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Oxidation and sulfidation resistance of a Nb-Cr alloy

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Abstract. — Cr and Cr-bearing alloys possess satisfactorily good oxidation resistance at high temperatures, but they sulfidize catastrophically in sulfur-bearing environments which are encountered frequently in energy conversion systems and in petrochemical industries. Nb, on the other hand, has good sulfidation resistance but poor oxidation resistance at high temperatures. A combination of Cr and Nb is shown to improve the corrosion resistance at high temperatures in oxidizing and sulfidizing environments. Kinetic and microstructural studies of oxidation and sulfidation of Cr-40wt%Nb alloys were preformed at 1173 K in sulfur vapor ($P_{S_2} = 0.74$ atm). This two phase alloy consists of an fcc Cr_2Nb intermetallic phase and small amount of Cr base alloy and shows very good oxidation resistance and appreciable sulfidation resistance in comparison with Fe-45Cr, pure Nb and Fe-40Mo. The dominant oxidation product is Cr_2O_3 , while the sulfidation products are rhombohedral Cr_2S_3 as an external scale and a Nb sulfide inner scale between the Cr_2S_3 and substrate.

1. Introduction.

It is well known that structural base metals Fe, Co and Ni are resistant neither to oxidation nor to sulfidation when exposed to oxidizing and sulfidizing environments at high temperatures and that, additionally, these metals sulfidize at rates orders of magnitude greater than the corresponding oxidation rates [1]. Cr and Cr-bearing alloys provide satisfactory oxidation resistance [1], but fail to provide sulfidation resistance; even preformed Cr_2O_3 scales are rapidly degraded by quite low sulfur levels in H_2 - H_2O - H_2S gas mixtures (e.g., $P_{O_2} = 10^{-10}$ atm, $P_{S_2} = 10^{-6.5}$ atm for Fe-45Cr alloy at 1173 K) where Cr_2O_3 is the only thermodynamically stable phase [2].

On the other hand, it has been established that both Nb and Mo have outstanding sulfidation resistance [3-5]. Unfortunately, the oxidation resistance of these refractory metals is extremely poor and limits their application in high temperature environments with high oxygen partial pressure. In most fuel energy systems, however, oxygen partial pressure is usually low and sulfur partial pressure is relatively high. For example, in a number of energy systems, metallic materials are exposed at elevated temperatures to gaseous environments containing oxygen in a general range $P_{O_2} = 10^{-10} \sim 10^{-20}$ atm and sulfur in a general range $P_{S_2} = 10^{-7} \sim 10^{-10}$ atm [10]. The good resistance of Nb and Mo to sulfidizing corrosion thus arouses interest for their use as potential alloy bases or alloy additions for developing protective scales resistant to S-bearing atmospheres.

Douglass [6-9] has led his UCLA research group in studying the effects of Mo and Nb on the sulfidation kinetics of Ni, Co and Fe. They concluded that the addition of up to 40 wt.%Nb failed to form a continuous, protective layer of NbS_2 , and that the addition of Mo to those base metals is a best choice for lowest sulfidation rate. Considering the satisfactory oxidation

resistance of Cr and Al, as well as sulfidation resistance of Nb and Mo, it seems to us more natural to select such binary alloys as Cr-Nb, Cr-Mo, Al-Nb or Al-Mo to study their sulfidation and oxidation properties.

The present work reports our recent results for a Cr-Nb alloy in high temperature oxidation and sulfidation studies. As far as we know, this is the first system reported to exhibit simultaneous oxidation resistance and sulfidation resistance.

2. Experimental conditions.

Finger-shaped Cr-40wt.%Nb (27.17 at.%Nb) alloy ingots were prepared for us by Ames laboratories, Ames, IA using a nonconsumable electric arc melting technique in high purity argon atmosphere. This alloy locates in a two-phase region comprising Cr_2Nb intermetallic compound and Cr-base alloy. Each as-cast ingot was encapsulated in a quartz tube flushed with high purity argon, with Ta as an oxygen getter, then annealed at 1373 K for 50 hours. Since this alloy is very brittle, in order to prevent mechanical damage during slicing, the ingots were potted inside a steel tube with a five-minute epoxy resin; then, each potted ingot was sliced into disks of 0.5-1 mm in thickness. Prior to exposure to reaction gas mixtures at high temperature, specimens were cleaned in acetone and methyl alcohol. The weight and size of each specimen were measured with an electronic balance and a micrometer, respectively, and its area was calculated. Specimens were then degreased ultrasonically in acetone and methanol. After drying for 10 to 30 minutes, the specimens were ready for oxidation and sulfidation experiments. Oxidation experiments were conducted at 1173 K in ambient atmosphere. Sulfidation experiments were carried out in sulfur vapor with P_{S_2} levels relatively higher ($P_{\text{S}_2} \approx 0.74$ atm) than previous experiments, the sulfur vapor being produced directly from liquid sulfur in this work. In general, sulfur vapor consists of several forms of sulfur molecules S_n , where $n = 1, 2, \dots, 8$, or even higher values. The boiling point of sulfur is calculated as 721.1 K from thermodynamic data cited by Kubaschewski and Alcock [12]. The volume fraction of S_2 in the sulfur vapor is approximately 98% at the 1173 K reaction temperature. One set of samples was oxidized 2 h at 1173 K and subsequently exposed for 1 h to sulfur vapor at 1173 K.

3. Kinetic results.

The Cr-40Nb alloy showed both oxidation and sulfidation resistance at 1173 K. The scaling rate was determined by measuring average scale thickness, and both sulfidation and oxidation rates appear to follow a parabolic rate law, as shown in figure 1. Sulfidation of this alloy resulted in a duplex scale. X-ray energy dispersive spectroscopy (XEDS) examination indicated that the external scale is rich in Cr and S, while the inner scale is rich in Nb and S. Oxidation and sulfidation rates of Fe-45Cr, Nb and Fe-40Mo at 1173 K are also plotted in figure 1b for comparison. The sulfidation scaling rate for Fe-40Mo alloy was calculated from the data of Carter *et al.* [13]; this alloy exhibited the best sulfidation resistance of the refractory metal alloys investigated by the UCLA group [6-9].

Fig. 1. — a) Scale growth kinetics for the overall sulfidation scale (D1), outer scale (D2) and inner scale (D3) formed on Cr-40Nb alloy in sulfur vapor $P_{S_2} = 0.74$ atm; b) scale growth kinetics for oxidation of Fe-45Cr (A), Cr-40Nb(B) and Nb(F) in air; for sulfidation of Nb(C) in H_2 - H_2S $P_{S_2} = 10^{-9}$ - $10^{-4.62}$ atm; Cr-40Nb(D) in sulfur vapor $P_{S_2} = 0.74$ atm; Fe-40Mo(E) in sulfur vapor $P_{S_2} \approx 10^{-4}$ atm; and for oxidation/sulfidation of Fe-45Cr(G) in H_2 - H_2S - H_2O , $P_{S_2} = 10^{-6.5}$, $P_{O_2} = 10^{-19}$ atm.

4. Oxidation scale.

X-ray diffraction results for an as-oxidized Cr-40Nb alloy exposed to air at 1173 K for two hours are shown in figure 2. The phases identified are Cr_2O_3 (solid triangles) in the overlying oxidation scale and cubic Cr_2Nb (solid circles) in the underlying substrate. A few additional weak peaks were consistent with Cr and a Nb_2O_5 phase. No ternary Nb-Cr oxides were

found in the oxidation product. Figure 3 shows the surface morphology of such an oxidized specimen and a fractograph across a transverse section. Some areas show particles of Nb_2O_5 on top of a Cr_2O_3 scale. When the oxidation time was extended to 20 hours, no appreciable differences were observed in the X-ray diffraction patterns. This alloy exhibited excellent oxidation resistance in comparison to that of pure Cr, Fe-45Cr, and type 310 stainless steel (Fe-20Cr-12Ni).

Z17342 4/18/91 S= 0.050 T=10.000 2 HOUR OXID.

Fig. 2. — X-ray diffraction profiles from Cr-40Nb oxidized in air for 2 h at 1173 K; solid circles refer to Cr_2O_3 and solid triangles to Cr_2Nb .

5. Sulfidation scale.

The slow sulfide scale growth kinetics presented in figure 1 show that sulfidation resistance without loss of oxidation resistance is clearly achieved. The sulfidation scale has been identified as a rhombohedral Cr_2S_3 external scale overlying a thin NbS_2 inner scale. The corresponding X-ray diffraction profiles are presented in figure 4. The rhombohedral Cr_2S_3 scale has a very similar morphology to that observed in the sulfidation of Nb in H_2 - H_2S , with $\{10\bar{1}0\}$ planes preferentially parallel to the scale surface. This texture also indicates that the hexagonal c axis is parallel to the scale/substrate interface. The sulfide scale morphology is shown in figure 5. The corresponding morphology for samples preoxidized at 1173 K and subsequently sulfidized is shown in figure 6.

Fig. 3. — SEM secondary electron image of oxide scale on Cr-40Nb alloy oxidized for 2 h at 1173 K in air. a) Surface morphology. b) Fractured cross-section revealing a very thin but continuous Cr_2O_3 scale.

Fig. 4. — X-ray diffraction profiles for two Cr-40Nb specimens after a) 1 h sulfidation in $P_{\text{S}_2} = 0.74$ atm at 1173 K; b) 2 h preoxidation in air followed by 1 h sulfidation in $P_{\text{S}_2} = 0.74$ atm at 1173 K.

6. Discussion.

The present experiments demonstrate the benefits of combining both Cr and Nb in high temperature oxidation and sulfidation environments. The Cr-Nb alloy showed excellent oxidation resistant and satisfactory sulfidation resistance at 1173 K.

Fig. 5. — a) SEM secondary electron image of surface morphology of assulfidized Cr-40Nb specimen after 1 h in $P_{S_2} = 0.74$ atm at 1173 K. b) SEM fracture cross-section revealing external Cr_2S_3 scale and inner niobium sulfide scale.

Fig. 6. — a) SEM secondary electron image of surface morphology of Cr-40Nb specimen after 2 h oxidation in air + 1 h sulfidation in $P_{S_2} = 0.74$ atm at 1173 K. b) SEM fracture cross-section revealing external Cr_2S_3 scale and an inner scale rich in Nb and S.

Selection of this alloy was guided by the composition of AISI type 310 stainless steels [14], one of several typically oxidation-resistant alloys for high temperature environments, which contain a minimum of 24-26wt.% (26-28at.%) Cr in order to form continuous chromia scales. As a first order guess, one might expect a similar minimum Nb content to achieve high temperature sulfidation resistance of Cr-Nb alloys. The Nb-Cr phase diagram reveals that the chosen alloy composition (40wt.%Nb, 27.17at.%Nb) is in a two-phase region rich in Cr and close to the intermetallic compound β' . According to level rule, this two phase alloy contains approximately 90wt.% of β' phase (Cr_2Nb) and 10wt.% of Cr terminal solid solution. Since this Cr terminal alloy contains < 5wt.%Nb, it is possibly not a sulfidation resistant alloy, but this difficulty may be overcome by the lateral growth of a niobium sulfide inner scale.

On the other hand, by choosing the alloy composition in the Nb-rich two-phase region (Nb alloy + Cr_2Nb), sulfidation resistance may be purchased at the possible expense of oxidation

resistance. The order of sulfidation resistance of the Cr-Nb system should be:

$$\text{Cr} < (\text{Cr} + \text{Cr}_2\text{Nb}) < \text{Cr}_2\text{Nb} < (\text{Nb} + \text{Cr}_2\text{Nb}) < \text{Nb},$$

while corresponding order of oxidation resistance should be

$$\text{Cr} > (\text{Cr} + \text{Cr}_2\text{Nb}) > \text{Cr}_2\text{Nb} > (\text{Nb} + \text{Cr}_2\text{Nb}) > \text{Nb}.$$

This crude conclusion is based on an assumption of non-interfering Cr and Nb corrosion processes. In practice, the oxidation resistance of $(\text{Cr} + \text{Cr}_2\text{Nb})$ or Cr_2Nb may be better than that of pure Cr due to interaction and doping effects.

Therefore, good oxidation resistance was expected of the Cr-40Nb alloy $(\text{Cr} + \text{Cr}_2\text{Nb})$, but its sulfidation resistance was unknown before the present experiments- and doubtful given its 60wt.% (73at.%)Cr content and our previous experience that catastrophic sulfidation occurs for Cr and Cr-bearing alloys. To our surprise (and delight), the scaling rate of the sulfide scale was satisfactorily slow, even though a much higher sulfur level ($P_{\text{S}_2} = 0.74$ atm) was employed in this work than in previous experiments.

According to the *Powder Diffraction File* [15], there are ten chromium sulfides identified, and Rau [16] reported that five phases are stable. The present X-ray diffraction experiments indicated that rhombohedral Cr_2S_3 is the only chromium sulfide formed as an external scale. The sulfidation rate of this Cr-40Nb alloy was found to be lower by 3 - 4 orders of magnitude than the rates for sulfidation of pure Cr and Fe-45Cr alloy.

That Cr_2S_3 grows as an external scale, while a niobium sulfide (NbS_2 , possibly) grows as an inner scale between the alloy substrate and the Cr_2S_3 scale, suggests that Cr_2S_3 grows by the outward migration of Cr, which is in agreement with two marker experiments for sulfidation of pure Cr [17, 18]. The formation of a continuous inner niobium sulfide scale creates a barrier to the outward diffusion of Cr; consequently, the sulfidation rate of the alloy was > 1000 times smaller than that of pure Cr.

7. Conclusion.

- Sulfidation scales formed on a Cr-40Nb alloy are continuous and duplex. The external scale is rhombohedral Cr_2S_3 with the c axis lying preferentially parallel to the scale/alloy interface; the inner scale is a niobium sulfide (possible 3R-NbS_2).
- The sulfidation rate of this alloy is more than 1000 times smaller than that for sulfidation of pure Cr and the Fe-45Cr alloy.
- The oxidation rate is 10^5 times smaller than the oxidation of Nb under the same conditions and about equal to the oxidation rate of pure Cr.

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