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The importance of grain size relative to grain boundary character on the sensitization of metastable austenitic stainless steel

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Austenitic stainless steel (AISI 304L), which was thermomechanically processed by introducing cold deformation followed by annealing, was sensitized. The percentage of coincident site lattice boundaries did not correlate well with the degree of sensitization (DOS). The material with grain sizes below 10 μm was found to be the least sensitized, while specimens with larger grains showed an increase in DOS with sensitization time. The DOS is shown to have an inverse correlation with the grain boundary area, decreasing exponentially with increasing grain boundary surface area.

Keywords: Austenitic stainless steel; Grain boundary engineering; Coincident site lattice; Degree of sensitization; Grain boundary surface area

Austenitic stainless steels sensitize in the temperature range 550–800 °C and consequently suffer from intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) in corrosive environments. These typical failure modes have been identified as common reasons of premature collapse of structural components. A number of methods have been used to reduce sensitization and related failures, e.g. reduction of carbon (below 0.03 wt.%), and addition of nitrogen and strong carbide formers (such as titanium/niobium) to the existing stainless steels. These alterations have met with various degrees of success; however, they have increased the cost of materials without producing a sensitization-free material [1–3]. The concept of 'grain boundary engineering' (GBE), based on the coincident site lattice (CSL) model, introduced by Watanabe, has emerged as a cheaper alternative to improve various properties, including corrosion resistance, of low stacking fault energy materials [4]. Sensitization in stainless steel can be minimized by enhancing the lattice sites common to two or more grains and thus reducing the 'grain boundary energy'. Such boundaries are known to have special properties and are designated by Σ. Thermomechanical processing (TMP) with multicycle (iterative) deformation and annealing treatments have recently been shown to improve sensitization, IGC and IGSCC resistance [5–11], plasticity [12–15], etc., compared to TMP in a single step. These iterative treatments would, however, increase the cost of the GBE process.

Refs. [10,11] report the application of a wide range of deformation (0–80%) to stainless steels followed by annealing at 950–1300 °C in order to increase the special boundaries ($1 \leqslant \Sigma \leqslant 29$). It has been shown that increasing the frequency of CSL boundaries enhances the sensitization resistance. GBE research has led to the conclusion that distribution of CSL boundaries and disruption of connectivity of random boundaries play a crucial role, in addition to high CSL boundaries concentration, on IGC, IGSCC and stress corrosion cracking (SCC) [16–18]. On the other hand, it has also been reported that the degree of sensitization is significantly reduced beyond a critical percentage of random boundaries [11]. While correlating CSL or random boundary proportion with sensitization or IGC, other metallurgical changes such as grain size, which has a bearing on sensitization, have not been extensively investigated [19–21]. Changes in grain size occur with changes in the thermomechanical parameters, such as annealing temperature, time and degree of deformation, used for GBE. The performance of stainless steels in terms of

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the effect of changes in grain size vis-à-vis CSL boundaries on the sensitization, in particular, need to be critically assessed. We present in this paper an attempt to correlate such changes, after introducing large cold deformation prior to annealing and sensitization, with the degree of sensitization.

AISI 304L stainless steel with chemical composition C 0.02, Cr 18.54, Ni 9.8, Mn 1.8 and Si 0.54 (wt.%) was chosen for this study. After solution annealing at 1070 °C for 1 h followed by water quenching, materials were unidirectionally cold rolled to reduce their thickness by 90%. Coupons $20 \times 15 \times 2.5$ mm^3 were cut from the rolled sheets and subjected to annealing at 800–950 °C for 15, 30 and 60 min followed by water quenching. Specimens were then subjected to sensitization treatment at 675 °C for 2 h as well as 53 h.

The sensitized stainless steel coupons were evaluated for DOS by employing the double-loop electrochemical potentio-kinetic reactivation (DL-EPR) method in 0.5 M H_2SO_4 + 0.01 M KSCN solution at room temperature. Before DL-EPR tests, the surface of the samples were mirror polished with 0.5 μm diamond paste. After the specimens attained a stable open circuit potential (OCP), they were polarized from −0.1 V vs. OCP to +0.3 V (with respect to a saturated calomel electrode) and then reversed at a scan rate of 1.67 mV s^{-1}. The ratio of the peak current associated with reactivation (I_r) and activation loop (I_a) is the DOS of the material. The post-EPR specimens were characterized using electron backscattering diffraction (EBSD), and mapping of the CSL boundaries was carried out. The CSL boundary classification was based on the Brandon criteria $\Delta\theta = 15°\Sigma^{-1/2}$, where $\Delta\theta$ is the angular deviation from the exact CSL boundary [22]. In the present study, grain boundaries with $\Sigma \leqslant 29$ were considered as low Σ, and random boundaries were considered to be those beyond $\Sigma \geqslant 29$.

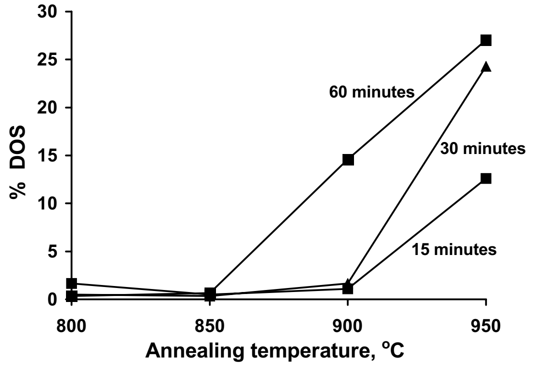

Figure 1. Influence of annealing temperature and time on % DOS.

The variation of DOS experienced by specimens sensitized at 675 °C for 53 h after different annealing conditions is presented in Figure 1. It has been observed that samples subjected to higher annealing temperatures after cold working prior to sensitization had higher DOS. DOS increases to very high values after annealing for 15 min at temperatures of 950 °C. Similarly, an increase in annealing time at a given annealing temperature prior to sensitization caused an increase in DOS. It was also observed that with increasing annealing time, a high DOS can be obtained at lower temperatures. Samples that were sensitized at 675 °C for 2 h had low DOS values (<2.6%). The specimens sensitized for 53 h were subjected to EBSD in order to estimate the fraction of CSL boundaries. The evolution of CSL boundary formation is shown in Table 1 as a function of the annealing conditions prior to sensitization. The results obtained did not show a significant increase in the percentage of CSL boundaries as compared to that in the solution-annealed stainless steel (~23%). The maximum proportion of CSL boundaries obtained was 41% after annealing at 950 °C for 30 min; however, no specific trend correlating the proportion of CSL boundaries with either temperature or time of annealing has been observed. In this study, unlike previous literature reports, an increase in the fraction of CSL boundaries did not translate into an improvement in the sensitization resistance. For instance, as shown in Table 1, the fraction of the CSL boundaries was slightly higher for samples annealed at 950 °C than that of other samples; the 950 °C-annealed samples, however, showed the lowest resistance to sensitization. It appears that resistance to sensitization modified by prior TMP is not dependent on grain boundary character alone. One of the earlier findings has shown that the AISI 304 and 316 that were deformed more than 80% prior to annealing at 1050 °C produced the best resistance against sensitization and IGC though it had the lowest percentage of CSL boundaries [11]. Extreme randomization (high percentage of random boundaries) has been suggested to be the possible reason for such results [11], though one-to-one correspondence between DOS and random boundaries could not be seen in our study (see Table 1). The highest percentage of random boundaries ($1 - \Sigma$CSL = 81%) resulted in the lowest DOS (0.35%); however, the lowest $1 - \Sigma$CSL (59%) was not necessarily the one that produced the highest DOS (24.3%).

In view of the fact that the grain size is the other important microstructural parameter that is affected by the TMP, an attempt was made to investigate the effects

Table 1. Percentage of coincident site lattice and low-angle (<15°) boundaries as a function of annealing conditions

Annealing temperature (°C)	Annealing time (min)								
	15			30			60		
	ΣCSL	(Σ3)	<15°	ΣCSL	Σ3	<15°	ΣCSL	Σ3	<15°
800	22	16	0.13	25	19	0.13	25	19	0.13
850	21	16	0.10	19	16	0.45	24	21	0.28
900	25	22	0.12	25	22	0.40	25	22	0.35
950	37	33	0.40	41	37	0.21	26	23	0.46