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OXIDATION BEHAVIOR OF $Cr-Cr_2Nb$ ALLOYS

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Oxidation of hypoeutectic $Cr-Cr_2Nb$ alloys containing 6 and 12% Nb at 950°C resulted in the formation of a multiproduct scale consisting of a continuous Cr_2O_3 outer layer and an inner region of discrete $CrNbO_4$ products interspersed with Cr_2O_3. Overall oxidation behavior resembled that of chromium as reactions with the Cr-rich phase tended to dominate. Oxidation resistance, in terms of reaction kinetics and scale adherence, increased with increasing volume fraction of the $Cr-Cr_2Nb$ eutectic phase. A model for the oxidation of these alloys based on the growth of Cr_2O_3 on the Cr-rich matrix regions and the formation of a slower growing $CrNbO_4$ on the Cr_2Nb-enriched phase can qualitatively explain the development of the multiproduct scale and the observed gravimetric and spallation results. Possible microstructural/compositional modifications to improve oxidation resistance are suggested.

MASTER

INTRODUCTION

Despite the commercial importance of numerous multiphase alloys, studies of the high-temperature oxidation, sulfidation, or carburization of such materials have been relatively limited. This is particularly true with respect to modeling and experiments aimed at developing a basic knowledge of the relevant reaction processes and the resulting corrosion product structures. In recent years, however, there has been increased activity in these areas – see, for example, refs. 1-7 – and a better understanding of the relationships among high-temperature environmental reactions, alloy microstructure, and the resulting scale structures is now forthcoming. Consequently, it was considered timely to analyze the oxidation behavior of selected $Cr-Cr_2Nb$ alloys.

Some aspects of the nature of scales formed on binary $Cr-Cr_2Nb$ (6 and 12 at. % Nb) alloys have been described previously (8,9). Multiple corrosion products formed on an alloy consisting of a Cr-rich solid solution and a $Cr-Cr_2Nb$ eutectic phase. Oxidation resistance (as determined by mass change kinetics and scale adherence) increased with an increasing starting volume fraction of the eutectic phase. No positive effect of modest additions of Al, Re, Fe, and Ni to Cr - (6 - 12 at.%)Nb on oxidation was found (9). This paper contains additional data on the oxidation behavior of binary Cr-Nb compositions, particularly with respect to scale characterization, and some results for alloys with modified microstructures resulting from adding molybdenum. The present and previous results are then analyzed in terms of some possible models that can be applied to the high-temperature gaseous corrosion of two-phase alloys.

The alloy compositions included in this study (Cr -6 and -12 at.% Nb) are in the hypoeutectic two-phase region of the Cr-Nb system (10). The microstructure consists of a

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matrix of Cr-rich solid solution surrounded by an interconnected eutectic structure (9,11). An example of such a structure is shown in Fig. 1. In the as-cast condition, the Cr-rich regions are supersaturated with Nb [solubility is about 1.7 at. % at 1000°C (ref. 10)], but, upon annealing at 900-1200°C (for up to 100 h), a uniform distribution of fine Cr_2Nb particles develops in this phase (11). As discussed below, the Cr-Cr_2Nb system is not ideal for studying the oxidation of multiphase alloys as the microstructures are somewhat complex (9-11). Oxidation studies of these alloys are primarily motivated by interest in developing materials with exceptional strengths at high temperatures based on incorporation of a Laves phase (Cr_2Nb in the present case). Significant progress has been made in this regard (12), but improvements in the room-temperature toughness and oxidation resistance of developmental compositions are still being pursued by alloying and processing modifications. A better mechanistic understanding of the oxidation behavior of this two-phase system is sought so as to establish the relationships between scale structure and substrate microstructure. This should then help to better guide alloy design, through manipulation of the composition and microstructure of Cr-Cr_2Nb and similar alloys, so as to develop materials with increased oxidation resistance via more protective oxide scales.

MATERIALS AND EXPERIMENTAL PROCEDURES

The Cr-Cr_2Nb alloys were prepared by arc melting and drop casting into a copper mold preheated to 300°C. High-purity Nb and Cr metal chips were normally used as charge materials, and the alloys were melted in a vacuum (10^{-3} Pa) furnace. The oxygen and carbon contents of the Nb chips were less than 200 and 50 wt ppm, respectively, and the oxygen levels in the alloys were typically less than 500 wt ppm. Table I lists the alloy compositions used in this study. (All concentrations noted hereafter are in at.%.) In the case of alloys CN-60 and -73, molybdenum was added to refine the coarse eutectic structure normally found in the binary (and other) alloys (compare Fig. 2 to Fig. 1). Such microstructural manipulation improved the toughness of the Cr-Cr_2Nb alloys by breaking up the blocky interconnected Cr_2Nb particles (13).

Table I. Nominal compositions of Cr_2Nb-Cr (CN) alloys.

Alloy Number	Concentrations of Major Elements (at. %)
CN-4	Cr-12Nb
CN-7	Cr-6Nb
CN-60	Cr-12Nb-6Mo-4Re-2Al
CN-73	Cr-5.6Nb-6Mo-1.5Al-0.1Zr

Thermogravimetric analysis (TGA) was used to assess overall reaction kinetics associated with the oxidation of the Cr-Cr_2Nb alloy; specimens (typically 7–15 mm x 5–10 mm x 1–2 mm were isothermally exposed to flowing, preheated, dried air (2 cc/s) at 950°C for up to 240 h. Weight changes were continuously measured using Cahn 1000 microbalances and a computer-controlled data acquisition system. At the end of each experiment, the specimens were furnace cooled and visually checked for loss of corrosion products by spallation. They were not re-exposed. In a few cases, specimens of selected compositions were held in laboratory air in a horizontal tube furnace at 950°C and withdrawn at intervals of 24 - 72 h, cooled to room temperature, visually examined, weighed, and returned to the furnace. This latter type of experiment was used to qualitatively assess the effect of repeated damage from thermal cycling on the integrity of the corrosion product scales.

Selected specimens from isothermal or cyclic exposures were examined by optical imaging of polished cross sections, scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDS), and/or electron microprobe analysis. In some of the cases when significant scale detachment/spallation occurred, the corrosion products from an individual specimen were collected, pulverized to a fine powder, and analyzed by x-ray diffraction (XRD).

RESULTS

Previously, it was shown that the Cr - 6% Nb binary alloy suffered higher mass gains and oxidation rates than Cr - 12% Nb at both 900 and 950°C (8). Alloying both compositions with molybdenum (CN-60 and -73), which modified the two-phase structure (see above), had a substantial negative effect on the oxidation rates. This is shown by the TGA data in Fig. 3, which compares the behavior of CN-60 and CN-73 with that reported earlier for the respective Cr -Nb binary alloys (8). As with the binary compositions, the alloy with the lower Nb content (CN-73) showed greater weight gains. The combination of Mo and lower Nb content resulted in very rapid, linear oxidation kinetics (Fig. 3). For CN-60 and CN-73, thermal cycling exacerbated the rate of metal consumption due to extensive scale damage (see, for example, Fig. 4) and spallation. Examination of oxidized surfaces that suffered partial scale loss revealed that much of the spallation occurred on the Cr-rich phase of the substrate (8,9). This can be illustrated by comparing an SEM image of cyclically oxidized CN-4 with one of the as-processed microstructures (Fig. 5). The spallation pattern resembles the grain structure of the substrate.

Spalled scales from CN-7, CN-60, and CN-73 were analyzed by XRD. Most of these products appeared to spall with little remaining scale on the metal surface. In each of the three cases, Cr_2O_3 and $CrNbO_4$ were identified (see Fig. 6). Previous EDS analysis of oxidized specimens of CN-4 and CN-7 showed products rich in Cr or Cr-Nb (8), and it was assumed that these were oxides. The present XRD results confirm the existence of these oxide products. Microprobe data also indicated that these products formed as oxides and that little unreacted metal was incorporated into the multiproduct scale (Fig. 7). Additionally, these results showed that the structure of the scale consisted of an outer continuous base-metal oxide (Cr_2O_3) and underlying discrete $CrNbO_4$ products in Cr_2O_3.

During oxidation, pores formed under the reaction products (see the electron image in Fig. 7 and ref. 8). The development of porosity is also illustrated by an examination of a fracture cross section of the scale formed on CN-4 after 180 h at 950°C (Fig. 8). As shown in Fig. 7 and elsewhere (8), underlying porosity tended to be associated with the Cr-rich phase.

DISCUSSION

The present XRD and microprobe results clearly indicate that chromia and $CrNbO_4$ are the principal reaction products when Cr - (6 – 12%) Nb alloys are oxidized at 900 and 950°C. Based on thermochemical stability considerations (14,15), which indicate that the oxides of niobium (Nb_2O_5, NbO_2, and NbO) are more stable than Cr_2O_3, the presence of chromia as the outer layer (Fig. 7) of a multiproduct scale is not unexpected. An outer scale of pure Cr_2O_3 also was observed upon oxidation of a Cr - 27% Nb alloy (hypereutectic part of the Cr-Cr_2Nb region) at 900°C (16).

It is interesting to examine the possible mechanisms by which the chromia scale can seamlessly form over a mixed oxide region and both phases of the Cr-Cr_2Nb alloy (Fig. 7). As recently discussed by Gesmundo and Gleeson (6), a number of possible scale structures can form upon high-temperature exposure of a two-phase alloy to a single-oxidant environment. These include (i) a layer consisting of discrete A- and B- oxides that results from the matrix and second phases of an A-B alloy oxidizing independently of one another; (ii) a uniform (AB)-oxide surface product formed by cooperative oxidation of the two phases; and (iii) a continuous B-type oxide scale that grows because the B-enriched second phase acts as a solute reservoir. However, although the reaction products on the Cr-Cr_2Nb alloys of this study do not match any of these generalized cases, the operative process may simply be a later manifestation of the oxidation reactions underlying the scale structure described in (i). In this regard, there is some similarity between the present results and recent observations associated with the sulfidation of Fe-Nb (and other) two-phase alloys (17). In the sulfidation case, the scales formed on the Fe-(20-30%)Nb alloys consisted of an outer layer of iron sulfide and an inner complex region consisting of $FeNb_2S_4$, iron and niobium sulfides, and unreacted metal. Initial reaction occurred over the solvent- (Fe-) rich phase and lateral overgrowth of sulfide islands led to a continuous outer scale of this product. This layer grew by outward cation diffusion, while the inner region grew by inward sulfur transport.

The similarities between the sulfide scale structure described immediately above and the observed oxide product layers on Cr-Cr_2Nb suggest that the reaction processes may well be the same in both cases as similar driving forces exist. A generalized model for the development of such scale structures has been described by Gesmundo et al. (3). Applying it in the context of the present alloy system shows that, if Cr_2O_3 grows by means of outward diffusion of cations (as is generally considered to be the case [18]), then a duplex scale of outer chromia and a mixed inner layer of the oxides of Cr and Nb and, possibly, the Cr_2Nb phase would result. This is in qualitative agreement with what is observed (see Fig. 7), but strict application of this model to the present case is not appropriate as some of the assumptions on which it is based (related to the absence of ternary products and the respective rates of oxidation of the A- and B-type binary oxides) are not necessarily met (3). However, consideration of a similar model in which, initially, a pure chromia layer grows over the Cr-rich regions of the alloy while $CrNbO_4$ (or $Cr_2O_3/CrNbO_4$) forms over the Nb-enriched phase can describe the development of the observed multiphase scale structure on Cr-Cr_2Nb alloys.

As shown in Figs. 7 and 8, the oxidation of the Cr-Cr_2Nb alloys also led to the development of underlying porosity. The pores can probably be ascribed to the Kirkendall effect arising from the preferential outward flux of chromium in conjunction with the growth of the outer chromia layer (18). The evidence that the porosity forms most readily over the Cr-rich phase (Fig. 7, ref. 8) may indicate a reduced chromium flux out of the Cr_2Nb-eutectic regions and would be consistent with a lower growth rate of the product formed on this phase (which was a necessary assumption for the modified scale development model described above). Underlying Kirkendall porosity associated with one phase of an oxidized two-phase alloy has been observed in other alloy systems - see, for example, ref. 19. The observed tendency for spallation to occur over the Cr-rich regions of the substrate (Fig. 5) may suggest that there is a relationship to the observed porosity distribution (8). However, while this porosity may be associated with the reacting matrix phase, it is not necessarily at the oxide-metal interface (Fig. 7, ref. 19) and thus does not directly influence scale adherence.

It has previously been shown that the binary Cr - (6 – 12%) Nb alloys oxidized at rates that fall into the band of those reported for chromia growth and that there were other aspects of their oxidation behavior (such as isothermal scale cracking) that resembled the oxidation of pure chromium (8,9). This is not surprising, as the thermogravimetric data (such as shown in Fig. 3) should reflect the oxidation characteristics of the major component of a multiphase structure (20). The decrease in weight gain as the Nb concentration of the binary and Mo-containing hypoeutectic Cr-Nb alloys was increased from ~6 to 12% (Fig. 1) is consistent with an increase in the volume fraction of the Cr_2Nb eutectic if the more slowly growing $CrNbO_4$ forms on this phase, as hypothesized above. In other work (summarized in ref. 21), the ratio of the oxidation rates of Cr-Nb alloys to that of Cr decreased as the Nb concentration increased from 7 to 37%, so it is reasonable to assume that this is the case.

Gesmundo et al. (3) have shown that, during oxidation of simple two-phase alloys, the matrix phase will oxidize faster, and dominate the oxidation behavior, if the second-phase particles are large. This is consistent with the results reported for the Cr-Cr_2Nb alloys of this study. Wang et al. (1) also concluded that conditions for the formation of a predominant solute oxide are favored when the second phase is finely distributed in the alloys. Therefore, refining the coarse Cr_2Nb eutectic microstructure should decrease the measured weight gains by promoting formation of $CrNbO_4$ at the expense of Cr_2O_3 grown over the Cr-rich regions. However, even though molybdenum does break up the interconnected network of Cr_2Nb-enriched phase (see Fig. 2 and ref. 13), its presence in the alloy led to greater increases in mass upon oxidation (Fig. 3). This may be partly due to the fact that the distribution of the matrix phase is also finer (compare Figs. 1 and 2), but the chemical effects of increased reactivity due to the molybdenum may outweigh any effects related to the modification of the two-phase microstructure.

The alloy compositions included in the present study are not ideal for rigorously studying and modeling the oxidation behavior of two-phase materials. Niobium can form a variety of oxide scales, which differ considerably from one another in terms of thermochemical stability, oxidation rate, and the time-dependence of its growth (18). The stability of the most noble of the oxides of niobium, Nb_2O_5, is not much different from that of Cr_2O_3. Furthermore, at least one ternary product, $CrNbO_4$, can form. More importantly, the microstructure of these alloys is quite complex and not easily modeled for oxidation studies: fine Cr_2Nb particles are precipitated in the matrix phase during high-temperature treatment of as-cast material and the Cr_2Nb eutectic structure contains small Cr-rich patches (9,11). In essence, the phase distribution in these alloys is nested. Nevertheless, as mentioned in the Introduction, the Cr - (6 - 12%) Nb alloys hold significant promise with respect to mechanical strength at high temperature and it is important to understand their oxidation behavior as part of overall alloy development. In this regard, the previous (8) and present findings would suggest that increased oxidation resistance could perhaps be attained by manipulating the microstructure and/or increasing the niobium concentration to try to promote the formation of more slowly growing $CrNbO_4$ or even a continuous inner $CrNbO_4$ or NbO barrier layer. (The NbO product is very stable and relatively slowly growing at low partial pressures of oxygen [18]. It could serve as a barrier if it developed as an underlying layer, but only if the partial pressure of oxygen was continuously maintained at a sufficiently low level by the presence of a robust outer scale.) Concerns about the effect of an increased volume fraction of the brittle Laves phase on