

## Effect of Processing Technique on Microstructure and Oxidation Behavior of Rare Earth Oxide Dispersion Containing Steels

M.F. Pillis and L.V. Ramanathan

Energéticas e Nucleares, Instituto de Pesquisas, P.O.Box 11049,  
CEP 05422-970 São Paulo SP, Brazil

**Keywords:** Oxidation, Rare Earth

**ABSTRACT.** Rare earths are often added to high temperature alloys to help form protective scales. The method of addition and distribution of rare earths(RE), affect overall oxidation resistance of these alloys. This paper presents the influence of powder preparation technique on the microstructure and oxidation behavior of RE oxide dispersion containing AISI 316L compacts. The microstructures of sintered compacts of AISI 316L with various amounts of ceria and yttria, produced from steel and RE oxide powders mixed in: (a) a 'turbula' type mixer and (b) a high energy attritor have been compared. Evaluation of the oxidation behavior of these compacts at 1000°C revealed a marked increase in oxidation resistance of the RE oxide containing compacts prepared from powders mixed in the attritor. This is due to the homogeneous distribution of the oxide dispersions.

### INTRODUCTION

Materials for use in high temperature oxygen containing environments rely for their protection on a continuous and slow growing oxide scale. Ideally, this scale should be non-volatile, adherent, coherent, stress free, pore free, crack free and have a low concentration of ionic defects. The oxides, chromia, alumina and silica have these capabilities and alloys that form the former two are used to a great extent. The addition of reactive elements such as rare earths (REs), aid the formation of more protective scales on chromia and alumina forming alloys.[1-14] The REs have been added in one of three forms: (a) as elements to the alloy; (b) as oxide dispersions to the alloy or (c) applied to the alloy surface as an oxide or some other compound. The effect of adding REs to Fe-Cr alloys, in the three different forms, has been investigated and reported [15-18]. During these investigations, significant variations in the oxidation behavior of the Fe-Cr alloys were observed and often attributed to the form and distribution of the REs in the alloy. This paper addresses the influence of the powder metallurgical technique used to obtain RE oxide dispersion containing AISI 316L, on the microstructure and oxidation behavior of the alloy.

### METHODS AND MATERIALS

AISI 316L powder with composition of: 16.91%Cr; 13.55%Ni; 1.60%Mo; 1.02%Mn; 0.355%Si; 0.044%C; 0.008%S and balance iron (in weight %) was used to prepare mixtures with ceria and yttria. The powder mixtures were prepared using:

1. A "turbula" type mixer: Powders of AISI 316L, AISI 316L+1%ceria and AISI 316L+1%yttria were homogenised for 20 minutes in a turbula type mixer. The powder mixtures were then compacted at  $6\text{tf/cm}^2$  in a uniaxial press, to render pellets that were subsequently sintered in hydrogen for 1 hour at 1250°C. The dimensions of the sintered specimens as well as their hydrostatic densities were determined. The final dimensions of the pellets were  $4\text{mm}\varnothing \times 1.5\text{mm}$ . The pellet specimens were then rinsed, degreased and dried.

2. A high energy mechanical attritor: Powders of AISI 316L, AISI 316L+0.5%, 1.0% and 1.5% ceria as well as AISI 316L+0.5% yttria were mixed in a high energy attritor mill for 15h under a nitrogen atmosphere. The powder mixtures were then compacted in a uniaxial press. The compression force for the various specimens in the press varied, to render specimens with the same green density of 5.5g/cc. The specimens were then sintered for 1h at 1250°C under hydrogen. The sintered specimens were then cut to size – 3 x 3 x 1mm and their surfaces finished to 220 mesh. The specimens were subsequently degreased in acetone.

The different specimens were oxidised at 1000°C for upto 16h in a thermogravimetric analyser. The overall weight gain during oxidation took into account, where ever relevant, the weight of the spalled oxide. A scanning electron microscope coupled to an energy dispersive analyzer was used to examine the specimens, both prior to and after oxidation. X-ray diffraction analysis of the surface oxides was also carried out.

## RESULTS AND DISCUSSION

### Specimens produced by mixing in a turbula type mixer

The microstructure of longitudinal sections of sintered AISI 316L+1%ceria and AISI 316L+1%yttria are shown in figures 1a and 1b respectively. They reveal inhomogeneous distribution of the RE oxides. The RE oxides are located at the steel particle boundaries. The ceria agglomerates are more uniformly distributed in the metallic matrix compared to the yttria agglomerates, which are large and non-uniformly distributed.

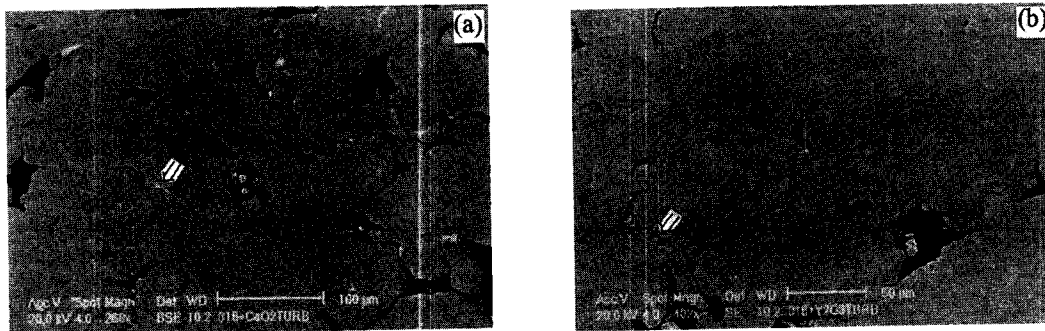


Fig. 1 Longitudinal section of AISI 316L with additions (turbula type mixer): (a) 1%CeO<sub>2</sub>; (b) 1%Y<sub>2</sub>O<sub>3</sub>.

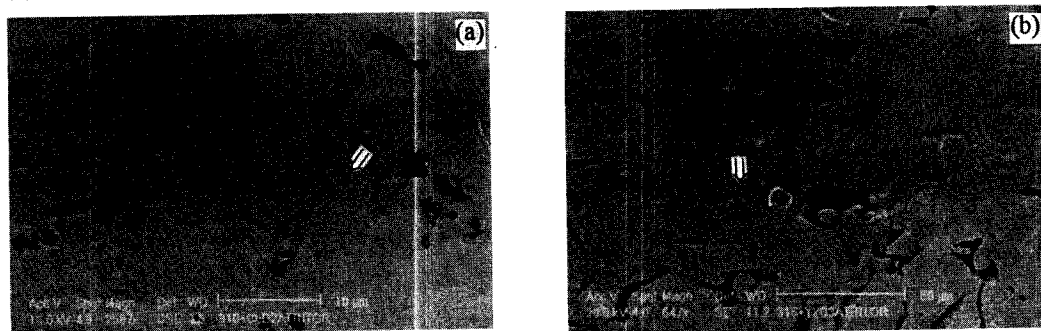


Fig. 2. Longitudinal section of AISI 316L with additions (high energy attritor): (a) 1% CeO<sub>2</sub>; (b) 1% Y<sub>2</sub>O<sub>3</sub>.

Specimens produced by mixing in a high energy attritor

The micrographs of the longitudinal section of sintered specimens containing ceria and yttria produced by mechanical alloying are shown in figures 2a and 2b respectively. It can be seen that the RE oxides formed small agglomerates and were uniformly distributed throughout the metallic matrix. Comparison of figures 1a and 2a as well as 1b and 2b reveal reduction in RE oxide size and more uniform distribution in specimens produced by the mechanical alloying technique.

#### OXIDATION MEASUREMENTS

The mass gain per unit area versus time curves for the different specimens prepared by simple powder mixing in the turbula is shown in figure 3. The overall oxidation behavior of the specimens without and with rare earth oxide dispersions are quite similar, although the specimens with the rare earth oxides showed a slight improvement in oxidation resistance. No scaling was observed. The isothermal oxidation behavior of the specimens prepared by mixing powders in the attritor are shown in figure 4. Significant reductions, of almost an order of magnitude, in oxidation mass gains can be observed. This is probably due to the formation of an oxide layer on the steel particle surfaces during mixing. The specimens with rare earth dispersions showed a marked reduction in oxidation rate, compared to AISI 316L. The ceria containing specimens were the most resistant. This is attributable to the more homogeneous distribution of ceria in the specimens.

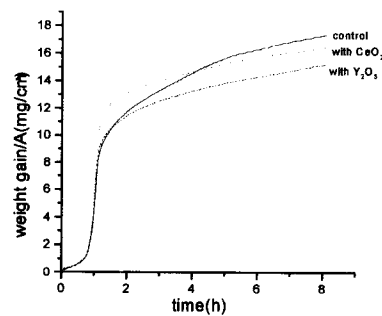


Fig. 3. Mass gain per unit area of AISI 316L, AISI 316L+1%CeO<sub>2</sub>, and AISI 316L+1%Y<sub>2</sub>O<sub>3</sub> specimens prepared from powders mixed in the turbula mixer and oxidised at 1000°C.

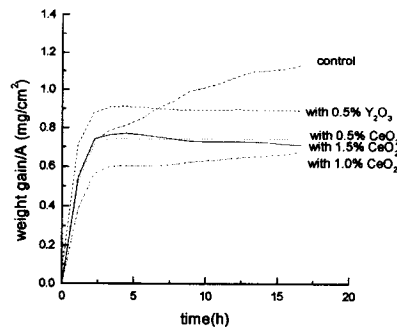


Fig. 4. Mass gain per unit area of AISI 316L, AISI 316L+CeO<sub>2</sub>, and AISI 316L+Y<sub>2</sub>O<sub>3</sub> specimens prepared from powders mixed in the attritor mill and oxidised at 1000°C.

The surfaces of AISI 316L, AISI 316L+0.5%ceria, and AISI 316L+0.5%yttria produced with the attritor and subsequently oxidised at 1000°C for 16h are shown in figure 5. The AISI 316L specimen surface reveals oxide scaling. The oxides formed on the ceria and yttria containing specimens were homogeneous and adherent. X-ray diffraction analysis of the oxidised surfaces revealed the presence of chromia and the spinel  $\text{FeCr}_2\text{O}_4$ . Scanning electron micrographs of the surface and cross section of AISI 316L oxidised for 5h at 1000°C is shown in figure 6. The surface oxide, found to be chromia by x-ray diffraction analysis, did not spall. Figure 6b reveals the presence of interconnected pores. The surfaces of AISI 316L+1%ceria and AISI 316L+1%yttria prepared with the turbula and oxidised at 1000°C for 5h are shown in figures 7a and 7b. Smooth and adherent chromia was found on both surfaces.

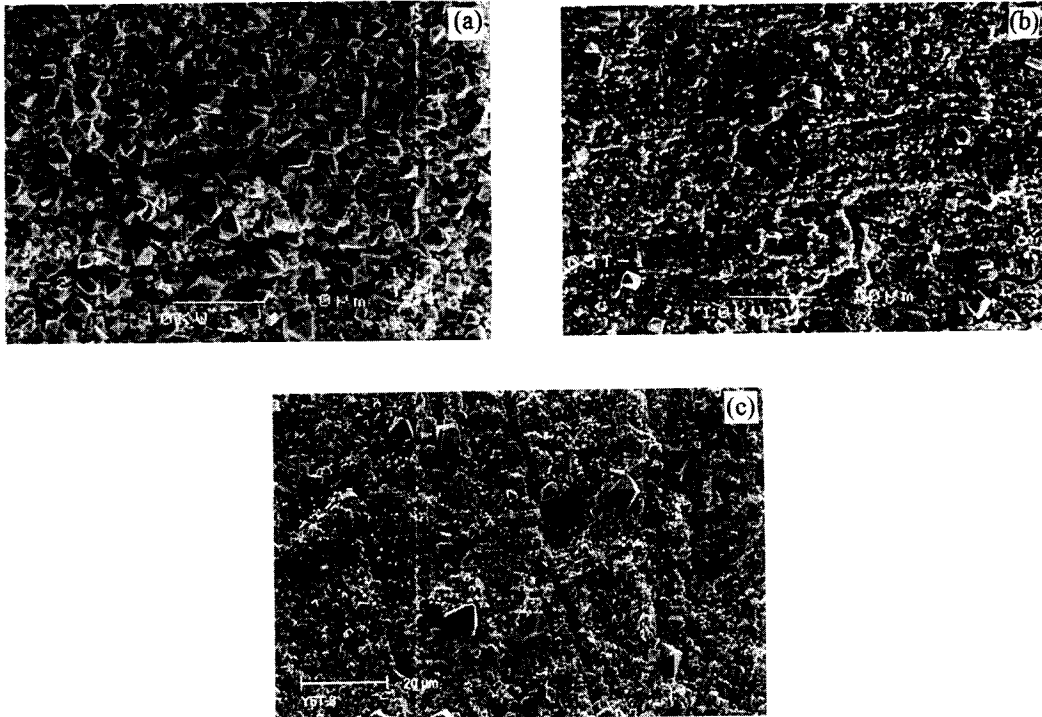


Figure 5. Surface of specimens oxidised for 16h at 1000°C (a) AISI 316L ; (b) AISI 316L+1%  $\text{CeO}_2$ ; (c) AISI 316L+1%  $\text{Y}_2\text{O}_3$

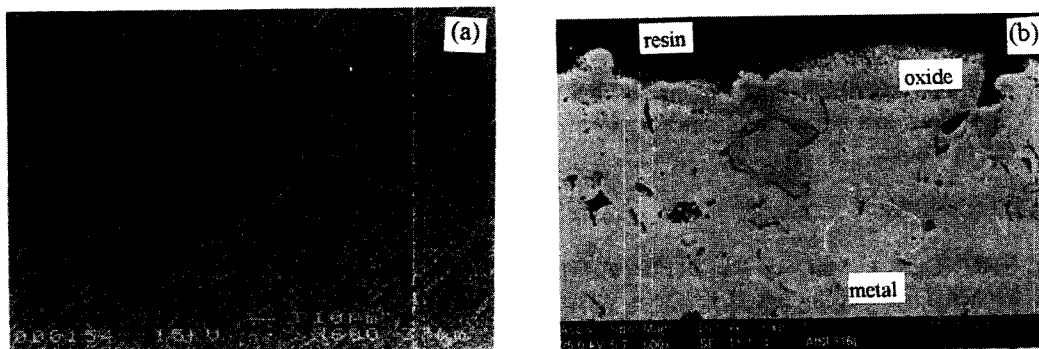


Fig. 6. AISI 316L oxidised at 1000°C for 5h. (a) surface; (b) cross-section.

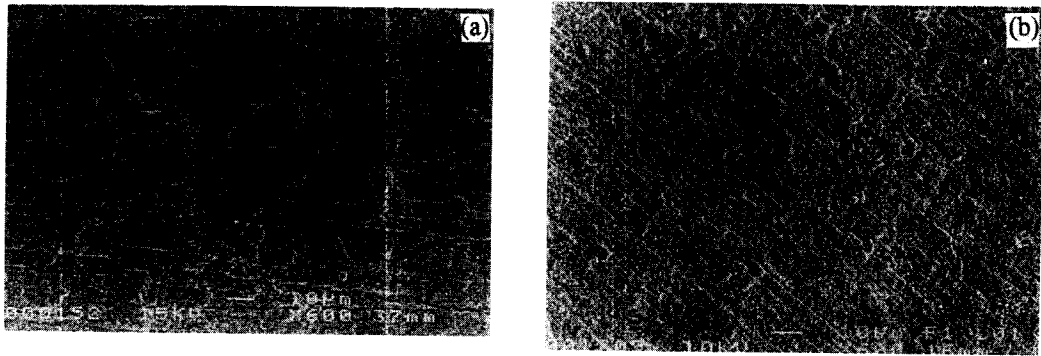


Fig. 7. Surface of specimens oxidised for 5h at 1000°C (a) AISI 316L+1% CeO<sub>2</sub>; (b) AISI 316L+1% Y<sub>2</sub>O<sub>3</sub>.

### GENERAL DISCUSSION

The reduced mass gains for RE dispersion containing specimens prepared from powders mixed in the attritor mill, as compared to those prepared from powders mixed with the turbula mixer can be attributed to the reduced powder particle size in the former. The rare earth oxide powders are also present at the alloy particle boundaries in the former. Reduced powder particle size also resulted in more homogeneous distribution of RE oxides, and the probable presence of an oxide layer on the metal powder particles.

The oxidation rate of AISI 316L at 1000°C decreased upon addition of rare earth oxide dispersions. The chromia formed on the specimen surface was more adherent and did not spall. The increased adhesion of the oxide layer is probably due to various factors. The reduced oxide layer thickness coupled with the large number of pores on the specimen surface (which accommodate the oxide), probably contributed to the reductions in tensions within the oxide layer. Besides, the many reentrances on the specimen surfaces possibly enabled the surface oxide to anchor strongly to the specimen.

### CONCLUSIONS

1. Preparation of specimen powders using the mechanical attritor resulted in reduced overall particle size, more uniform rare earth oxide particle distribution and more homogeneous alloys.
2. The addition of rare earth oxides, ceria and yttria as dispersions to AISI 316L using the attritor mill resulted in a significant increase in oxidation resistance at 1000°C.
3. The increased oxidation resistance of RE dispersion containing AISI 316L specimens prepared from powders mixed in an attritor is attributable to the homogeneous distribution of the rare earth oxides.

### REFERENCES

1. STRINGER, J., *Mat. Sci. Eng.*, A120 (1989), p.129.
2. RHYS-JONES, T.N.; GRABKE, H.J.; KUDIELKA, H., *Corr. Sci.*, 27, 1 (1987) p.49.
3. MOON, D.P., *Mat. Sci. Techn.*, 5 (1989), p.754.
4. HUNTZ, A.M., *Mat. Sci. Eng.*, 87 (1987), p.251.
5. COTELL, C.M.; YUREK, G.J.; HUSSEY, R.J.; MITCHELL, D.F.; GRAHAM, M.J., *Oxid. Met.*, 34, 3/4 (1990), p.173.

6. TIEN, J.K.; PETTIT, F.S., *Metall. Trans.*, 3 (1972), p.1587.
7. GIGGINS, C.S.; KEAR, B.H.; PETTIT, F.S.; TIEN, J.K., *Metall. Trans.*, 5 (1974), p.1685.
8. RHYS-JONES, T.N.; GRABKE, H.J., *Mat. Sci. Technol*, 4 (1988), p.446.
9. WHITTLE, D.P.; STRINGER, J., *Philos.Trans.R.Soc.London*, A295 (1980), p.309.
10. ALLAM, I.M.; WHITTLE, D.P.; STRINGER, J. *Oxid. Met*, 12, 1 (1978), p.35.
11. HOU, P.Y.; STRINGER, J., *Mat. Sci. Eng.*, 87 (1987), p.295.
12. PIERAGGI, B.; RAPP, R.A., *J.Electrochem. Soc*, 43, 11 (1995), p.4015.
13. YIFAN, Z.; ZHU, D.; SHORES, D.A, *Acta Metall. Mater*, 43, 11 (1995), p.4015.
14. RHYS-JONES, T.N.; GRABKE, H.J.; KUDIELKA, H., *Corr. Sci.*, 27, 1, (1987), p.49.
15. RAMANATHAN, L.V., *Corr. Sci.*, 35 (1993), p.871.
16. PILLIS, M.F., FEITOSA, D.; RAMANATHAN, L.V., *Proc. 2<sup>nd</sup> NACE Latin American Region Corrosion Congress*, 1996, Rio de Janeiro, Brazil.
17. PILLIS, M.F.; RAMANATHAN, L.V., *Proc. 5<sup>th</sup> Brazilian Conference on Microscopy of Materials*, 1996, Rio de Janeiro, Brazil.
18. RAMANATHAN, L.V., *Corrosion Prevention and Control*, 45 (1998), p.5.

## **Advanced Powder Technology II**

doi:10.4028/www.scientific.net/KEM.189-191

## **Effect of Processing Technique on Microstructure and Oxidation Behavior of Rare Earth Oxide Dispersion Containing Steels**

doi:10.4028/www.scientific.net/KEM.189-191.322