

Effect of Addition of Rare Earth Oxide Concentrates on Oxidation Behavior of AISI 304L Stainless Steel

Pillis, M.F.; de Araújo, E.G.; Ramanathan, L.V.

Instituto de Pesquisas Energéticas e Nucleares; Av. Prof. Lineu Prestes, 2242; Cidade Universitária; São Paulo, 05508-000; Brazil

Abstract

Rare earth elements are often added to chromium dioxide forming alloys to improve its high temperature oxidation resistance. The rare earths can be also added as oxide dispersions. Significant cost reductions are possible if rare earth oxide concentrates can be used instead of pure rare earth oxides, the former being the precursor to obtaining pure rare earth oxide. In this study the effect of adding pure and concentrates of rare earth oxides to AISI 304L on its oxidation behavior has been evaluated. AISI 304L stainless steel powder compacts containing 2 vol% of pure lanthanum and yttrium oxides or their concentrate were prepared by milling followed by pressing. The compacts were vacuum sintered and isothermally oxidized in air for up to 200h at 900°C. The reaction products were examined using a scanning electron microscope. The compacts with pure rare earth oxides and the concentrates exhibited similar oxidation behavior.

Experimental Procedure

Rare earth (RE) oxide concentrates are prepared using the solvent extraction technique. Starting with RE chlorides, the first stage of extraction of REs consists of separating them as light, medium and heavy REs. Within each group, after various stages of extraction and precipitation, further separation of concentrates of lanthanum and yttrium oxides is carried out. Powders of AISI 304L (0.01 C, 0.01 S, 11.3 Ni, 19.1 Cr, 0.9 Si, 0.159 O, 0.056 N, 0.2 Mn and balance Fe) and 2 vol.% pure oxides or concentrates of lanthanum and yttrium were mixed for 1h in a vibratory mill to obtain the powder mix. This mix was compacted in a uniaxial press and the compacts were sintered in vacuum for 1h at 1250°C. The specimens were then oxidized isothermally in a muffle furnace. The specimens were oxidized for 200h at 900°C. Curves of mass gain versus exposure time were obtained. The mass gain determined included that of the spalled oxide, where pertinent. The specimens oxidized for 100h were examined in a scanning electron microscope. Chemical analyses of micro-regions were carried out by energy dispersive spectroscopy (EDS).

Results and Discussion

The mass gain versus time curves of specimens oxidized in the muffle furnace are shown in Fig.1. The specimen without RE oxides showed the highest mass gain. The addition of both pure RE oxides and concentrates of RE oxides decreased the overall mass gain of the specimens as compared to that without RE oxide additions. The surface oxides formed on all specimens oxidized for 20h did not spall. However, after 50h of oxidation, the surface oxides on specimens without RE additions and with Y_2O_3 spalled. Oxide spalling on specimens with Y_2O_3 was slight and was in the form of a fine powder; whereas the oxide that spalled from the surface of specimens without RE additions was in the form of large scales. Fig. 1 also shows that during the first 20h of oxidation, the effect of the different RE oxide additions was similar. Beyond 20h of oxidation, the difference in the effects of the various RE oxide additions was more pronounced.

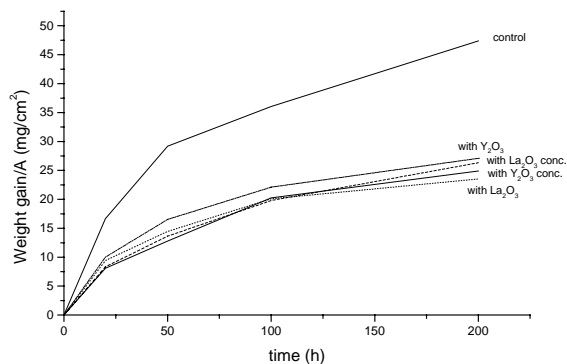


Fig. 1: Oxidation curves of specimens oxidized in a muffle furnace at 900°C.

Figure 2 shows the surface of AISI 304L oxidized for 100h at 900°C. The oxide in region 1 is rich in iron. It also shows acicular regions (region 2), containing iron and some nickel. Large parts of the surface where the oxide had spalled were also observed, and in these regions only iron were detected.

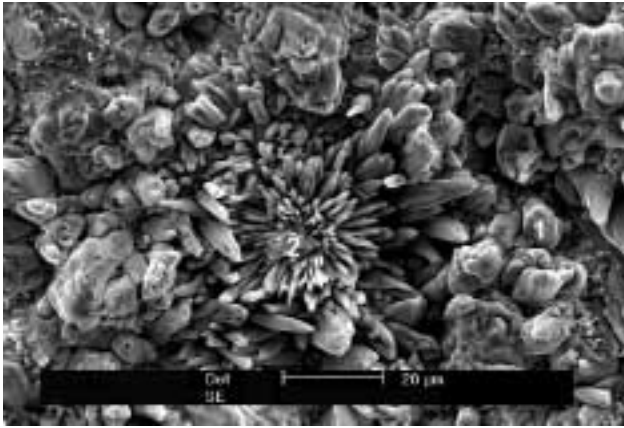


Fig. 2: Surface of AISI 304L oxidized for 100 h at 900°C in a muffle furnace.

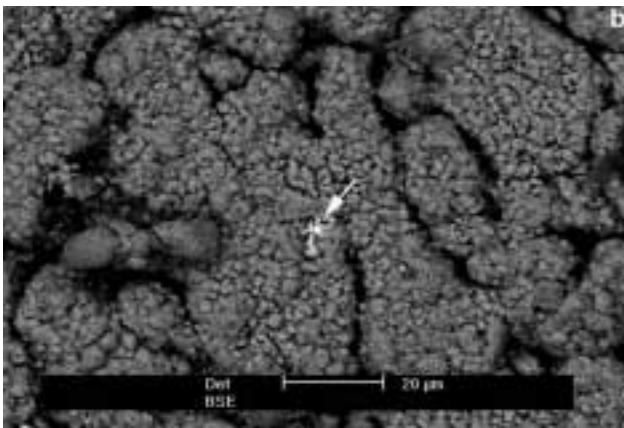
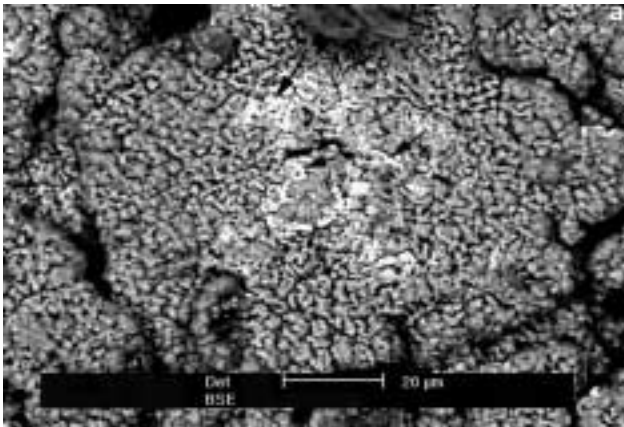


Fig. 3: Surfaces of: (a) AISI 304L + La_2O_3 and (b) AISI 304L + La_2O_3 concentrate, oxidized for 100h at 900°C in a muffle furnace..

Figure 3a is the surface of the alloy containing La_2O_3 after 100h of oxidation. No spalling was observed. The lighter regions, shown with arrows, are La_2O_3 . Specimens of the alloy containing concentrates of La_2O_3 did not spall after 100h at 900°C, but a number of surface cracks were seen,

as shown in Fig. 3b. Large quantities of Fe, Cr and some Ni were detected. The region shown with an arrow is an agglomerate of La_2O_3 concentrate. The presence of this RE oxide at the oxide/gas interface indicates that the scale grows at the metal/oxide interface and due to predominant anion diffusion. Alloys containing the other RE oxide additions were also examined and they showed similar microstructures.

Of the various mechanisms that have been proposed [1-5] to explain the effect of reactive element additions on oxidation behavior, presently the one most accepted is the change in the species that diffuses predominantly upon addition of RE. In Fe-Cr alloys without reactive elements, Cr_2O_3 grows by diffusion of both oxygen and Cr along the grain boundaries, and the oxide layer is thick [1]. Oxide growth stresses causes spalling. On the other hand in Fe-Cr alloys containing reactive elements, Cr_2O_3 grows by predominant oxygen diffusion [2, 3]. The oxide layer is thin and has a higher degree of plasticity. Adhesion of the oxide layer to the alloy is also higher. The RE ions segregate to the grain boundaries [5] of the alloy and the oxide scale, close to the metal/oxide interface. The large ionic radii of the RE (compared to the radii of Fe, and Cr ions) make cation diffusion more difficult, and anion transport the main mechanism for chromia layer growth.

Conclusions

1. The addition of RE oxides decreased the oxidation rate of AISI 304L at 900°C. This effect lasted for at least 200h of oxidation.
2. The oxidation behavior of AISI 304L containing pure RE oxide and RE oxide concentrates was similar.

Acknowledgements

The authors wish to thank FAPESP for the financial support given through Project no: 01/13748-6.

References

1. Golightly, F.A.; Stott, F.H.; Wood, G.C. **Oxid.Met.**, v.10, n.3, 1976, p.163-187.
2. Cotell, C.M.; Yurek, G.J.; Hussey, R.J.; Mitchell, D.F.; Graham, M.J. **Oxid. Metals**, v.34, n.3/4, 1990, p. 173-200.
3. Yurek, G.J.; Przybylski, K.; Garratt-Reed, A.J. **J.Electrochem.Soc.**, 1987, p.2643-2644.
4. Funkenbusch, A.W.; Smeggil, J.G.; Bornstein, N.S. **Metall.Trans.A**, 16A, 1985, p.1164-1166.
5. Pint, B.A. **Oxid. Metals**, v.45, n.1/2, 1996, p. 1-37.