STRUCTURAL STABILITY OF HIGH NITROGEN AUSTENITIC STAINLESS STEELS

Jana Bakajová[1,*], Mária Dománková[1], Peter Gogola[1]

[1] STU Bratislava, Faculty of Materials Science and Technology inTrnava, Paulínska 16, 917 24 Trnava, Slovak Republic.
*corresponding author: Tel.: -, Fax.:-, e-mail: jana.bakajova@stuba.sk

Resume

This paper deals with the structural stability of an austenitic stainless steel with high nitrogen content. The investigated steel was heat treated at 800°C using different annealing times. Investigation was carried out using light microscopy, transmission electron microscopy and thermodynamic calculations. Three phases were identified by electron diffraction: Cr_2N, σ – phase and $M_{23}C_6$. The thermodynamic prediction is in good agreement with the experimental result. The only is the $M_{23}C_6$ carbide phase which is not thermodynamically predicted. Cr_2N is the majority secondary phase and occurs in the form of discrete particles or cells (lamellas of Cr_2N and austenite).

Available online: http://fstroj.uniza.sk/PDF/2011/05-2011.pdf

Article info

Article history:
Received 22 February 2011
Accepted 5 May 2011
Online 11 May 2011

Keywords:
High nitrogen austenitic stainless steel
Transmission electron microscopy
Electron diffraction
Precipitation

ISSN 1335-0803

1. Introduction

Austenitic stainless steels are preferred construction materials used in medicine, chemical, petrochemical and energetic industry. Development of new grades includes the substitution of the classic CrNi grades with CrMnN grades [1]. This way production costs can be saved by replacing the expensive Ni with cheaper elements like Mn and N. These steels show high strength, very good resistance to cavitation wear, pitting and crevice corrosion [1,2,3,4]. During annealing of these steels in the temperature range between 500 and 1050 °C Cr-rich precipitates can be formed and the corrosion resistance of these steels can be significantly reduced [1,5]. In addition to the Cr_2N nitride, which is formed preferentially, also σ-phase can be formed. Nitrogen can't be dissolved by σ-phase particles; therefore this type of precipitates is formed mainly in nitrogen depleted zones [6]. Aim of this work is to characterize the type and morphology of various precipitation particles depending on the annealing time.

2. Experimental methods

Chemical composition of the experimental high nitrogen austenitic stainless steel is listed in Table 1.

Table 1
Chemical composition of experimental material

Element	content [wt.%]
Cr	21
Mn	23
Ni	1.5
C	max. 0.04
V	max. 0.2
N	0.85

The steel was annealed at 800 °C using a variety of annealing times ranging from 5 min to 100 h. Designation of the samples is shown in Table 3.

Table 2

Designation of samples

Annealing time	Designation
5 minutes	P005
10 minutes	P0010
30 minutes	P0030
60 minutes	P0060
10 hours	P0010h
30 hours	P0030h
100 hours	P00100h

The samples were prepared for the light microscopy by standard metallographic preparation finished with electrochemical etching in a 10% water solution of oxalic acid at a current density of 1 $A.cm^{-2}$. NEOPHOT 32 light microscope, equipped with a CCD camera, was used for the documentation.

Two stage carbon replicas were prepared for the TEM measurements.Identification of the secondary phase particles was done by transmission electron microscopy (TEM) using electron diffraction (ED) and EDX analysis (JEOL 200kV and Philips 300kV).

3. Results

Fig. 1 documents the microstructures of the investigated samples annealed at 800 °C with different annealing times. The microstructure is formed by typical polyhedral austenitic grains with annealing twins visible in the grains. Already after 5 min (Fig. 1a) local precipitation on the grain boundaries can be observed. After 30 min (Fig. 1c) also disconti-nuous precipitation was documented. So called cells were formed consisting of lamellas (austenitic lamellas + lamellas of nitrides).

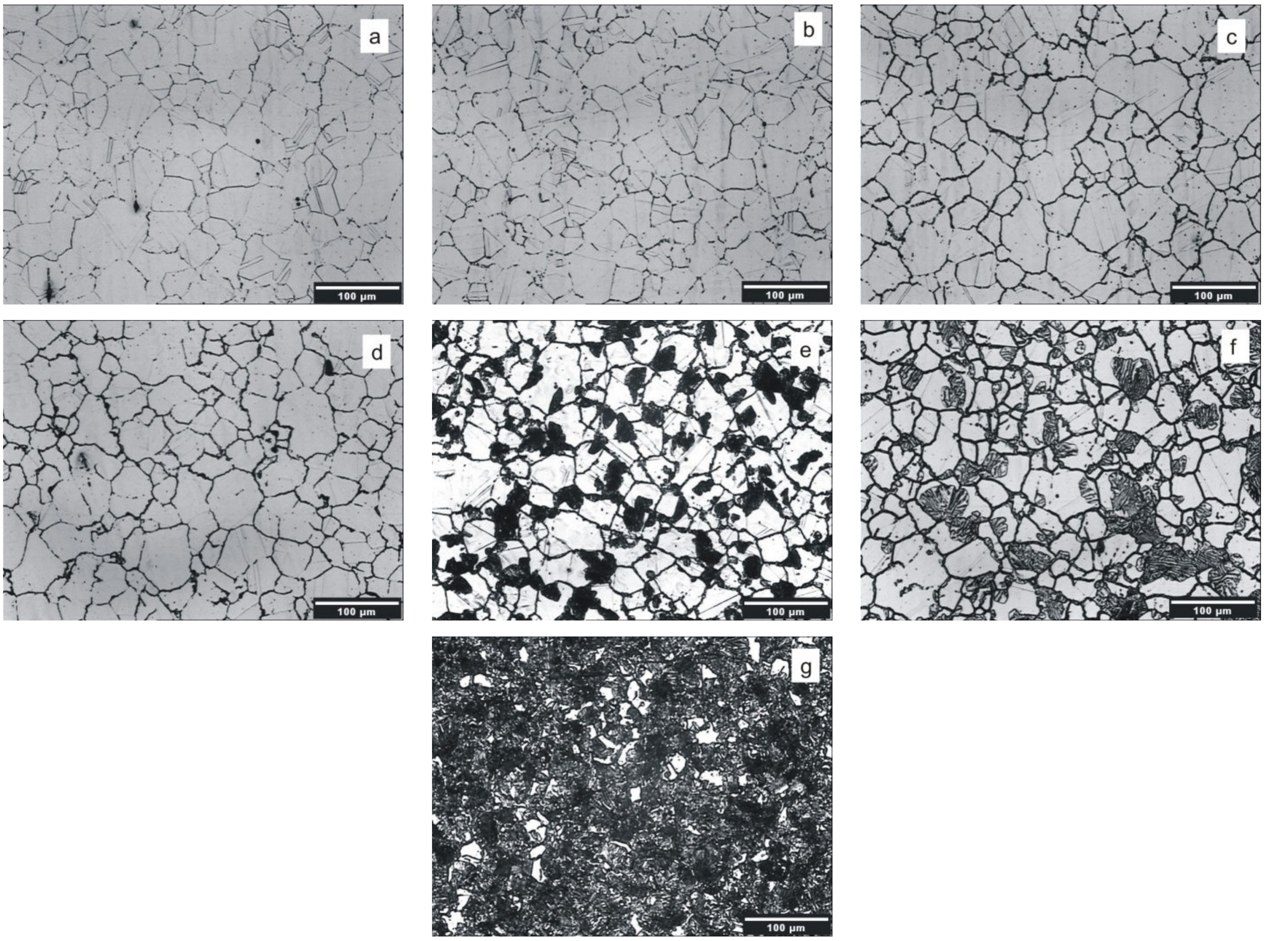

Fig. 1. Microstructure of high nitrogen austenitic stainless steel after different time of annealing on the 800 °C a) P005, b) P0010, c) P0030, d) P0060, e) P0010h, f) P0030h, g) P00100h

With longer annealing times the proportion of secondary particles was increasing. In the Table 3 phases identified by ED in the experimental steel are listed.

Table 3

Phases identified by ED

Sample Designation	Type of the phase Cr_2N	σ – fáza	$M_{23}C_6$
P005	✓		
P0010	✓		
P0030	✓		✓
P0060	✓		✓
P0010h	✓	✓	⊗
P0030h	✓	✓	⊗
P00100h	✓	✓	◈

✓ - Phases identified by ED
◈ - Phases expected according to EDX measurements
⊗ - Phases expected, but not proved by ED nor EDX

Fig. 2 shows some details of the grain boundaries investigated by TEM. The morphologically different particles observed were identified by ED as Cr_2N (Fig. 2a), σ-phase (Fig. 2b) and carbide $M_{23}C_6$ (Fig. 2c). In Table 4 average chemical composition of the investigated particles, measured by EDX, is listed.

Table 4

Average chemical composition of the identified phases

Elements	Type of the phase Cr_2N	σ phase	$M_{23}C_6$*
Cr	86.5 ± 1.2	28.8 ± 0.4	43.8
Mn	7.9 ± 0.7	21.7 ± 0.5	17.4
Fe	2.5 ± 0.9	47.5 ± 0.7	34.9
Ni	0.2 ± 0.2	0.9 ± 0.4	0.8
Mo	2.9 ± 0.7	1.2 ± 0.3	3.1

*only one particle of 80 particles measured was investigated as $M_{23}C_6$

The phase equilibria and the molar fractions of equilibrium phases were calculated for systems corresponding to the investigated steel in the temperature range of 600 – 1200 °C by Thermocalc software using the database STEEL17X formulated by Kroupa et al. [7]. In the calculation procedure the total Gibbs energy of the system consisting of contributions of individual phases is minimized at constant temperature and pressure. In the calculations, the elements Fe, C, N, Si, Mn, Cr, Mo, Ni and V were considered, and the phases δ-ferrite (b.c.c.), austenite (f.c.c.), Cr2N (h.c.p.), M6C (f.c.c.), M23C6 (f.c.c.) and σ (tetragonal) were taken into account [8].

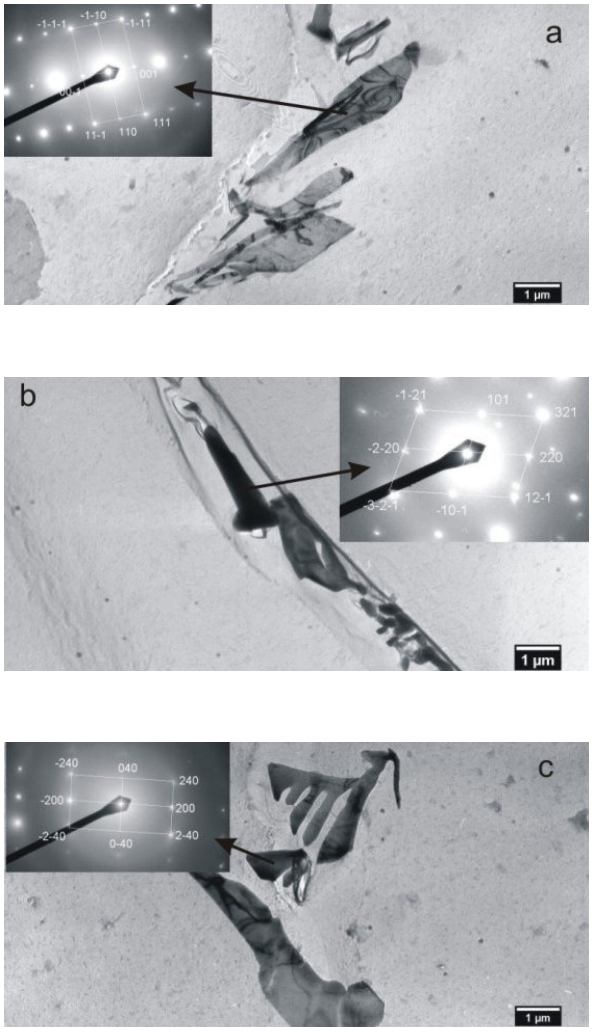

Fig. 2. Microstructure of the investigated steel with corresponding diffraction patterns of the marked particles a) P0010, particle of Cr_2N, b) P0010h, particle of σ phase, c) P0030, particle of $M_{23}C_6$

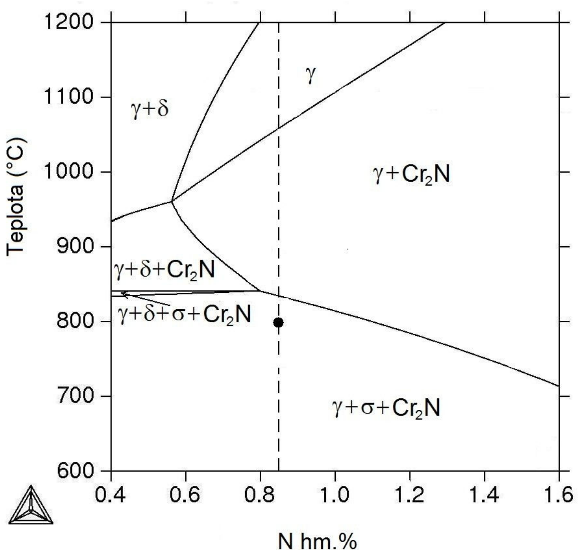

Fig. 3. Isopleths showing calculated phase equilibria for systems corresponding to CrMnN steel [8]

4. Discussion

The study of secondary phases formed in the experimental steel during annealing at 800°C showed local precipitation already after 5min of annealing time. With longer annealing time the proportion of secondary phases increased and after 30 min discontinuous precipitation was observed. Lamellar cells formed by austenite and Cr_2N nitride were created. The same precipitation procedure was investigated in the steel Fe-18Cr-18Mn-0,43N-0,09C by F. Shi et. al. [5] and also in the steels Fe-22Cr-16Mn-0,9N-0,11C and Fe-22Cr-14Mn-0,9N-0,03C by Ma Yu-Xi et. al. [9]. The presence of the investigated phases was confirmed by multiple authors, especially the presence and precipitation procedure of the Cr_2N particles [3, 5, 6, 10]. However the precipitation of the σ-phase particles was confirmed only by one of the authors. Tae – Ho Lee et. al. [6] identified σ-phase particles in the nitrogen depleted zones; in the same areas as identified by our experiments. The comparison of thermodynamic calculation and experimental results are in good agreement. Particles of $M_{23}C_6$ are the only exception. These particles were not predicted by thermodynamic calculations; however they were identified experimentally by ED. It can be assumed that these are only particles of a transition phase.

5. Conclusion

- The microstructure of the experimental material is formed by typical polyhedral austenitic grains with annealing twins and secondary phase particles visible.
- The proportion of precipitation particles increases with increasing annealing time. After 5 and 10 minutes only local precipitation on the grain boundaries was observed. After 30 min the start of discontinuous precipitation could be observed.
- Two stage carbon replicas were created from all experimental samples. Investigation of these replicas showed the presence of Cr_2N particles. When the annealing time exceeded 10 h, σ–phase was formed additionally. The average chemical composition of the identified particles is shown in Tab. 4. In the samples annealed for 30 and 60 min also $M_{23}C_6$ carbide particles were identified.
- Thermodynamic calculations predicted for the given annealing temperature (800 °C) three possible phases: austenite, Cr_2N and σ-phase. The transition temperature between the „$\gamma+Cr_2N+\sigma$" area and the „$\gamma+Cr_2N$" area is 834°C. Between the „$\gamma+Cr_2N$" area and the austenite area is 1058°C.

Acknowledgements

This article was prepared thanks to the support provided within the program for research and development for the project Centre for Development and Application of Progressive Diagnostic Methods in the Process of Metallic and Non-metallic Material's Processing, ITMS: 26220120014, co financed by the European fund for regional development.

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