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IDENTIFICATION OF PRECIPITATES IN Cr-Mn-N BASED STEEL AFTER THERMAL EXPOSURES

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Abstract

The paper deals with the identification of precipitates in the Cr-Mn-N steels after thermal exposure. The purpose of the study is to clarify the M_2N precipitation by isothermal annealing at the temperatures of 750 and 900 °C with a holding time of 5, 10, 30 min, 1 hr. and 10 hrs. Microstructure of austenitic steel was characterised by the typical presence of annealing twins. Stepwise etching was observed at the holding time of 5 and 10 minutes, but at the holding time of 30 minutes, secondary particles were precipitated at the grain boundaries. Corrosion tests revealed that holding time significantly affected steel structure. M_2N is the dominant precipitate, but the occurrence of σ-phase was occasionally observed especially at the interface of discontinuous precipitation and austenitic matrix. Slight increase of hardness at the grain boundaries was caused due to the precipitation of secondary phases during isothermal holding. The maximum hardness of 294 HV was measured on the sample isothermally annealed at 750 °C and holding for 10 hrs. The research provides theoretical basis for the heat affecting of steels, such as, for example, in welding.

Key words

stainless steel, precipitation, corrosion, corrosion resistance

INTRODUCTION

The main reason of invention and further development of stainless steels was to increase technical parameters of equipment and machines in the industry.

These materials have a longer lifetime and ensure safe operation even longer. Increase of the corrosion resistance is accompanied by the efforts to improve the mechanical properties,

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creep resistance, weldability and strength properties at low temperatures, while maintaining good ductility and toughness. The given type of steel maintains an austenitic structure at room temperatures as well as at very low ones (1).

If interstitial elements dissolve in the solid solution, the strength of austenitic stainless steels increases without any significant loss of stiffness and ductility. Excellent properties of the high nitrogen austenitic stainless steels may be affected by the precipitates formed after the heat treatment of steels (2, 3).Stainless steels are susceptible to intergranular corrosion, which is related to the emergence of new phases at the grain boundaries of the solid solution. These are particularly the carbide or nitride precipitates that are formed when heating the steel above 400 °C (usually in the range of 500 – 850 °C) for a long time exposure. The main reason of the nitride and carbide precipitation is the dependence of C and N solubility on γ-Fe and α-Fe. The high temperature ensures dissolution of greater amount of phases. Precipitation of secondary phases at the austenite grain boundaries may result in a reduction of the Cr content in the boundary areas, which may cause sensitisation of the steel and its susceptibility to intergranular corrosion (4, 5, 7, 8, 9, 10).

Factors affecting the degree of sensitisation modify the thermodynamics and kinetics of the formation of carbides at the grain boundaries, which may accelerate or slow down the process of precipitation (11). Precipitation is highly dependent on the chemical composition of the steel and heat treatment before aging. The purpose of the study was to clarify the morphology and kinetics of the M_2N precipitation during isothermal annealing (2, 3, 11). The research provides theoretical basis for the heat affecting of steels, such as, for example, in welding.

EXPERIMENTAL METHODS

The Cr-Mn-N steel was used as experimental material. The chemical composition of the steel is given in Table 1. The samples were subjected to isothermal annealing process at the temperatures of 750 and 900 °C with the holding time of 5, 10, 30 min, 1 hr. and 10 hrs.

CHEMICAL COMPOSITION OF Cr-Mn-N STEEL Table 1

Content of elements [%]						
C	**Si**	**Mn**	**Ni**	**Cr**	**Mo**	**N**
0.03 - 0.05	0.15 - 0.25	22.7 - 23.3	1 - 2	20.8 - 21.3	0.2 - 0.3	0.81 - 0.86

Light microscopy was applied to the microstructure analysis of metallographically prepared surface. The changes of microstructure during isothermal annealing were investigated. Transmission electron microscopy (TEM) using a two-stage replica was applied to a more detailed study of the precipitation process. Analysis was complemented by X-ray diffraction analysis, in order to identify excluded secondary precipitated phases at the austenite grain boundaries. An accelerated corrosion test method according to ASTM A262 A was carried out to study of the corrosion resistance of the experimental steels (12).

Experimental methods were complemented by Vickers hardness test with a load of 1 kg. Microstructure of experimental steel was formed by austenite with the typical presence of annealing twins. Mean grain size was calculated by the linear secant method.

RESULTS AND DISCUSSION

The microstructure showed moderate heterogeneity in the grain size, which ranged from 15 to 70 microns. Calculated mean grain size diameter d was 30 ± 8 microns. The grain size did not change significantly during isothermal annealing.

Fig. 1a shows the microstructure of the steel after isothermal annealing. The polyhedral structure of the steel after annealing at 750 °C/30 min is documented in Fig. 1. Intensive etching of grain boundaries can be caused by the process of precipitation of secondary phases at the grain boundaries.

Fig. 1b documents the microstructure of the experimental steel after isothermal annealing at 750 °C/10hrs. Only local manifestation of precipitation at grain boundaries, but also discontinuous precipitation was observed during this annealing.

Examples of microstructure after annealing at 900 °C are documented in Fig. 1c, d.

Intense etching of the grain boundaries, which may be caused by precipitation of secondary phases, was observed again.

However, discontinuous precipitation was observed at this temperature. Microstructural Changes that may affect the corrosion resistance of the experimental steel were observed by light microscopy. Thus, accelerated corrosion test method according to ASTM A262 A (12) was applied.

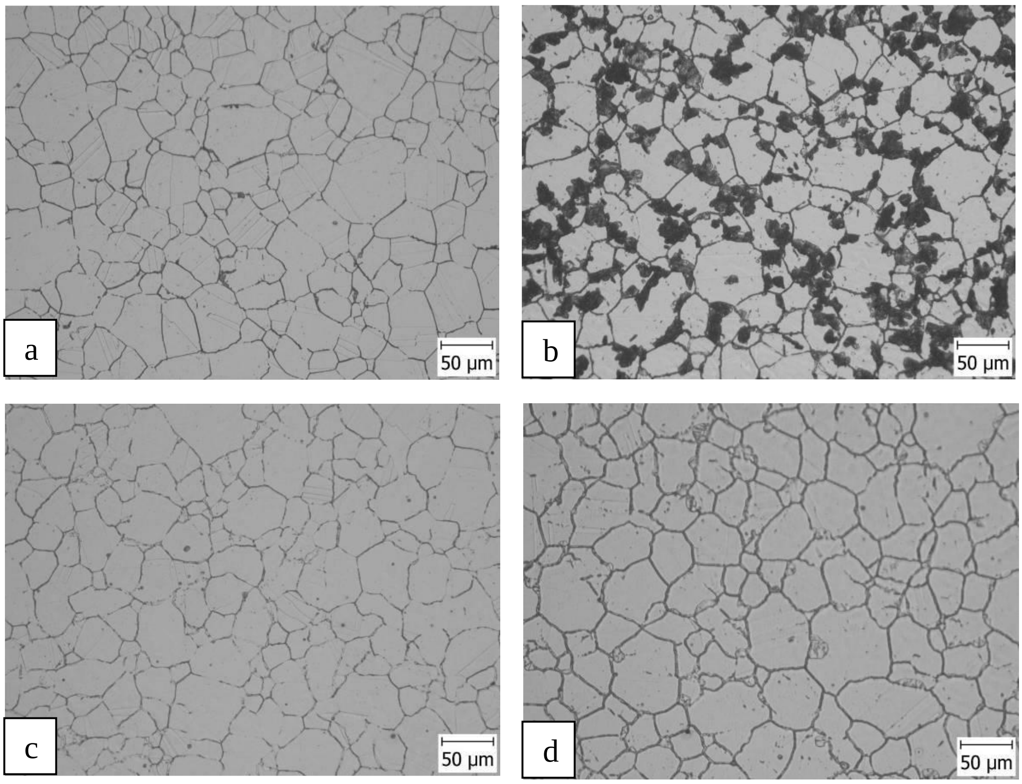

Fig. 1 *Microstructure of the steel after isothermal annealing under conditions a) 750 °C/30 min; b) 750 °C/10 hrs.; c) 900 °C/30 min.; d) 900 °C/10 hrs.*

Etchant of 10 % oxalic acid solution at 20 °C, voltage 10 V, time 90 s and current of 1 A/cm^2 were used in the corrosion test. The analysis is used for a preliminary assessment of intergranular attack of the material. The attack was subsequently rated as:

- the step for different dissolution rates, absence of chromium-rich carbides (at grain boundaries), different grain orientation of the material only result in the creation of steps between grains,
- dual with several ditches at the grain boundaries, without ditches surrounding the whole grain, which is indicative of the partial precipitation at the boundaries,
- ditch when the grain boundary contains an amount of chromium carbides that well after the test merge to relate the trench surrounding at least one grain boundary.

Dual attack was observed after the application of the corrosion test of the steel annealed at 750 °C for 5 minutes holding time. Grains are partially surrounded by the ditches, which may be caused by precipitation of secondary phases. The state is not classified as sensitised despite the occurrence of secondary phases at the grain boundaries. Microstructure developed at the holding time of 10 minutes exhibits dual attack. However, after a holding time of 30 min. (Fig. 2a) grains are affected by ditches. The observed microstructure is ranked as sensitised and susceptible to intergranular corrosion. Similar nature of the microstructure was observed even when the sample was annealed at 750 °C/1hr. Pitting attack occurred at the holding time of 10 hrs. (Fig. 2b) Microstructure is again evaluated as sensitised.

Similar character of the microstructure was also observed in the case of annealing at 900 °C. Microstructure observed after holding times of 5 and 10 minutes was classified as dual. This condition is evaluated based on the standard as sensitised. Significantly affected structure was observed with increasing the holding time, which was classified after applying the corrosion tests as ditch attack (Fig. 2c and 2d). Such a microstructure is sensitised and prone to intergranular corrosion.

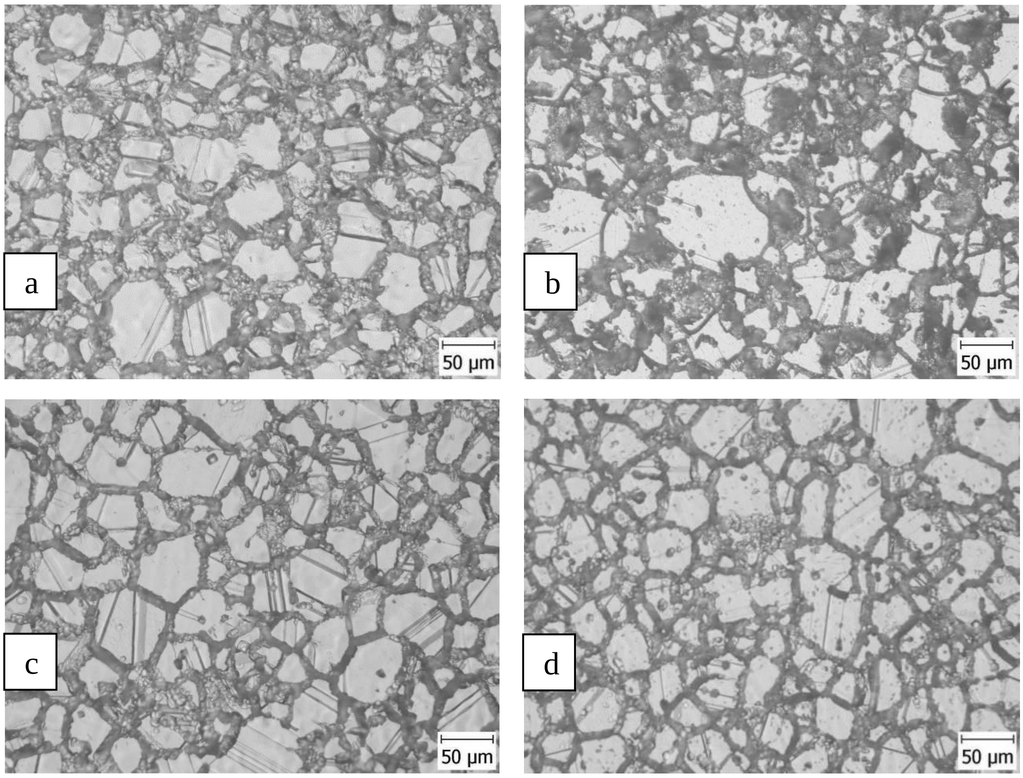

Fig. 2 *Microstructure of steel P560 after corrosion tests under conditions: a) 750 °C/30min; b) 750 °C/10 hrs.; c) 900 °C/30 min.; d) 900 °C/10 hrs.*

Measuring the Vickers hardness with load of 1 kg was an additional experimental method. Fig. 3 documents the changes in hardness HV1 at the temperatures of 750 and 900 °C with increasing the holding time. Slight increase in hardness, which may be due to the precipitation of secondary phases during isothermal holding, was observed. Etching of the grain boundaries, which may be due to the precipitation of secondary phases, was found by light microscopy. Transmission electron microscopy was conducted for a more detailed observation of the nature of the microstructure at the grain boundaries. Particles of irregular shape rarely precipitated at the grain boundaries after heat treatment at 750 °C and holding time of 5, 10 min. The presence of M_2N nitride was confirmed by using X-ray diffraction analysis. Grain boundaries coarsening caused by the precipitation of secondary phases was observed after 30 min. holding time. Precipitated secondary phases extended into the austenite grains. Particles of M_2N nitride were identified by electron diffraction.

Fig. 4 shows an example of the microstructure of grain boundaries observed by TEM by application of two-stage replica. As can be seen from the documented microstructures, density of precipitates at the grain boundaries increased with increasing the holding time. Location of the initial stage of discontinuous precipitation is also visible in Fig. 4c.

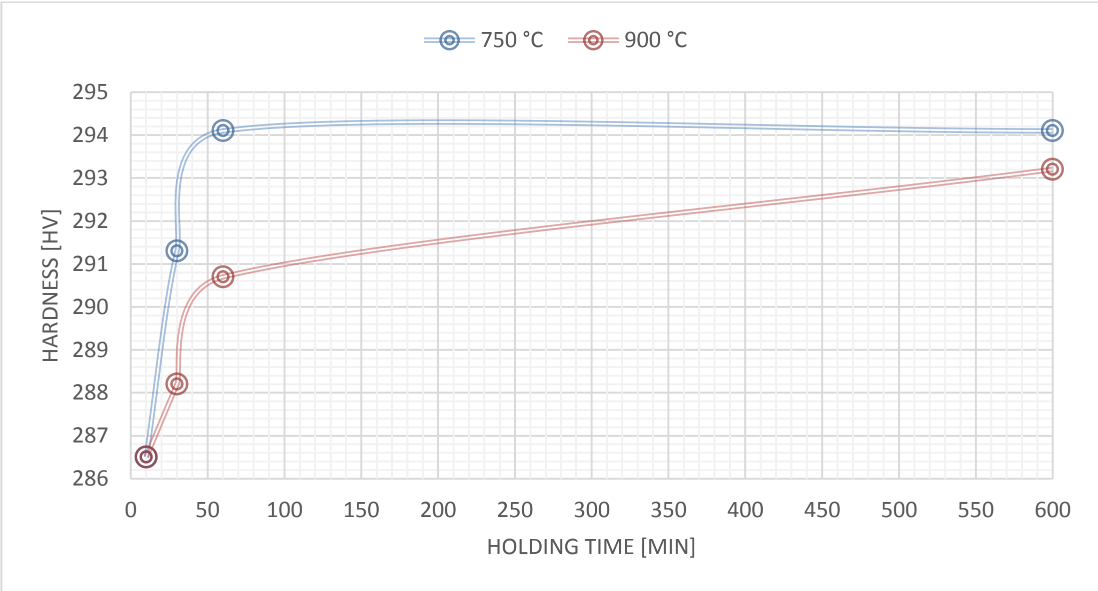

Fig. 3 *Dependence of steel hardness on holding time before and after heat treatment*

M_2N is the dominant precipitate, but the occurrence of σ-phase was occasionally observed especially at the interface of discontinuous precipitation and austenitic matrix. The approximate chemical composition of the identified phases measured by semiquantitative chemical EDX microanalysis is shown in Table 2.

The results of EDX analysis confirmed the presence of two types of phases that precipitated in the experimental steel during isothermal holding: M_2N nitride with indicative chemical composition: ~5% Mo; ~80% Cr; ~7% Mn; ~6%Fe; ~2%Ni and σ-phase with indicative chemical composition: ~1% Mo; ~29% Cr; ~20% Mn; ~48% Fe; ~1%Ni.

THE CHEMICAL COMPOSITION OF PHASES FORMED
AFTER THERMAL EXPOSURE

Table 2

Annealing temperature	Holding time	Chemical elements [wt. %]					Secondary phase
		Mo	Cr	Mn	Fe	Ni	
750 °C	5 min.	5.85	75.73	8.83	5.53	4.03	M_2N
	10 min.	5.28	80.78	7.65	3.05	3.08	
	30 min.	3.01	78.21	7.73	9.68	1.33	
	1 hr.	3.11	86.41	7.38	2.26	0.81	
	10 hrs.	3.18	88.48	5.78	1.82	0.72	
	10 hrs.	1.16	29.16	20.51	48.34	0.83	σ-phase

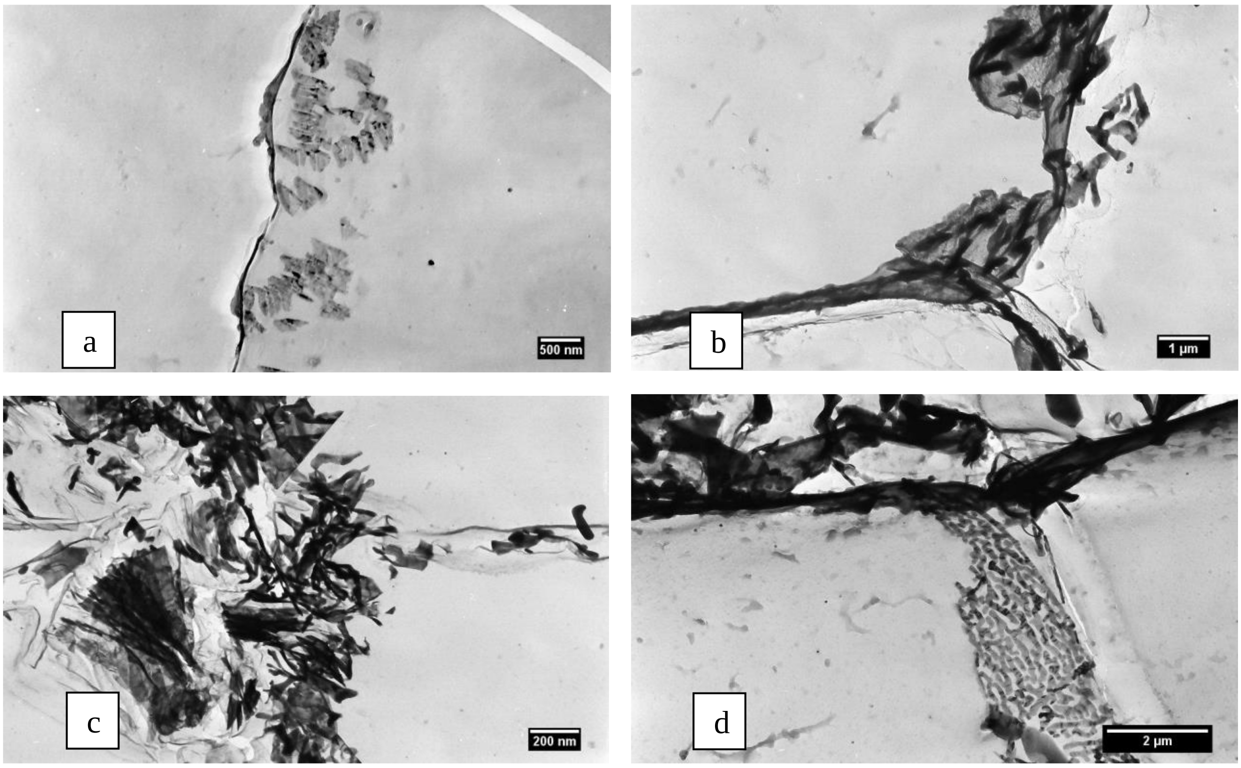

***Fig. 4** The grain boundaries observed by transmission electron microscope, steel annealed at 750 °C for holding time of a) 10 min.; b) 30 min.; c) 1 hr.; d) 10 hrs.*

CONCLUSION

Characteristic changes of microstructure which were due to influence of heat treatment were observed by light microscopy. Typical austenitic grains of the size ranging from 23 microns to 30 microns were observed at the annealing temperature 750 °C, annealing twins were observed at each temperature holding time. Step etching was recorded in the case of the samples annealed with the holding time of 5 and 10 minutes. Other samples were etched more strongly. Density precipitation increased with increasing the holding time.

Characteristic austenite grains of the size ranging from 21 microns to 32 microns were observed again after annealing at the temperature of 900 °C. Secondary precipitated particles were observed at the grain boundaries after holding time of 30 minutes. Etching was smaller than that observed at the previous temperature. Vickers hardness measurements at the grain boundaries confirmed an increase in hardness after heat exposure by an average of 32.4 HV. The maximum hardness of 294 HV was measured on the sample isothermally annealed at 750 °C for 10 hrs. Transmission electron microscopy was used to identify the phases present in the steel annealed at the temperature of 750 °C. Values of d_{hkl} interplanar spacings were calculated by analyzing the diffraction pattern and then compared with the tabulated values. The presence of M_2N nitride and σ-phase was confirmed.

In order to verify the phase identification by X-ray diffraction, EDX microanalysis was applied. The detected chemical composition of secondary particles confirmed the presence of M_2N nitride and σ-phase.

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