Role of Rare Earth Oxide Coatings on Oxidation Resistance of Chromia Forming Alloys

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Abstract- This paper presents the influence of different rare earth oxides on the oxidation behavior of an iron-chromium alloy. Correlations have been drawn between the extent of influence of the rare earths, their ionic radii, oxide morphology and the coverage of the oxide on the alloy surface.

The use of rare earths (RE) to increase high temperature oxidation resistance of chromium dioxide and alumina forming alloys is well known. The rare earths can be added as elements (or oxides) to the alloys or applied as an oxide coating to the alloy surface. The sol-gel technique is very efficient to apply nano-sized oxide coatings. The influence of various rare earth oxide gels such as La_2O_3, CeO_2, Pr_2O_3, Nd_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Y_2O_3, Er_2O_3, and Yb_2O_3 on cyclic oxidation behavior (RT-900ºC) of Fe20Cr alloy was studied. The weight gain during oxidation was due to formation of Cr_2O_3 on the specimen surfaces. The cyclic oxidation resistance, expressed as the number of cycles varied with the RE oxide. Table I presents the cyclic oxidation resistance of Fe20Cr specimens coated with the different RE oxides and the ratio of the radius of the RE ion to the radius of the chromium ion (R_{RE}/R_{Cr}). Specimens coated with RE oxides with R_{RE}/R_{Cr} ratios less than 1.45 withstood only half as many cycles compared with specimens coated with RE oxides with R_{RE}/R_{Cr} ratios more than 1.45.

Marked differences in the morphology of RE oxides were observed. Specimens coated with RE oxides with cube, rod or needle-like morphology withstood a higher number of oxidation cycles compared with those coated with RE oxides with platelet or cluster morphology. The area fractions, or coverage, of the different RE oxides on the specimens varied and this could be correlated to cyclic oxidation resistance. The ionic radii of the REs are 1.3 to 1.65 times that of Cr. The extents to which RE elements affect oxidation rates have been found to be proportional to their sizes. Direct correlation between RE ion radius and cyclic oxidation resistance lends further proof to the segregation theory mechanism by which REs influence chromium dioxide scale growth. That is, the presence of RE ions at the oxide scale grain boundaries effectively blocks Cr ion movement and thereby makes inwards oxygen ion movement predominant. The Cr_2O_3 layer thickness varied with the RE in the coating. The time required for the Cr_2O_3 layer to reach critical thickness for spalling, and consequently, cyclic oxidation resistance depends on characteristics of the RE oxides. These in decreasing order of influence are: RE ion radius, RE oxide morphology, RE oxide coverage and adhesion or resistance to thermal or scale growth stresses.

Table I: Cyclic oxidation resistance of RE oxide coated Fe20Cr specimens and ratios of the RE ion radius to chromium ion radius.

Oxide of	Number of cycles at spall	R_{RE}/R_{Cr} ratio
Lanthanum	15+	1.64
Cerium	9	1.60
Praseodymium	15+	1.57
Neodymium	12	1.54
Samarium	12	1.50
Gadolinium	15+	1.46
Dysprosium	6	1.42
Yttrium	7	1.39
Erbium	7	1.37
Ytterbium	4	1.34