CORROSION AND GRAIN BOUNDARY CHARACTER DISTRIBUTION (GBCD) IN 316L AUSTENITIC STAINLESS STEEL

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ABSTRACT

IGC (Inter-granular corrosion), in a single phase materials, is expected to depend on (a) Chemistry, (b) Grain size and (c) GBCD(Grain boundary character distribution). In the present study, 316L austenitic stainless steel was deformed to different extent by unidirectional and by cross rolling. Subsequent solutionizing , i.e. a combination of pri mary recrystallization and grain growth, did not bring any noticeable difference in bulk texture. The GBCD, especially the 23 twin boundaries, were, however, significantly differ ent. A difference of more than five times in low CSL (coincident site lattice) boundaries were obtained. An effort was made to relate the effect of GBCD on corrosion - by DL- EPR (Double loop electrochemical potentiokinetic reactivation).

INTRODUCTION

Austenitic stainless steels play an important role in the global industry and because of their unique properties, are widely used in application areas including chemical, paper, energy, transport, machinery, consumer products (foods beverage and catering). The most attractive property of austenitic stainless steel is its corrosion resistance. Corrosion resistance especially IGC (Inter-granular corrosion) and IGSCC (Inter-granular stress corrosion cracking) is expected and also reported (1) to depend on nature of GB (grain boundary). Manipulation of such nature, the so-called GBE (grain boundary energy) is one of the thrust areas in today's material development.

Watanabe (2) introduced the concept of "grain boundary design and control", in which he proposed that even the bulk properties of materials could be improved by controlling the grain boundary nature. The grain boundary structure can be described by coincident site lattice (CSL) model, which gives the degree of coincidence of lattice from adjacent grains and hence is rough measure of the grain boundary energy (3). A number of authors have suggested that an increased in fraction of CSL may improve specific properties of material (4) e.g. low CSL boundaries exhibit high resistance to sliding, corrosion, sensitization and solute segregation as well as reduced mechanism of creep rate and inter-granular stress corrosion cracking (5,6). Subsequently, a significant influence of grain boundary character distribution (GBCD) on the overall resistance to inter-granular corrosion of polycrystalline materials was reported for alloy 600(7), alloy 800(8) and lead (9). These results showed that the increase in the fraction of low Σ CSL type grain boundaries ($\Sigma \leq 29$) decreased the penetration depth by inter-granular attack.

Most of such studies (7,8,9) have used local and limited data on grain boundaries to demonstrate relation freedom from carbide precipitation or crack growth. Objective of the present study is to 'appreciate' effect(s) of overall GB nature on bulk IGC measurement.

EXPERIMENTAL

The material under investigation was in the form of plate of 32-mm thickness. The composition of these stainless steels is given in table. 1.

Table 1 : *Chemical composition of 316L austenitic stainless steel used in this investigation weight percentage (wt %).*

C	S	P	Si	Mn	Cr	Ni	Mo	Cu	N	Fe
0.025	0.07	0.025	0.46	1.58	17.11	11.69	2.57	0.026	0.007	Bal

These materials were rolled to different percentage of reduction i.e. 20, 40, 60 and 80 in unidirectional as well as in cross-rolled. The final thickness is obtained by giving number of pass of each reduction. For all reduction annealing was carried out at 1050°C for one hour and subsequent water quenching, to obtain different grain size. In order to produce a mirror-like finished and deformation free surface, the specimen were electroploished in an electrolyte containing 1 part of perchloric acid and 3 part ofmethanol.

The data set for determining GBCD of recrystallized 316L sample were obtained by a commercial TSL package (on a xl-30 Philips SEM) was used. Different step rises depending in the grain size, were used for OIM measurement. Approximately, 200 to 300 grain boundaries per sample were characterized for CSL identification; Brandon's criterion (10) was used.

Corrosion studies were carried out by Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR), the test conducted following the recommendations of Majidi and Streicher (11). Samples were cut from bulk with a size about lOmmXIOmm. All sample were first solution treated i.e. annealed at 1050^{0}C for one hour followed by water quenching (WQ) and sensitization treatment were given to all 316L deformed samples i.e. 750□C for 48 hrs and WQ. A Stainless steel wire is soldered to one side of the sample to provide electrical contact to the specimen. The entire assembly was then mounted in super fast, cold setting resin (plast powder / liquid) by placing it in a round, 20mm diameter, and 20 mm-deep mold. The mounted specimen was polished to 1-am, diamond -paste finish and rinsed in distilled water before test.

A fresh solution of 0.5 M H_2SO_4 and 0.01 M KSCN was used in each test. The platinum sheet and saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. The solution was de-aerated by passing argon gas before as well as during the test. The DL-EPR conditions used in the study are listed in the following table 2.

Table. 2 : *Condition for DL-EPR test.*

Polishing	1 -μm (Diamond paste)
Electrolyte	0.5 M H2S04 + 0.01M KSCN
Temperature	25 ±2°C
OCP	-360 to -380 mV
Initial Potential	OCP
Vertex Potential (I)	0.3V
Vertex Potential(II)	-0.4V
Final potential	-0.45V
Scan rate	1.667mV/sec

RESULTS & DISCUSSION

Summary of the results on the fraction of near CSL-boundaries is shown in table 3.

Table 3.

The relation between percentage of reduction and fraction of Σ3 - Σ29 at 5° and 15°

Brandon's criteria: Δ9 = 152^{1/2}

Sample	Σ3-Σ29		Σ3	
	15°	5°	15°	5°
0%	0.505	0.35	0.389	0.34
20%U	0.412	0.31	0.344	0.306
40%U	0.378	0.215	0.328	0.214
60%U	0.377	0.292	0.319	0.286
80%U	0.325	0.235	0.279	0.234
20%CR	0.358	0.252	0.27	0.236
40%CR	0.27	0.166	0.191	0.191
60%CR	0.24	0.137	0.166	0.132
80%CR	0.148	0.099	0.134	0.098

All samples were solutionized 1050° Ih. Where U stand for Unidirectional and CR stand for Cross-rolled.

A general trend is drop in Σ3-E29. Sl« 10% at all condition, except 20% cross rolled Slw4%. Different treatments did not make significant differences in bulk texture, but difference in grain size and more importantly in relative GBCD it could create. For similar grain size distribution also different GBCD could be obtained - nearly 5 times difference in GBCD could be achieved. GBCD change with increasing reduction can be summarized as drop in total CSL fraction and no significant- change of proximity to exact CSL. In other word, increasing the percentage of reduction increases number of random boundaries. Degree of sensitization was measured with the help of DL-EPR. All experiment was carried out in standard solution recommended by ASTM -A-262 for 304L.

Table 4 : DL-EPR results

Percentage of Deformation	316L Ir/Iax 100	
	Unidirectional	Cross-rolled
0%	0.4	0.4
20%	0.0308	1.14
40%	0.0779	0.926
60%	0.115	0.0174
80%	0.006	0.003

Table-4 show that degree of sensitization decrease with increase in percentage of reduction, increases in-between and again it decreases in case of unidirectional rolled samples. While in cross-rolled, degree of sensitization increases with increasing reduction and finally decreases, in both cases, there is decrease in corrosion rate.

From table 4., DL-EPR results showing some different trend, which is so far reported by many authors. 80% deformation with maximum random boundaries gives the lowest degree of sensitization. To explain this the following hypothesis is proposed, which is based on the formation and effectiveness of sensitized zone on grain boundary which will depend upon: (a) nucleation probability-this should depend on nucleation rate, which is proportional to exp. ($-\Delta G^*/RT$), Where as ΔG^* is activation energy barrier to heterogeneous nucleation, which should be proportional to ($1/\gamma$), where γ is the grain boundary energy. Effectiveness of sensitized zone will depend on relative contribution from bulk versus grain boundary. More chromium carbide precipitates will form on grain boundary which having low energy as chromium will be coming from matrix rather than bulk. While in case of high-energy boundary it will be reverse.

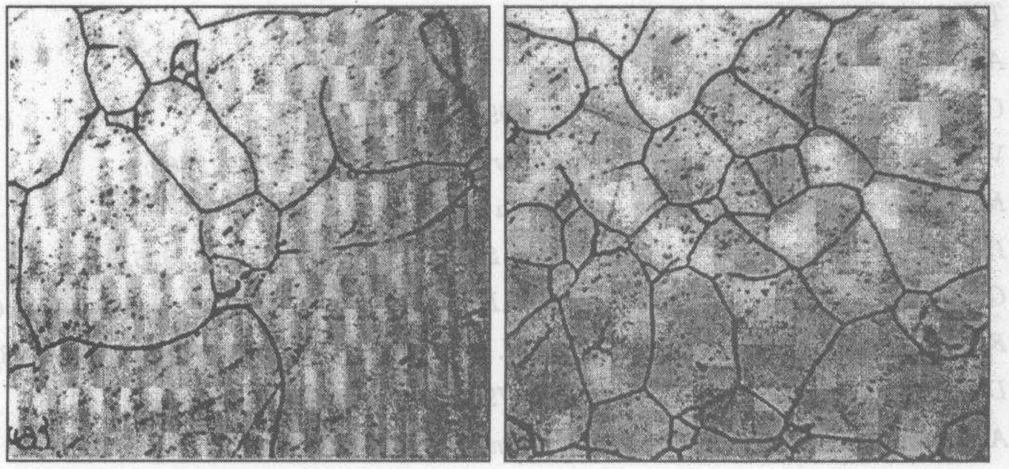

Figure. 1 : *Optical photomicrograph of the (a) 0% 316L and (b) 80% cross rolled as received after DL-EPR (annealing 1050°C for lhr+ sensitization 750°C for 48hrs) (Magnification 160X)*

Figure l(a) show that degree of sensitization is more compare to figure l(b).

CONCLUSION

1. Drop in CSL population with increase in reduction.
2. IGC do not show a monotonic change with increase or decrease in special boundary concentration.
3. A model explaining the observed experiment observation is proposed.

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