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THE EFFECT OF COLD WORK ON THE SENSITISATION OF AUSTENITIC STAINLESS STEELS

VPLIV HLADNE DEFORMACIJE NA POVEČANJE OBČUTLJIVOSTI NERJAVNIH JEKEL

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The sensitisation behaviour of austenitic stainless steel is greatly influenced by several metallurgical factors, such as the chemical composition, the degree of prior deformation, the grain size, and the ageing temperature and time. The precipitation behaviour of AISI 316 and 304 austenitic stainless steels has been investigated after ageing at various temperatures from 500 °C to 900 °C for 0.1 h to 1000 h. The TTS diagrams of the experimental steels after an oxalic-acid etch test ASTM A262 practice A were constructed. It was demonstrated that the C curves of the TTS diagrams were displaced towards shorter times by the increment of 20 % cold work (CW), since the sites inside the grain matrix have a high energy and the carbides can nucleate there easily. Cold work increases the number of dislocations/dislocation pipes along which the diffusion rate of chromium is very high. The sensitisation of the experimental steels accelerated the precipitation of $M_{23}C_6$. Besides $M_{23}C_6$, the σ-phase and M_6C were detected at the grain boundaries and in the austenitic matrix in the case of the cold-worked samples.

Key words: austenitic stainless steels, sensitisation, precipitation, cold working, intergranular corrosion

Občutljivost nerjavnih jekel je odvisna od več metalurških dejavnikov, npr. od kemične sestave, predhodne deformacije, velikosti zrn, časa in temperature staranja. Izločilno vedenje jekel AISI 316 in 304 je bilo raziskano po različno dolgem staranju od 0,1 h do 1000 h pri temperaturah med 500 °C in 900 °C. TTS diagrami eksperimentalnih jekel so bili pripravljeni po oksalnem preizkusu po ASTM 262 – metoda A. Dokazano je, da so C-krivulje TTS-diagramov premaknjene h krajšim časom po 20-odstotni hladni deformaciji (CW), zato ker imajo tudi v zrnih mesta z veliko energijo, kjer nastanejo karbidni izločki. Hladna deformacija poveča število dislokacij/dislokacijskih cevk, kjer je difuzija kroma zelo hitra. Povečanje občutljivosti jekel je povečalo hitrost izločanja karbidov $M_{23}C_6$. σ-fazo in M_6 karbide smo v hladno deformiranem jeklu opazili ob kristalnih mejah in v avstenitni matrici.

Ključne besede: avstenitna nerjavna jekla, povečanje občutljivosti, hladna deformacija, interkristalna korozija

1 INTRODUCTION

The intergranular corrosion (IGC) and stress-corrosion cracking (SCC) of austenitic stainless steels are the most important corrosion processes that affect the service behaviour of these materials. Exposure to temperatures in range 500–800 °C leads to the grain-boundary precipitation of chromium-rich carbides $(Fe,Cr)_{23}C_6$ and to the formation of chromium-depleted regions. If the mass fraction of chromium content near the grain boundaries drops under the passivity limit of 12 %, the steel becomes sensitised. 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 the hot working of the material. The degree of sensitisation (DOS) is influenced by factors such as the steel's chemical composition, the grain size, the degree of strain or temperature and the time of isothermal annealing. The sensitisation involves both the nucleation and growth of carbides at the grain boundaries. Depending on the state or the energy of the grain boundaries they can provide preferential sites for carbide nucleation and act as a favoured diffusion path for the growth of carbides. Therefore, it has been suggested that the nature of grain boundaries could also influence the DOS and IGC [1–4].

In this article we report on some preliminary comparisons of the combined effects of chemical composition, deformation, temperature and aging time on sensitisation in AISI 304 and 316 stainless steels.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

The chemical composition of the experimental steels is given in **Table 1**. The steels were mostly investigated in the as-received condition with some in the solution-annealed condition. The solution annealing was conducted on the as-received materials at 1050 °C for 60 min followed by water quenching.

The steels were 20–40 % cold rolled by controlling the thickness of the plates. The cold-worked samples were heat treated at various temperatures in the range 500–900 °C for times of 0.1 to 1000 h. The samples were then water quenched after the heat treatment.

The oxalic-acid etch test (ASTM A262 practice A) was used to determine the steels' sensitivity to inter-granular corrosion. The specimens were electrolytically etched in 10 % oxalic acid for 90 s at a current density of

Table 1: Chemical composition (in mass fractions, *w*/%) of the austenitic stainless steels
Tabela 1: Kemična sestava (v masnih deležih, *w*/%) avstenitnih nerjavnih jekel

steel	C	N	Si	Mn	P	S	Cr	Ni	Mo	Fe
AISI 304	0.04	0.012	0.54	1.08	0.0032	0.008	18.52	8.47	0.21	bal.
AISI 316	0.05	0.032	0.47	0.86	0.0026	0.001	17.55	11.56	2.10	bal.

1 A/cm^2. The etched microstructure was then examined at 250x, and was characterised as a step, dual or ditch microstructure [5].

For the individual secondary-phase identification transmission electron microscopy (TEM) of the carbon extraction replicas was applied. TEM observations were performed using a JEOL 200 CX operating at 200 kV. The carbon extraction replicas were obtained from mechanically polished and etched surfaces. The replicas were stripped from the specimens in the solution of CH_3COOH : $HClO_4$ = 4 : 1 at 20 °C and 20 V.

3 RESULTS

The results of the light microscopy examination are summarised in **Figure 1**. The microstructure of AISI 304 after solution annealing consists of polyhedral austenitic grains with twinning typical of an fcc microstructure. The average austenitic grain size in this state is about 45 µm (**Figure 1a**). A small amount of δ-ferrite was also observed. No precipitates were detected at the grain boundaries (GBs) of the solution-annealed steels. **Figure 1b** shows the microstructure of the AISI 304 after 40 % of CW. The microstructures of the aged states are shown in **Figure 1c** and **Figure 1d**. **Figure 1c** shows the evolution of secondary phases precipitated at the

GB in the isothermally aged specimen (650 °C/0.5 h) without cold work. The microstructure of the isothermally aged specimen (650 °C/0.5 h) and 40 % CW is shown in Figure 1d. The precipitation of secondary phases was observed at the GB and intragranularly and within the matrix.

To compare the results of two austenitic stainless steels, time-temperature-sensitisation (TTS) diagrams for these steels for different degrees of CW ranging from 0 % to 40 % are presented in **Figure 2**. From the TTS diagrams it can be seen that the nose of the C curve corresponding to the maximum rate of sensitisation

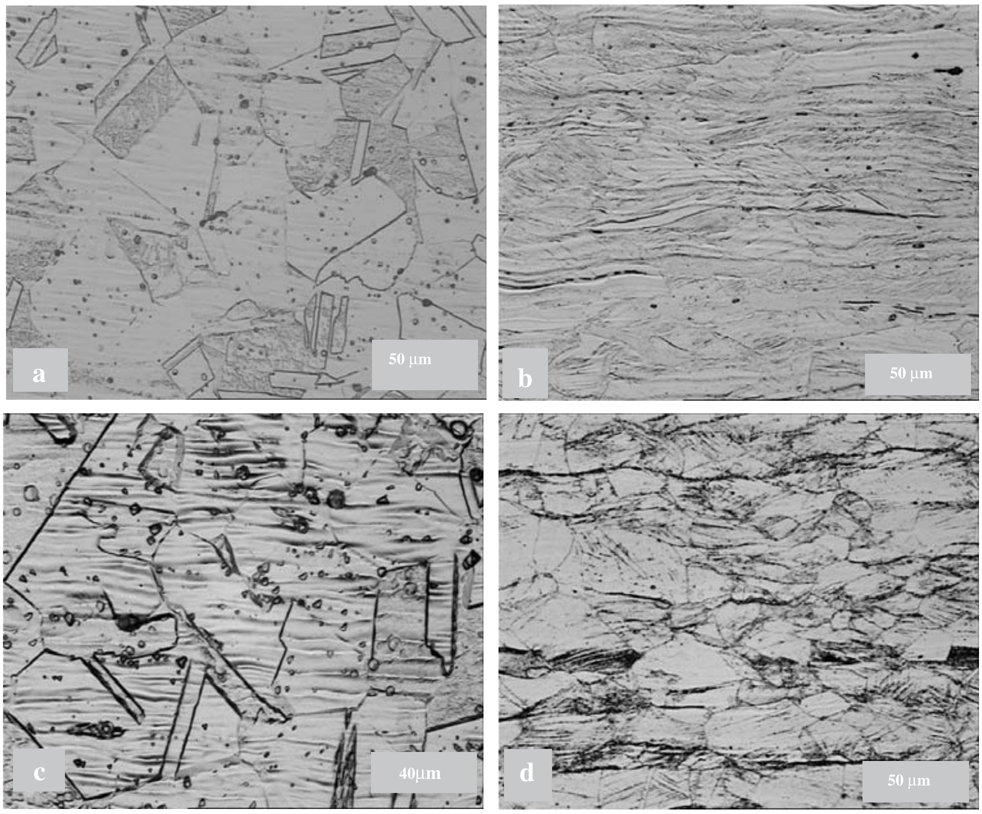

Figure 1: Microstructure of the AISI 304 a) after solution annealing – 0 % CW, b) after solution annealing – 40 % CW, c) after aging at 650 °C/0.5 h, 0 % CW, d) after aging at 650 °C/0.5 h, 40 % CW

Slika 1: Mikrostruktura jekla AISI 304 a) po topilnem žarjenju – 0 % CW, b) po topilnem žarjenju – 40 % CW, c) po staranju 650 °C/0,5 h, 0 % CW, d) po staranju 650 °C/0,5 h, 40 % CW

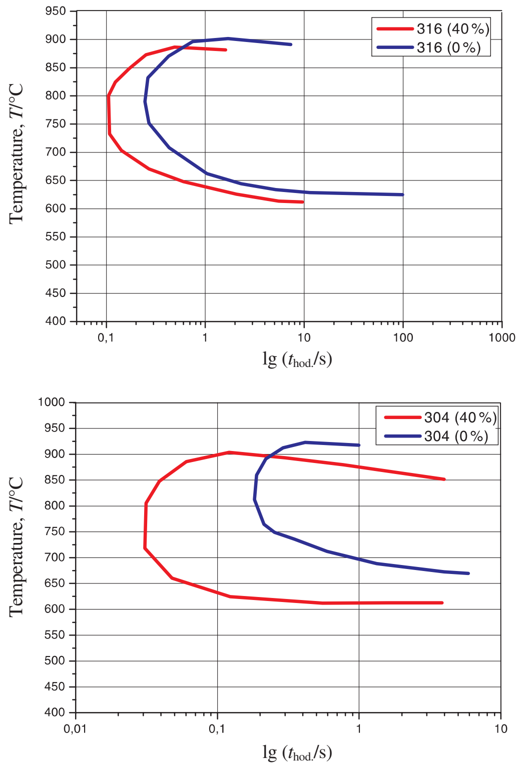

Figure 2: TTS diagrams for AISI type 316 and 304 stainless steels with various degrees of CW established as per ASTM A262 practice A test
Slika 2: TTS diagrama za nerjavni jekli 316 in 304 pri različni stopnji deformacije, določeni z ASTM A262-preizkusom

occurs at 800 °C for the AISI 316 in the 0 % CW condition. As the degree of CW increases, the nose temperature remains almost that same, but t_{min} decreases with the increase in % CW up to 20 % and remains constant thereafter. The TTS diagram of AISI 304 is shifted towards shorter times than the 0 % CW material. The tendency of the shift of the AISI 304 C curve is similar to the case of AISI 316.

To identify the type of secondary phases precipitated at the grain boundaries (GBs) during the isothermal

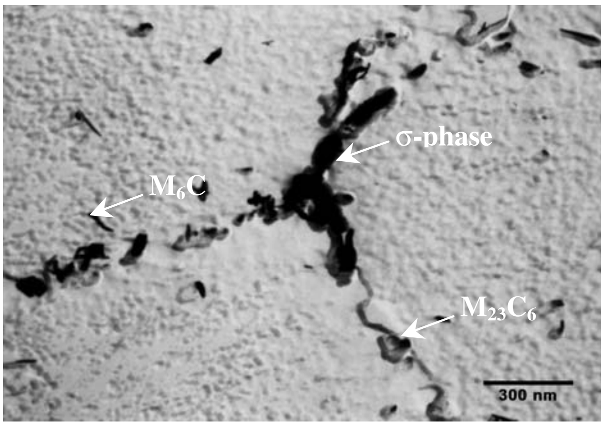

Figure 3: Microstructure of AISI 316 (650 °C/300 h) – TEM
Slika 3: Mikrostruktura jekla AISI 316 (650 °C/300 h) – TEM

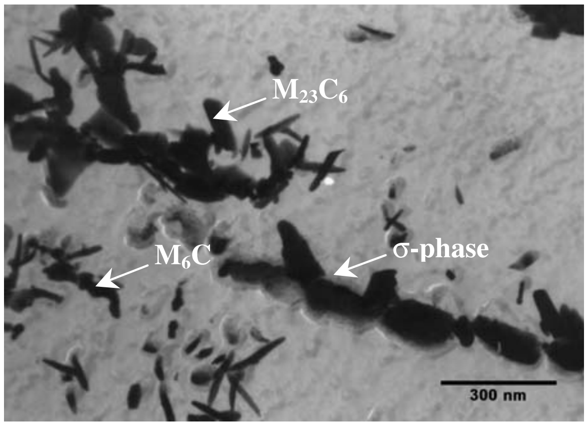

Figure 4: Microstructure of AISI 316 (650 °C/1000 h) - TEM
Slika 4: Mikrostruktura jekla AISI 316 (650 °C/1000 h) – TEM

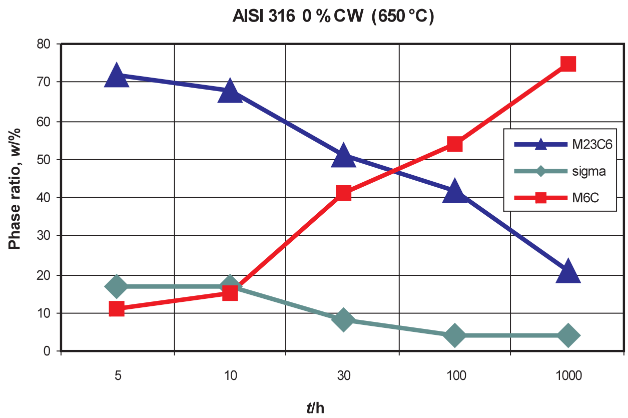

Figure 5: Phase ratio in AISI 316 after aging at 650 °C
Slika 5: Razmerje faz v jeklu AISI 316 po staranju pri temperaturi 650 °C

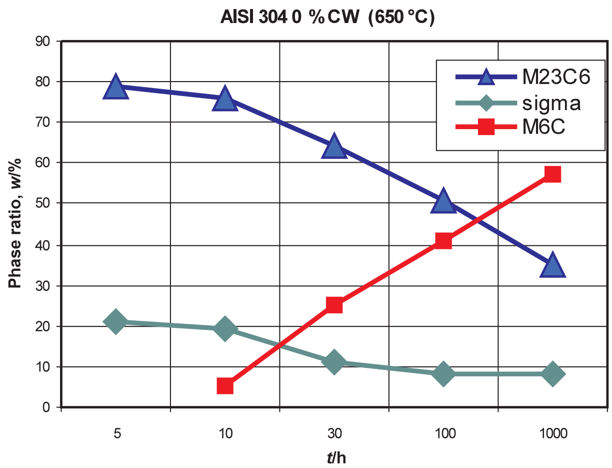

Figure 6: Phase ratio in AISI 304 after aging at 650 °C
Slika 6: Razmerje faz v jeklu AISI 304 po staranju pri temperaturi 650 °C

treatment, TEM analysis was carried out. First, $M_{23}C_6$ was detected at the grain boundaries after aging. In addition to $M_{23}C_6$, the σ-phase and M_6C were detected at the grain boundaries (**Figure 3 and Figure 4**). Similar precipitation trends were detected using TEM analysis at the grain boundaries of the AISI 304 steel. The identified secondary phases in the experimental steels and the phase ratio are shown in **Figures 5 and 6**.

4 CONCLUSIONS

The precipitation behaviour of AISI 316 and 304 austenitic stainless steels was investigated during aging at various temperatures in range from 500 °C to 900 °C for times from 0.1 to 1000 h. The following conclusions can be drawn:

TTS diagrams of the experimental steels after the oxalic-acid etch test ASTM A262 practice A show that the C curves of the TTS diagrams are displaced towards shorter times with increasing amounts of CW.

After ≈20 % cold working, even the sites inside the grain matrix have high energy and carbides can nucleate there also. Cold work increases the number of dislocations/dislocation pipes along which the diffusion rate of chromium is faster.

Sensitisation of the experimental steels accelerated the precipitation of $M_{23}C_6$. In addition to this carbide, σ-phase and M_6C were detected at the grain boundaries and in the austenitic matrix in the cold-worked samples.

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