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Study of precipitation in Cr-Mn-N austenitic stainless steels annealed in the temperature range from 650°C to 900°C

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Abstract. The precipitation behaviour of secondary phases during isothermal aging in the temperature range from 650°C to 900°C was studied in CrMnN austenitic stainless steels. Metallographic observation, transmission electron microscopy with energy dispersive spectroscopy and selected area diffraction analysis were applied for the study of precipitation. The results showed that the phase composition of the precipitates depended on the chemical composition of the experimental steels and the conditions of the thermal expositions. The nose temperature of secondary phases is about 800°C, with the corresponding incubation period of 100s.

Keywords: austenitic stainless steels, precipitation, sensitisation, intergranular corrosion

1 Introduction

High-nitrogen austenitic stainless steels (HN ASSs) exhibit high strength, toughness, cold work capacity, corrosion resistance and low magnetic susceptibility. Therefore HN ASSs become more and more important in the class of austenitic stainless steels [1-4]. The development of the HN ASSs was motivated by the economy for reduction of the strategic element such is nickel. Nickel is the most widely used alloying element which can impart the face-centred-cubic (fcc) crystal lattice to stainless steels. The price of nickel is too high and therefore nickel is replacement by manganese [5].

Austenitic stainless steels are the most favoured construction materials of various components required in chemical, petrochemical and nuclear industries. The selection of these materials is made basically due to a good combination of mechanical, fabrication and corrosion resistance properties.

If the ASSs are heat affected in the temperature range of 500-900°C it can lead to the grain boundary precipitation of secondary phases. Precipitation of secondary phases causes of chromium depletion regions. If the chromium content near the grain boundaries drops under the passivity limit 12 wt. %, the steel becomes to be sensitised. In the sensitised condition, the steels are quite susceptible to the intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) that can result in premature failures of the fabricated components. The sensitisation temperature range is often encountered during isothermal heat treatment, slow cooling from the solution annealing temperature, the improper heat treatment in the heat affected zone of the welds or welding joints or hot working of the material. Degree of the sensitisation (DOS) is influenced by factors as the steel chemical composition, grain size, degree of strain, or temperature and time of isothermal annealing [6-10].

We report on some preliminary comparisons of the combined effects of chemical composition, temperature and aging time on precipitation in three experimental Cr-Mn-N steels in this research article.

2 Experimental procedures

The three experimental steels with the chemical composition in Table 1 was solution heat treated (1100°C/30 min. followed by water quenching) and then annealed in the temperature range from 650 to 900°C for holding time 5 min. to 100 hours.

Table 1 Composition (wt.%) of the main alloying elements of the experimental steel

Experimental steel	C	Mn	Cr	N	Mo
CrMnN1	0.18	10.50	17.60	0.49	3.30
CrMnN2	0.04	18.30	17.90	0.81	1.90
CrMnN3	0.04	22.90	21.00	0.85	0.25

The specimens for light optical microscopy (LOM) examination were polished up to fine diamond (~1μm) finish. The specimens were etched chemically for 60 s. using the solution: 10 ml H_2SO_4 + 10 ml HNO_3 + 20 ml HF + 50 ml distilled H_2O. Then the screening of microstructures was done using a light microscope NEOPHOT 32 equipped with the CCD camera.

For the individual secondary phases identification transmission electron microscopy (TEM) of the dual stage replicas was utilised. Thin foils suitable for TEM observation were prepared from each of the samples. Small discs of 3 mm in diameter and thick about 0.1 mm were jet-electropolished in electrolyte $HNO_3 : CH_3OH = 3 : 7$, at -10°C and 15V to obtain transparent areas near the central hole. The jet-electropolishing was done by TenuPol 5. TEM observations were performed using JEOL 200 CX operated at 200 kV and Philips CM 300 operating at 300 kV equipped with energy-dispersive X-ray spectrometer (EDX), which was used for the microchemical analyses. The analysis was supplemented by selected area electron diffraction (SAD) for the phase identification.

3 Results

The microstructure of experimental steels after solution annealing is shown by Fig.1. The microstructure consists of polyhedral austenitic grains with twinning typical for fcc microstructure. Heterogeneity of grains size was observed. No precipitates were observed at the grain boundaries. The microstructure is characteristic for the state after solution annealing.

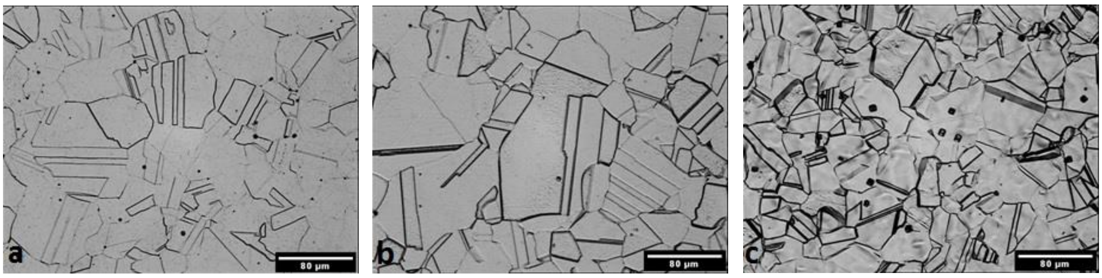

Fig. 1. Microstructure of experimental steels after solution annealing: a)CrMnN1, b)CrMnN2, c)CrMNn3

Fig.2 summarises the microstructure of the experimental steels after heat treatment 800°C/4 hours. Precipitation of secondary phases was observed at the grain boundaries (local precipitation), inside of the grains (continuous or discontinuous precipitation) in the case of the experimental steel CrMnN1 (Fig.2a). The character of the microstructure of the experimental steels CrMnN2 and CrMnN3 was very similar. There was observed local and discontinuous precipitation (Fig.2b and 2c). The grain boundaries or small parts of the grains were etched intensive what can be caused by precipitation of secondary phases.

TEM observation was used for the detailed analysis of the microstructure. The experimental technique with resolution lower than 10^{-6} m is necessary to use for manifesting of the precipitation. Therefore TEM observation was used for the detailed analysis of the microstructure. Fig.3a shows the characteristic microstructure of experimental steel CrMnN1 observed by TEM using carbon replica. The picture shows the detail of grain boundaries with precipitates of the irregular shape and small precipitates of regular geometric shape inside the austenitic grains. The big particles at the grain boundaries were identified by electron diffraction as carbide $M_{23}C_6$ (Fig.3b). The small particles inside grains were identified as χ-phases.

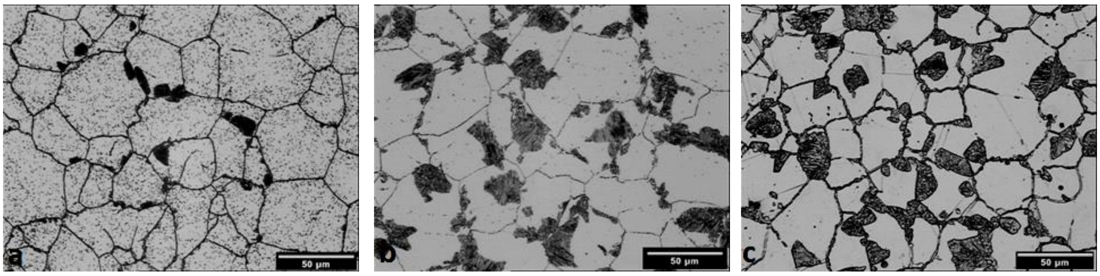

Fig. 2. Microstructure of experimental steels after annealing 800°C/4 hours: a)CrMnN1, b)CrMnN2, c)CrMNn3

Fig.4a shows detail of the discontinuous precipitation in the experimental steels CrMnN2 observed by TEM using carbon replica. Fig.4b documents detail of microstructure of the experimental steels CrMnN3 observed by TEM using thin foil. The picture shows detail of the grain boundary and lamellar area of discontinuous precipitation in austenitic grains.

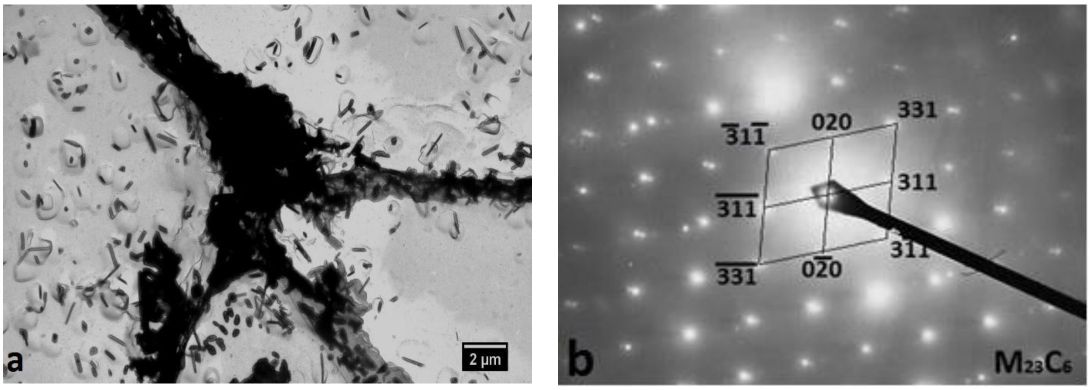

Fig. 3. Detail of the grain boundaries with the precipitates of irregular shape and small particles of regular geometric shape inside the grains (a) and electron diffraction pattern of big particles at the grain boundaries (b) – experimental steel CrMnN1 after annealing 850°C/10 hours

TEM analysis confirmed processes of precipitation during annealing. Precipitation had the different character in the experimental steels. The local precipitation was observed in the case all annealed state. Discontinuous precipitation was observed after holding time 4 hours in the case of all experimental steels. Continuous precipitation of the small regular shape particles inside austenitic grains was observed after annealing 800°C/3 hours in the experimental steel CrMnN1. Table 2 summarises identified phases in the experimental steels annealing at the temperature 800°C with different holding times.

The nose temperature of precipitation was determined to be about 800°C, with corresponding incubation period of precipitation 100 s [11].

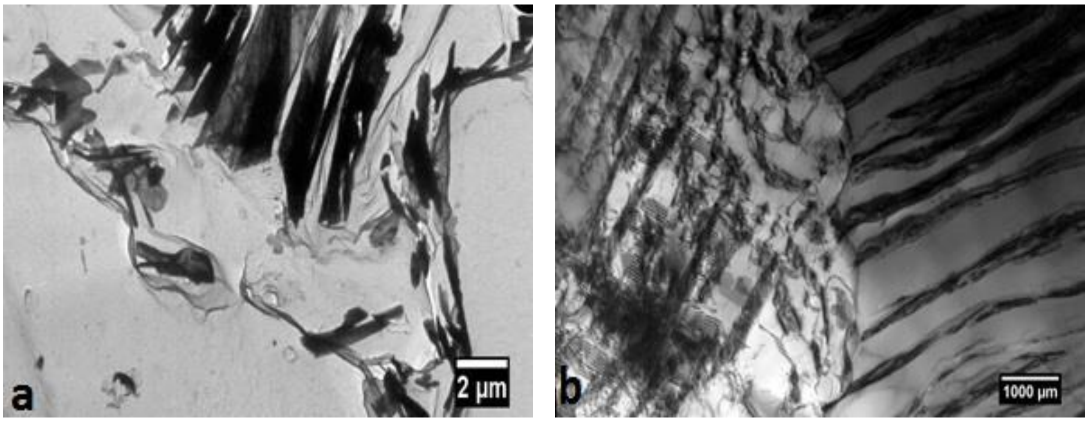

Fig.4. Detail of the grain boundaries with the precipitates of irregular shape and lamellar area of the discontinuous precipitation after annealing 850°C/10 hours: a) experimental steel CrMnN2 (replica), b) experimental steel CrMnN3 (thin foils)

Table 2 Identified phases in the experimental steels annealed at the temperature 800°C [11]

Condition of annealing	Experimental steels		
	CrMnN1	CrMnN2	CrMnN3
800°C/5 min	$M_{23}C_6$	M_2N	M_2N
800°C/10 min	$M_{23}C_6$, M_2N	M_2N	M_2N
800°C/30 min	$M_{23}C_6$, M_2N, chi	M_2N	M_2N, $M_{23}C_6$
800°C/60 min	$M_{23}C_6$, M_2N, chi	M_2N	M_2N, $M_{23}C_6$
800°C/10 h	$M_{23}C_6$, M_2N, chi	M_2N, $M_{23}C_6$, sigma	M_2N, sigma
800°C/30 h	$M_{23}C_6$, M_2N, chi	M_2N, $M_{23}C_6$, sigma	M_2N, sigma
800°C/100 h	$M_{23}C_6$, M_2N, chi	M_2N, $M_{23}C_6$, sigma	M_2N, sigma

4 Conclusions

The precipitation behaviour of CrMnN high nitrogen austenitic stainless steels has been investigated in the temperatures range from 650 to 900°C for duration range from 5 min. to 100 h. The following conclusions were drawn:

- Precipitation of secondary phases was observed in all analysed states of the experimental steels. The character of precipitation was different according to annealing conditions.

- $M_{23}C_6$ carbide, M_2N nitride and chi phase were identified in the experimental steel CrMnN1 by electron diffraction and EDX semi-quantitative chemical analysis. Increased content of carbon supports precipitation of carbide $M_{23}C_6$ and restrains precipitation of nitride M_2N on the other side.
- M_2N, $M_{23}C_6$ and sigma phase were identified in the experimental steels CrMnN2 and CrMnN3.
- The morphology of M_2N precipitation is transformed from initial irregular shape at the grain boundaries to lamellar ones in the cell as the annealing time increases.

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