Susceptibility to the intergranular attack in austenitic stainless steels

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Abstract. Intergranular corrosion is very dangerous local corrosion form that often leads to the dislodgment of individual grains and to the intensive negative influence on the mechanical properties of the material. The susceptibility of the austenitic stainless steels to the intergranular corrosion is connected with their exposition in the temperature range of 500-800 °C (“critical temperatures”) and with consequent slow cooling in the air which leads to the precipitation of chromium-rich carbides at the grain boundaries. This process consumes chromium from a narrow band along the grain boundaries and the steel becomes to be sensitized and susceptible to the intergranular corrosion in aggressive environments. This article deals with the susceptibility to the intergranular corrosion of three austenitic stainless steels (AISI 304, 316L, 316Ti). Both “as received” and improperly heat treated specimens (sensitization for 10 hours at 650 °C, cooling in the air) were tested by ASTM A262 standard method, A and E practices. Optical microscopy and SEM analysis were used for the assessment of the obtained results.

1. Introduction
Intergranular corrosion is the special form of local corrosion, which can occur in many alloy systems when the corrosion rate of the grain-boundary areas is higher than that of the grains interiors. The result is the corrosion of a narrow path preferentially along the grain boundaries. This localized attack is very dangerous because the surface damage of the material is usually easily overlooked but it often leads to the dislodgment of individual grains and to the intensive negative influence on the mechanical properties. Although the detailed mechanism of intergranular corrosion varies with each metal system, its physical appearance at the microscopic level is quite similar for most systems [1-4].

Intergranular corrosion is very typical corrosion attack in austenitic stainless steels. In common oxidizing environments these steels have good corrosion resistance due to the formation of passive protective surface film. However, under the action of aggressive halide ions, local breakdown of passivity occurs, causing pitting corrosion [2, 5-6]. The susceptibility of the austenitic stainless steels to the intergranular corrosion is connected with their exposition in the temperature range of 500 – 800 °C (“critical temperatures”) and with consequent slow cooling in the air which leads to the precipitation of $\text{M}_{23}\text{C}_6$ chromium-rich carbides on the grain boundaries [7-9]. The precipitation of chromium carbides consumed the main alloying element - chromium from a narrow band along the grain boundary and this makes the zone anodic to the unaffected grains. If the chromium content near the grain boundaries drops under the passivity limit (11.5 wt. %), the steel becomes to be sensitized...
and susceptible to the intergranular corrosion in aggressive environments. The chromium depleted zone becomes the preferential path for corrosion attack or crack propagation if under tensile stress [1-4, 7]. The sensitisation temperature range is often encountered during isothermal heat treatment, slow cooling from the solution annealing temperature, improper heat treatment in the heat affected zone of the welds or weld joints or hot working of the material. Degree of the sensitisation is influenced by the factors such as the steel chemical composition, grain size, degree of strain, or temperature and time of isothermal annealing [7].

This article deals with the susceptibility to the intergranular corrosion of three austenitic stainless steels (AISI 304, AISI 316L, and AISI 316Ti). Both “as received” and improperly heat treated specimens (sensitization for 10 hours at 650 °C, cooling in the air) were tested by ASTM A262 standard method, A and E practices. Optical microscopy and SEM analysis were used for evaluation of the obtained results.

2. Experimental material

AISI 304, AISI 316L and AISI 316Ti austenitic stainless steels with chemical compositions in table 1 were used as the experimental material. They were purchased in sheets (1000 x 2000 mm) of 1.5 mm thickness. Their production processes were based on continuous casting in electric arc furnace. Then they were annealed (AISI 304 at 1040 – 1100 °C, AISI 316L and 316Ti at 1050 °C). The IIB surface finish (smooth and matte metallic glossy surface) was realized by pickling after slightly smoothing rolling [10]. Microstructures of “as received” steels (figure 1) are polyhedral, created by austenitic grains with numerous twins, which could be created by annealing or by rolling.

|             | Cr   | Ni   | Mo | Ti | Mn  | N    | C    | Si   | P    | S    | Fe    |
|-------------|------|------|----|----|-----|------|------|------|------|------|-------|
| AISI 304    | 18.00| 8.01 | -  | -  | -    | 1.40 | 0.075| 0.027| 0.38 | 0.031| 0.0037| balance |
| AISI 316L   | 16.79| 10.14| 2.03| -  | -    | 0.82 | 0.05 | 0.02 | 0.31 | 0.03 | 0.001 | balance |
| AISI 316Ti  | 16.54| 10.56| 2.02| 0.303| 1.07 | 0.009| 0.023| 0.48 | 0.032| 0.006| balance |

Table 1. Chemical compositions of experimental stainless steels (wt. %).

Figure 1. Microstructures of the experimental stainless steels in “as received” state, longitudinal sections: A) AISI 304 (glycerine + HNO₃ + HCl etch.); B) AISI 316L (Kallings 2 etch.); C) AISI 316Ti (Kallings 2 etch.).
The steels are of different size of grains. The orange colored cuboid-shaped titanium carbides are markedly seen in AISI 316Ti microstructure (figure 1C).

3. Experimental procedure
The rectangular specimens (14 mm x 40 mm x 1.5 mm) were prepared for experiments. A part of specimens were improperly heat-treated to evoke a sensitization. Then both “as received” and heat-treated specimens were tested by ASTM A262 standard method A and E practices for an assessment of their susceptibility to the intergranular corrosion.

Heat treatment of specimens was performed in furnace at 650 °C for 10 hours with consequent slow cooling to create suitable diffusion conditions for precipitation of chromium carbides. The temperature of 650 °C was chosen according to the graph of carbon solubility in austenite [5].

The oxalic acid etch test was performed according to A practice of ASTM A262 standard method under the conditions listed in table 2 [11]. The specimen surfaces were mechanically treated by grinding (500 and 1000 mesh) before the electrochemical etching process. For the etching, each specimen was immersed into electrolyte and connected to the positive pole of the power source as an anode. A cathode was of the same material as the anode [11]. The etched surfaces (the specimen sides facing the cathode) were evaluated by the ZEISS Observer 21M microscope.

Table 2. Conditions of the electrochemical etching (ASTM A262, A practice).

| Solution component | Content (wt. %) | Temperature (°C) | Current density (A.cm$^{-2}$) | Time (s) |
|--------------------|----------------|------------------|-------------------------------|----------|
| oxalic acid        | 10             | 20 ± 3 °C        | 1.0                           | 90       |
| demineralized water| 90             |                  |                               |          |

The specimens for E practice of ASTM A262 standard method (Strauss test) were metallographically prepared. Then they were placed on electrolytic copper pieces and immersed into solution. The test was carried out according the conditions listed in table 3 [11]. The specimens after Strauss test were studied by the ZEISS Observer 21M microscope and by SEM analysis (Tescan Vega microscope).

Table 3. Conditions of Strauss test (ASTM A262, E practice).

| Solution component        | Content (wt. %) | Temperature (°C) | Time (hours) |
|---------------------------|-----------------|------------------|--------------|
| copper sulfate (anhydrous)| 6               | 100 °C           | 15           |
| sulfuric acid             | 16              |                  |              |
| demineralized water       | 78              |                  |              |

4. Experiment results and discussion
The microstructure of specimens after heat treatment (sensitization) visualized by classical chemical etching (Kallings 2) shows no radical changes (figure 2) only some grain boundaries are highlighted compared to the "as received" state. On the AISI 316Ti specimen (figure 2C), titanium carbides are concentrated into clusters (similar clusters are not visible in the "as received" state). Due to the minimal differences between the "as received" and post-heat treatment states can be deduced that the chemical etching used did not enable to visualize a possible precipitation of chromium carbides at the grain boundaries caused by the given improper heat treatment.

The oxalic acid etch test is used in connection with other tests as a rapid method for identifying those specimens which are certain to be free of susceptibility to the rapid intergranular attack in the various hot acid tests (4 to 240 hours of exposure) [11]. The assessment of the susceptibility to the intergranular corrosion is based on the classification of grain boundaries attack [3, 7, 11] that distinguishes three types of etch structures (step, dual and ditch structures). If there are no ditches at grain boundaries only steps between grains the structure is marked as the step one. This structure type indicates the highest resistance to the intergranular corrosion.
The presence of ditches indicates the dissolution of carbides at the grain boundaries during the previous etching process. When no single grain is completely surrounded by ditches, the structure is marked as the dual one. The ditch structure is reflected by one or more grains completely surrounded by ditches [3, 7, 11].

According to microstructures after the etch test (figures 3 and 4) AISI 304 and AISI 316L steels showed strong differences in intergranular corrosion susceptibility between the “as received” and the sensitized state.

The step structures in the “as received” state could be caused by the different dissolution rates of the variously oriented grains and they are probably not related to the chromium carbides precipitation. Therefore can be concluded that these steels were not exposed to critical temperatures in the production process, and thus they were not sensitized.
A)  B)

Figure 4. Microstructure of AISI 316L after the etch test: A) “as received” state; B) the state after heat treatment (sensitization).

As shown in figures 3B and 4B the microstructures of 304 and 316L steels after sensitization can be classified as the ditch ones. Carbides, precipitated at grain boundaries during the heat treatment, dissolved during the etching process and ditches were formed. Ditches in AISI 316L microstructure (figure 4B) are lighter-colored than the ones in the AISI 304 specimen (figure 3B). A lighter color of the etched ditches indicates their smaller depth compared to the dark ones. Accordingly, AISI 304 steel after sensitization exhibited higher susceptibility to the intergranular corrosion than AISI 316L steel. Also the authors [7] observed similar ditch structures of austenitic steels.

Unlike 304 and 316L steels, AISI 316Ti steel stabilized by titanium reflected the minimal difference between the “as received” and the sensitized state (figure 5), without the grains surrounded by ditches. According to performed etch test it points to the highest resistance to the intergranular corrosion.

A)  B)

Figure 5. Microstructure of AISI 316Ti after the etch test: A) “as received” state; B) the state after heat treatment (sensitization).

Strauss test (E practice of ASTM A262 standard method) is usually used for a confirmation of the susceptibility to the intergranular corrosion in the case of the positivity of the etch oxalic acid test (appearance of ditch structures). In this study the Strauss test was carried out on all specimens regardless of results of the etch test. The aim was to compare the both tests and to find out which one is more precise, comfortable and which one suits to the quick assessment the susceptibility of austenitic steels to the intergranular attack. The microstructures after Strauss test are shown in figures 6–8.
Figure 6. Microstructure of AISI 304 after Strauss test: A) the “as received” state; B) the state after heat treatment (sensitization); C) the state after heat treatment (sensitization) – detail of the attacked grain boundaries (SEM).

Figure 7. Microstructure of AISI 316L after Strauss test: A) “as received” state; B) the state after heat treatment (sensitization).

Strauss test confirmed a susceptibility of AISI 304 stainless steel exposed to the critical temperatures to the intergranular corrosion (figure 6B, 6C). 15-hour exposition of the sensitized specimen in aggressive acidic hot solution evoked marked corrosion attack at the chromium depleted zone along the grain boundaries. As can be seen in figure 7B, unlike the etch test AISI 316L influenced by the critical temperatures did not reflect any corrosion attack at the grain boundaries. This result points to the relevance of the both independent tests in the case of light colored (= shallower) ditches at the grain boundaries obtained by the etch test. Both performed tests confirmed the high resistance of AISI 316Ti stainless steel to the intergranular corrosion (figure 8).
Figure 8. Microstructure of AISI 316Ti after Strauss test: A) “as received” state; B) the state after heat treatment (sensitization).

5. Conclusion
Based on the results of performed experiments, it can be concluded:

- Microstructures after heat treatment (sensitization) visualized by classical chemical etching (Kallings 2) showed no radical changes compared to the “as received” state and a precipitation of the chromium carbides at the grain boundaries was not observed.

- The microstructures of the tested steels after the etch test (A practice) in the "as received" state did not show ditch structures caused by the dissolution of chromium carbides at the grain boundaries. After improper heat treatment (sensitization), the microstructures of AISI 304 and AISI 316L steels after etch test showed a ditch attack at the grain boundaries. In the AISI 316Ti microstructure the similar ditch structures were not observed.

- Strauss test (E practice) confirmed high susceptibility of improperly heat treated AISI 304 and high resistance of AISI 316Ti stainless steels to the intergranular corrosion. Strauss test did not confirm results of the etch test of the sensitized AISI 316L, the intact grain boundaries indicated high resistance to the intergranular corrosion.

- All three steels in “as received” state showed high resistance to intergranular corrosion and it means they were not exposed to critical temperatures during the production process (they were not sensitized).

According to the performed experiments the etch test can be considered more comfortable than Strauss test. Unlike Strauss test the microstructures obtained by the etch test were well readable even without metallographic preparation of the specimens. Except for AISI 316L specimen (ditch structure with light coloured shallow ditches) the etch test brought clear results.

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