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Effect of addition of rare earth oxide concentrates on oxidation resistance of AISI 304L

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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 900ºC. The parabolic rate constants were determined and the reaction products examined using a scanning electron microscope. X-ray diffraction analysis of the reaction products was also carried out. The compacts with pure rare earth oxides and the concentrates exhibited similar oxidation behavior.

Introduction

Alloys for use at high temperatures should have adequate mechanical strength and resist degradation caused by reactions between the alloy and the environment [1,2]. Almost all structural alloys are Fe, Ni or Co based. The surface oxide formed on these alloys in oxidizing environments is not sufficiently protective above 550ºC. These alloys are therefore alloyed with Cr and/or Al to establish more protective surface oxides of chromia or alumina respectively [3]. The addition of other reactive elements such as Y, Zr, Ce , and others to these alloys further improves the protective properties of the surface oxides. Similarities in the chemical nature of the rare earth (RE) elements make their separation, one from the other, one of the most difficult processes in inorganic chemistry. In almost all investigations about the effect of RE on oxidation behavior of chromia and alumina forming alloys, the RE have been added as either elements [4-21] or as pure oxide dispersions [3, 4, 6, 10-12]. The RE oxide concentrate is a precursor in the production of pure RE oxides and the processing costs involved in obtaining pure RE oxides is significant. Hence, the influence of adding pure RE oxides and RE oxides concentrates on oxidation behavior of a chromia former has been studied. Various mechanisms have been proposed to explain the effect of RE element on improving oxidation resistance [3-6, 13-16]. The mechanism most widely accepted explains the improvements observed in high temperature oxidation of alloys containing RE, as being due to diffusion of the RE ions to oxide scale grain boundaries and blocking of alloy cation diffusion along these paths [17-20].

Materials and Methods

RE oxide concentrates are prepared from minerals containing all the rare earth elements.. Starting with RE chlorides, the first stage of extraction of individual REs consists of separating the mix into light, medium and heavy REs. Within the light REs and the heavy REs, after various stages of extraction and precipitation, further separation of concentrates of lanthanum and yttrium oxides respectively, are carried out. In this investigation 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 1250ºC. The specimens were then oxidized isothermally in a muffle furnace or in a thermogravimetric analyzer. In the muffle furnace, the specimens were oxidized for 200h at 900ºC. In the thermogravimetric tests, the specimens were oxidized in oxygen for 20h at 900ºC. Parabolic oxidation rate constants were calculated and the specimens oxidized for 20h and 100h in the muffle furnace were examined in a scanning electron microscope. Chemical analyses of micro-regions were also carried out by energy dispersive spectroscopy (EDS).

Results and Discussion

The chemical composition of the RE oxide concentrates, as determined by x-ray fluorescence analysis is shown in Table 1.

Table 1: Chemical composition of rare earth oxide concentrates (wt %).

	Y_2O_3 concentrate	La_2O_3 concentrate
SO_3	0.06	0.03
CuO	0.03	-
Y_2O_3	85.7	0.06
Tb_2O_3	0.21	-
Dy_2O_3	7.78	-
Ho_2O_3	0.01	-
Er_2O_3	3.83	-
Yb_2O_3	2.36	-
SiO_2	-	0.02
CaO	-	0.03
Pr_2O_3	-	2.76
Nd_2O_3	-	7.44
Cl	-	0.04
TiO_2	-	0.29
ZrO_2	-	0.01
La_2O_3	-	89.00
Sm_2O_3	-	0.41

The mass gain versus time curves of specimens oxidized in the thermogravimetric analyzer 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. Fig. 1 also shows that the different RE oxides affected oxidation rate to the same extent. The parabolic rate constants were determined from the steady state regions of these curves. Decrease in the parabolic rate constants with addition of reactive elements can be seen in Table 2. The alloy without additions revealed the highest rate.

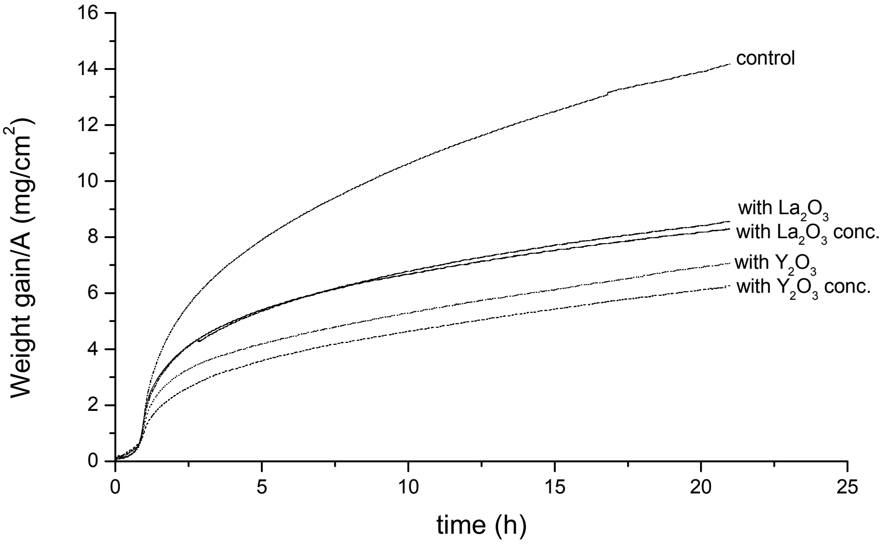

Fig.1: Oxidation curves obtained in a thermogravimetric balance at 900°C.

Table 2: Parabolic rate constants (Kp) at 900°C

Alloys	Kp ($g^2.cm^{-4}.s^{-1}$)
AISI 304L	2.26×10^{-9}
AISI 304L + Y_2O_3	5.82×10^{-10}
AISI 304L + La_2O_3	6.67×10^{-10}
AISI 304L + Y_2O_3 conc.	4.44×10^{-10}
AISI 304L + La_2O_3 conc.	6.06×10^{-10}

The decrease in the parabolic rate constant of alloys containing reactive element additions can be attributed to reduction in Cr^{3+} ion flux through the oxide layer [7, 8, 10]. The rate of diffusion of Cr^{3+} is significantly higher than that of oxygen in chromia forming alloys. Therefore when transport of this cation is suppressed, there is a marked effect on the oxidation rate [11]. Results obtained so far suggest that the effect produced by the addition of RE oxide or its concentrates are similar. There is therefore no adverse effect on the oxidation resistance of the alloy upon addition of the RE oxide concentrate instead of the pure RE oxide, the latter being significantly more expensive. Similarity in the overall effect is due probably to the impurities in the RE oxide concentrate, and these are oxides of other REs.

Fig. 2a shows the surface of AISI 304L oxidized for 100h at 900ºC. The oxide in region 1 is rich in iron. It also shows acicular regions (region 2), containing iron and some nickel. Regions of the surface where the oxide had spalled were also examined, and only iron was detected in these regions. Fig. 2b shows a cross section of the same specimen. The oxide/metal interface is undulating and oxidized regions around the pores within the alloy can be observed. EDS analysis across the section revealed only the presence of iron along the outer part of the layer (region 1). In region 2, traces of chromium were observed. In the light grey region 3, Fe and Ni were also detected, besides Cr. The oxide/metal interface, (region 4) was rich in chromium.

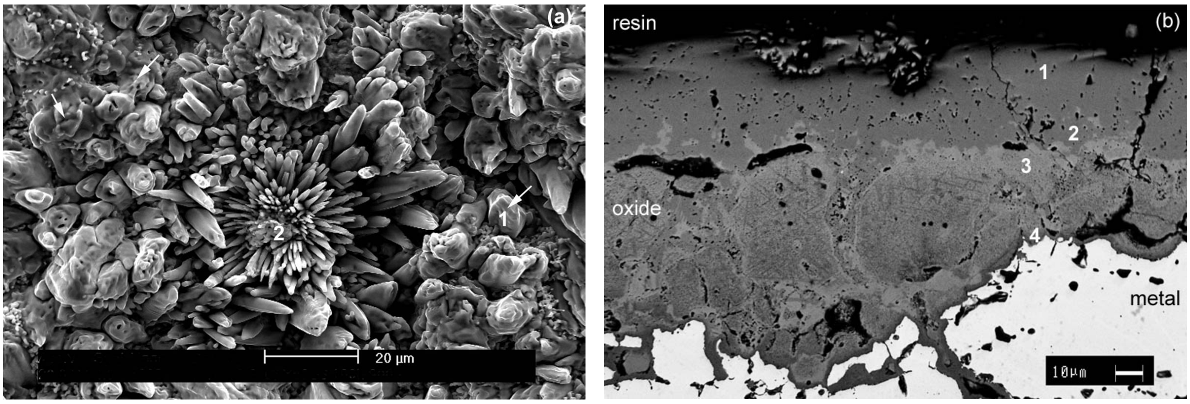

Fig. 2: AISI 304L oxidized for 100 h at 900°C in a muffle furnace; (a) surface; (b) cross sectional.

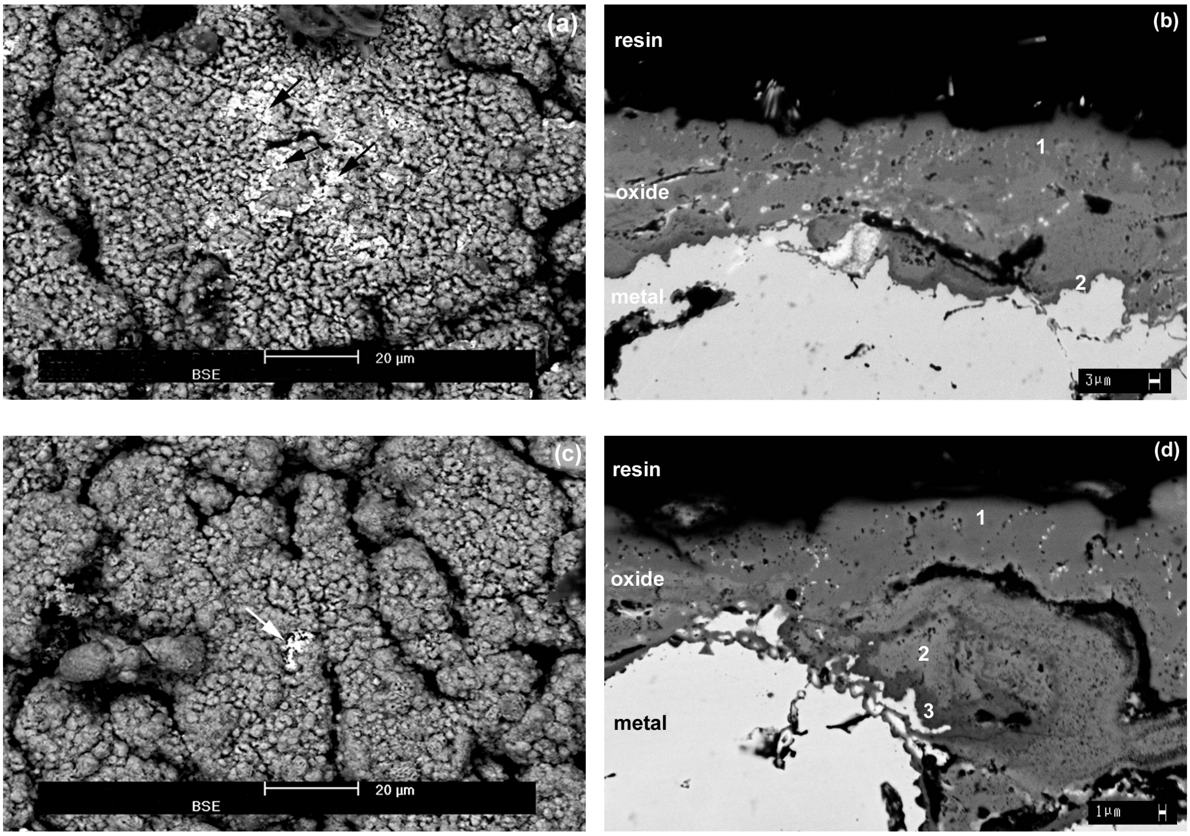

Fig. 3: (a) AISI 304L + La_2O_3 surface oxidized for 100h at 900°C in a muffle furnace; (b) cross sectional of (a); (c) AISI 304L + La_2O_3 concentrate surface oxidized for 100 h at 900°C; (d) cross sectional of (c).

Fig. 3a is the surface of the alloy containing La_2O_3 after 100h of oxidation in the muffle furnace. No spalling was observed. The lighter regions, shown by arrows, are La_2O_3.

Fig. 3b is a cross section of the same specimen. Region 1 is rich in Fe and contains traces of Cr and region 2, close to the interface metal/oxide, contains large quantities of Cr. Specimens of the alloy containing La_2O_3 concentrate did not spall after 100h at 900ºC, but a number of surface cracks were seen, as shown in Fig. 3c. Large quantities of Fe, Cr and some Ni were detected. The region shown with an arrow is an agglomerate of La_2O_3 concentrate. Fig. 3d shows a cross section of this alloy. The outer region 1 contains large quantities of Fe, Cr and Ni. In the interface region 3, the oxide is rich in Cr. The light particles distributed all along the oxide layer are La_2O_3 concentrates. The distribution of this RE oxide, from the oxide/gas interface, indicates that the preferential direction of growth of the surface oxide is by predominant anionic diffusion. Alloys containing the other RE oxide additions were also examined and they showed similar microstructures.

Of the various mechanisms that have been proposed [3-6, 13-20] to explain the effect of reactive element additions on oxidation behavior, the one most widely accepted attributes the increased resistance to a 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 [21]. Oxide growth stresses lead to spalling. On the other hand in Fe-Cr alloys containing reactive elements, Cr_2O_3 grows by predominant oxygen diffusion [7, 21]. 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 of the alloy and the oxide scale, close to the metal/oxide interface [8]. The large ionic radii (compared to the radii of Fe, and Cr ions) of the RE make cation diffusion more difficult, and anion transport predominating during chromia layer growth.

Conclusions

1. The addition of RE oxides and concentrates decreased the oxidation rate of AISI 304L at 900ºC.
2. The oxidation behavior of AISI 304L containing both pure RE oxide and RE oxide concentrates was similar.
3. The marked reduction in chromium dioxide growth rate with RE addition is due to oxygen ions being the predominantly diffusing ions and growth of new oxide at the metal/metal oxide interface.

Acknowledgements

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