A New Etching Route for Revealing the Austenite Grain Boundaries in an 11.4% Cr Precipitation Hardening Semi-Austenitic Stainless Steel

D. San Martín^{1*}, P.E.J. Rivera Diaz del Castillo¹, E. Peekstok² and S. van der Zwaag¹

¹Fundamentals of Advanced Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

²Department of Materials Science and Engineering, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands

(NOTE: Since 2008, David San Martín works in the National Centre for Metallurgical Research, CENIM-CSIC, Madrid, Spain, dsm@cenim.csic.es)

Abstract: A detailed metallographic characterization of a precipitation hardening semi-austenitic stainless steel is described. A new etching procedure based on the Lichtenegger and Blösch color etching solution, which is frequently used in duplex stainless steels to differentiate delta ferrite from austenite, has been used to differentiate martensite, austenite and the Chi-phase in this stainless steel. By changing the etching conditions, this etchant now reveals the austenite grain boundaries when the steel is in the austenitic state. Moreover, this solution is able to reveal also the prior austenite grain boundaries when the steel is in its martensitic state. This etching procedure represents a great advantage because it reveals, at the same time, different features of the microstructure.

Keywords: Stainless Steel, Martensite, Austenite, Grain Boundaries, Etchant.

*Corresponding author.

1. Introduction

Precipitation hardening semi-austenitic stainless steels are a class of high alloyed Cr and Ni containing steels that provide an optimum combination of high strength, relatively good ductility and moderate corrosion resistance [1]. The semi-austenitic condition comes from the fact that these steels retain their austenitic structure on cooling to room temperature but form martensite when treated at sub-zero temperatures (below 0 °C). The formation of martensite followed by the precipitation of fine intermetallic phases during annealing at intermediate temperatures (400-600 °C) [2] provide their final mechanical properties. In the present steel an ultimate tensile strength exceeding 3000 MPa has been attained in wires after the precipitation hardening heat treatment [3, 4].

To enable metallurgists to make high quality steels, reliable and suitable metallographic techniques need to be available to characterize both microstructural features, such as phases, grain boundaries and precipitates. Available metallographic methods generally combine very precise instructions concerning sample preparation and etching processes. Moreover, the etching result is strongly dependent on the composition of the phase; thus slight alterations in the composition of the steel give rise to different etching outcomes. The complexity of a number of these methods makes them usually inoperative for a wide range of alloy compositions. It can be found that some methods extensively demonstrated to be effective in revealing certain phases in some commercial alloys are unsuccessful or produce different etching results when applied to these new steels. Thus, the search for new metallographic procedures or the application of the existing ones to new steels always reveals new ways or new features.

In this work, the metallographic characterization of a precipitation hardening semi-austenitic stainless steel is described. The Lichtenegger and Blösch color etching solution [5], which is frequently used in duplex stainless steels to differentiate δ -ferrite from austenite [6], has been used to differentiate martensite, austenite and the χ -phase in this stainless steel. Moreover, this solution was also able to reveal the prior austenite grain boundaries in the martensitic state after austenite was transformed isothermally (below 0 °C) to martensite. It may be possible to use this etching solution to reveal the austenite grain boundaries in other austenitic stainless steels by changing the etching conditions.

2. Materials and Experimental Procedure

The steel studied is being manufactured by Sandvik AB. It is a relatively newly developed steel grade that has been studied within the last ten years by a number of workers [2-4, 7-9]. The composition (Table 1) of the main alloying elements of the steel was determined by X-ray fluorescence. Carbon and nitrogen content were determined using a Leco CS 225 and a Leco TC436 induction furnace, respectively. The as-received material was delivered as strips of 31 mm width and 0.5 mm thickness.

Previous XRD and metallographic studies indicate that the phases usually present in the steel are austenite, titanium nitrides and the χ -phase [10]. The χ -phase [11] is a hard and brittle intermetallic usually found in austenitic steels alloyed with molybdenum.

Characteristic crystallographic features of typical phases present in stainless steels are shown in Table 2. Further information concerning these phases and additional ones can be found elsewhere [12, 13]. A typical composition of the phase is $\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$,

although it usually contains other elements like titanium or nickel. The morphology of this phase varies from rod-shaped to globular particles. It usually forms first at grain boundaries, then on incoherent twins and finally intragranularly [14]. On the other hand, titanium nitrides have also been detected in this steel. In high alloy steels like the one studied in this work, titanium is added for two reasons: to increase the strength of the steel and to bind the residual nitrogen and/or carbon content into the form of TiN or TiC [15]. The improvement in strength is achieved via an ageing treatment at 400-600 °C, during which Ni_3Ti fine precipitation is induced in the martensite. However, it is well known that carbon and nitrogen have a detrimental effect on the martensite transformation kinetics and on the toughness of the steel. Therefore, their levels should be minimized (they are usually kept below 0.03 wt %) or eliminated by the addition of a nitride and/or carbide forming elements such as titanium. The martensite can be induced in this steel by deformation [16] or by isothermal holding below 0 °C [8, 10].

The samples used to characterize the austenite and martensite by light optical microscopy (LOM) were cut into 5 mm squares and mounted in bakelite, ground and polished in different lap clothes, finishing with 1 μm diamond paste. In order to reveal the martensite metallographically, samples had to be aged at 550 °C for 30 minutes. Thus, fine precipitation is preferentially induced in the martensite [9] and this phase is more sensitive to etching due to the existence of these precipitates.

3. Results and Discussion

The samples of the studied steel were transformed isothermally at -40 °C for 384 h to partially transform the austenite into martensite. Later, they were aged at 550 °C in

order to make the martensite more sensitive to chemical reagents due to the formation of precipitates. Without this aging step martensite could not be revealed. The etching reagent used to reveal martensite in the microstructure at room temperature is described in Table 3. Used at room temperature, austenite was slightly etched with a light brown color and martensite was strongly etched with a dark brown color. Samples need to be freshly polished for proper etching response. The etching time needed to disclose the martensite phase is only of a few seconds. The martensite volume fraction was determined using LOM with the help of an image analyzer [17]. The volume fraction of martensite measured in this way was 50%. A typical microstructure for a partially transformed material is shown in Figure 1.

An important step in the characterization of an austenitic steel is to reveal the austenite grain boundaries. The different chemical etching solutions explored in this work are given in Table 4. Kalling's No. 2 [18], glyceresia [19] and electrolytic etching [20] have been reported to reveal the austenite grain boundaries in stainless steels. However, no satisfactory results were obtained in this work using similar conditions to those found in the literature. Kalling's No. 2 resulted in similar etching of the microstructure compared to Kalling's No. 1; no improvement was observed. The electrolytic etching resulted in severe darkening of the surface in just a few seconds but no grain boundaries were revealed. The voltage was varied and still no improvement was obtained. Glyceresia also darkens the surface very quickly. Alternative etching solutions that combine hydrochloric and nitric acids such as aqua regia and dilute aqua regia were also unsuccessful in revealing the austenite grain boundaries.

The first positive results were obtained using Vilella's reagent, which is a variation of glyceric acid. Initially, only after a few seconds, the interface between the χ -phase and austenite is etched black, and austenite and the χ -phase are slightly darkened. After 30-60 s, some grain boundaries are revealed in the microstructure (see center grains in Figure 2a). A big titanium nitride particle is also present in this micrograph as well as the χ -phase precipitates (visible mostly as dark points). The micrograph reveals that the austenite grain size is very small, of the order of 5-10 μm . This might be a reason why the austenitic microstructure of this steel is very difficult to expose [21]. Further etching for up to 5 minutes darkens the surface with a slight improvement in showing the grain boundaries. After this severe etching, both matrix and grain boundaries are revealed, but the contrast is not good enough and a light polish in the 1 μm lap cloth for a few seconds is needed until the etched matrix is removed (at the same time some grain boundaries are also removed). Only after several cycles of etching and polishing were the grain boundaries revealed properly, although not all of them were visible (Figure 2b). This process is very tedious and time consuming, taking up to one hour for only one sample and with no fully satisfactory results. This reagent should be discarded and changed when it turns to a yellow/orange color.

The Lichtenegger and Blösch reagent [5, 6] is a color etching solution that is generally used to reveal the microstructure resulting from solidification of duplex and austenitic stainless steels [22]. When using ammonium difluoride ($\text{NH}_4\text{F} \cdot \text{HF}$) one should take into account that in contact with water, it will decompose to ammonium fluoride (NH_4F) and hydrofluoric acid (HF). The HF content of the resulting solution makes it very corrosive, toxic and hazardous. Therefore, this solution must be handled with care. In

order to dissolve the ammonium difluoride, the water should be warmed because the decomposition reaction is endothermic. This reagent colors the austenite and leaves the δ -ferrite intact. Etching with this solution, at room temperature, gives very similar results to those obtained using Kalling's No.1; martensite and austenite are etched dark brown and light brown respectively. However, if the sample is left for longer periods of etching than those required to etch the martensite (>1 minute), the χ -phase is made visible in white color. Compared to Kalling's No.1 the sample needs a bit more time to attain the same color intensity in the martensite. However, it has been found that when this etching solution is used hot, around 60-80 °C, more features of the microstructure are revealed. Only after 10 s the austenite is colored in light white-blue and martensite becomes almost unetched. Traces of grain boundaries are visible in the austenite phase. After 45 s, austenite turns to a variety of colors from white and light blue to light red and light brown. Martensite is etched brown. Grain boundaries are visible in both austenite and martensite, although the austenitic microstructure is more clearly revealed. After 90 s, austenite keeps the same variety of colors and martensite turns to dark grey color. Grain boundaries are then well revealed in both phases although darkening of the overall microstructure has also taken place. A compromise has to be found in order not to stain or color the microstructure too much, while the grain boundaries remain visible. From the very first stages of the etching the χ -phase is revealed with an intense white color that contrasts very well with the matrix, especially with the martensite phase.

In Figure 3a the microstructure obtained after etching for 90 s is shown at low magnification. In Figures 3b and 3c, fully martensitic and austenitic regions of the microstructure are shown, respectively. Grain boundaries are clearly visible in both

phases. Light color regions in Figure 3b corresponds to retained untransformed austenite. Figures 3b and 3c show that the χ -phase is present preferentially at austenite grain boundaries. The presence of this phase might make the steel susceptible to intergranular corrosion as already discussed. However, its presence can be avoided by changing the thermal conditions during the final stages of the hot rolling process.

Finally, the comparison of the prior austenite grain size of isothermally transformed martensitic regions with the austenite grain size of untransformed austenitic regions gives information on the influence, if any, of the size of the austenite grains on the kinetics of the martensitic transformation.

Conclusions

A new etching procedure based on the Lichtenegger and Blösch color etching solution has been developed to disclose austenite, martensite and the χ -phase present in a precipitation hardening semi-austenitic stainless steel. This procedure was used to reveal the austenite grain boundaries when the steel was in the austenitic state. Moreover, this solution was able to reveal also the prior austenite grain boundaries when the steel was in its martensitic state after martensite was isothermally transformed below 0 °C. This etching procedure represents a great advantage for metallographers because it reveals simultaneously different features of the microstructure.

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Table 1. Chemical composition of the studied steel [wt.%] with balance Fe.

Cr	Ni	Mo	Ti	Al	Si	Cu	Mn	S	P	C, N
11.4	8.7	3.4	1.1	0.7	0.3	2.5	0.3	0.04	0.03	< 0.01

Table 2 Secondary phases present in stainless steels

Phase	Symbol	Type	Formula	Temperature Range, °C	Structure	Lattice constant, nm
Carbide	-	M ₇ C ₃	(Cr, Fe, Mo) ₇ C ₃	950-1050	Orthorhombic	a=0.452; b=0.699; c=1.211
Carbide	-	M ₂₃ C ₆	(Cr, Fe, Mo) ₂₃ C ₆	600-950	Cubic (fcc)	a=1.057-1.068
Carbide	-	M ₆ C	(Cr, Fe, Mo, Cb) ₆ C	700-950	Cubic (diamond)	a=1.093-1.128
Nitride	-	M ₂ N	(Cr, Fe) ₂ N	650-950	Hexagonal	a=0.478, c=0.446
Nitride	Z	MN	(Nb, Cr)N	700-1000	Tetragonal	a=0.303, c=0.737
Carbo-nitride	-	MC	Ti(CN)	700-1400	Cubic (fcc)	a=0.432-0.424
Carbo-nitride	-	MC	Nb(CN)	700-1350	Cubic (fcc)	a=0.442-0.438
Sigma	σ	AB	(Fe, Ni, Cr, Mo)	550-1050	Tetragonal	a=0.886-0.892, c=0.454
Chi	χ	A ₄₈ B ₁₀	Fe ₃₆ Cr ₁₂ Mo ₁₀	600-900	Cubic (bcc)	a=0.886-0.892
Alpha prime	α'	-	CrFe (Cr 61-83 %)	350-550	Cubic (bcc)	a=0.2877
Laves	η	A ₂ B	(Fe, Cr) ₂ (Mo, Nb, Ti, Si)	550-900	Hexagonal	a=0.473-0.482; c=0.726-0.785
R	R	-	(Fe, Mo, Cr, Ni)	550-650	Hexagonal	a=1.0903; c=1.9347
Tau	τ	-	-	550-650	Orthorhombic	a=0.405; b=0.4.84; c=0.286
G	G	A ₁₆ B ₆ D ₇	Ni ₁₆ (Nb, Ti) ₆ Si ₇	500-850	Cubic (fcc)	a=1.12

Table 3 Chemical etching solution to reveal the martensite phase

Name	Composition
Kalling's No.1	1.5 g CuCl_2 (cupric chloride) + 33 ml HCl (hydrochloric acid) + 33 ml $\text{C}_2\text{H}_5\text{OH}$ (ethanol) + 33 ml of distilled water

Table 4. Chemical etching solution attempted to reveal the austenite grain boundaries.

Name	Composition
Kalling's No. 2	5 g CuCl_2 (cupric chloride) + 100 ml HCl (hydrochloric acid) + 100 ml $\text{C}_2\text{H}_5\text{OH}$ (ethanol)
Vilella's reagent	45 ml $\text{C}_3\text{H}_8\text{O}_3$ (glycerol) + 30 ml HCl (hydrochloric acid) + 15 ml HNO_3 (nitric acid)
Glyceregia	45 ml HCl (hydrochloric acid) + 30 ml $\text{C}_3\text{H}_8\text{O}_3$ (glycerol) 15 ml HNO_3 (nitric acid)
Electrolytic etch	60% HNO_3 (nitric acid) + 40 % distilled water
Aqua regia	45 ml HCl (hydrochloric acid) + 15 ml HNO_3 (nitric acid) + 20 ml CH_3OH (methanol)
Dilute aqua regia	15 ml HCl (hydrochloric acid) + 5 ml HNO_3 (nitric acid) + 100 ml distilled water
Lichtenegger-Blöch (L-B)	20 g $\text{NH}_4\text{F} \cdot \text{HF}$ (ammonium difluoride) + 0.5 g $\text{K}_2\text{S}_2\text{O}_5$ (potassium metabisulfite) + 100 ml of distilled water

Figure 1 Microstructure obtained after holding the sample at -40°C for 384 h.

Martensite and austenite are the dark and light phases respectively.

Figure 2 (a) Microstructure obtained after etching with Vilella's reagent for 30-60 s; (b) Microstructure after repeated cycles of etching and polishing with the same reagent.

Figure 3 Microstructure revealed using hot L-B etching solution. (a) Martensite (dark phase) and austenite (light phase). (b) Prior austenite grain boundaries revealed in isothermally transformed martensitic regions. Light color regions correspond to untransformed austenite. (c) Austenite grain boundaries revealed in the untransformed austenite phase. White dots correspond to the χ -phase.