RESEARCH PAPERS
FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA
SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

2014 Volume 22, Special Number

STUDY OF THE SENSITIZATION ON THE GRAIN BOUNDARY IN AUSTENITIC STAINLESS STEEL AISI 316

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ABSTRACT

Intergranular corrosion (IGC) is one of the major problems in austenitic stainless steels. This type of corrosion is caused by precipitation of secondary phases on grain boundaries (GB). Precipitation of the secondary phases can lead to formation of chromium depleted zones in the vicinity of grain boundaries. Mount of the sensitization of material is characterized by the degree of sensitization (DOS). Austenitic stainless steel AISI 316 as experimental material had been chosen. The samples for the study of sensitization were solution annealed on 1100 °C for 60 min followed by water quenching and then sensitization by isothermal annealing on 700 °C and 650 °C with holding time from 15 to 600 min. Transmission electron microscopy (TEM) was used for identification of secondary phases. Electron backscattered diffraction (EBSD) was applied for characterization of grain boundary structure as one of the factors which influences on DOS.

KEY WORDS

Austenitic stainless steel, microstructure, precipitation, grain boundary

INTRODUCTION

Austenitic stainless steels are the largest group in the stainless steel family. These alloys are commonly used as structural materials due to their combination of good mechanical properties and high corrosion resistance. The most widely used is AISI 300 series, a system of Fe-Cr-Ni alloys. Type AISI 316 has good corrosion resistance and high-temperature strength because of high alloying content. Corrosion resistance is provided by the formation of a chromium-rich passive layer. In service, when steel is exposed to temperatures between 450 and 900 °C, chromium-rich carbides tend to precipitate at grain boundary (GB). Significant carbide precipitation can result in severe chromium depletion near the GB, referred to as sensitization (1-3). A number of methods have been used to reduce sensitization and related failures, e.g. reduction of carbon (below 0.03 wt. %), and addiction of nitrogen and strong

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carbide formers (such as titanium/niobium) to the existing stainless steels (SS). However, all of these methods have drawbacks (4).

Many recent studies of grain boundary engineering (GBE) have demonstrated that GB characters can influence the DOS and IGC of stainless steel. Special grain boundaries are often characterized by the Coincidence Site Lattice (CSL) model. This model says that the GBs are special if they have a given fraction of atoms in the grain boundary plane which are coincident to both lattices separated by the grain boundary. These boundaries are classified in terms of Σ values. The Σ value denotes the fraction of atoms in coincidence, e.g. in a Σ3 boundary every third atom is at coincident site. Sensitization in SS can be minimized by enhancing the lattice sites common to two or more grains and thus reducing the "GB energy". Such boundaries are known to have special properties and are designated by Σ. GB with $1<\Sigma<29$ are regarded as low-ΣCSL boundaries or special boundaries (4-6).

This study is focused on the sensitization of GBs by the precipitation of secondary particles in austenitic stainless steel AISI316 after heat treatment.

EXPERIMENTAL PROCEDURES

Two series of austenitic SS AISI 316 specimens were used in this study. Chemical composition and properties of the heat treatment are summarizing in Table 1, 2.

CHEMICAL COMPOSITION OF AISI 316 Table 1

wt. %							
C	Si	Mn	P	S	Ni	Cr	Mo
0.04	0.54	1.08	0.03	0.008	11.48	18.52	2.1

To study the effects of solution heat treatment on IGC, the specimens were solution annealing at 1100 °C for 1h followed by water quenching, then sensitized by isothermal annealing at 650 °C and 700 °C for 15, 30, 60, 300 and 600 min respectively.

SIGNATURE OF SPECIMENS AND PARAMETERS OF SOLUTION TREATMENT Table 2

Temperature	Isothermal annealing				
	15 min	30 min	60 min	300 min	600 min
650 °C	S21	S22	S23	S24	S25
700 °C	S31	S32	S33	S34	S35

For determination the steels sensitively to intergranular corrosion on oxalic acid etched test (ASTM A262 practice A) was used. Metallographic samples were prepared using standard metallographic mechanical grinding and polishing techniques. The polished samples were electrolytically etched with oxalic acid (10 ml $C_2H_2O_4$ + 90 ml H_2O) at 10 V, to reveal the microstructures.

For the detail observation of GBs and precipitates a double stage replicas were used. Observation of replicas was carried on the transmission electron microscopes (TEM) Philips 300CM (EDX) and JEOL 200CX (ED). Observation by EBSD method on scanning electron microscope (SEM) JEOL 7600F was used to identify type of GB.

RESULTS

On the Fig. 1(a - e) is microstructure of austenitic stainless steel AISI 316 after isothermal annealing at 700 °C with the different holding time. Microstructure of sample S31 (15 min) has polyedrical grains with grain size heterogeneity and is characterized mostly with step etch (Fig. 1a). Sample S32 (30 min) Fig.1b) has identical microstructure, but GBs are intensively etched with some ditches on GBs (Fig. 1b). This type of etch is known as dual (7). Both samples are not sensitized and are not prone to IGC. Sensitization was observed on samples on Fig.1 c - e (60 - 600 min). Microstructure of these samples is characteristic by intensive etch on GB. This appearance of GB is result of precipitation of the secondary particles. For the clear identification of these precipitates, TEM microscopy was used.

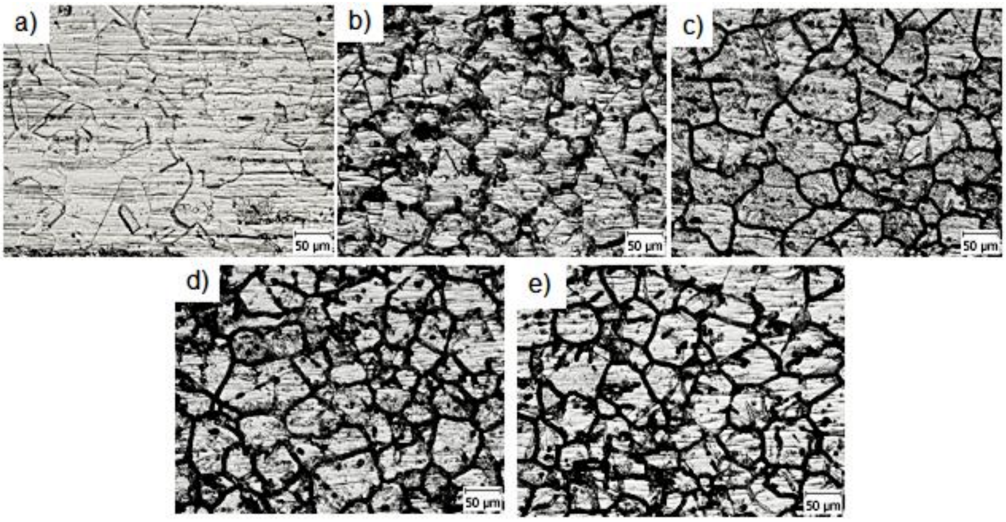

Fig. 1 *Microstructure of the specimens sensitized at 700 °C for: a) S31 – 15 min, b) S32 – 30 min, c) S33 – 60 min, d) S34 – 300 min, e) S35 – 600 min.*

From the analysis on TEM it is possible to say that sample S31 (700 °C, 15 min) has no precipitation of secondary particles on GB (Fig. 2a). Sensitized grain boundary with secondary particles is shown on Fig 2b (sample S35). From the ED analysis these precipitates were identified as $M_{23}C_6$ carbide (Fig. 2c). Besides $M_{23}C_6$ carbide, σ phase was identified on GBs too.

Fig. 2 *TEM analysis of grain boundary of ASIS 316 a) detail of not sensitized GB, b) detail of sensitized GB (S35), c) diffraction pattern of $M_{23}C_6$ carbide*

EBSD method was used for study of the GB character and calculation of the CSL parameter. On the Fig. 3 (a - d) are samples after isothermal annealing at 650 °C with different holding time (Table 2). Microstructure on all samples is polyedrical with various size of grains. All samples contained annealing twins which are typical for austenitic grain. Course GBs were observed in the case of all samples, which were heat treated with holding time longer than 300 min. It was caused by intensive precipitation of the secondary phases on the GBs.

Program Tango was used to process SEM micrographs and identify type of GB. On the Fig. 4 are GBs highlighted CSL grain boundaries. Each colour represent different CSL with various value of S. From the literature (5, 8) is well know that in austenitic stainless steel AISI 316 are mostly presented CSL grain boundaries with S3 (e.g. annealing twins) whose are represented on Fig. 4 by red colour. In addition to S3 on the Fig. 4 were identified another CSL grain boundaries like S9 (pink colour) and S27 (green colour).

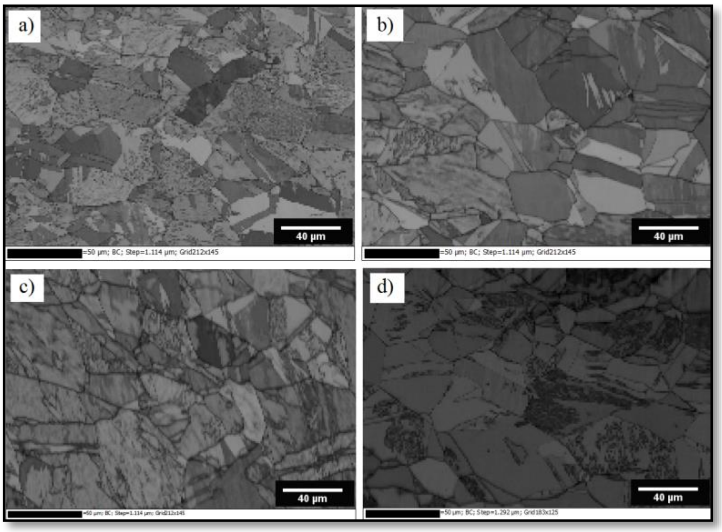

Fig. 3 *SEM backscattered electron microscopy of specimens sensitized at 650 °C for: a) S22 - 30 min, b) S23 – 60 min, c) S24 – 300 min, d) S25 –600 min*

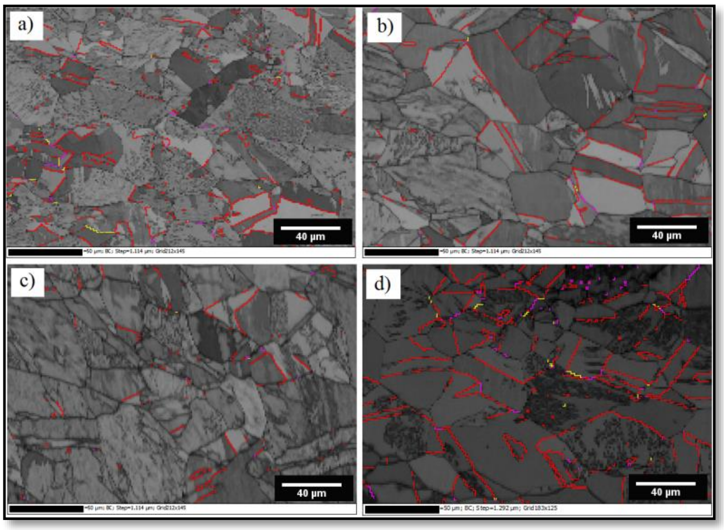

Fig. 4 *Highlighted CSL: a) S22, b) S23, c) S24, d) S25. In orientation maps are colour coded as follows: Σ3 – red, Σ9 – pink, Σ27a,b – green*

In Table 3 are summarised the values of CSL grain boundaries for samples whose were isothermally annealed at 650 °C with time of hold: 30, 60, 300 and 600 min. By analysis on

EBSD, the number of CSL grain boundaries and number of CSL grain boundaries with precipitates was calculated. Each sample was analyzed at three different places.

Table 3 shows that samples after isothermal annealing with hold time 30 and 60 min contains minimal number of precipitates. Because of this little number it was not possible to identify these precipitates with SEM. On the samples with longer holding time (300 and 600 min) was observed coursing of grain probably because of higher rate of precipitation of secondary particles on GBs during isothermal annealing.

Analysis of the sample S24 (700 °C/300 min) was found 20.5% sensitized random GBs, while CSL GBs were sensitized only 10.3%. Ratio of GBs was increased with increasing of holding time. EBSD analysis showed 25.3% sensitized random GBs and 13.4% sensitized CSL GBs at heat treatment 650 °C/600 min (Tab. 3).

FRACTION OF COINCIDENT LATTICE AND OTHER LOW ΣCSL GB AS A FUNCTION OF SOLUTION TREATMENT — Table 3

Annealing temperature	**Annealing time**	**Percentage of CSL GB**				**Percentage of GB with precipitates [%]**	
		Σ3	Σ9	Σ27(a,b)	Other low ΣCSL	Random GB	CSL GB
650 °C	30 min	4.24 ±0.31	0.18 ±0.08	0.04 ±0.03	0.11 ±0.03	Without precipitates*	
	60 min	6.17 ±1.45	0.33 ±0.20	0	0.14 ±0.04	Without precipitates*	
	300 min	1.69	0.06 ±0.01	0.01	0.07 ±0.01	20.50 ± 2.15	10.28 ±0.6
	600 min	9.27 ±2.03	0.82 ±0.25	0.31 ±0.27	0.15 ±0.06	25.24 ± 3.78	13.39 ±0.90

*Precipitates weren’t identified by SEM.

CONCLUSION

The precipitation behaviour of AISI 316 austenitic stainless steel was investigated during heat treatment at the temperatures 650 and 700 °C with different holding time. The following conclusions were down:

- Corrosion test ASTM A262 practice A, showed that samples S31 (700 °C/15min), S32 (700 °C/30 min) had not contain GBs attacked by IGC. No sensitization was observed. Precipitation of secondary phases was observed in the case of the samples S34 (700 °C/300 min), S35 (700 °C/600 min). Microstructure of these samples was classified as sensitised and susceptible to IGC.
- The TEM analysis was focused especially on identification of secondary phases at the grain boundaries. At first $M_{23}C_6$ carbide at the austenitic grain boundaries was detected and subsequently σ-phase was detected.
- EBSD analysis was used to detail study of GBs for samples S22 - S25 (650 °C/ 30 min – 600 min). SEM analysis of the sample S22 and S23 shows low count of precipitates on GBs.
- Number of random sensitized GBs on sample S24 was set to 20.5%, while number of sensitized CLS grain boundaries was only 10.3%. For samples S25 number of random

sensitized GBs increased to 25.3% and also the number of sensitized CLS GBs increased up to 13.4%.

ACKNOWLEDGMENT

The authors wish to thank the financial support of Scientific Grant Agency of Slovak Republic (VEGA) under grant No. 1/0402/13.

This contribution/publication is the result of the project implementation: Center for development and application of advanced diagnostic methods in processing of metallic and non-metallic materials, ITMS:26220120014, supported by the Research & Development Operational Programme funded by the ERDF.

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