EFFECT OF DEFORMATION AND HEAT TREATMENT ON GRAIN BOUNDARY SENSITISATION IN AUSTENITIC STAINLESS STEELS

DOMÁNKOVÁ, M.*, MAREK, P.*, MAGULA V.**

*Katedra materiálového inžinierstva, MtF STU Trnava, Slovakia
** IBOK, a.s., Bratislava, Slovakia

ABSTRACT
Sensitisation behaviour of austenitic stainless steel are greatly influenced by several metallurgical factors such as chemical composition, degree of prior deformation, grain size, aging temperature-time. We deal with the influences of deformation on sensitisation behaviour in AISI 304 and AISI 316 austenitic stainless steels. Sensitisation kinetics was studied in the temperature range of 500 to 900°C for different degrees of cold work, ranging from 20 to 40%. It has been well-established that the nose of the time-temperature-sensitisation (TTS) diagrams by increasing of cold work is displaced towards lesser time. Evaluation of TTS diagrams was performed by the method: ASTM A262 practice A. In order to understand the cause of the enhanced rate of sensitisation with deformation, transmission electron microscopy was carried out. The identification, morphology and size of grain boundary precipitates, which are responsible for sensitisation, were characterised for samples aged at 650°C for ageing duration corresponding to the onset of sensitisation.

1. INTRODUCTION
Austenitic stainless steels are the most favoured construction materials of various components required in chemical, petrochemical and nuclear industries. The selection of these is made basically due to a good combination of mechanical, fabrication and corrosion resistance properties. The exposition in the temperature range of 500-800°C leads to the grain boundary precipitation of chromium rich carbides \((\text{Fe,Cr})_2\text{C}_6\) and to the formation 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 [1-4]. 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 [5-6]. 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. The sensitisation involves both nucleation and growth of carbides at the grain boundaries. Depending on the state or energy, the grain boundaries provide preferential sites for the carbide nucleation and act as favoured diffusion path for growth of carbides. Therefore it has been suggested that the nature of grain boundaries would also influence the DOS and IGC.

Sensitisation resulting from isothermal exposure is normally represented by time-temperature-sensitisation (TTS) diagrams, which are plots of aging time versus temperature necessary for sensitisation. These are “C” shaped curves, which separate sensitised and non-sensitised regions. The TTS diagrams show the time required for isothermal sensitisation at various temperatures and can be used to solve problems such as the selection of conditions of annealing which will not result in sensitisation. The nose of this curve specifies the critical temperature at which the minimum time \((t_{\text{min}})\) is required for sensitisation.
Sensitisation may also result from cooling through the sensitisation temperature range, this is of great practical importance. Dayal and Gnanamoorthy [7] have reported a method to predict the extent of sensitisation during continuous cooling/heating of the material. The critical linear cooling rate (CCR) can also be calculated from the TTS diagram. Based on the CCR and the TTS diagram, the continuous-cooling-sensitisation (CCS) diagram can be established. Influence of the plastic deformation on the sensitisation of ASSs is frequently analysed problems [2,3,6,7]. Effects of annealing and plastic deformation on ASSs are mostly considered as a complex phenomenon of the synergetic nature. As an example, the process of thermo-mechanical treatment can be used, which affects the optimisation of the ASS mechanical properties. Study of the plastic deformation influence on sensitisation of ASSs is concentrated on the detailed analysis of the material texture, misorientation and grain boundary character distribution. An influence of the degree of strain on the position of “C” curves and the critical linear cooling rate was proved [2,3,8].

In this research 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

2.1 Materials, heat treatment and cold working
The chemical compositions of experimental steel are given in Table 1. These materials were mostly studied in the as received condition with some in the solution annealed condition. Solution annealing was conducted on the as received materials at 1050°C for 60 min followed by water quenching.

Table 1. Chemical composition (in wt.%) of austenitic stainless steels used in this study

<table>
<thead>
<tr>
<th>steel</th>
<th>C</th>
<th>N</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304</td>
<td>0.04</td>
<td>0.012</td>
<td>0.54</td>
<td>1.08</td>
<td>0.0032</td>
<td>0.008</td>
<td>18.52</td>
<td>8.47</td>
<td>0.21</td>
<td>bal.</td>
</tr>
<tr>
<td>AISI 316</td>
<td>0.05</td>
<td>0.032</td>
<td>0.47</td>
<td>0.86</td>
<td>0.0026</td>
<td>0.001</td>
<td>17.55</td>
<td>11.56</td>
<td>2.10</td>
<td>bal.</td>
</tr>
</tbody>
</table>

The steels were cold rolled ranging from 20 to 40% by controlling the thickness of plates. The degree of cold work (CW) was used to express the reduction ratio in thickness. Specimens of 15 mm length and 8 mm width with reduced thickness were cut from the cold rolled strips for sensitisation testing.

The cold worked samples were heat treated at various temperatures range from 500 – 900°C for duration range from 0.1 to 1000 h. The samples were water quenched after the heat treatments.

2.2 Specimen preparation
The specimens for ASTM A262 practice A test were mounted in an epoxy resin and were polished up to fine diamond (~1µm) finish. The specimens were etched electrolytically using 5 % oxalic acid solution for microstructural characterisation.

2.3 Sensitisation test
For determination the steels sensitivity to intergranular corrosion an oxalic acid etched test (ASTM A262 practice A) was used. The specimens were electrolytically etched in 10% oxalic acid for 90 sec. at a current density of 1 A/cm². The etched structure is then examined at 250 x and was characterised as step, dual or ditch structure. The specimen showing step or dual structure was considered to be free from sensitisation whereas the specimen showing ditch structure was classified as sensitised.
2.4 Construction of time-temperature-sensitisation diagrams
These diagrams were obtained by plotting sensitisation test results on a temperature versus log
soaking time axes and drawing a line which demarcates the sensitised and non sensitised
regions.

2.5 Phase identification
For individual secondary phase identification transmission electron microscopy (TEM) of
extraction carbon replicas was utilised. TEM observations were performed using
JEOL 200 CX operated at 200 kV. Carbon extraction replicas were obtained from
mechanically polished and etched surfaces. The replicas were stripped from the specimens in
solution of CH$_3$COOH : HClO$_4$ = 4 :1 at 20°C, 20 V.

3. RESULTS
3.1 Microstructural characterisation
The results of light microscopy investigation, summarised in Fig.1, microstructure of AISI
304 after solution annealing is composed of polyhedral austenitic grains with twinning typical
for fcc structure. The average austenitic grain size of this state is about 45 µm (Fig.1a). The
small amount of δ-ferrite was also recorded. No precipitates were observed at the grain
boundaries (GB) of solution annealed steels. Fig.1b shows microstructure of AISI 304 in the
40% CW condition. Microstructure of aged states is documented in Fig.1c and Fig.1d. Fig.1c
shows the evolution of secondary phases precipitation at the GB in the isothermally aged
specimen (650°C/0,5 h) and 0%CW. The microstructure of the isothermally aged specimen
(650°C/0,5 h) and 40% CW is showed in Fig.1d. Precipitation of secondary phases was
observed at the GB and intragranularly within the matrix too.

Fig.1. Microstructure of AISI 304 a) after solution annealing - 0% CW, b) after solution
annealing - 40% CW
3.1 Corrosion behaviour
The rapid oxalic acid etch test was used for analysis of the grain boundary sensitisation development. Examples of microstructure obtained by etch test for AISI 316 are given in Fig. 2.
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 collectively presented together in Fig. 3. From the TTS it can be seen that the nose of the C-curve corresponding to the maximum rate of sensitisation occurs at 800°C for AISI 316 in the 0% CW condition. As the degree of CW increases, nose temperature remains almost same but $t_{\text{min}}$ decrease with increase in % CW up to 20% and thereafter remains constant. For AISI 304, the TTS diagrams are shifted towards lesser time than that of 0% CW material. Minimum time required for sensitisation at nose temperature ($t_{\text{min}}$) was determined from TTS diagrams and are presented in Table 2.

### Table 2. Variation of $t_{\text{min}}$ with degree of CW

<table>
<thead>
<tr>
<th>% CW</th>
<th>AISI 316</th>
<th>AISI 304</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>$t_{\text{min}}$ (h)</td>
</tr>
<tr>
<td>0</td>
<td>800</td>
<td>0,25</td>
</tr>
<tr>
<td>20</td>
<td>800</td>
<td>0,1</td>
</tr>
<tr>
<td>30</td>
<td>800</td>
<td>0,1</td>
</tr>
<tr>
<td>40</td>
<td>800</td>
<td>0,1</td>
</tr>
</tbody>
</table>

### 3.3 Secondary phases identification

Fig.4 shows the microstructure of AISI 316(40%CW) in the solution annealing state observed by TEM. Fig. 5 shows a typical GBs formed in an early stage of the aging treatment (650°C/10 min.), only a few particles of secondary phases were observed on GB using TEM. As first $M_{23}C_{6}$ carbides at grain boundaries were detected after aging. Besides $M_{23}C_{6}$ carbides, σ-phase and $M_6C$ carbide were detected at grain boundaries (Fig.6 and Fig.7).

Table 3 summarised the average metal composition and frequency (Fig.8) of identified secondary phases in steel AISI 316 (40%CW) after the aging treatment.
Table 3 Average metal composition in wt.% of identified secondary phases in steel AISI 316 (40%CW) after aging treatment

<table>
<thead>
<tr>
<th>aging treatment</th>
<th>phase</th>
<th>metal composition (wt%)</th>
<th>frequency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>Fe</td>
</tr>
<tr>
<td>650°C/5 h</td>
<td>$M_23C_6$</td>
<td>64.1</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>$M_6C$</td>
<td>21.3</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>σ-phase</td>
<td>19.6</td>
<td>59.7</td>
</tr>
<tr>
<td>650°C/10 h</td>
<td>$M_23C_6$</td>
<td>61.7</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>$M_6C$</td>
<td>14.5</td>
<td>30.2</td>
</tr>
<tr>
<td></td>
<td>σ-phase</td>
<td>18.6</td>
<td>60.3</td>
</tr>
<tr>
<td>650°C/30 h</td>
<td>$M_23C_6$</td>
<td>64.7</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>$M_6C$</td>
<td>11.1</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>σ-phase</td>
<td>24.2</td>
<td>59.3</td>
</tr>
<tr>
<td>650°C/100 h</td>
<td>$M_23C_6$</td>
<td>61.4</td>
<td>18.1</td>
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<tr>
<td></td>
<td>$M_6C$</td>
<td>13.6</td>
<td>30.6</td>
</tr>
<tr>
<td></td>
<td>σ-phase</td>
<td>26.3</td>
<td>57.3</td>
</tr>
<tr>
<td>650°C/1000 h</td>
<td>$M_23C_6$</td>
<td>72.9</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>$M_6C$</td>
<td>9.6</td>
<td>29.4</td>
</tr>
<tr>
<td></td>
<td>σ-phase</td>
<td>23.3</td>
<td>68.5</td>
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</tbody>
</table>
4. CONCLUSIONS
The precipitation behaviour of AISI 316 and 304 austenitic stainless steels have been investigated at the aging at various temperatures range from 500 to 900°C for duration range from 0.1 to 1000 h. The following conclusions were drawn:

1. TTS diagrams of experimental steels after oxalic acid etch test ASTM A262 practice A were constructed. It was demonstrated that C-curve of TTS diagrams are displaced towards lesser time by increasing of cold work,

2. after ~20% cold working, even the sites inside the grain matrix have high energy and carbides can nucleate there easily. Cold work increases the number of dislocations/dislocation pipes along which diffusion rate of chromium is very high,

3. sensitisation of the experimental steels accelerated the precipitation of the carbide $M_23C_6$, besides $M_23C_6$ carbide, $\sigma$-phase and $M_6C$ carbide were detected at grain boundaries and in the austenitic matrix in the case of cold working samples.

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REFERENCES


