EFFECT OF SENSITIZATION TREATMENT ON THE MICROSTRUCTURES AND PROPERTIES OF 204C2 AUSTENITIC STAINLESS STEELS *

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Abstract
Influence of different sensitization temperatures and times on 204C2 austenitic stainless steel was studied in this research. Mechanical properties for the experimental steels were studied by tensile and hardness test. The samples were sensitization-treated at three different times and four different temperatures. SEM and TEM were used to characterize the evolution of carbides and the chemical component was investigated using EDS. Results show that the strength and elongation decrease with the increase of sensitization temperature and time. Compared with the solid solution sample, the ultimate tensile strength, yield strength and elongation respectively decreased by 101MPa (11.1%), 86MPa (16.0%) and 8.6% (17.3%) at the 800℃. This is closely related to the precipitation of carbides. Carbide precipitation along the wider grain boundary (corrosion groove) is easy to be observed after sensitization treatment. Precipitate phases are mainly composed of chromium, manganese and carbon elements. The chromium-depleted zones appear around the precipitate phases. With the increase of sensitization time and temperature, the quantity and size of precipitates increase. The chromium in the chromium-depleted zones becomes lower levels and intergranular corrosion is more likely to occur when the sensitization time and temperature increase.
Keywords: 204C2 Cr-Mn austenitic stainless steel; Microstructure and mechanical properties; Sensitization temperature and time; Precipitation.

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1 INTRODUCTION

Stainless steels are common material of construction as these offer a wide range of corrosion resistance along with good fabrication and mechanical properties to many industrial environments [1]. In case of austenitic steels, the most important corrosion forms are the intergranular and the stress corrosion. Intergranular corrosion refers to the process of material corrosion along the grain boundary. It leads to a reduction in the binding force between grains, resulting in a reduction in the strength of the material [2]. It causes frequent failure in application of actual engineering. One of the main causes of intergranular corrosion to the stainless steel is sensitization. The term sensitization is defined as the destruction in corrosion resistance which may occur if austenitic stainless steels anneal in the particular temperature range. This is in sharp contrast to the excellent corrosion resistance of conventional solid solution treatment. Sensitization has long been attributed to the precipitation phase. It will cause the depletion of Cr in the zones of the matrix immediately adjacent to grain boundaries. Those zones in which the local Cr content reduces to less then12% lose the original ability to form a passive film. It causes the area to be preferentially corroded [3]. Moreover, in certain circumstances, sensitized steels corrode preferentially along the grain boundary. Many efforts have been made to find ways of controlling the precipitation of carbides precipitation in austenitic stainless steels. Therefore, several methods, such as reducing the carbon and adding titanium, niobium, or zirconium content, which can effectively avoid intergranular corrosion were presented [4].

Although a great deal of research has been done on carbides precipitation during sensitization processing of 300 series (Cr-Ni) austenitic stainless steels, the existence of the precipitation in 200 series (Cr-Mn) austenitic stainless steels is not well documented in the previous literature. Cr-Mn austenitic stainless steels have been considered as an important replacement for the Cr-Ni austenitic stainless steels in many industries by the reason of high price of nickel element [5]. 204C2 stainless steels are the main group of the Cr-Mn austenitic stainless steels with a face-centered cubic structure. It is essentially non-magnetic by solid solution treatment. In 200 series stainless steels, nickel element is replaced partially by manganese. They are used to take the place of the Fe-Cr-Ni alloys [6,7]. They have a lower density (Mn element is lighter than Ni element). Meanwhile, they have so higher strength relative to 300 series stainless steels [8].

Due to the decrease of nickel and the increase of manganese, Cr-Mn austenitic stainless steel is easier to precipitate at grain boundary compared with Cr-Ni austenitic stainless steel. It is more prone to intergranular corrosion. The manganese precipitation influences the mechanical properties of 204C2 austenitic stainless steel. It will be in a manner similar to that of the M23C6 carbide. However, no systematic study of the development of alloy elements precipitate during the sensitization process has been performed by the different sensitization times and different sensitization temperatures for Cr-Mn austenitic stainless steel.

The aim of the present paper is to concentrate on building quantitative aspects of the size of particles at grain boundaries. There is a wide temperature range for sensitization of austenitic stainless steel about 450-850℃ [9]. Therefore, sensitization treatments of the study are at the temperatures of 500℃，600℃，700℃ and 800℃ for 5minutes，10minutes and15minutes. The effect of chromium and manganese to the precipitation was analyzed for the 204C2 austenitic stainless steel by macroobservation. Mechanical properties for the experimental samples at different sensitization temperatures and times for the experimental steels were studied.

2 DEVELOPMENT

2.1 Materials and Methods

The chemical composition of the investigated and contrasting material was determined by chemical titration. In the present study, the experimental material was processed with dimension of 150 × 150 × 1.5 mm. Before any sensitization treatments, it was necessary to eliminate original precipitates that may have formed of the sample. All twelve samples were given an initial solution annealing heat treatment at 950℃ for 5 minutes followed by water quenching. They were then annealed at temperatures between 500℃ and 800℃ for 5 minutes to 15 minutes in annealing furnace followed by water quenching. For the study of mechanical properties, tensile tests were carried out. The surfaces of all the samples were ground using sandpaper, polished with paste and finally washed in an ultrasonic cleaner in an acetone bath before performing tensile tests. The room temperature tensile tests were operated by the electronic universal experiment machine at a constant rate of 1 mm/min. The microstructure was observed after etching with aqua regia (5ml nitric acid is added to 15ml hydrochloric acid) by Zeiss Ultra 55 scanning electron microscopy (SEM). The samples for transmission electron microscopy (TEM) were sliced into 0.30 mm thick discs. The discs were gradually sanded down to a thickness of 50-60 µm by different kinds of sand paper (from 240# to 2000#). These samples were finally electropolished in a twin-jet and stored in ethanol and finally examined in a Tesla BS-540 transmission electron microscope.

2.2 Results and Discussion

The composition of the 204C2 and 304 stainless steel is shown in Table 1.

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

Brand	Cr	Ni	Mn	N	Ti	C
204C2	16.5	1.98	9.05	0.17	0.02	0.083
304	18.2	8.02	1.03	0.18	none	0.049

Compared with 18-8 austenitic stainless steels, nickel element is mostly replaced by manganese and copper element in 204C2 austenitic stainless steel. The carbon element is twice as much as 304. To the austenitic stainless steels, the intergranular corrosion rate increases with the increase of carbon content. The corrosion rate increases sharply especially when the carbon content is more than 0.06% [10]. According to this, it is easier to precipitate at grain boundary and the intergranular corrosion is more likely to occur. It is worth mentioning that titanium was added in 204C2 stainless steel for stabilization to avoid intergranular corrosion.

The mechanical properties of the 204C2 stainless steel is shown in Table 2.

Table 2 Mechanical properties of the experimental steel

Number	Temperature/℃	Time/min	R_m/MPa	$R_{0.2}$/MPa	A/%
0	**950**	**5**	**905**	**539**	**49.8**
1		5	864	503	46.1
2	500	10	857	481	45.9
3		15	847	470	45.7
4		5	847	489	44.8
5	600	10	835	475	44.2
6		15	820	464	43.1
7		5	835	478	44.7
8	700	10	823	464	44.0
9		15	812	453	43.3
10		5	818	471	41.3
11	800	10	810	464	41.2
12		15	804	453	41.2

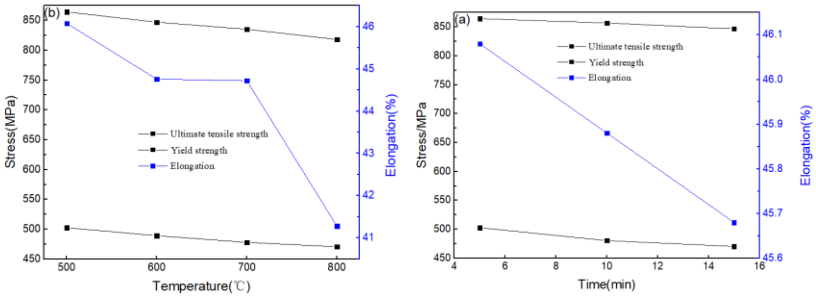
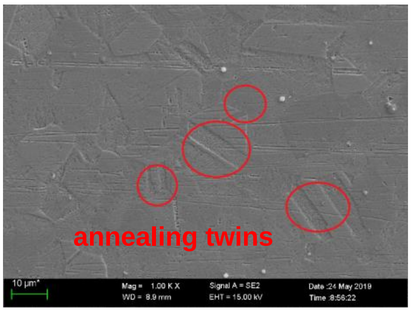


Fig. 1 Mechanical properties of the experimental steel(a) different times, (b) different temperatures

Table 2 depicts the overall trend mechanical properties of 204C2 austenitic stainless steel. Strength and elongation occur slight variations at the same temperature with different times or the same time with different temperatures. Fig. 1 shows the result of the ultimate tensile strength, yield strength and elongation in the method of controlled variable. It is observed that strength and plasticity decrease simultaneously with the increase of both time (Fig. 1(a)) and temperature (Fig. 1(b)) during the range for sensitization, which is caused by the different size and amount of carbide precipitation. In addition to this, strength and elongation are much lower than those of standard solid solution treatment. The following research will show that it is strongly influenced by the existence of grain boundary precipitates. Strength and plasticity reach a minimum at 800℃ for 15minutes in this experiment. Compared with the solid solution sample, the ultimate tensile strength, yield strength and elongation respectively decreased by 101MPa (11.1%), 86MPa (16.0%) and 8.6% (17.3%) at the minimum.



The microstructure of the standard solid solution treatment samples, observed by the scanning electron microscopy, was full austenitic structure which is shown in Fig. 2. It eliminates original precipitates that may have formed of the sample before any sensitization treatments. Investigation reveals equiaxial austenite grain intersected with annealing twins [11].

Fig. 2 SEM micrographs for samples of standard solid solution treatment (950℃ for 15minutes)

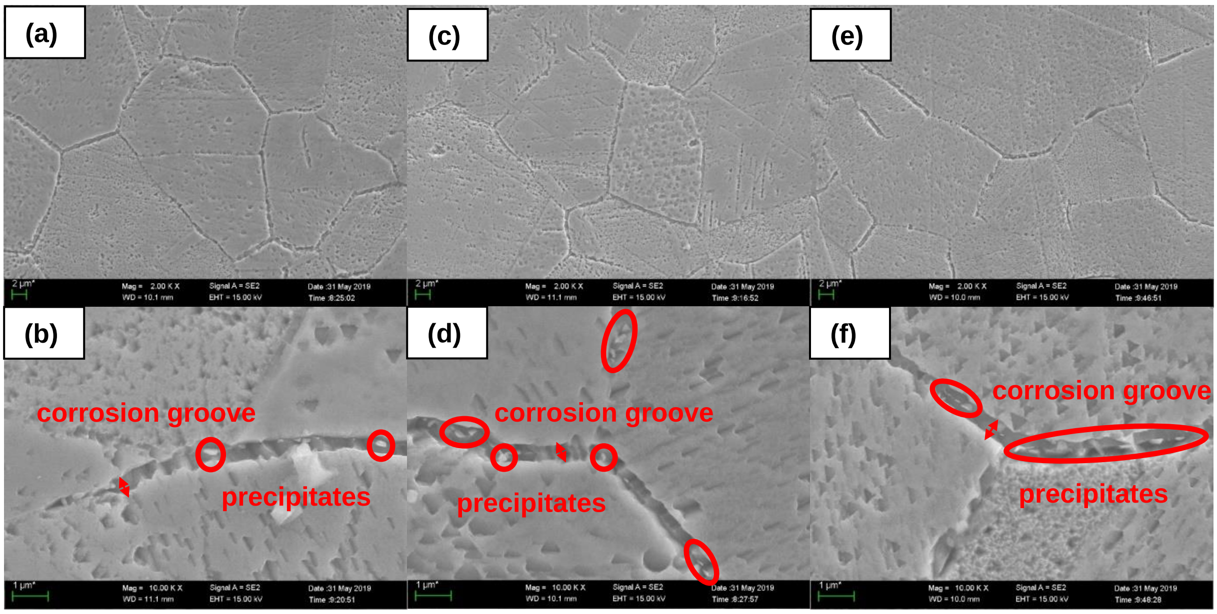


Fig. 3 SEM micrographs for samples of sensitization treatment at 500℃

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(a)2000X at 5min; (b) 10000X at 5min; (c)2000X at 10min;
(d)10000X at 10min; (e)2000X at 15min; (f)10000X at 15min

In order to study the effect of different sensitization times to the 204C2 austenitic stainless steel, sensitization treatment was taken by the time of 5minutes, 10minutes and 15minutes at the same temperature. Fig. 3 shows the microstructure of the sensitization treatment samples at the temperature of 500℃ with different times. As shown in the picture, the width of the grain boundary region is evident. When the sample is sensitized, the grain boundary will become wider at first. Then the precipitate phases appear along the grain boundary. The wide grain boundary region is called corrosion groove. It occurs during eroding with aqua regia and maybe caused by the lower chromium content of the grain boundary region.

The corrosion grooves become wider with the increase of sensitization time. It is due to the increase of precipitation quantity and size. According to the results of chemical composition, precipitation in 204C2 austenitic stainless steel could be (Cr, Mn) C, which is similar to $Cr_{23}C_6$. The nucleation and growth of precipitation at grain boundaries in the samples consist a linear function of sensitization treatment time. With the increase of sensitization time at the same temperature, the quantity and size of precipitates increase. This results in lower levels of chromium in the surrounding area and promotes corrosion.

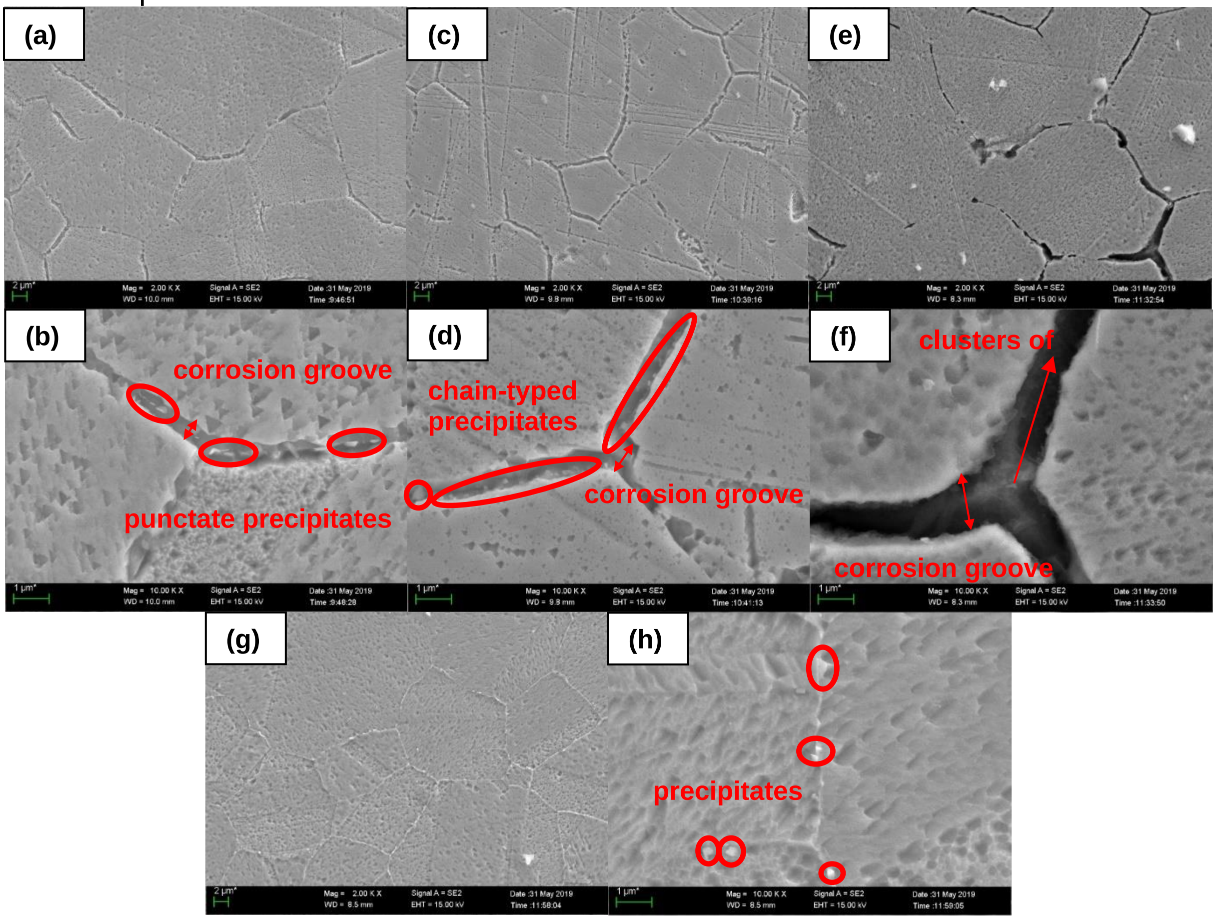
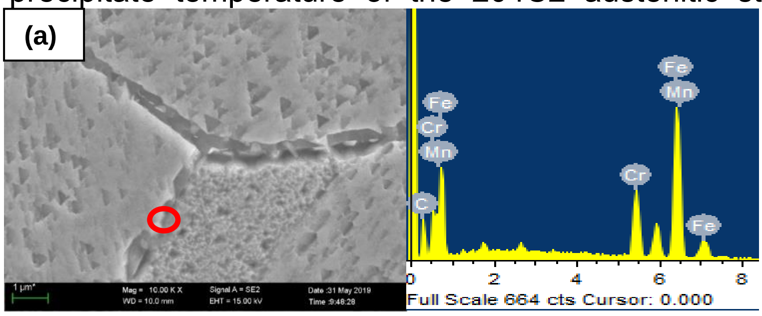
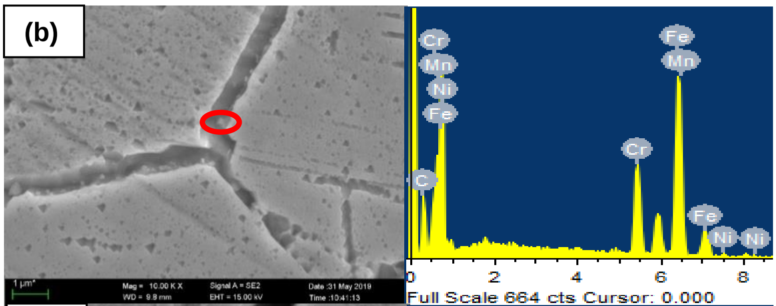


Fig. 4 SEM micrographs for samples of sensitization treatment at 15min
(a)2000X at 500℃; (b) 10000X at 500℃; (c)2000X at 600℃;(d)10000X at 600℃;
(e)2000X at 700℃; (f)10000X at 700℃; (g)2000X at 800℃; (g)10000X at 800℃;

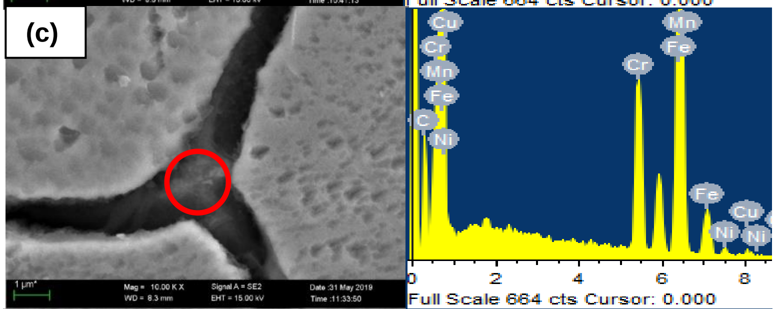
Sensitization treatment was taken by the temperature of 500℃, 600℃, 700℃ and 800℃ at the same time. Fig. 4 shows the microstructure of the sensitization treatment samples at the time of 15min with different temperatures. Temperature is also an important variable in the distribution of precipitates at grain boundaries in these steels. As shown in the Fig. 4(b), some punctate precipitates can be seen intermittently along the corrosion groove (grain boundary) at the temperature of 500℃. In the Fig. 4(d), as a result of the amount of the punctate precipitates increases with the temperature increment, the punctate precipitates link together to form chain-typed precipitates along the corrosion groove at the temperature of 600℃. In the Fig. 4(f), clusters of precipitates are found in the corrosion groove at the temperature of 700℃. With the increase of sensitization temperature, the quantity and size of precipitates increase. The auxetic punctate precipitates link into clusters. As the sensitization temperature continues to increase, the corrosion grooves disappear at the temperature of 800℃ in the Fig. 4(h). The quantity of clusters increases with the increase of sensitization temperature. The wide corrosion groove zones are filled with clusters. This causes the corrosion grooves to disappear. In addition to this, the precipitate at grain boundaries starts to grow into the grain at the temperature of 800℃. The temperature of 800℃ may be the most sensitive precipitate temperature of the 204C2 austenitic stainless steel. Due to the time s h



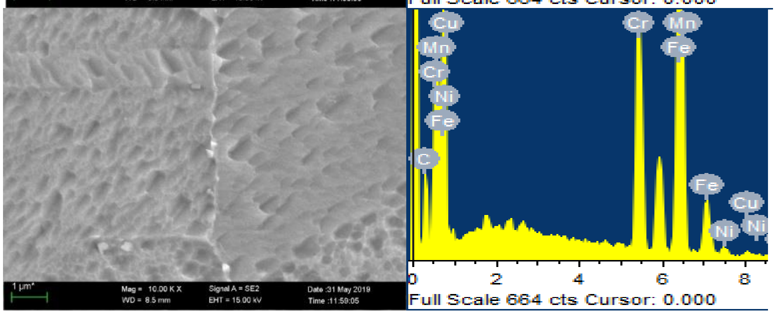
Element	Wt./%
C	11.62
Cr	15.93
Mn	9.50
Fe	62.95



Element	Wt./%
C	12.53
Cr	17.20
Mn	9.86
Fe	59.98



Element	Wt./%
C	13.64
Cr	18.69
Mn	10.06
Fe	55.36

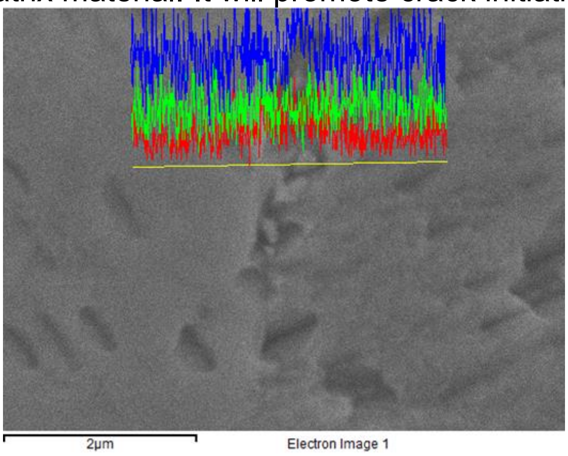


Element	Wt./%
C	10.99
Cr	20.29
Mn	11.23
Fe	54.28

Fig. 5 spot scanning for samples of sensitization at 15min (a) 500℃; (b) 600℃; (c)700℃;(d) 800℃;

Energy dispersive spectroscopic analysis (EDS) was used to study the variations in the precipitates. Fig. 5 shows the qualitative analysis of the precipitates. The spectrum and table of the grain boundary precipitate shows that manganese and chromium element content in the precipitates increase as the sensitization temperature rises. When the precipitates such as $Cr_{23}C_6$ is formed, the chromium is 17 times than carbon content. It results in aggravated poor chromium around the precipitate. Passivation capability in the chromium-depleted zone is insufficient or even disappears. The chromium-depleted zone near grain boundary dissolves preferentially under the corrosive medium, which results in intergranular corrosion [12].

Significant chromium enrichment is see chromium in precipitates is higher than th compositions, precipitates have different matrix material. It will promote crack initiati



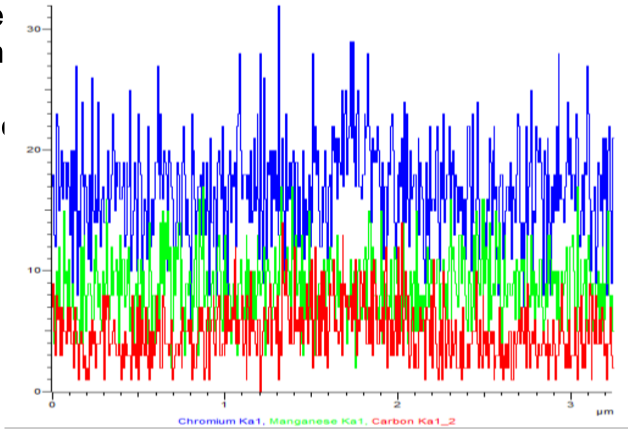
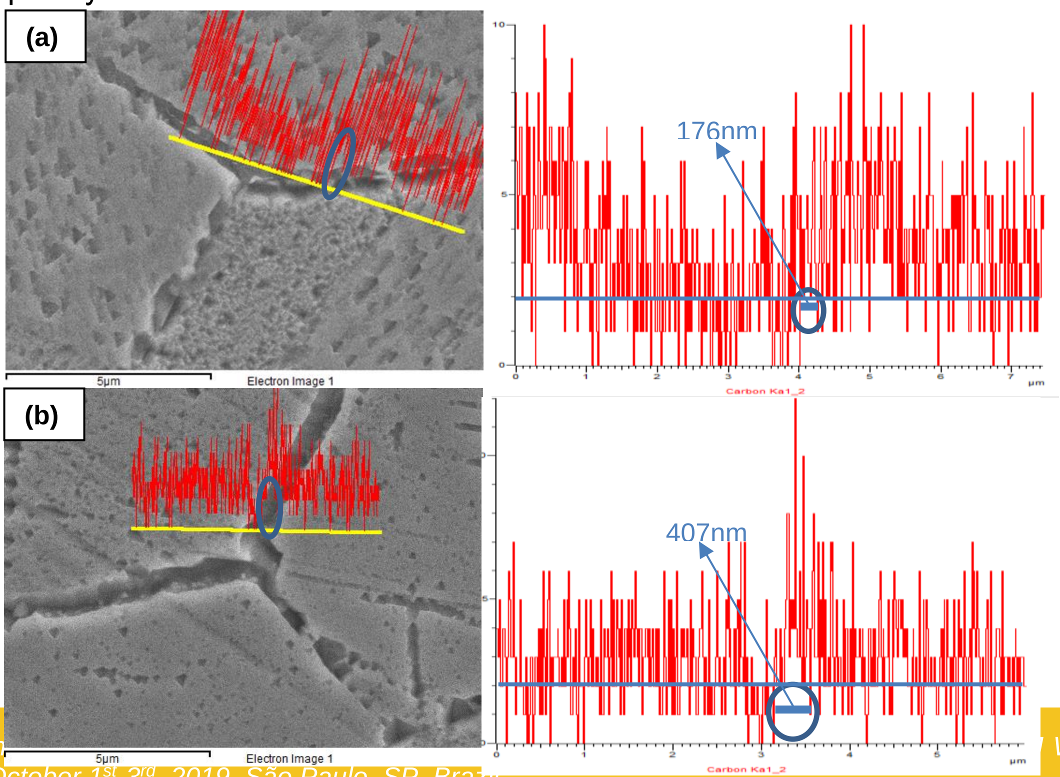


Fig. 6 linear scanning for samples of sensitization at 500℃ for 5min

Line scanning is used to measure the width of corrosion grooves and chromium enrichment zone. As shown in the Fig. 6, the change trend of chromium, manganese and carbon is identical. The manganese and carbon will not be mentioned subsequently.



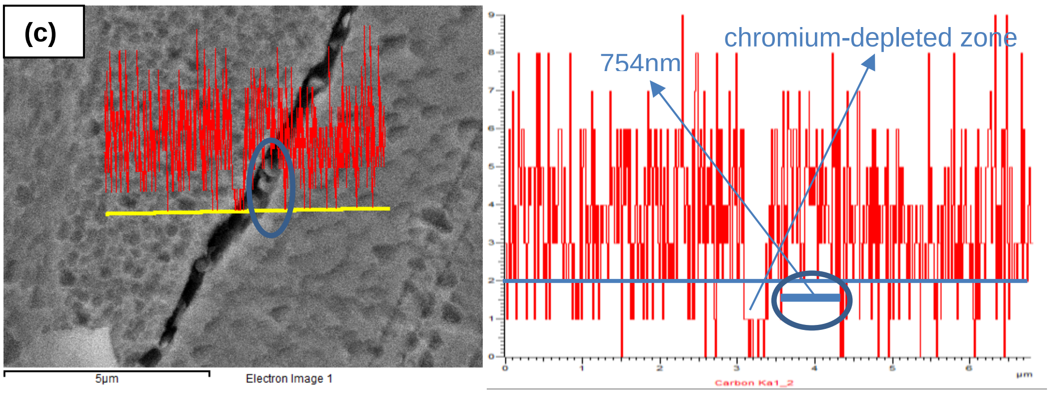


Fig. 7 linear scanning for sensitization at 5min (chromium) (a) 500℃; (b) 600℃; (c)700℃

The result of linear scanning along the along the width of the precipitates is shown in the Fig. 7. Due to the corrosion grooves disappear at the temperature of 800℃, it's not studied here. With increasing temperature (or time), one major effect which is seen is that the width of the chromium enrichment zone increases. And the examination of the microstructures reveals that in general some coarsening corrosion grooves was observed. The width of the chromium enrichment zone is found to be on the order of a few hundred nanometers, 175nm at 500℃, 407nm at 600℃ and 754nm at 700℃. The valleys of the chromium-depleted zone are found at the temperature of 700℃, which results in corrosion.

The structure of matrix is clearly apparent, but the grain-boundary regions are not evident. Precipitates at grain boundary is carried out through transmission electron microscopy of higher multiples.

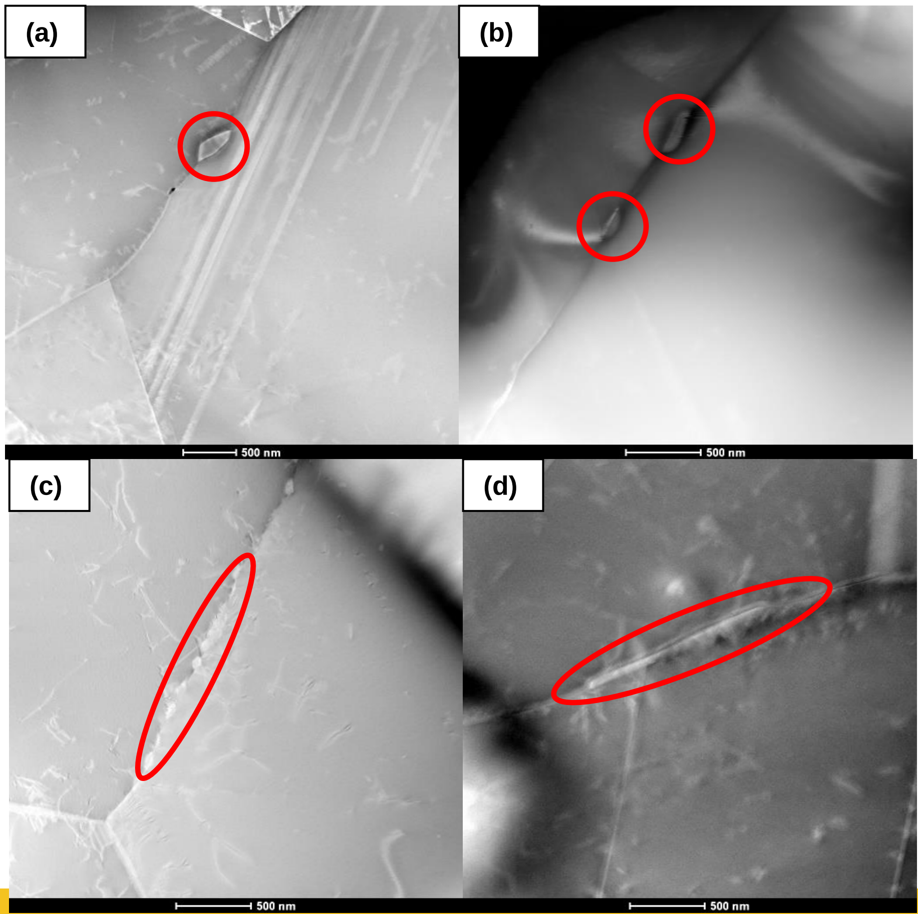


Fig. 8 TEM micrographs for samples of sensitization at 5min (a) 500℃; (b) 600℃; (c)700℃; (c)800℃

Fig. 8 shows the microstructure of the sensitization treatment samples at the time of 5min with different temperatures by TEM. It is clearly verified the results of Fig. 4. The distribution of precipitates at grain boundaries have four stages of change: (1) punctate precipitates at 500℃; (2) chain-typed precipitates at 600℃; (3) clusters of precipitates at 700℃; (4) precipitates start to grow into the grain at 800℃. On the flat grain b es.

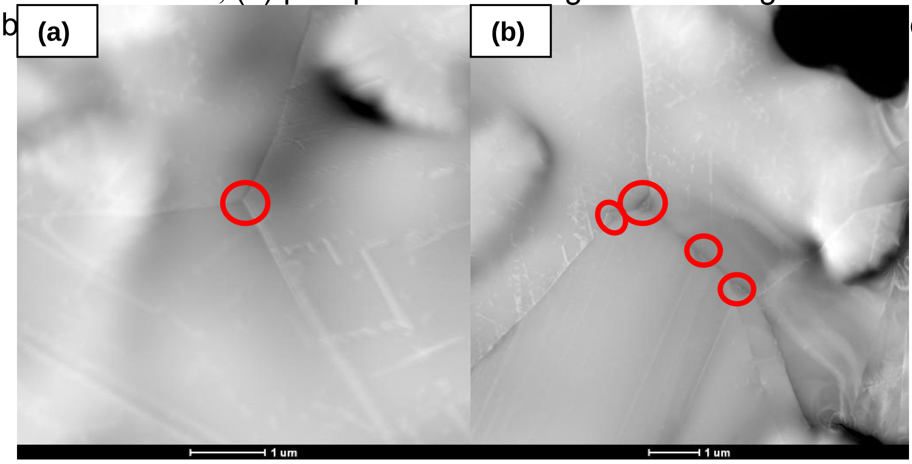


Fig. 9 TEM micrographs for the same sample (a) without precipitates; (b) precipitates

Fig. 9 shows the microstructure of the same sample of sensitization. In the images, it is apparent that the precipitates distribution is disunity in the same sample. The precipitates distribution is different at the three boundaries which come together in the center. Some grain boundaries within the same sample may exhibit vast precipitates, while other boundaries show even no precipitates at all. It is a reflection of differences in the misorientation between the two grains comprising the boundary. Each grain boundary has its own sensitivity. Grain boundary orientation can affect the nucleation and growth of carbides precipitates [14].

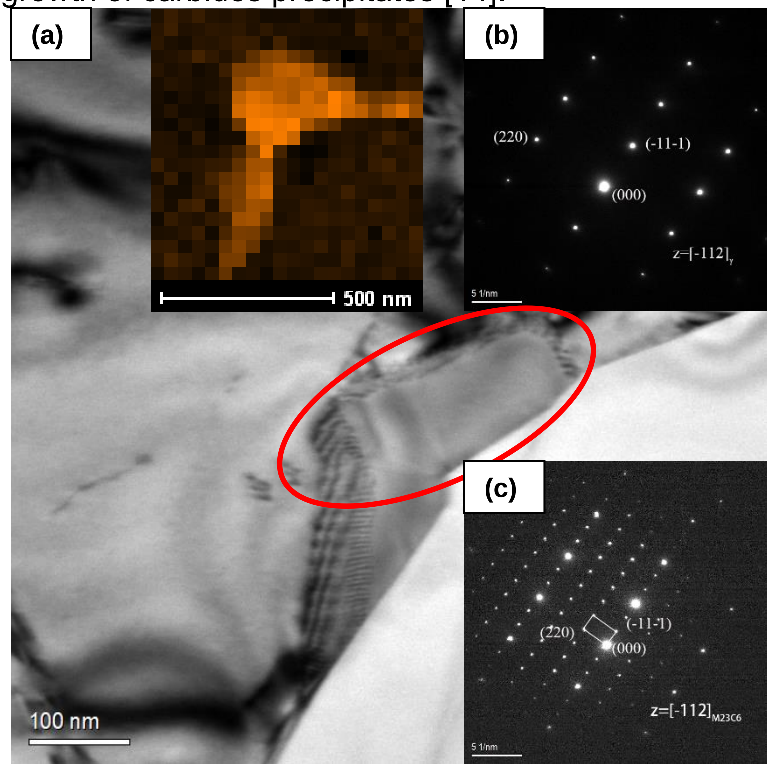


Fig. 10 TEM micrographs for the precipitate grows into the grain
(b) diffraction mottle of matrix; (c) diffraction mottle of precipitates

Fig. 10 shows the microstructure of the precipitate grows into the grain at 800℃. It can be seen the precipitate has an orientation relationship with the austenite grain (matrix).

Conclusions

In the present investigation we have shown that by applying sensitization treatments at different time and temperature to 204C2 austinite stainless steel the following conclusions can be drawn:

1) Nickel is mostly replaced by manganese and copper in 204C2 austenitic stainless steel. The carbon element in it is twice as much as 304. It is easier to precipitate at grain boundary and the intergranular corrosion is more likely to occur

2) Strength and plasticity decrease simultaneously with the increase of both time and temperature during the range for sensitization. Strength and plasticity reach a minimum at 800℃ for 15minutes in this experiment. Compared with the solid solution sample, the ultimate tensile strength, yield strength and elongation respectively decreased by 101MPa (11.1%), 86MPa (16.0%) and 8.6% (17.3%) at the minimum.

3) When the sample is sensitized, the precipitate phases appear along the wider grain boundary (corrosion groove). Some grain boundaries within the same sample may exhibit vast precipitates, while other boundaries show even no precipitates at all. It is a reflection of differences in the misorientation between the two grains comprising the boundary. Precipitate phases are mainly composed of chromium, manganese and carbon elements. The chromium-depleted zones appear around the precipitate phases.

4) With the increase of sensitization time and temperature, the quantity and size of precipitates increase. The width of corrosion groove increases from 176nm to 754nm as a result of this. The distribution of precipitates at grain boundaries have four stages of change: (1) punctate precipitates at 500℃; (2) chain-typed precipitates at 600℃; (3) clusters of precipitates at 700℃; (4) precipitates start to grow into the grain at 800℃. The chromium-depleted zone near grain boundary dissolves preferentially under the corrosive medium, which results in intergranular corrosion. The chromium in the chromium-depleted zones becomes lower levels and intergranular corrosion is more likely to occur when the sensitization time and temperature increase.

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