, 1100, and 1200 °C gives an activation energy of 114.8 kcal/mole.

Fig. 4.

Fig. 5.

Fig. 4. — Effect of aluminum content on oxidation kinetics of Nb-Al alloys oxidized in air.

Fig. 5. — Oxidation kinetics of NbAl_3 -AlN alloy in air at 900 to 1400 °C.

Coincidentally, this value is very close to that cited for oxygen diffusion in single crystal Al_2O_3 [8]. Also included in figure 6a are oxidation data for Nb-Ti-Al-V alloys in oxygen from the work of Perkins and Meier [10], the triangles representing oxidation rates for these alloys when complex Nb-Ti-Al oxides were formed, while the data points represented by closed circles are oxidation kinetics when these alloys formed a scale of basically protective Al_2O_3 .

Fig. 6. — Arrhenius plots for oxidation of $\text{NbAl}_3\text{-AlN}$ alloy: a) assuming single oxidation mechanism; b) assuming a change in mechanism at 1400 $^\circ\text{C}$.

Fig. 7. — Optical cross section of $\text{NbAl}_3\text{-AlN}$ oxidized at 1200 $^\circ\text{C}$.

The line drawn through these latter points is that representing the rate of oxidation of NiAl, when a reliably protective Al_2O_3 scale was formed. The data points generated at 1000 and 1200 °C in the present work fall very close to this line, while the data point at 1400 °C is closer to the line representing the formation of complex Nb-Al-containing oxides. This might suggest that the oxidation behavior of the NbAl_3 -AlN alloy is controlled by diffusion through a protective Al_2O_3 layer at the two lower temperatures, but that at 1400 °C, a continuous alumina scale is not formed, so that the oxidation behavior is then controlled by a complex Nb-Al-containing scale. Figure 6b shows a graphical representation of this interpretation. The suggestion that an Al_2O_3 scale is formed at the lower temperatures but not at 1400 °C is, however, in direct contrast to the behavior of Perkins and Meier's Nb-Ti-Al-V alloys, which were only able to form a continuous Al_2O_3 layer at the higher temperatures. Note also that a data point from Singheiser, *et al.* [7] for the oxidation of NbAl_3 at 1000 °C also falls close to the line for the growth of alumina on NiAl.

Figure 7 shows a metallographically-polished cross section of NbAl_3 -20AlN after oxidation for 76.5 hours at 1200 °C. The metal-oxide interface appears to be essentially flat, and the two-layered structure of the scale is evident. The inner layer was shown by energy-dispersive X-ray analysis to be enriched in Al. X-ray diffraction analysis indicated that α - Al_2O_3 was the major phase present. The outer, apparently porous layer was Nb-rich, and presumably represented the transient scale that formed during the time required for the basal layer of Al_2O_3 to become continuous. These data appear to confirm that a continuous basal oxide layer of essentially Al_2O_3 is formed on this alloy and controls the oxidation rate.

Although unmodified NbAl_3 contains sufficient Al to initially form an Al_2O_3 scale, Steinhorst and Grabke [9] have shown that such scales are rapidly disrupted and that oxidation at a linear rate ensues. This is a result of the formation in the Al-depleted region beneath the scale of the next-lower intermetallic, Nb_5Al_3 , which oxidizes rapidly once exposed to the environment. Al-rich NbAl_3 was demonstrated to form consistently protective scales.

Any explanation of the effects of the dispersed reservoir phase on the development and maintenance of a protective Al_2O_3 scale on NbAl_3 must account for the facts that, since Nb oxides grow by anion diffusion, there is no injection of vacancies, nor accumulation of oxidized reservoir particles beneath the outer scale, as in the case of the Ni-SiC alloy [4], and that there is no volatilization to assist the accumulation of dispersoid particles at the alloy surface, as in the case of the Mo-based alloy. In this case, the formation of a protective scale is thought to be strictly controlled by the initial composition of the alloy, and the initial distribution of AlN in the alloy. One possible function of the AlN reservoir phase in the NbAl_3 -AlN alloy may have been to compensate for the Al consumed to form the protective scale, and to prevent the degradation of NbAl_3 to Nb_5Al_3 .

The other mode in which a dispersed-reservoir phase has been observed to promote the formation of a protective, external scale on a Ni-SiC alloy is by dissociating ahead of the advancing oxidation front, and releasing the protective scale-forming element to diffuse to the oxidation front. Because of the rapid, initial oxidation rate of the Nb-based alloys, there is probably insufficient time for this mode of protective scale formation to occur. However, after the formation of the initial Al-Nb-containing scale on the NbAl_3 -AlN alloy, for instance, the effective oxygen partial pressure beneath this semi-protective scale (which will contain incorporated AlN particles) may be sufficiently low to allow AlN particles in the subjacent alloy to dissociate and contribute to the formation of a continuous alumina scale on a local level.

4. Conclusions.

The experimental results reported demonstrate that the ability to form a protective oxide scale can be incorporated into Mo and NbAl₃ by using the dispersed-reservoir approach described. The use of appropriate reservoir phases, for instance, should allow the formation of any of the three practically-useful oxides or, in principle, any other desired oxide, providing the reservoir phase meets the appropriate thermodynamic criteria. However, this ability comes at the price of incorporating into the alloy a dispersion of second phase particles, which has implications for the mechanical properties of the alloy. At the level and size used in earlier work in a Ni-SiC alloy [4], the dispersed particles resulted in a reduction of the room-temperature ductility of the alloy to 3 percent. While the alloys investigated in this program were obviously not optimized in terms of the minimum volume fraction and particle size of the dispersed second phase, their effect on mechanical properties is obviously an important consideration. Further research is required to translate these concepts to the design of practical, high-temperature components, but the underlying principles appear to offer promise.

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