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Microstructural Characterization and the Effect of Phase Transformations on Toughness of the UNS S31803 Duplex Stainless Steel Aged Treated at 850 °C

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Duplex stainless steels, with ferritic-austenitic microstructure, have excellent mechanical properties and corrosion resistance. However, when duplex stainless steels are exposed to temperatures between 600 and 1000 °C, some phase transformations can occur such as chromium nitrides precipitation, chromium carbides precipitation and the sigma phase formation. The formation of such compounds leads to loss in both corrosion resistance and fracture toughness. The negative effects of the formation of chromium nitrides, carbides and the sigma phase are due to the chromium depletion in the matrix. The phase transformations cited above occur initially at ferritic-austenitic interfaces and at the grain boundaries. The aim of this work is to identify and characterize the phase transformations, which occur when aging heat treatments are carried out at temperatures at which the kinetics is the fastest for the reactions mentioned. At first, the samples were annealed at 1100 °C for 40 min. The aging heat treatments were then carried out at 850 °C for 6, 40 e 600 min. Microstructural characterization was done by using optical microscopy with different etchings, in order to identify each phase formed in the duplex stainless steel during aging heat treatments. The toughness was also evaluated by using Charpy impact test. Impact tests show that loss of toughness was related to phase transformations.

Keywords: *duplex stainless steel, the sigma phase, toughness*

1. Introduction

The duplex stainless steels, with ferritic-austenitic microstructure, have better corrosion resistance than the austenitic stainless steel and better mechanical properties than the ferritic stainless steel[1]. However, when these steels are exposed to temperatures ranging from 300 to 500 °C the α' phase formation can occur. At higher temperatures other solid-state phase transformations may also occur. At temperatures ranging from 500 to 1000 °C (Fig. 1), phase transformations such as the sigma phase formation, chromium nitrides and carbides precipitation are favored[2].

The occurrence of these phases can often cause loss of toughness and a decrease in corrosion resistance. Especially the sigma phase formation has been the object of many studies. The sigma phase presents the fastest kinetics in the range of temperatures reached during welding or thermo-mechanical processing[4-6].

The sigma phase is a hard and fragile one and its formation causes loss of toughness as described in reference[2]. Moreover, for sigma phase consumes chromium and molybdenum of the matrix, which leads to the depletion in these elements. As a result, there is a loss in corrosion resistance[7]. In the Fe-Cr-Ni systems, the sigma phase has a Fe-Cr composition and a tetragonal crystalline structure with 30 atoms per unit cell[8]. Depending on the alloy composition, the sigma phase can also contain molybdenum, silicon and tung-

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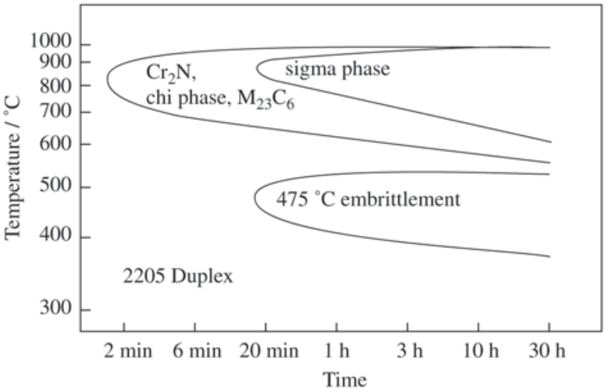

Figure 1. Precipitation diagram of UNS S31803Duplex stainless steel[3].

sten. In a general way, the ferrite stabilizing alloy elements favor the sigma phase formation. Molybdenum, for instance, which is generally added to duplex stainless steels to improve pitting corrosion resistance, also favors the sigma phase formation[7]. Besides the chemical composition, other factors can propitiate the sigma formation such as grain size - the smaller the grain size the greater the tendency towards the sigma formation. The sigma phase is more easily formed in high energy regions such as grain boundaries and interfaces[2]. The temperature of annealing heat treatment influences the sigma phase formation in two ways: Higher annealing temperatures cause an increase in grain size, which reduce the tendency towards the sigma phase formation. On the other hand, at higher temperatures, high-temperature-ferrite can occur, facilitating the sigma phase formation during aging heat treatments. The precipitation of carbides ($M_{23}C_6$), can also occur in duplex stainless steel, and can present the same negative effects caused by the formation of the sigma phase. The $M_{23}C_6$ precipitation also occurs in regions of high energy. Nitrides also occur in stainless steel. The main nitrides that occur in stainless steel are CrN and Cr_2N[2]. In duplex stainless steel, the precipitation of Cr_2N type nitrides is favored in the ferrite-austenite interfaces. However, its precipitation has also been observed in ferrite-ferrite boundary[2,5].

The identification and the characterization of the sigma phase, of the chromium carbides and of the chromium nitrides as well as of other phases can be made by using several complementary techniques of microstructural analysis, such as the X-ray diffraction. However, efficient indirect techniques are used in the verification of the occurrence of phase transformations, such as the Vickers microhardness and the Charpy impact test. The identification of phases using optical microscopy can also be made. Optical microscopy is one the most important and also accessible complementary techniques. The identification of the phases by its morphology and the colour acquired after the metallographic etching can be made in a conclusive way because many of the phase transformations occurred during aging heat treatment are well known[9].

The aim of this work is to characterize the phase transformations in duplex stainless steel after aging at 850 °C, as well as to show a relationship between phase transformations and the loss of toughness. In this study the duplex stainless steel UNS S31803 was used. The samples were annealed at 1100 °C for 40 min and later aged at 850 °C for different periods of time. A metallographic procedure was also developed for microstructural characterization and identification of the phases. The procedure developed consisted of using three types of metallographic etchings. Each etching disclosed with differentiated intensity and characteristic colors the morphology of the phases in the steel, facilitating their identification.

2. Experimental Procedure

The chemical composition of the UNS S31803 (22%Cr-5%Ni) ferritic-austenitic duplex stainless steel studied is shown in Table 1. The samples were withdrawn from a rolled sheet.

The stainless steel studied was solution annealed at (1100 ± 3) °C for 40 min. After the annealing heat treatment was done, the samples were aged at (850 ± 3) °C for 6, 40 and 600 min. All the heat treatments were carried out in a muffle and were followed by quenching in water.

The metallographic sample preparation consisted of grinding with # 600 emery paper, 1 µm diamond polishing and further etching. Different etchings were used to characterize the microstructure of the samples after annealing and aging heat treatments. The procedure is described as follows:

1. Behara II. Austenite and ferrite have different colours after etching with Behara II for 15 s. Ferrite becomes blue and austenite yellow.
2. KOH. The electrolytic etching composition was a solution of KOH 10 N. 2.5 V was applied for about 60 s in the samples inside the solution of KOH. This etching differentiates the sigma phase from the other phases.

Table 1. Chemical composition (wt %) of the UNS S31803 steel.

C	Si	Mn	P	S	Cr	Ni	Mo	N
max	max	max	max	max				
0.03	1.0	2.0	0.030	0.015	22	5.5	3.2	0.18

3. NH_4OH. The electrolytic etching with NH_4OH was done by applying 1.5 V in the sample for 40 s. This etching differentiates carbides and nitrides from the other phases.

The microstructures were analysed by using mainly optical microscopy. The other technique used to identify phase transformations in the steel studied was the Charpy impact test. The impact test measures the energy absorbed during impact and gives a relationship between the type of material and its toughness. The test was carried out according to ASTM E-23 Standards (1998)[10].

3. Results

Annealing heat treatment

Table 2 shows the result of the Charpy impact tests after annealing at 1100 °C for 40 min.

After annealing the samples were etched with different etchings. Figure 2 shows the results of the annealing samples after the etching with Behara II. Two phases are distinguishable. The yellow phase (lighter) is austenite and the blue(darker) one is ferrite.

Aging heat treatments

The phase transformations, which occurred in the first few minutes of the aging heat treatments, caused a significant loss in toughness.

Table 3 shows the result of the Charpy impact tests after annealing at 850 °C for 6 min, 40 min and 600 min. The results of aging heat treatments are shown in Fig. 3 to 8.

Figures 3, 4 and 5 show the microstructures of the sample aged at 850 °C for 6, 40 and 600 min, respectively. The samples showed in Figs. 3, 4 and 5 were etched with KOH solution that differentiates the sigma phase from the carbides and nitrides. Chi phase is also etched with KOH. An increase in the amount of the sigma phase can be observed in longer aging heat treatments.

Figures 6, 7 and 8 show the results of the aging in samples etched with NH_4OH, revealing carbides and nitrides. Chromium carbides and nitrides precipitation occurred mainly in ferritic-austenitic interfaces as observed in Figs. 6, 7 and 8 by using dark field optical microscopy. In Figs. 7 and 8, an increase in the amount of carbides and nitrides precipitation can be observed for longer aging heat treatments.

Table 2. Results of the Charpy impact tests of the sample annealed.

Sample	Energy absorbed during Charpy impact test (J)
Annealed at 1100 °C for 40 min	> 368*

* The others values are above Charpy Impact Machine Test Scale.

Table 3. Results of the Charpy impact tests of the samples aged at 850 °C.

Samples aged at 850 °C (min)	Energy absorbed during Charpy impact test (J)
6	264 ± 46
40	80 ± 26
600	75 ± 10

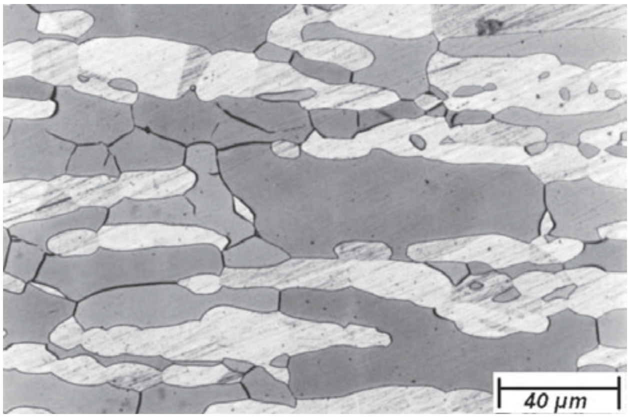

Figure 2. Optical microscopy. Sample annealed at 1100 °C for 40 min and quenched in water. The austenite is yellow (lighter) and ferrite is blue (darker). Etching: Behara II.

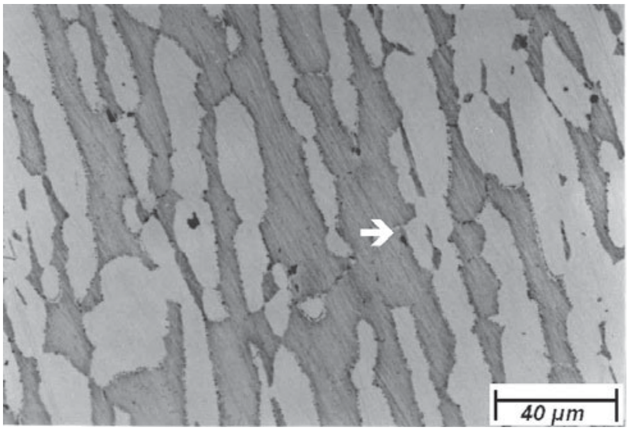

Figure 3. Optical microscopy. Sample aged at 850 °C for 6 min and quenched in water. The ferrite regions are darker than the austenite ones. The sigma phase formation occurred mainly in the ferrite-austenite interface. The arrow indicates the sigma phase. Etching: KOH solution.

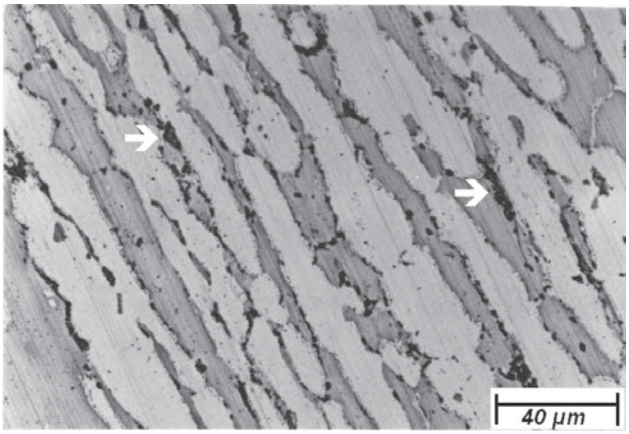

Figure 4. Optical microscopy. Sample aged at 850 °C for 40 min and quenched in water. The ferrite regions are darker than the austenite ones. The sigma phase formation occurred mainly in the ferrite-austenite interface. The arrow indicates the sigma phase. Etching: KOH solution.

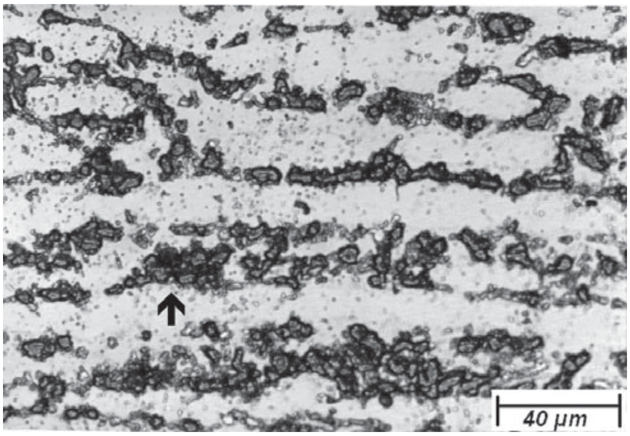

Figure 5. Optical microscopy. Sample aged at 850 °C for 600 min and quenched in water. The ferrite grains regions are darker than the austenite ones. The sigma phase formation occurred mainly in the ferrite-austenite interface. The arrow indicates the sigma phase. Almost all ferrite was consumed in the sigma phase formation. Etching: KOH solution.

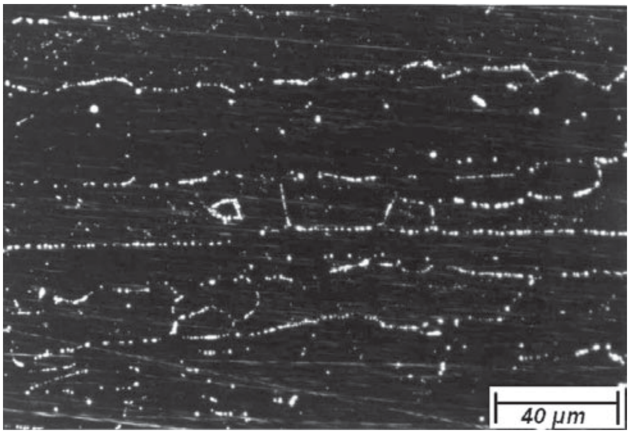

Figure 6. Dark field optical microscopy. Samples aged at 850 °C for 6 min and quenched in water. The brighter regions indicate chromium nitrides and carbides precipitation. Etching: electrolytic etching with NH_4OH.

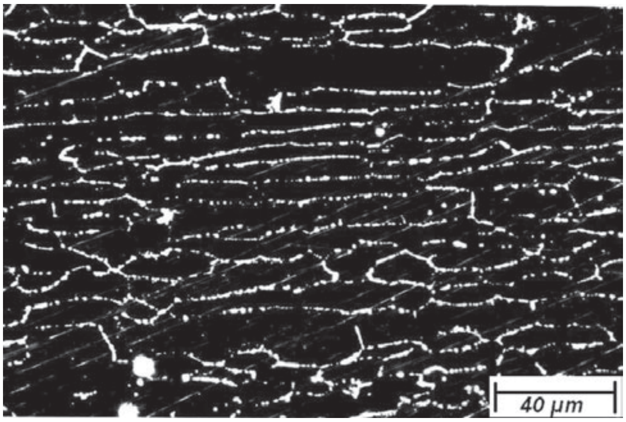

Figure 7. Dark field, optical microscopy. Samples aged at 850 °C for 40 min and quenched in water. The brighter regions indicate chromium nitrides and carbides precipitation. Etching: electrolytic etching with NH_4OH.

4. Discussion

The annealing heat treatment was carried out at an ordinary temperature of annealing for stainless steels. The Behara II etching differentiates very clearly the ferritic from the austenitic regions in the annealed sample. It can be observed that volumetric fractions of ferrite and austenite are almost the same in the sample annealed. In the aged samples, the use of different etchings made it possible to distinguish the sigma phase formation from carbides and nitrides precipitation.

The aging heat treatments were carried out at the temperature of fastest kinetics of the phase transformations for the steel studied. At 850 °C, the beginning of sigma phase formation takes only few minutes, but is somewhat slower than the precipitation of carbides and nitrides. Chromium carbides and nitrides precipitation takes only few seconds. In the figures showed could be observed carbides and nitrides precipitation occurred almost completely in the first few minutes. On the other hand, the sigma phase formation took longer than 40 min.

The chromium carbides and nitrides precipitation are

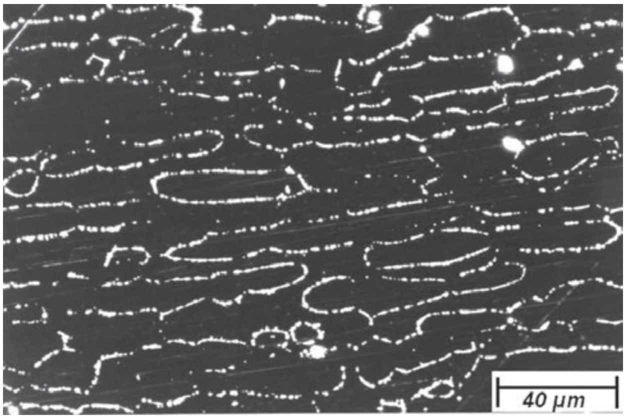

Figure 8. Dark field, optical microscopy. Samples aged at 850 °C for 600 min and quenched in water. The brighter regions indicate chromium nitrides and carbides precipitation. Etching: electrolytic etching with NH_4OH.

favoured by the decrease in the solubility of carbon and nitrogen in austenite at temperatures below the annealing temperature. Earlier studies[5] have showed that the carbide precipitated in the UNS S31803 is of the $M_{23}C_6$ type. This kind of carbide tends to appear in low carbon stainless steels[4]. The case of nitrides, Cr_2N precipitation is expected. It is important to mention that carbides and nitrides precipitation also depends on the content of these chemical elements. Higher volumetric fractions of chromium nitrides are expected as compared to the chromium carbide. However, the techniques used cannot distinguish nitrides from carbides.

The sigma phase occurs after chromium nitrides and carbides precipitation. The sigma phase formation in ferritic-austenitic duplex stainless steels can be described by the eutectoid transformation of ferrite into the sigma phase plus austenite as follows: $\alpha \rightarrow \sigma + \gamma$. The sigma phase particles nucleated on the ferritic-austenitic interfaces and grew inwards into the ferritic phase. The sigma phase presented massive morphology and the particles were very large when compared to chromium carbides and nitrides. During the longer aging heat treatments, the sigma phase consumed almost the ferrite available. On the other hand, the austenite of 22%Cr-5%Ni duplex stainless steel, with ordinary levels of nitrogen, does not transform during aging heat treatments.

The Charpy impact tests and microestrutural characterization lead to the conclusion that chromium carbides and nitrides cause a decrease of toughness but the effect of the sigma phase formation is stronger. Volumetric fractions of about 5% of the sigma phase are enough to render fragile the studied steel[6].

5. Conclusions

1. The use of different etchings made it possible to disclose almost all the phases in the microstructure of the studied stainless steel. Two mechanisms of phase transformations were identified: chromium nitrides and carbides precipitation and the sigma phase formation.
2. Aging heat treatments at 850 °C for more than 6 min rendered fragile the steel. The chromium carbides and nitrides precipitation certainly cause loss of toughness as well as sigma phase formation.
3. The Charpy impact test cannot be used to quantify or identify the sigma phase formation.

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