

## INFLUENCE OF THE HEAT TREATMENT ON THE TENDENCY TO INTERGRANULAR CORROSION OF AUSTENITIC STAINLESS STEEL AISI 321

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***Abstract:** The paper presents the results of electrochemical testing on intergranular corrosion of stainless steel AISI 321. AISI 321 was subjected to quenching at 1050°C, sensitization at 650°C and stabilizing annealing at 850°C. Experiments were done in a 5% H<sub>2</sub>SO<sub>4</sub> water solution to determine the susceptibility of the steel in different conditions to intergranular corrosion attacks. The open circuit potential was measured till reaching a stable value of the steady state potential, and then anodic polarization was performed in the range -300...+1600 mV. The results from potentiodynamic polarization allowed to choose an etching potential in the transpassive region to reveal the tendency of the steel to intergranular attacks and to observe the microstructure. It was found that the sensitization for one hour at 650°C led to microstructural changes favourable to an increased tendency to intergranular corrosion. This result suggests that, though AISI 321 is alloyed with titanium, additional heat treatment must be taken to overcome the possibility of intergranular corrosion provoked by the changed microstructure during different technological processes, such as welding.*

***Keywords:** Stainless steel, Intergranular corrosion, Microstructure, Electrochemical corrosion.*

### INTRODUCTION

Austenitic stainless steels are usually used as a resistant to atmospheric corrosion material for household items and constructions, for transportation and chemical industries. They owe their corrosion resistance to a thin passive film, based on chromium oxide, that protects their surface from corrosive environments. For this film to form and stand protective, stainless steels must contain enough chromium that is known to transfer its ability to passivate to steels. For this to occur, chromium content in the solid solution ( $\alpha$  or  $\gamma$ ) must exceed 11.7 mass %. Austenitic stainless steels, alloyed with chromium and nickel, lose their resistance to corrosion after being heated at temperatures in the range between 450°C and 850°C and next slow cooling. In the abovementioned temperature range, chromium carbides such as Cr<sub>23</sub>C<sub>6</sub> precipitate at grain boundaries (Cihal & Prazak, 1960), (Davis, 2000). Furthermore, for the significantly lower atomic mobility of chromium compared to that of carbon, in the formation of these carbides take part chromium atoms only from the vicinity of the grain boundaries but carbon atoms diffuse through the bulk of the grains. A corollary of this is the formation of a thin, 20 nm (Aaltonen, Aho-Mantila, & Hännien, 1983), area next to grain boundaries where chromium content is lower than the required for a protective layer to form and maintain (Cihal & Prazak, 1960), (Aaltonen, Aho-Mantila, & Hännien, 1983), (Dabossi, Beranger, & Baroux, 1994). This phenomenon is displayed as the formation of a microgalvanic corrosion cell where an anode is the thin, low in chromium, boundary area of the austenitic grains, while the chromium carbides located at the boundaries play the role of a cathode. A structural state as the described leads to intergranular corrosion of stainless steels and a serious deterioration in their mechanical properties.

Lowering the tendency for intergranular corrosion of stainless steels can be achieved by two main approaches. The first one aims to decrease the possibility of chromium carbides formation either by reduction of carbon content or by stabilizing the steel with stronger than chromium carbide-forming elements (Ti and Nb). The second approach is based on suitable heat treatment, including heating at temperatures at which chromium carbides are dissolved into austenite, and next quenching with a sufficiently fast cooling rate that does not allow the formation of carbides.

The aim of the presented here experiment is to establish the tendency of an austenitic stainless steel AISI 321 to intergranular corrosion.

## EXPERIMENTAL METHODS

The tested material was AISI 321 stainless steel. The specimens were of dimensions 15x15x7 mm. The chemical composition was determined using JEOL SUPER PROBE 733 scanning electron microscope and is as follows (in mass %): 17.8% Cr; 10.5% Ni; 1.1% Mn; 07% Ti.

Beforehand, the specimens were heat treated as it is shown in Table 1.

Table 1. Used modes of heat treatment of AISI 321 stainless steel

Heat treatment	Temperature, °C	Soaking time, min	Cooling medium
Quenching	1050	20	Water at room temperature
Sensitization	650	60	Air at room temperature
Stabilization	850	30	Air at room temperature

Next, the specimens were prepared as metallographic specimens – i.e., grounded and polished. Prior to electrochemical testing, the specimens were degreased using acetone.

Electrochemical tests were carried out in a 5% water solution of H<sub>2</sub>SO<sub>4</sub> open to air and at room temperature. The tested area was 0.4 cm<sup>2</sup>. Anodic polarization was used to determine the tendency to intergranular corrosion, using a standard three-electrode cell, containing the tested specimen as a working electrode, saturated calomel electrode SCE as a reference electrode, and a platinum counter-electrode. The values of the potentials in the present report were calculated to the normal hydrogen electrode and are presented as values to the normal hydrogen electrode (NHE). The cell was connected to a RADELKIS OH405 potentiostat. The data from the potentiostat was gathered using a NATIONAL INSTRUMENTS USB-6008 controller attached to a PC. The applied potential was changed with a rate of 1 mV/s in the range of -300 mV (NHE) to +1600 mV (NHE). Before polarization, the specimens were allowed to stabilize until reaching a steady state potential, thus the change in the open circuit potential with time was observed. The information from the obtained potentiodynamic polarization curves was proceeded using eL-ChemViewer software (Hrbac, Halouzka, Trnkova, & Vacek, 2014) to determine corrosion potentials and corrosion current densities of the tested specimens. Using the obtained values, the corrosion rate CR was calculated as described in (G102-89, 1999).

Potentiodynamic curves served to determine the potential for fixed potential testing to etch grain boundaries and assess the tendency to intergranular corrosion. During fixed potential tests the samples were held at a fixed potential for 30 minutes. Next, the tested surfaces were observed using an optical metallographic microscope Epityp 2 with a digital camera attached to it. The tendency to intergranular corrosion was assessed by the degree of grain boundaries etching and their thickening during the fixed potential test.

## RESULTS AND DISCUSSION

Figures 1 and 2 represent the results of the electrochemical testing. Measured and calculated electrochemical characteristics are shown in Table 2.

Figure 1 demonstrates the influence the heat treatment had on the open circuit potential and the steady state potential of AISI 321. The data in Figure 1 shows that processes that worsened the corrosion resistance of AISI 321 occurred during heat treatment as the open circuit potential and steady state potential of the untreated specimen had more positive values than those of the heat-treated samples. Thus, it can be speculated upon the thermodynamical stability of the treated samples as it is a well-known fact that the steady state potential can be used to assess this stability of a metal.

Quenching from 1050°C did not change the behaviour of AISI 321 during polarization in the used 5% H<sub>2</sub>SO<sub>4</sub> water solution as can be seen in Figure 2. This is confirmed from the data in Table 2 – corrosion current densities  $i_{cor}$  and corrosion rates CR of the as-received specimen and of the quenched specimen were of the same order, corrosion potentials  $E_{cor}$  of both specimens differed by less than 100 mV, and transpassivation potentials were practically equal.

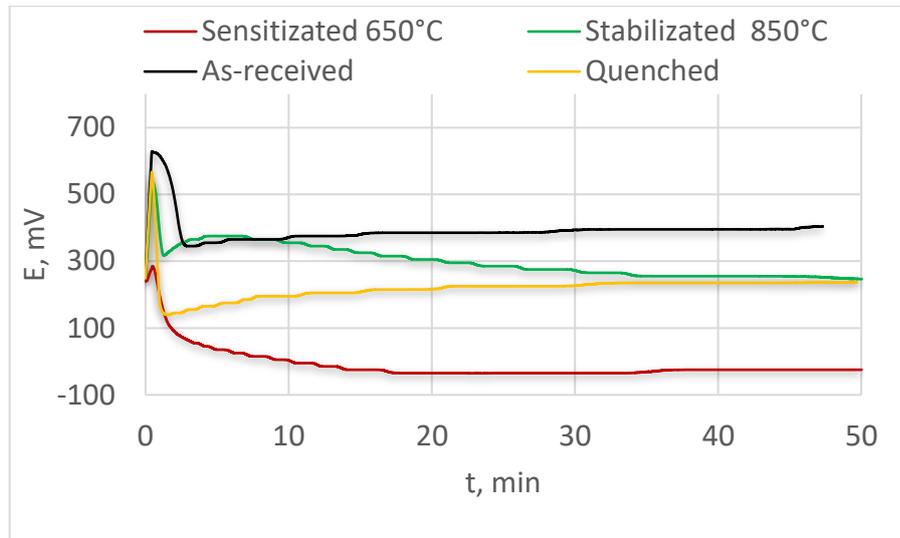


Fig. 1. Open circuit potential of AISI 321 in different conditions in 5% H<sub>2</sub>SO<sub>4</sub> water solution

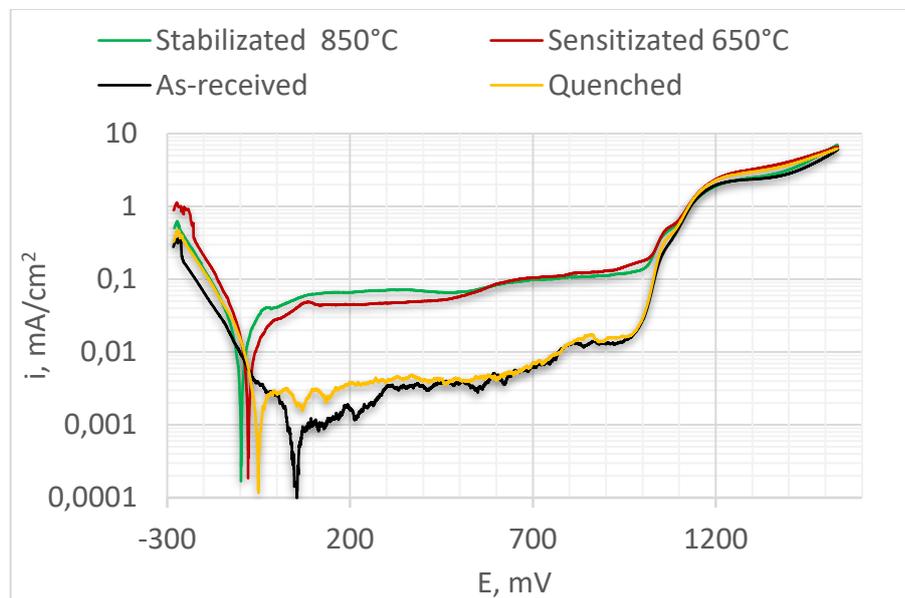


Fig. 2. Potentiodynamic polarization curves of AISI 321 in different conditions in 5% H<sub>2</sub>SO<sub>4</sub> water solution

This is not the case after sensitization and stabilization. It can be seen in Figure 2 that these treatments led to a worsening in the behaviour of AISI 321 in the used aggressive media. Both heat treatments (sensitization and stabilization) resulted in an increase in the current densities of AISI 321 by one order of magnitude compared to the specimen in as-received condition and after quenching. As the anodic branches of potentiodynamic curves are plotted as a sum of intergranular dissolution and dissolution within the bulk of the grains, the anodic current densities cannot plainly express the tendency of the specimens to intergranular corrosion. Thus, to correctly assess the tendency to intergranular corrosion, fixed potential testing was applied.

The fixed potential was chosen considering the known from the specialized literature fact that the anodic dissolution of austenitic steels occurs at two potential ranges – at the transition from active to passive state of potentiodynamic curves, and at the transition from passive to transpassive state (Landolt, 2007). As the curves obtained from our experiments did not show a transition from an active to a passive state, the fixed potential was chosen in the transpassive state. The specific value of the fixed potential was +1500 mV (to be sure all the specimens were in a transpassive state). When stainless steels are in the transpassive state, preferable dissolution of Cr<sub>23</sub>C<sub>6</sub> occurs. Furthermore, for the change of the passive layer in acid media from an insoluble Cr<sub>2</sub>O<sub>3</sub> to a soluble Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, an increased rate of intergranular dissolution is observed even for steels that were not

sensitized (that do not have precipitates of chromium carbides on grain boundaries) (Fauvet, et al., 2008).

Figure 3 represents the change of current densities with time during fixed potential testing. Optical micrographs of the tested surfaces can be seen in Figure 4. Figure 3 shows that during fixed potential testing all the specimens dissolved with close current densities – between 6 and 8 mA cm<sup>-2</sup>. The highest current density during the anodic dissolution was measured for the sensitized specimen, and one can speculate that after sensitization at 650°C, AISI 321 had the highest tendency to intergranular corrosion. This was confirmed by the state of the tested surfaces, visible in Figure 4.

Table 2. Electrochemical characteristics of AISI 321 in different conditions

Steel condition	E <sub>ss.</sub> , mV	E <sub>cor.</sub> , mV	E <sub>tr.</sub> , mV	i <sub>cor.</sub> , μA cm <sup>-2</sup>	CR, mm/yr
As-received	403	52	965	0,17	0,002
Quenching 1050°C	237	-47	965	0,64	0,007
Sensitization 650°C	250	-76	1015	1,52	0,016
Stabilization 850°C	-25	-98	1036	1,15	0,015

E<sub>ss.</sub> – steady-state potential; E<sub>cor.</sub> – corrosion potential; E<sub>tr.</sub> – transpassivation potential; i<sub>cor.</sub> – corrosion current density; CR – corrosion rate.

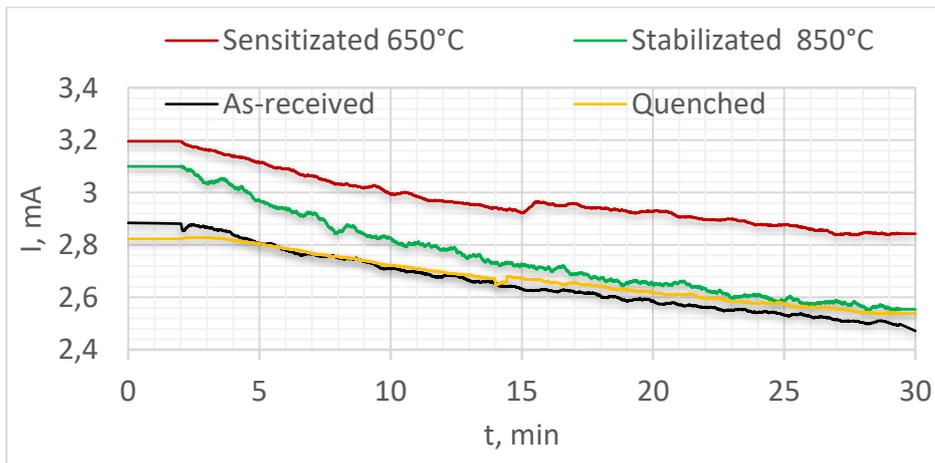
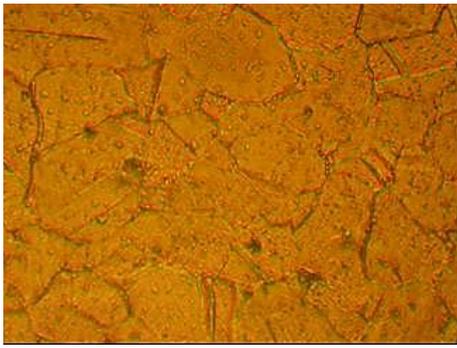


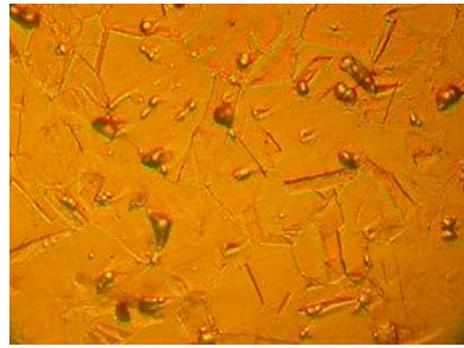
Fig. 3. Curves of anodic dissolution of AISI 321 in different conditions in 5% H<sub>2</sub>SO<sub>4</sub> water solution

The microstructure of the as-received steel demonstrated dissolution on only a portion of the grain boundaries – Figure 4a. The outlined grain boundaries were thin, and this suggested a low tendency to intergranular corrosion. The quenched specimen of AISI 321 had a surface in relief of preferred dissolution of differently oriented grains and twins in the austenitic grains, while their boundaries were not outlined – Figure 4b. This demonstrates that during quenching from 1050°C, chromium carbides did not precipitate and AISI 321 was resistant to intergranular corrosion.

The microstructure of the sensitized AISI 321 is shown in Figures 4c and 4e. It can be seen from these microphotographs that sensitization at 650°C led to the full dissolution of grain boundaries during fixed potential testing, and the outlined grain boundaries were thick. Therefore, sensitization at 650°C had as a corollary the formation of an uninterrupted network of chromium carbides on the grain boundaries, despite the fact the steel had been alloyed with titanium. Similar behaviour of an alloyed with titanium stainless steel is described in (Padilha & Rios, 2002) too. The higher current densities during the anodic dissolution of the sensitized specimen were due to the relatively high anodic area of this specimen (the thin area, low in chromium content next to grain boundaries). The sensibilization at 850°C also led to grain boundaries dissolution but not all boundaries were affected – Figures 4d and 4f.



a) AISI 321 in the as-received state, x500



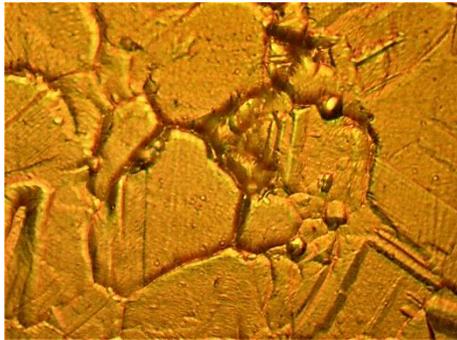
b) AISI 321, quenched from 1050°C in water, x500



c) AISI 321, sensitized at 650°, and air-cooled, x500



d) AISI 321, stabilized at 850°, and air-cooled, x500



e) AISI 321, sensitized at 650°, and air-cooled, x1000



f) AISI 321, stabilized at 850°, and air-cooled, x1000

Fig. 4. Microstructure of AISI 321 in different conditions after anodic dissolution in 5% H<sub>2</sub>SO<sub>4</sub> water solution at a fixed potential of +1500mV for 30 minutes

## CONCLUSIONS

The experimental results show that, despite the stabilization of stainless steel AISI 321, under some working conditions or during some technological processes, such as welding, this steel can achieve a tendency to intergranular corrosion damage. Thus, the working conditions and technological parameters should be monitored, and suitable heat treatment should be included in the technological schemes to prevent future intergranular corrosion of stainless steel AISI 321.

The presented experiment allows the following conclusions to be made:

1. Quenching from 1050°C in water of stainless steel AISI 321 does not change the ability of the steel to passivate during the polarization test till the transpassivation potential.
2. Stainless steel AISI 321 tends to intergranular corrosion after sensitization at 650°C for one hour.

3. To avoid possible corrosion damage, stainless steel AISI 321, despite being alloyed with titanium, must be heat treated if during operation or technological treatments the steel is heated to temperatures, close to 650°C.

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