Rare-earth Information Center INSIGHT

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Corrosion and Coatings

The use of rare earths for corrosion protection has been known for many years. In the October issue of the **MRS Bull. 19** [10] (1994), a series of six papers discuss recent developments in this field, four of which are reviewed below.

In the lead paper, J. C. Colson and J. P. Larpin (pp. 23-25) note that the best high temperature oxidation resistant alloys contain < 1 wt.% of yttrium or cerium. It is believed that rare earth additions reduce the growth rate of Cr_2O_3 and/or Al_2O_3 protective scales by slowing down the outward diffusion of the cations (Cr^{3+} or Al^{3+}) and allowing the inward transport of oxygen to predominate. However, in sulfidizing environments (S_n and/or H_2S), the alloys do not hold up as well and there is no completely satisfactory solution today. As is the situation for oxidizing environments, steels containing Al (along with the rare earths) are more resistant to sulfur corrosion, than those alloys which do not contain Al. Clearly, a situation which needs much more study before we will have alloys with satisfactory corrosion resistance.

A paper by B. A. Pint (pp. 26-29) examines the use of Y_2O_3 coatings and implanted Y to improve the high temperature (~1200°C) oxidation resistance of β-NiAl. Both methods significantly reduce the rate of oxidation over the untreated β-NiAl, however, the Y_2O_3 coating holds up better at longer times than implanted Y. Pint suggests that a more uniform submicron Y_2O_3 dispersions in the coatings is essential for further improvements in protecting β-NiAl.

The role of yttria-stabilized zirconia (YSZ) in improving the oxidation and corrosion resistance of SiC ceramics at high temperature in oxidizing and reducing atmospheres, and in the presence of molten salts has been investigated by K. N. Lee, N. S. Jacobson and R. A. Miller (pp. 35-38). They note that mullite ($3Al_2O_3 \cdot 2SiO_2$) coatings work real well by itself in an oxidizing atmosphere with excellent adherence and thermal shock resistance. But in a reducing, or a cyclic oxidation/reduction situation, or in the presence of molten salts, mullite is not too effective in protecting SiC. However, YSZ used in a multilayer configuration, with the YSZ serving as the overlayer material, has considerable promise. The large differences in the coefficients of thermal expansion between the mullite and YSZ presents a problem, but by the use of graded coatings this situation can be mitigated.

The use of thermal-barriers has permitted significant improvements in the performance of turbines and aircraft engines by allowing them to operate at higher temperatures. Many thermal barriers consist of YSZ plasma-sprayed on a M-Cr-Al-Y bond coating (where M = Ni or Co). However, under service conditions other modes of damage, including erosion and hot-salt corrosion, can severely limit the life-time of the gas turbine or engine. F. H. Stott, D.J. de Wet and R. Taylor (pp. 46-49) studied the degradation of the thermal-barrier coatings by molten sands

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and glass debris between 1300 and 1600°C. They find that Y is absorbed in the molten salt or glass if their Ca contents are low, thus depleting the YSZ of the Y, which leads to failure of the YSZ coating. For the high Ca containing salts, both Y and Zr are removed from the coating and are replaced by the Ca which tends to stabilize the tetragonal modification of ZrO_2.

Sichuan Rare Earth Plant

Advanced Materials Resources, Ltd., Canada, (AMR), and Mianning County Mining Company (MCMC) recently signed a joint venture to construct a large scale rare earth processing plant in Mianning county, Sichuan province, the People's Republic of China (PRC). AMR will own an 80% interest in the joint venture and it will have exclusive rights to market all of the joint venture's production internationally. The feedstock for this plant will be a rare earth concentrate mined from the high grade ore deposits in Mianning county, which is reported to be the second largest in the PRC in terms of the amounts of rare earth reserves. This will be AMR's third joint venture in the PRC [see **RIC Insight 6**, [12] (December 1, 1993) and **7** [1] (January 1, 1994)], but it still requires government approval before becoming effective.

White Laser Light

A. A. Kaminskii and H. J. Eichler have proposed that white laser light could be generated by using visible stimulated emission of Pr crystalline lasers [**Phys. Status Solidi (b) 185**, K85-K88 (1994)]. Pr insulating crystals would be the most likely candidate materials among the lanthanide lasing ions, since it has eight "channels" (wavelengths) in the visible spectrum. The stimulated emissions in the $4f^2$-$4f^2$ intermanifold transitions can be induced by laser and Xe-flashlamp pumping. The authors present a simplified chromaticity diagram, showing the locations of the Pr channels, which can be mixed to create a white light. There are five red channels, two green and one blue. Although the one blue channel is sufficient to create this white light, the near future research will be focused on finding new Pr crystals which will have additional channels in the blue region. In addition to white light, one would be able to create many other mixed colors, which are necessary for the next generation of projection displays.

Corrosion Resistant High T_c Superconductors

J.-P. Zhou and co-workers (University of Texas, Austin, Texas) discovered a way to significantly improve the chemical corrosion resistance of the $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor. This development should speed up the use of YBCO in thin film applications. YBCO tends to degrade when exposed to water, acids, CO_2 and CO. Normally, when a YBCO sample is exposed to water at 25°C, or water vapor at 75°C, the surface becomes coated by $BaCO_3$ crystallites after 2 days. However, when Ca is substituted for the Y (30 to 40%), and by simultaneously replacing some of the Ba with La (15 to 20%), the dual-substituted-YBCO samples were remarkably stable — essentially no reaction was observed after soaking in water for one month. The larger the amount of substitution, the greater the corrosion resistance. The dual substitution reduces the bond-length disparities, and thus the internal stresses, while maintaining the electronic concentration which is necessary to retain the desirable superconducting behaviors. These results were published in the **J. Amer. Chem. Soc. 116,** 9389-9390 (1994).

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