HIGH NITROGEN AUSTENITIC STAINLESS STEEL PRECIPITATION DURING ISOTHERMAL ANNEALING

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Resume

The time-temperature-precipitation in high-nitrogen austenitic stainless steel was investigated using light optical microscopy, transmission electron microscopy, selected area diffraction and energy-dispersive X-ray spectroscopy. The isothermal precipitation kinetics curves and the corresponding precipitation activation energy were obtained. The diffusion activation energy of M_2N precipitation is 129 $kJ.mol^{-1}$. The results show that critical temperature for M_2N precipitation is about 825°C with the corresponding incubation period 2.5 min.

Available online: http://fstroj.uniza.sk/journal-mi/PDF/2016/10-2016.pdf

Article info

Article history:
Received 21 December 2015
Accepted 01 July 2016
Online 18 July 2016

Keywords:
Stainless Steel;
Annealing;
Sensitization.

ISSN 1335-0803 (print version)
ISSN 1338-6174 (online version)

1. Introduction

Nickel-free high nitrogen austenitic stainless steels (HN ASS) are highly attractive nowadays of their excellent mechanical and corrosion properties. They are also cheaper than nickel which has prospected possibility of allergic reactions in the human body. Also nickel is starting to be significantly deficient element what is also reflected in increasing prices of its alloys. Also the primary application of nickel is in jet engines [1 - 4], so in case of insufficient resources, manufacturing of stainless steels would have to be reduced in behalf of nickel alloys for aeronautic industry. The application field of nitrogen alloyed ASS is wide including power-generating industry, ship building, chemical equipment, biomaterials and petroleum industry. There are several attributes which makes the use of HN ASS favourable compared to the more conventional alloys. Some of these are high yield and tensile strength, high ductility, good strength fracture toughness combination, high strain hardening potential and favourable corrosion properties [5 - 7]. Generally austenitic stainless steels alloyed by chromium and nickel are considered as heat resistant up-to 800 °C [8, 9]. However, the excellent properties of HN ASS will be damaged if the precipitation of nitrides or other secondary phase occurs during thermal progress such as hot forming, heat treatment and welding [10, 11]. This means that HN ASS cannot completely replace Cr-Ni stainless steels, however in many applications they can be successfully used as a cheaper alternative and to save nickel, which is starting to be significantly deficit.

The purposes of the present study are to examine the morphology and the precipitation kinetics of M_2N precipitates in the isothermal annealing process and to provide some theoretical basis for the heat processes.

2. Experimental material and methods

The experimental steel with the chemical composition of Cr 21.0, Mn 23.0, N 0.85, C 0.04, V 0.2, Ni 1.5, Fe balance (in mass percent) 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 30 hours.

The specimens for light optical microscopy (LOM) examination were polished up to fine diamond (~1μm) finish. The specimens were etched chemically for 60 sec. using 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. Quantitative metallographic software adopted to measure the percentage of precipitates.

For the individual secondary phase 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 0°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 phases identification.

3. Results

Fig. 1a – 1d show microstructure of the experimental steel observed by light optical microscope (LOM). From the pictures is obvious the heterogeneity in the grain size of polyhedral austenitic matrix. The local precipitation at the grain boundaries was observed in the microstructure of samples annealed at 850°C/30 min. and 1 h, respectively (Figs. 1a and 1b). Fig. 1c shows microstructure of the sample annealed at 850°C / 10 h. The local precipitation at the grain boundaries is more intensive and there are some dark grains with lamellar shaped forms of discontinuous precipitation. The similar microstructure was observed in the case of the sample annealed at 850 °C / 30 h (Fig. 1d).

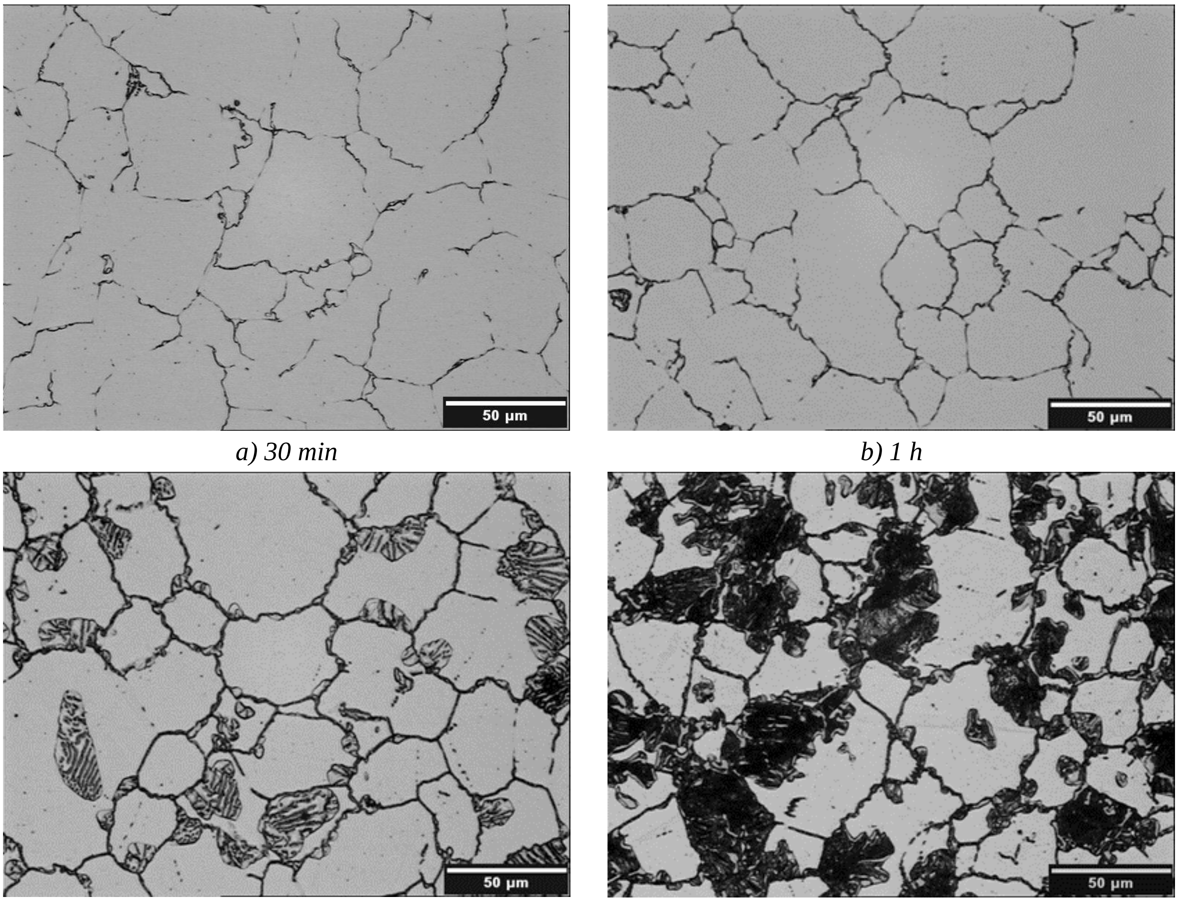
The detail of the grain boundary observed by TEM using replicas is show in Fig. 2a. The particles of the irregular shape were observed at the grain boundaries. These particles were identified as nitride M_2N using SAD (Fig. 2b). The chemical composition of nitride M_2N determined by EDX analysis is given in the Table 1.

Fig. 3a shows the bright-field image of the grain boundary serration observed by TEM using thin foils. The serration of grain boundary was caused by precipitation of nitride M_2N during annealing at 800 °C / 1 h. After the certain incubation time 5 h the cellular precipitation of M_2N started from grain boundaries (Fig. 3b).

The time-temperature-precipitation (TTP) diagrams were constructed on the base of statistical analysis of the precipitation. The nose temperature of M_2N precipitation was determined to be about 825° C, with corresponding incubation period of precipitation 2.5 min. Fig. 4 shows the relationship between volume fraction of precipitates and annealing time (t) at the different temperatures. The regression curves were constructed based on these data (Fig. 5). According to these curves the diffusion activation energy is determined as about 129 $kJ.mol^{-1}$. We use Arrhenius equation in logarithmic shape:

$$Q = \frac{R \ln\frac{t_1}{t_2}}{\frac{1}{T_1} - \frac{1}{T_2}} \qquad (1)$$

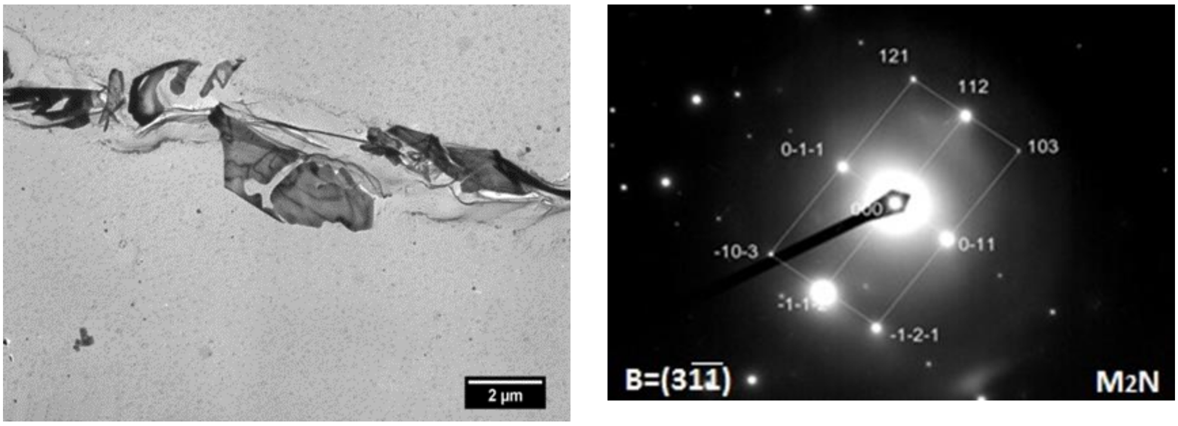
where t_1 and t_2 is time necessary for selected volume fraction of precipitates and T_1 and T_2 annealing temperature.



a) 30 min *b) 1 h*

c) 10 h *d) 30 h*

Fig. 1. Microstructure of samples after isothermal annealing at 850° C.



a) detail of grain boundary with the particles of irregular shape 750°C/1 h

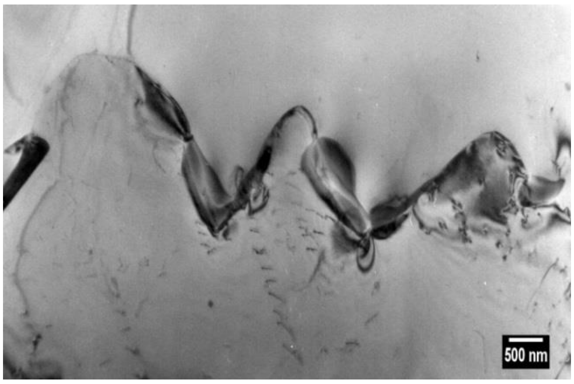
b) electron diffraction pattern of particles (SAD)

Fig. 2. TEM micrograph (replica).

Table 1

Chemical composition of the metal elements of the particles at the grain boundaries in the samples annealed 750 °C / 1 h.

particles	**chemical composition (mass %)**			
irregular shape (M_2N)	Cr 95.0 ± 2.5	Fe 3.5 ± 0.8	Ni 1.0 ± 0.5	Mo 0.5 ± 0.2



a) detail of the grain boundary serration with the particles of irregular shape (800 °C / 1h)

b) cellular precipitation of nitride M_2N inside grain (800 °C / 5h)

Fig. 3. TEM micrograph (thin foils).

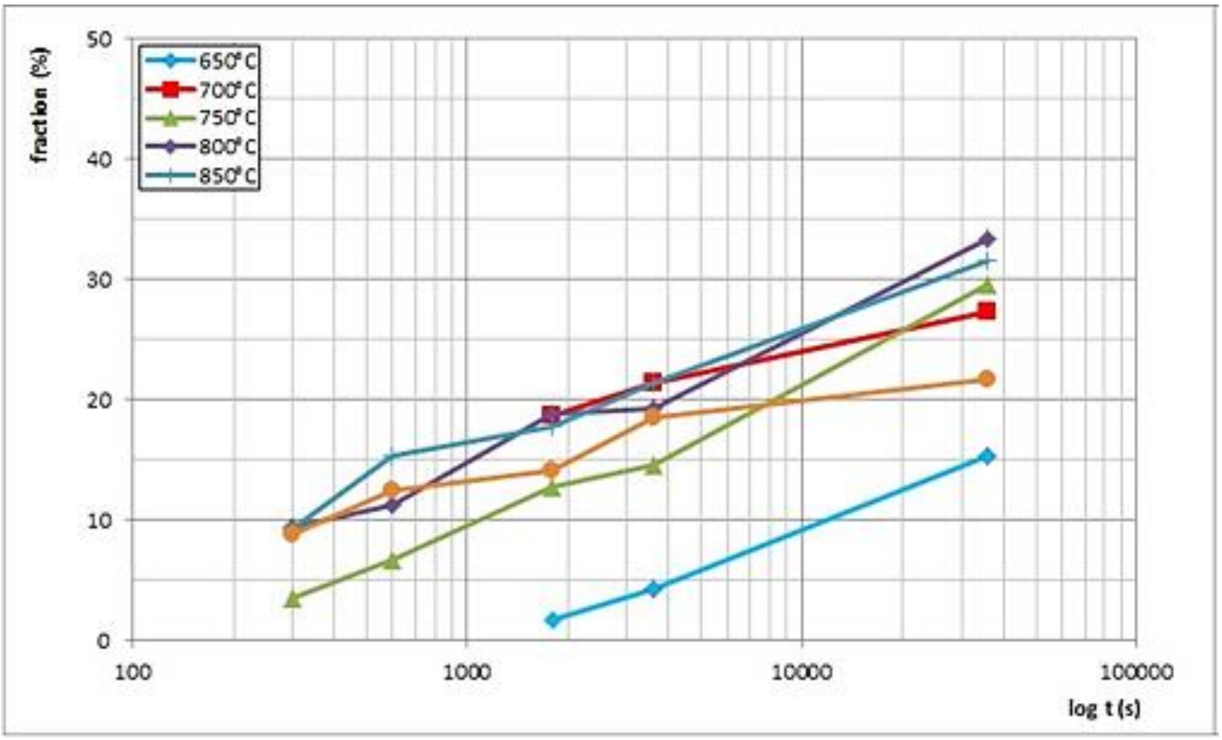


Fig. 4. Relationship between volume fraction of M_2N and annealing time at the different temperatures.
(full colour version available online)

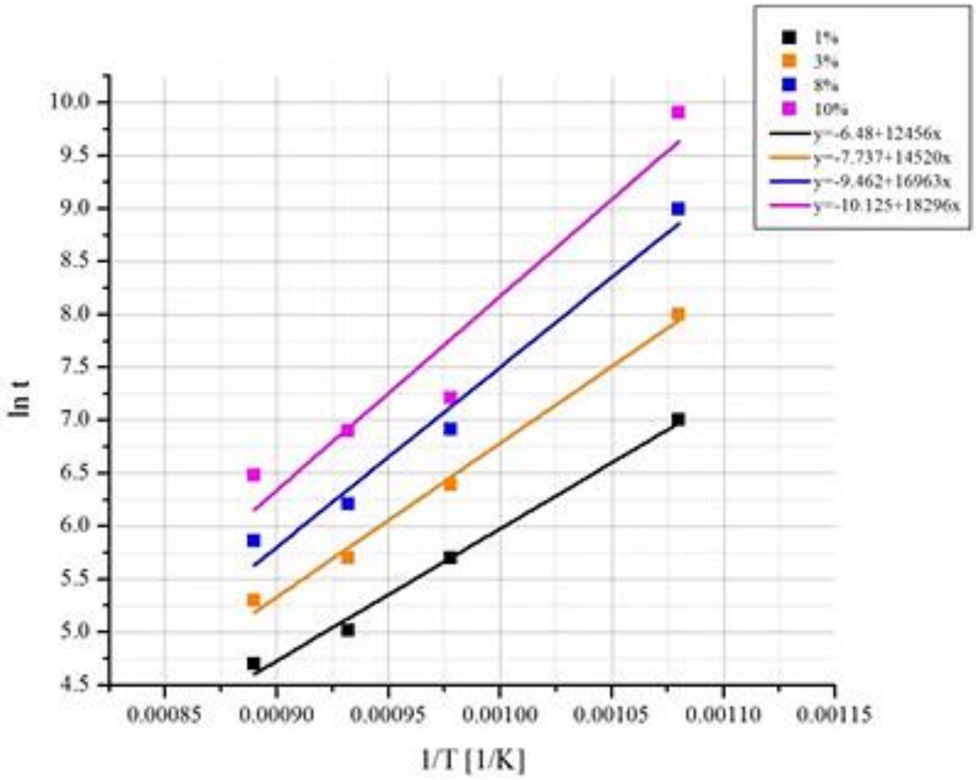


Fig. 5. Regression curves in lower annealing temperatures regions.
(full colour version available online)

4. Conclusions

The precipitation behaviour of CrMnN high nitrogen austenitic stainless steel has been investigated in the temperatures range from 650 to 900°C for duration range from 5 min to 30 h. The following conclusions were drawn:

1. 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. The precipitates are first observed to nucleate along grain boundaries in the samples, which were annealed shorter time than 10 hours. As the aging time increases, the precipitates start to grow inward austenitic grains by cellular precipitation, and precipitates in the cell at the early stage of aging are granular. With further increase in the aging time, the cellular precipitation region continues to grow and the granular precipitates in the cell are prolonged,
2. according to the isothermal precipitation kinetics curves of M_2N the nose temperature is about 825 °C with holding time 2.5 min.,
3. diffusion activation energy of M_2N precipitation is about 129 kJ.mol^{-1} for experimental steel.

Acknowledgements

The authors wish to thank the financial support of Scientific Grant Agency of Slovak Republic (VEGA) under grant No. 1/0402/13.

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