THE EFFECT OF ANNEALING TEMPERATURE ON QUALITY OF AUSTENITIC STAINLESS STEEL WITH DELTA FERRITE

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ABSTRACT
The aim of this work is to determinate the temperature start of precipitation of the secondary phases in austenitic stainless steels with delta ferrite. Presence of the delta ferrite in austenitic stainless steel promotes the precipitation of the secondary phases especially carbides and sigma phase whose have effect on quality of steel. The microstructure was characterized after a solution annealing at 1030 °C followed by annealing in temperature range from 550 to 1000 °C for the time of 30 minutes and cooling in air. Etched samples were observed using optical microscopy and scanning electron microscopy. The delta ferrite content was determined by a Feritscope MP30. Analysis of microstructure showed that the first phases precipitate between 550 and 650 °C at α/γ boundaries and delta ferrite. Sigma phase starts to precipitate between 650 and 750 °C at α/γ boundaries.

Keywords: austenitic stainless steel, annealing, delta ferrite, secondary phases, sigma phases

1. INTRODUCTION

Austenitic stainless steels (ASS) are the most widely used grade of stainless steel thanks to good mechanical properties and corrosion resistance. They have very good strength, toughness and formabilityamong the commercially available alloys from cryogenic to elevated temperatures.Other factors contributing to their increased use is long service life with low maintenance cost, ability to be recycled, and benign effect on the environment and human health [1]. ASS is nonmagnetic and has FCC structure. All these steels have at least 15 % chromium and certain amount of nickel, manganese,carbon, and nitrogen whose stabilize austenitic structure. It is known that except of chromium, the silicon too contributes to the improvement of the heat resistance of austenitic stainless steels. Silicon content can range from 1 to 3% and even 5% in exceptional conditions such as corrosion resistance in nitric acid. However, the silicon constricts the range of austenitic phase, i.e. it promotes the formation of delta ferrite [2,3]. The amount of delta ferrite depends of application. Especially, amount of delta ferrite is limited in the weld metal because it embrittles a weld metal and deteriorates corrosion property [4]. As mention before, microstructure of austenitic stainless steel is austenitic and it is stabile at room temperature but with heating (usually about500ºC) the microstructure becomes nonstabile. Because ASSisusually used at high temperatureregions it becomes important to study the microstructure stability because it influences on properties of these steel especially mechanical and corrosion properties.During annealing or welding these steels, the precipitation of the carbides ($M_{23}C_6$, MC, M_6C and M_7C_3) is the first that occur followed by precipitation of other intermetallic phases (σ, χ, η, G, R and other phases). Presence of the delta ferrite in austenitic stainless steel promotes the precipitationof thesecondary phases especially carbides and sigma phases[5,6].The aim of this work is to determinate the temperature start of precipitation of the secondary phasein austenitic stainless steels with delta ferrite.

2. EXPERIMENTAL

The material used in this study was ASS delivered in hot rolled state with 10% delta ferrite. The chemical composition of steel was tested at the Institute "Kemal Kapetanović" and is given in Table 1.

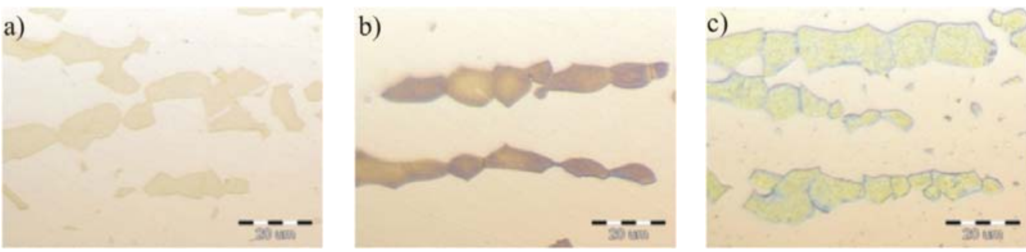
Table 1. Chemical composition of tested ASS

Chemical composition / wt.%							
C	Si	Mn	Cr	Ni	P	S	N
0.04	4.41	7.4	18.0	8.1	0.007	0.005	0.183

The delta ferrite content was determined by a Feritscope MP30 (Fisher, Germany) according to standard ASTM A800 /A800M-91.This is the magnetic induction method which takesadvantage offactthat the delta ferrite ismagneticwhile the austenite is not.Specimens for testing were cut from the testing material with diameter of 15 mm. Before annealing at different temperatures, all specimens were solution annealed at1030°Cfor 60minutes followed by water quenching which brings already precipitated carbides as well as most of other intermetallic phases back into solution.Second step was specimens annealing at 550, 650, 750, 850, 950 and 1000 °C for 30 minutes followed by cooling in the air. Heating rate was about 10 °C/min.The microstructural analysis was carried out by theOlympus optical microscopewith maximum magnification 1000xand the scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). Murakami's reagent (10 g $K_3Fe(CN)_6$, 10 g NaOH and 100 ml H_2O) was used for etching. Etching with Murakami's reagent at room temperature was used for identification of carbides while heated reagent (about 100 °C)was used for identification of the delta ferrite and sigma phase.

3. RESULTS AND DISCUSSION

Analysis of microstructure after solution annealing showed austenitic microstructure with a presence of the delta ferrite, Figure 1.a. The structure of elongated delta ferrite islands is observed in the longitudinal section. No secondary phases were detected.Etching with Murakami's reagent heated at 100 ^{0}C colored delta ferrite in brown and sigma phase in blue.



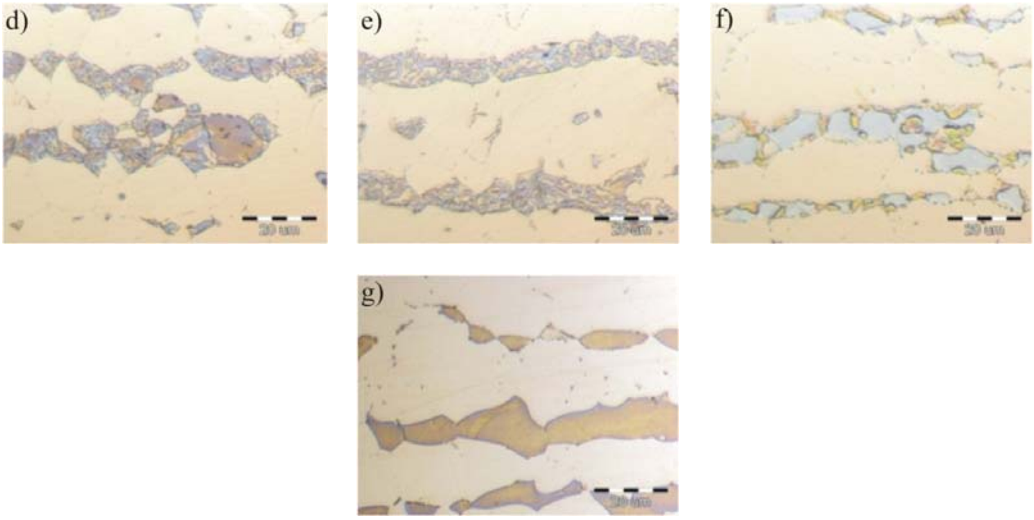
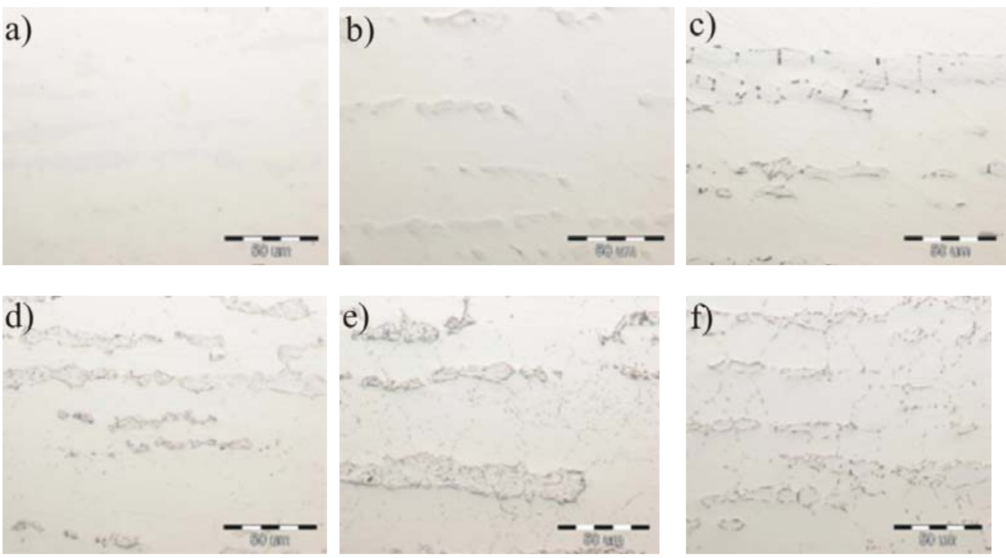


Figure 1. Microstructure of samples: a) solution annealed state and b-g) annealed at 550, 650,750, 850, 950 and 1000 ºC for 30 minutes, Murakami's reagent heated at 100 ºC, 1000x

At Figure 1. b-g.decomposition of the delta ferrite can be observed. Decomposition started at 650 ^{0}C and continues at 750, 850 and 950 ºC.The appearance of blue color implied on presence of sigma phase. During annealing at the high temperatures the delta ferrite transforms in carbides ($M_{23}C_6$), sigma phase and austenite (γ'). To prove presence of carbides etching with Murakami's reagent at room temperature was used. The results of microstructure analysis after etching with reagent on room temperature are presented on Figure 2.



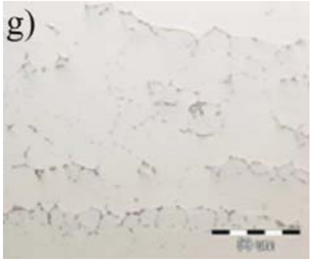


Figure 2. Microstructure of samples: a) solution annealed state and b-g) annealed at 550, 650,750, 850, 950 and 1000 °C for 30 minutes, Murakami's reagent at room temperature, 500x

From the results showed at Figure 2 precipitation of carbides at 550 °C and higher temperatures can be observed. On lower temperatures carbides precipitate on delta ferrite but at temperatures 750 °C and higher the carbides precipitate on austenitic grain boundaries too. The average value of the delta ferrite content for different annealing temperatures is presented in Table 2. The delta ferrite content was determined by the magnetic induction method. For each sample, five measures were done at transverse (T) and longitudinal (L) direction.

Table 2. The delta ferrite content for different annealing temperatures

	Delta ferrite / %						
Annealing temperature /°C	Solution annealed state 1030°C/60'	550	650	750	850	950	1000
T	10.38	9.68	10.26	0.94	0.33	4.02	9.62
L	7.84	7.52	7.48	0.97	0.26	3.02	7.4

*T-transverse direction, L- longitudinal direction

From the results given in Table 2 it could be see that decomposition of delta ferrite starts between 650 and 750 °C. The percent of the decomposition delta ferrite at 750 °C was about 90 %. Increasing of annealing temperature (above 850 °C) increases the content of the delta ferrite i.e. the content of delta ferrite at 1000 °C is almost the same as in initial solution annealed state. Figure 3 shows SEM samples analysis with a back-scattered electron detector (BSE) who has ability to differentiate between phases according to their mean atomic number without need of chemical etching. The present phases have a different chemical composition with less or more heavy elements and the grayscale contrast of these phases was expressed. The secondary phases are brighter than ferrite and austenite, according to their content ofelements with high atomic number (Z), of Mo and Cr.This method is recommended characterization technique in order to make difference between the intermetallic phases [7,8].

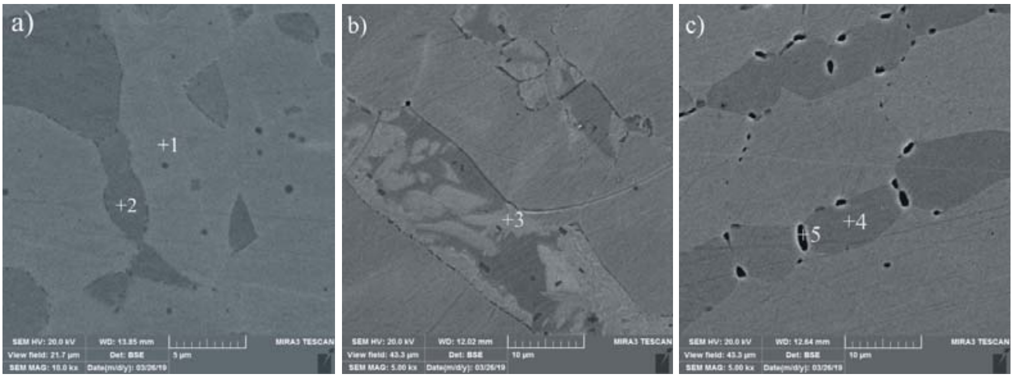


Figure 3. SEM-BSE image of annealed samples: a) 650, b)750 and c) 1000 ºC for 30 minutes, 10 000x

In Figure 3, the different phases can be identified as the delta ferrite (darkest phase), austenite (dark gray) and sigma phases (light gray). Dark spots at the interpahese between the delta ferrite and austenite are present too. These spots were also detected by other authors [7]. From the analysis of a chemical composition (EDS) it could be seen that the delta ferrite has higher content of chromium and silicon (alphagenic elements provide formation of delta ferrite) but lower content of a nickel (gamagenic elements provide formation of austenite), Table 3. Sigma phase has the highest content of chromium and lowest content of nickel. After annealing at 1000 ºCthe delta ferrite was again observed in the samples and there was no precipitation of the sigma phase. The black spots were still present and bigger in size comparing to previous annealing temperatures. Chemical analysis of the black spot showed increased content of carbon. Content of other elements were similar to delta ferrite what could imply that phase on this place was dissolved, especially because the black spot wasplaced within the delta ferrite. Analysis of results shows that precipitation of the sigma phase as well as the black spots start at ferrite/austenite, ferrite/ferrite boundary and inside of the ferrite.

Table 3. Chemical composition of phases after heat treatment of the samples according to Figure 3.

	Phases	Chemical composition / wt.%					
		C	Si	Cr	Mn	Fe	Ni
Spectrum 1	Austenite	0.92	3.76	17.77	7.80	61.03	8.72
Spectrum 2	Delta ferrite	1.34	4.45	21.07	7.06	59.26	6.82
Spectrum 3	Sigma phase	1.96	4.62	26.91	6.76	55.65	4.10
Spectrum 4	Delta ferrite	2.79	3.38	19.13	6.63	61.15	6.92
Spectrum 5	Black spot	3.19	3.49	19.90	6.38	59.99	5.76

At temperature 650 ºC and higher the delta ferrite is transformed in sigma phase. The delta ferrite becomes unstable because a loss of chromium and could transform in secondary austenite (γ'). In the same time, simultaneous enrichment of sigma phase with chromium lead to a diffusion of nickel to the delta ferrite [7]. From the results given in Tables 2 and 3 and Figure 3 it could be seen that more fraction of delta ferrite was transformed into sigma phase and secondary austenite.

4. CONCLUSIONS

The microstructural changes of the austenitic stainless steel with 10% of delta ferrite at different annealing temperatures have been investigated. The effect of annealing in temperature range from 550 to 1000 ºCfor the time of 30 minutes and cooling in air can be summarized as:

- Initial microstructure whose consist of austenite and delta ferrite in the form of islands elongatedin the longitudinal section is stabile to 550 ºC
- The first phases precipitate between 550 and 650 ºC at α/γ boundaries and delta ferrite. Etching with Murakami's reagent at room temperature suggeststhat present precipitates were carbides.
- Decomposition of the delta ferrite started at 650 ºC and continues to 850ºC where about 90% delta ferrite was decomposed. Further increasing of annealing temperatureincreases the content of the delta ferrite up to the initial content at 1000 ºC. The delta ferrite transforms in sigma phases, carbides and secondary austenite due to diffusion of chromium.
- Sigma phase starts to precipitate between 650 and 750 ºC at α/γ boundaries. Kinetic of precipitation is faster where concentration of some elements as chromium and silicon arehigher. The delta ferrite containshigher percent of silicon and chromium and is favorable place for precipitation of sigma phases.

5. REFERENCES

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