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Significant increase in the hardness of the ferritic phase due to structural changes at low temperatures in duplex stainless steels

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1. Introduction

Duplex stainless steels (DSSs) are used in a wide variety of applications, combining good corrosion resistance, weldability and high mechanical strength according to [1]. The corrosion resistance of these alloys is the same or higher than that of their austenitic analogues and they have higher strength, enabling gauge, weight and cost reductions according to [2].

The DSSs have been increasingly used as structural materials in various applications that require high mechanical strength and in highly corrosive environments such as chemical plants, offshore installations, thermal power plants, etc.

The properties of DSSs arise from an equilibrium of the austenitic (γ) and ferritic (α) phases obtained by either chemical composition or thermal treatment, and their best properties are achieved with a 50:50 α/γ ratio. DSSs are susceptible to the formation of additional phases that can influence their mechanical according to [3].

These phases correspond to the precipitation of various compounds such as chromium carbides, nitrides and several other intermetallic phases as defined [4].

These phases can be formed during solidification, subsequent heat treatment, or by plastic deformation or aging during their service life. As an example, pipes used in primary coolant water in pressurised nuclear reactors are designed for a 40-year service life and their long-term mechanical are of the utmost importance for safe operation.

However, ageing during service in some temperature ranges can degrade the material’s mechanical according to [5].

Long-term thermal ageing in the range of 300°C and 400°C produces an increase in hardness and tensile properties, together with a decrease in the impact properties, ductility and toughness according to [1] and [6].

Earlier studies according to [7, 8], have attributed such degradations of mechanical properties to a spinodal reaction occurring in the ferrite phase, in which the ferrite decomposes into an iron-rich phase and an enriched chromium α’ phase according to [9], but other precipitated phases, such as a complex nickel silicide known as G phase, have also been observed and reinforced for [10, 11].

The precipitates occur within the ferrite grain preferentially on dislocations and at α–γ interfaces according to [7, 8].

It has been reported by [8], that G phase precipitation occurs from chromium-rich α’ phase in the second stage of ageing, which corresponds to ageing of more than 3000 hours at 400°C [9].

Therefore, despite several studies about the effect of phase precipitation on duplex stainless steel properties, there is little information about DSS performance in the presence of precipitation at low temperatures, particularly about its hardness phases. In this study, an analysis was made of the properties of the phases of DSS with high chromium content after long-term ageing (3000 and 7000 hours) at 400°C particularly[10].

However it is important to note that the alpha-alpha' spinodal decomposition occurring in the iron-chromium-based ferrite is responsible for this aging susceptibility. It is then possible to predict the evolution of hardness of industrial components during service, based on the detailed knowledge of the involved aging process [12].

2. Experimental procedures

The samples used in this investigation were obtained from a hot rolled DSS whose composition is given in Table 1.

Table 1
Composition of the two analyzed DSS samples

Elements	Cr	Ni	C	Mn	Si	Mo	N
Higher Cr	22.6	5.38	0.024	1.57	0.35	2.58	0.13
Lower Cr	17.2	4.37	0.018	1.60	0.37	2.54	0.11

PS: P < 0.015 and S < 0.008

However the samples with higher chromium content (22%Cr-5%Ni) were heat treated at 1250°C during 1hour while the samples with lower chromium (17%Cr-5%Ni) content were heat treated at 1300°C during 1hour and quenched in water at 25°C, intending to approximate the ferrite-austenite percentage to 50:50%.

After the solubilization, the samples were aged in a horizontal electric furnace for 3000, 5000 and 7000 h at two different temperatures (300°C and 400°C) and then quenched in water at 25°C.

The sample structures were visualized using optical microscopy Olympus BX51and the phases percentages were measured with an image analyzer LEICA.

To understand these changes, the effect of ageing conditions on the hardness of the samples was investigated.

The hardness of the ferrite and austenite of the solubilized and the annealed samples were analyzed using the Nanoindenter XP equipment, with captured images using optical microscopy (Olympus BX51).

Transmission electron microscopy (TEM) was realised in microscope Philips model CM120, and was performed to characterize the annealed samples and identify the changes in the chromium rich phases precipitated during the heat treatment.

Quantitative elementary analysis (QEA) using scanning electron microscopy (SEM) was used in order to quantify the composition of the elements in both ferrite and austenite phases.

3. Results

The Fig. 1 and Fig. 2 following show the TEM micrographs for the annealed samples during 3000 h and 7000 h manly at 400°C, to be more representative according to literature, just to verify the precipitation of phases (α'and G) between the lowest and highest times of treatment in both ferrite and austenite phases.

It is observed that for the lower chromium content sample just one kind of chromium rich precipitate could be detected while for the higher chromium content two kind of chromium rich precipitate could be detected.

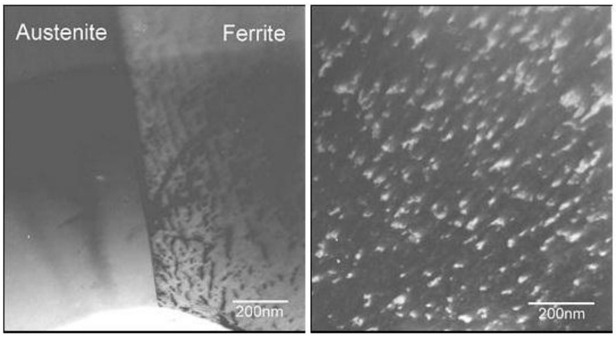
Concerning to the size of the precipitates it is plausible to infer that the lower chromium content sample has just G-phase precipitation and the higher chromium content have α' and G phase precipitation.

However it is known that in the temperature range of 300°C to 600°C is characterized by the spinodal decomposition of ferrite into chromium-poor α and chromium rich α' domains, which can cause embrittlement of duplex stainless steel alloy.

Spinodal decomposition and spinodally coarsening take place in ferrite by ageing become embrittlement after long-term thermal ageing treatment [13].

Other precipitation processes besides α' phase also occur between 300°C and 600°C in duplex stainless steel, such as G phase precipitation in ferrite and carbide, and γ2 phase precipitation at the grain boundaries. Among these processes, the main one is nickel, Si, Mo-rich G phase precipitation [11].

These particles are very small (1 nm, occasionally up to 50 nm) and are usually present in very high concentrations. They precipitate within the ferrite grain preferentially on dislocations and at α–γ interface.



a b

Fig. 1 TEM micrograph for the lower chromium content sample annealed at 400°C during: a) 3000 h bright field in the ferrite and b) G-phase at 7000 h dark field of the ferrite

Fig. 3 shows the ferrite percentage phase for the lower chromium content sample changes of 57% to 30-35% approximately, and the austenite percentage phase increases to 43% to about 65-70%.

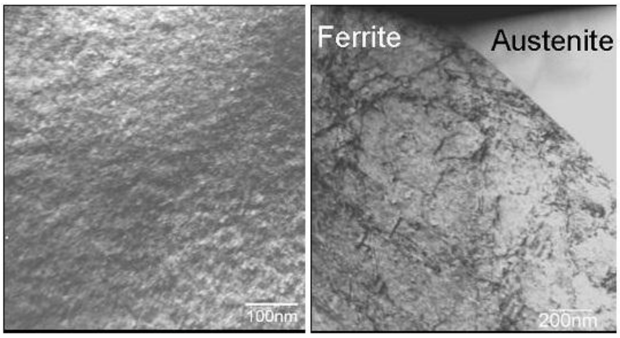


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Fig. 2 TEM micrograph for the higher chromium content sample annealed at 400°C during: a) 3000 h dark field and b) α' and G phase at 7000 h bright field of the ferrite

But for the higher chromium content sample the ferrite percentage phase increases to 50% to 60% approximately while the austenite percentage phase decreases to 50% to 40%.

The decreasing or increasing tendencies in the phase percentage is related to the original percentage phase of the hot rolled samples.

The lower chromium content sample in the hot rolled condition had 18% of ferrite phase and 82% of austenite phase. The higher chromium content sample had 55% of ferrite phase and 45% of austenite phase in the hot rolled condition.

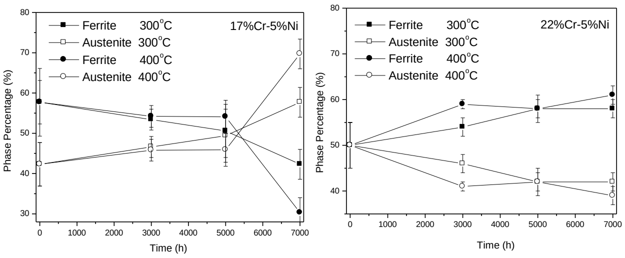

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Fig. 3 Phases percentage for both samples in function of the annealing time and temperature content a) lower chromium and b) higher chromium

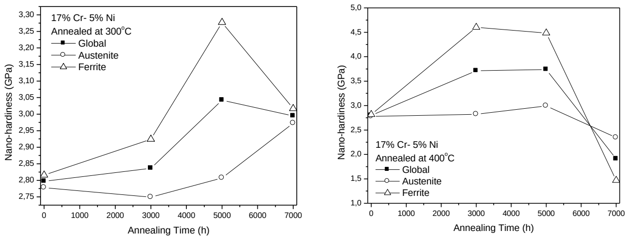

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Fig. 4 Hardness of the ferrite and austenite phases in function of the annealing time for the lower chromium content samples and annealed at: a) 300°C and b) 400°C

The Fig. 4 and Fig. 5 show the hardness of the ferrite and austenite phase for the lower and higher chromium content samples, annealed at 300°C and 400°C and the global hardness of the alloy as a function of the aging heat treatment conditions.

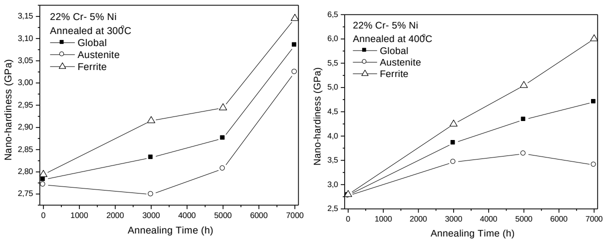

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Fig. 5 Hardness of the ferrite and austenite phases in function of the annealing time for the higher chromium content samples and annealed at: a) 300°C and b) 400°C.

The global hardness represents the average hardness of ferrite and austenite phases

The effect of aging time on the hardness of austenite was less significant than on that of the ferrite phase and the precipitated phases act as barriers against dislocation motion, resulting in increased global hardness of the alloy.

The results show in the Fig. 5 for the higher chromium content samples that the micro-hardness in ferrite gradually increases with increase of long thermal ageing time, while the effect of the long ageing time on the micro-hardness in austenite is negligible [14].

The ferrite hardening was very rapid in the initial stages of ageing at 400°C; thereafter the hardness increase was more gradual at all the ageing temperatures [15].

The Table 2 below shows the contents of the respective elements in austenite and ferrite phases in order to relate these to percentages with their hardness of these phases in isolation.

As can be seem, the presence of more than one Cr rich phase retards the kinetics of precipitation and the effects were not noticed at 300°C. The Cr content in the ferrite phase (24%) of the higher Cr content sample is about 30% bigger than the Cr content available in the ferrite phase (18%) of the lower Cr content sample.

Table 2

Composition of the ferrite and austenite phases in the samples solubilized higher chromium and lower chromium content

Elements	Composition(%)			
	22%Cr-5%Ni		17%Cr-5%Ni	
	Austenite	Ferrite	Austenite	Ferrite
Al	0.2322	0.3081	0.0453	0.0552
Si	0.3352	0.3771	0.3257	0.3678
Nb	0.0157	0.0174	0.0292	0.0136
Mo	1.9538	3.0629	2.2133	3.0047
Cr	21.2690	24.8970	16.9732	18.4332
Mn	1.7627	1.5137	1.7435	1.5515
Fe	67.8241	65.6945	72.7838	72.3212
Ni	6.6073	4.1293	5.8859	4.2528

4. Discussion

The micrographs show an increasing tendency of the ferrite phase percentage for the higher chromium content sample and a decreasing tendency of ferrite phase percentage for the lower chromium content sample. The original hot rolled sample had higher ferrite phase percentage (55%) for the 22%Cr-5%Ni alloy and lower ferrite phase percentage (18%) for the 17%Cr-5%Ni alloy.

The solubilization treatment changed the alloys of their equilibrium state and the annealing slowly took them back to the equilibrium state. For the higher chromium content sample the changes are less evident due to the small percentage of changes.

However for the lower chromium content the percentage of changes is bigger and it is noticeable the new austenite phases presence at the grain boundaries.

The ferrite percentage phase for the lower chromium content sample changes to 57% to 30-35% approximately. The austenite percentage phase increases to 43% to about 65-70%.

For the higher chromium content sample the ferrite percentage phase increases to 50% to 60% approximately while the austenite percentage phase decreases to 50% to 40%. It was visualized that in spite of such macro-structural changes there were micro-structural changes like chromium rich precipitations inside the ferrite grains which contributed to the global hardness increase or decrease. The global hardness of the higher chromium content annealed at 300°C continuous increases from 0 to 7000 h of annealing time.

However, the increase is more pronounced in the ferrite phase. The TEM showed that the chromium rich precipitation occurs markedly in this phase (probably G-phase). The global hardness of the lower chromium content annealed at 300°C still continuous increases from 0 to 5000 h of annealing time but after this time the hardness clearly decrease.

The probable effect associated with this decreasing tendency in the global hardness is the coalescence of the chromium rich phases.

The chromium content in the ferrite phase (24%) of the higher chromium content sample is about 30% bigger than the chromium content available in the ferrite phase (18%) of the lower chromium content sample. In the meantime the global hardness for the higher chromium content sample annealed at 400°C stilly showed a decreasing tendency. The lower chromium content sample also showed a decreasing in the global hardness when annealed at 400°C but this tendency starts at 3000 h instead of 5000 h as mentioned for this same sample annealed at 300°C.

5. Conclusions

1. The micro-structural changes due to effect of thermal aging affect the global properties remarkably the global hardness and the corrosion resistance, but this effect on the hardness of austenite was less significant than on that of the ferrite phase.

2. The chromium rich precipitation occurs manly in the ferrite phases.

3. There is a clearly difference between the kinet-

ics of precipitation of the lower chromium content sample and the higher chromium sample but the increase in hardness after 7000 h of aging indicates that this treatment increased the area per unit volume of the barriers to dislocation motion, probably due the high nucleation rate.

4. The phenomena of precipitation and coalescence of chromium rich phases must be related to the increasing and decreasing tendencies of hardness, respectively.

5. A possible increase in corrosion resistance for lower chromium content sample resulting from 7000 h of aging was related mainly to the diffusion of chromium from the matrix to the chromium-depleted area, which probably did not affect the material's hardness.

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RYŠKUS SUDVEJINTŲ NERŪDIJANČIŲJŲ PLIENŲ FERITINĖS FAZĖS KIETUMO PADIDĖJIMAS DĖL STRUKTŪRINIŲ POKYČIŲ ŽEMOSE TEMPERATŪROSE

Reziumė

Sudvejinto nerūdijančiojo plieno bandiniai 3000, 5000 ir 7000 valandų buvo sendinami žemose 300°C ir 400°C temperatūrose. Kaip keičiasi mikrostruktūros kietumas, buvo stebima atleidimo laikotarpiu optinio mikroskopo ir fazių procentiniais matavimais. Nanokietumas buvo panaudotas fazei, turinčiai įtakos bendrajam kietumui, identifikuoti. G fazės pasirodymo pagreitinimas ir α fazė dėl išcentrinės dekompozicijos buvo identifikuoti elektronų dekompozicijos vaizdo perdavimu. Nustatyta, kad mikrostruktūriniai pokyčiai veikia bendrąsias savybes, ypač bendrąjį kietumą. TEM rezultatai parodė, kad dažniausiai yra pagreitinamas chromu praturtintos feritinės fazės pasirodymas. Taip pat išryškėjo aiškūs skirtumai tarp mažesnio ir didesnio chromo kiekio bandinių kinetikos ir pagreitinimo. Pagreitinimo reiškinys ir chromu praturtintų fazių susijungimas turi būti susiję su kietumo didėjimo ir mažėjimo tendencijomis.

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SIGNIFICANT INCREASE IN THE HARDNESS OF THE FERRITIC PHASE DUE TO STRUCTURAL CHANGES AT LOW TEMPERATURES IN DUPLEX STAINLESS STEELS

Summary

Duplex stainless steel samples were aged at low temperatures of the 300°C and 400°C for 3000, 5000 and 7000 hours. The changes at the micro-structure were followed during the annealing time using an optical microscopy and measurements of phase percentages. Nanohardness was used in order to identify the phase responsible for the increasing in the global hardness. The G phase precipitation and α'phase due to spinodal decomposition was identified by transmission electron microscopy. It was detected that the micro-structural changes affect the global properties, remarkably the global hardness. TEM results showed that the chromium rich precipitation occurs mainly in the ferrite phases. The results also showed a clear difference between the kinetics of precipitation of the lower chromium content sample and the higher chromium sample. The phenomena of precipitation and coalescence of chromium rich phases must be related to the increasing and decreasing tendencies of hardness, respectively.

Keywords: Spinodal decomposition, hardness, G phase, precipitation.

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