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Corrosion behavior of sintered oxide dispersion strengthened stainless steels

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There is always a thrust to improve the mechanical and corrosion properties of powder metallurgy products. The properties of the powder metallurgy components can be improved by using novel sintering techniques [1] or by the addition of second phases [2–5]. The properties of sintered products are superior after liquid phase sintering compared with conventional solid state sintering, as the presence of high-diffusivity liquid allows for rapid densification. Supersolidus liquid phase sintering (SLPS) is a novel liquid phase sintering technique, wherein the liquid forms within the particles and this results in fragmentation of individual grains. Subsequent repacking occurs under the capillary action of the liquid, resulting in rapid densification. SLPS provides better sintered properties in highly alloyed materials [1]. Dispersion strengthening by addition of hard second phase particles improves the mechanical properties of powder metallurgy stainless steels [2–5]. Powder metallurgy is an ideal technique for producing dispersion-strengthened alloys as it produces a homogenous distribution of dispersoids in the matrix. The beneficial effect of dispersoids on mechanical behavior has been reported for Al_2O_3-dispersed ferritic stainless steels [2, 3] and Y_2O_3-dispersed austenitic stainless steels [4, 5]. Addition of Al_2O_3 (0 to 8 vol%) did not degrade the corrosion resistance in ferritic stainless steels in 1N sulfuric acid [2, 3]. The effect of Y_2O_3 addition on the sintering behavior of austenitic stainless steels was studied by Lal and Upadhyaya [4, 5]. They reported higher sintered densities and enhanced corrosion resistance in the 4 volume percent samples, which was attributed to the interaction of Cr_2O_3 with the dispersoids. The literature on the corrosion behavior of dispersion strengthened powder metallurgy stainless steels is limited. The present study was undertaken to evaluate the corrosion rates of ferritic (434L) and austenitic (316L) stainless steels processed by two sintering techniques, conventional solid state sintering and SLPS. The aim of the study was to evaluate the effects of sintering temperature and yttria content on the corrosion behavior.

Gas atomized stainless steel powders of 316L (in weight percent, C: 0.025, Ni: 12.97, Cr: 16.51, Mo: 2.48, Si: 0.93, Mn: 0.21, S: 0.008, P: <0.01, Fe: BAL) and 434L (C: 0.023, Ni: nil, Cr: 15.93, Mo: 1.00, Si: 0.71, Mn: 0.24, S: 0.013, P: 0.02, Fe: BAL) grades were supplied by AMETEK, USA. The 99.9% pure Y_2O_3-oxide powder, of average size 1 μm, were supplied by RE Acton, UK. Different proportions of Y_2O_3 (0, 2.5, 5, 7.5 and 10 weight percent) powder were mixed with stainless steel powder in a Turbula mixer. Green compacts of approximately 5 mm height were prepared in a die of 12.7 mm diameter. A uniaxial compaction pressure of 600 MPa was applied using a manually operated hydraulic press. The green densities of the samples varied from 75 to 80% of the theoretical density. Green samples were sintered in a laboratory tubular furnace at two different temperatures of 1250 °C (solid state sintering) and 1400 °C (SLPS), using hydrogen as the reducing atmosphere. A heating rate of 5 °C/min was maintained and the samples were held at the sintering temperature for 60 min. The samples were then furnace cooled. The theoretical densities of some of the powder metallurgy samples have been compared in Fig. 1. The theoretical density of the composite was calculated using the inverse rule of mixtures from the known densities of 316L (8.05 g/cc), 434L (7.96 g/cc) and yttria (5.71 g/cc). Electrochemical corrosion experiments were conducted using a 263A PAR potentiostat. Tafel scans were obtained in freely aerated 0.05 mol/l sulfuric acid at ambient temperature (~25 °C). The polarization experiments were carried out in a flat cell using Ag/AgCl in saturated KCl (SSC) standard electrode (+197 mV vs. SHE) and platinum counter electrode. The Tafel scans were carried out at a scan rate of 0.166 mV/s as per ASTM standards [6]. The samples were polished to 600 grit on SiC paper, and cleaned with distilled water and acetone before the start of each experiment. A 430 stainless steel specimen, supplied by PAR, was used as the standard for ferritic stainless steel, while a wrought specimen of 316 was used as the standard for austenitic samples.

Some typical Tafel plots are presented in Fig. 2. It was generally observed that the cathodic Tafel slope (β_c) could be defined from the Tafel plots, while the anodic Tafel slope (β_a) was not well defined due to the onset of passivation. The passivation behavior of these composites has been addressed in detail elsewhere [7]. The corrosion current density (i_{corr}) was obtained by extrapolating the linear cathodic portion of the Tafel plot to the horizontal line drawn at the zero current potential. These terms are defined in one of the Tafel plots in Fig. 2. The results of Tafel extrapolation experiments for the ferritic and austenitic steels have been tabulated

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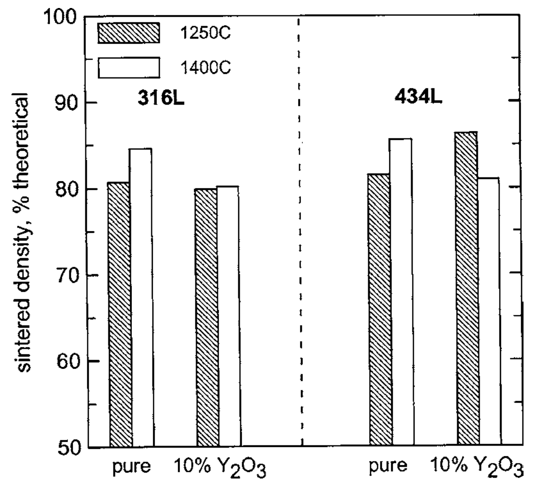

Figure 1 Sintered densities of powder metallurgy 316L and 434L stainless steel samples and the composites containing 10% Y_2O_3. The samples were sintered at 1250 °C (solid state sintering) and 1400 °C (supersolidus liquid phase sintering).

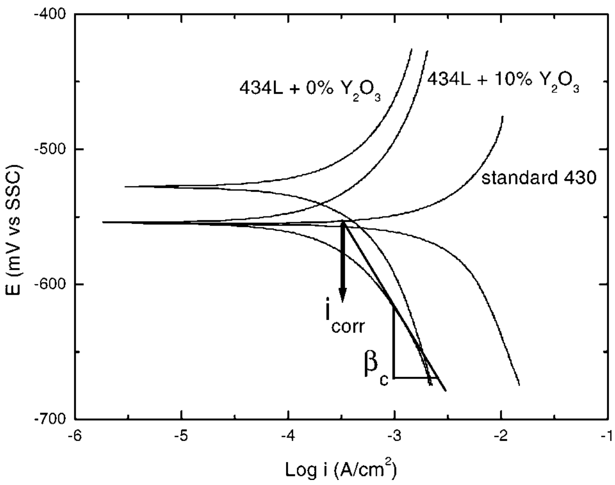

Figure 2 Tafel plots of 430 standard, powder metallurgy 434L stainless steel samples (containing 0% and 10% Y_2O_3) sintered at 1250 °C. The cathodic Tafel slope (β_c) and the corrosion current density (i_{corr}) have also been defined.

in Tables I and II, respectively. The anodic Tafel slopes are not provided in these tables because they were generally not well defined. The corrosion rates of austenitic stainless steels were lower by almost two orders of magnitude when compared to ferritic stainless steels (Tables I and II) and this is due to the presence of Ni in austenitic stainless steels [8]. The corrosion rates of the wrought stainless steel samples were comparable to the reported corrosion rates in the literature [8]. The corrosion rates of the powder metallurgy samples were also in accordance with the reported corrosion resistance of sintered austenitic and ferritic stainless steels [9, 10].

TABLE I Tafel extrapolation results for 430, 434L powder metallurgy and 434L powder metallurgy composites sintered at 1250 and 1400 °C

Temperature (°C)	Sample	i_{corr} (μA/cm^2)	β_c (mV/dec)	Corrosion rate (mm/y)
1250	430 (std)	2691	−124	27.30
	434L	269	−122	2.73
	434L + 2.5%yttria	389	−120	3.95
	434L + 5%yttria	295	−118	3.00
	434L + 7.5%yttria	360	−117	3.65
	434L + 10%yttria	316	−112	3.21
1400	434L	323	−128	3.28
	434L + 2.5%yttria	251	−110	2.55
	434L + 5%yttria	295	−132	3.00
	434L + 7.5%yttria	350	−124	3.55
	434L + 10%yttria	524	−124	5.32

TABLE II Tafel extrapolation results for 316, 316L powder metallurgy and 316L powder metallurgy composites sintered at 1250 and 1400 °C

Temperature (°C)	Sample	i_{corr} (μA/cm^2)	β_c (mV/dec)	Corrosion rate (mm/y)
1250	316L std	6	−129	0.06
	316L	7	−101	0.07
	316L + 2.5%Y_2O_3	10	−82	0.10
	316L + 5%Y_2O_3	15	−66	0.15
	316L + 7.5%Y_2O_3	15	−56	0.15
	316L + 10%Y_2O_3	8	−30	0.08
1400	316L	7	−59	0.07
	316L + 2.5%Y_2O_3	8	−46	0.08
	316L + 5%Y_2O_3	7	−52	0.07
	316L + 7.5%Y_2O_3	8	−56	0.08
	316L + 10%Y_2O_3	9	−33	0.09

There was no significant effect of sintering temperature on the corrosion rates of the powder metallurgy stainless steels (Table I). The corrosion rates of the powder metallurgy stainless steels were comparable. The sintered porosity did not significantly affect the corrosion rates. It is noted from Fig. 1 that, for all conditions, the sintered porosity remained greater than 8%, which is the limiting condition for the transition from interconnected to closed porosity. Therefore, the pores are predominantly interconnected. The microstructures obtained after sintering at these two different temperatures have been reported elsewhere [11]. Despite possessing interconnected porosity, the corrosion rates of powder metallurgy stainless steels, as determined by the Tafel extrapolation method, are comparable to their wrought counterparts. The corrosion rates need to be determined by immersion testing for understanding long-term corrosion behavior. The present investigation, nevertheless, indicates that stainless steels consolidated by powder metallurgy processing may not be inferior to their wrought counterparts as regards their corrosion resistance. An earlier study has also pointed out that porosity does not significantly affect the corrosion behavior of sintered austenitic and ferritic stainless steels [12]. It is, therefore, envisaged that by adopting better sintering strategies and judicious use of sintering activators and alloying additives, it may be possible to achieve near-full density stainless steels, which will presumably possess superior mechanical properties as well as comparable corrosion resistance.

In the case of ferritic stainless steels, the corrosion rates of the powder metallurgy samples were lower compared to the wrought samples and this is due to the presence of Mo in the powder metallurgy samples [12]. On the other hand, there was no significant difference between the corrosion rates of the austenitic powder metallurgy and wrought samples. This again revealed that the inherent porosity in the powder metallurgy samples did not drastically affect the corrosion rate.

The corrosion rates of the yttria-dispersed stainless steels were of the same order of magnitude as the sintered stainless steels (Tables I and II). The corrosion rates of austenitic stainless steel composites were lower compared to ferritic stainless steel composites. There was no significant effect of yttria content on the corrosion rate in both types of stainless steels, thereby indicating that the matrix stainless steel phase, by large, determined the corrosion behavior of the composites.

In summary, the corrosion behavior of powder metallurgy ferritic (434L) and austenitic (316L) stainless steels, dispersed with yttria (Y_2O_3), were studied in 0.05 mol/l sulfuric acid. The powder metallurgy stainless steels were sintered at two temperatures, 1250 and 1400 °C. The effect of sintering temperature and dispersoids addition on the corrosion behavior was addressed. The powder metallurgy austenitic stainless steels possessed comparable corrosion resistance to wrought 316 stainless steel. The powder metallurgy 434L stainless steel exhibited higher corrosion resistance than wrought 430 stainless steel and this has been attributed to the presence of Mo in 434L. The austenitic stainless steels exhibited enhanced corrosion resistance compared to the ferritic stainless steels. A higher sintering temperature did not result in significant changes in corrosion resistance in the powder metallurgy samples. Addition of Y_2O_3 to both austenitic and ferritic powder metallurgy stainless steels did not degrade the corrosion resistance. The ferritic stainless steel composites exhibited higher corrosion rates than the austenitic stainless steel composites. Primarily, the stainless steel matrix material determines the corrosion behavior of the composites.

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