

AN AES INVESTIGATION OF BRUSHED AISI 304 STAINLESS STEEL AFTER CORROSION TESTING

AES-PREISKAVE KRTAČENEGA NERJAVNEGA JEKLA AISI 304 PO KOROZIJSKEM PRESKUSU

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During a test in a wet salt (NaCl) chamber rusty spots and elongated pits appeared on the brushed surface of a prototype casing for a household device made from AISI 304 stainless steel. The corrosion pits only formed on the brushed surface and on the deformed edges. Metallography revealed deformation-induced martensite and delta ferrite in the microstructure. In the wet salt environment the brushed surface showed a lower corrosion resistance than the non-brushed surface. The corrosion was explained as being due to damage to the protective oxide layer with brushing, insufficient re-passivation and the presence of iron particles. The corrosion propensity of the brushed surface of the casing was increased by the presence of deformation-induced martensite, delta ferrite and, probably, the remains of iron particles. The use of AISI 316 stainless steel, alloyed with molybdenum, would be more appropriate for avoiding the formation of corrosion pits due to chloride ions in a wet environment.

Key words: stainless steel, pitting corrosion, passivation, deformation-induced martensite, AES analysis

Ohišje prototipne gospodinjске naprave je bilo izdelano iz nerjavnega jekla AISI 304. Iz dekorativnih razlogov je bila površina krtačena. Med preskusom v vlažni slani komori se je pojavila korozija v obliki rjastih madežev in podolgovatih jamic vzdolž zakrivljenega roba. Predstavljeni so rezultati metalografske preiskave in analiza korozijskih produktov. Korozijske jamice se opazi samo na predhodno krtačeni površini in po deformiranih robovih. Z metalografskimi preiskavami smo odkrili v mikrostrukturi po deformiranih robovih prisotnost deformacijskega martenzita in delta ferita. V vlažnem slanem (NaCl) okolju je krtačena površina pokazala slabšo korozijsko odpornost v primerjavi z neobdelano površino. Glavna razloga za korozijo sta med krtačenjem poškodovan oksidni sloj in slaba repasivacija po krtačenju. Dodatno so lahko k pojavu korozije prispevali še deformacijski martenzit, delta ferit in ostanki delcev železa na površini. Posledica slabše korozijske odpornosti je pojav jamičaste korozije v vlažnem, slanem okolju. Za zmanjšanje možnosti pojava jamičaste korozije bi bila bolj primerna izbira nerjavnega jekla AISI 316, ki je legirano z molibdenom in s tem bolj odporno proti pojavu jamičaste korozije.

Ključne besede: nerjavno jeklo, jamičasta korozija, pasivacija, deformacijski martenzit, AES analiza

1 INTRODUCTION

The passive film on a stainless-steel surface consists of a mix of iron oxide and chromium oxide. The chromium oxide film is formed instantaneously in the air, if the stainless steel surface is clean and dry. However, complete passivation cannot be achieved if the product-contact surfaces are not clean or they contain surface defects. The polishing of the stainless steel's surface, therefore, improves the corrosion resistance¹. The resistance to pitting corrosion is also increased by alloying the stainless steel with molybdenum. The beneficial effect of molybdenum on the corrosion resistance of stainless steels is widely recognized^{2,3,4} and has been attributed to several factors⁴, such as: the enrichment of Cr in the oxide layer; the enrichment of Mo in the passive film or in the alloy layer just below the passive film; the thickening of the passive film; and the stabilisation of the Cr oxides by the presence of six-valence Mo⁵.

The interaction between the different oxides and the passivation/corrosion characteristics of stainless steel are very complicated and not yet fully understood.

Different surfacing techniques are applied to stainless steel to obtain a special visual effect on the surface. The brushing of stainless steel's surface is popular because it gives an attractive look to the surface. The protection from contamination of the steel surface requires the brushing of the stainless steel to be with stainless-steel brushes. In the event that iron particles on the stainless-steel surface are not removed by cleaning or by passivation in acid, subsequent pitting corrosion usual appears in a wet environment⁶.

An additional influence on the corrosion resistance of the material comes from different constituents of the microstructure, like carbides, martensite, delta ferrite and inclusions. Also well known is the harmful influence of deformation-induced martensite^{7,8}, which forms during the cold working of stainless steel. After cold working the stainless steel needs to be annealed at 1050 °C in order to transform the martensite to austenite. Furthermore, residual stresses in the material can induce stress-corrosion cracking and accelerate the appearance of other corrosion forms when the material is exposed to a corrosive environment. Pitting corrosion due to chloride ions can cause considerable damage to the steel

surface; it penetrates deep into the material and causes local weak points or even perforations of the wall.

The process of pitting corrosion is well defined, but frequently the reasons for its starting are not clearly defined. The pit can form only in places where the passive layer is interrupted. The well-known standard work on corrosion ⁸ states that pits form more readily on etched or ground surfaces than on a polished surface, and the presence of cold working can increase the propensity to pitting.

The corrosion resistance of stainless steel also depends on the amount of carbon in the steel. The precipitation of carbides depletes the neighbourhood of chromium and accelerates the intercrystalline and pitting corrosion. Besides martensite and the presence of iron particles, the corrosion is also accelerated by delta ferrite and sulphide inclusions.

When the pits start to grow, the corrosion process diminishes the pH in the pit bottom and chloride ions move towards the pit. This accelerates the pit growth in terms of depth, which can lead to the perforation of the sheet and a leak in the wall or the failure of the structure. For these reasons, many factors should be considered for the selection of suitable stainless steel. The investigated stainless steel showed failures typical for pitting corrosion.

The aim of the investigation was to analyse the corrosion residue on the stainless steel's surfaces and to identify the main reasons for the corrosion.

2 EXPERIMENTAL

The investigated samples were from a corrosion-tested AISI 304 stainless-steel casing with a previously brushed surface. The composition of the investigated steel is listed in **Table 1**.

The corroded surface of the casing was carefully visually and macroscopically surveyed and typical corroded samples were cut for a metallographic investigation and for an AES analysis. The samples for metallographic observation were prepared by the standard procedure and etched in aqua regia. The microstructure was investigated with an optical microscope, the surface defects were observed with a stereo microscope and in a scanning electron microscope. The corrosion products were analysed by Auger spectroscopy (AES). Before the AES analysis, the surface was cleaned for 45 min with ion etching. For the AES analysis an electron source of Mg Ka (1253.6 eV) was used, and the results were compared with the

reference database of binding energies ⁹ accessible at the URL: <http://srdata.nist.gov/xps/>.

3 RESULTS AND DISCUSSION

A careful visual and stereo-microscope examination revealed spots of rust, white remnants identified as sodium chloride (**Figure 1**) and corrosion pits on the surface of the case. After the corrosion test a difference was observed when comparing the brushed (**Figure 2**) and non-brushed surface (**Figure 3**) of the case. The corrosion pits were only observed on the brushed surface, while the non-brushed surface was without any corrosion damage.

The rusty spots in **Figure 1** represent the remains of dried rust and were easily removed from the non-brushed surface. Most of the surface below the rusty spots was without any corrosion damage. The possible sources of rust were cut edges, holes for screws and deformed regions where the sheet was bent. It is also important not to neglect the remnants of other material that was in contact with the sheet, like for instance, fragments of the brush. It seems that a liquid, contaminated with rust, was spread over the sheet, and after drying the rust spots remained on the non-corroded steel surface.

SEM microscopy of the brushed surface revealed individual corrosion pits and groups of corrosion pits (**Figure 2**). The longitudinal traces of brushing are evident on one side of the sheet, while the opposite side

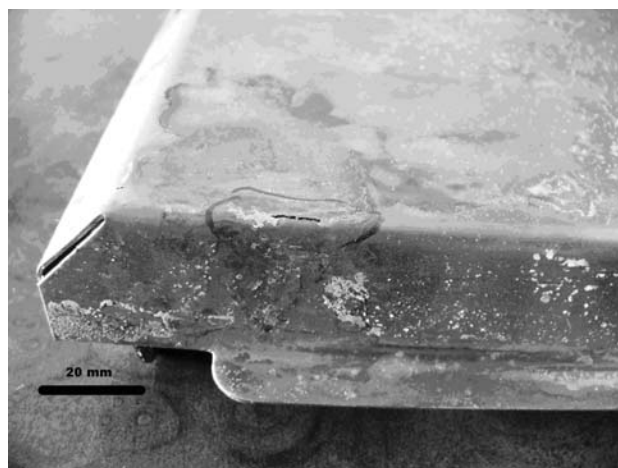


Figure 1: Remains of rust and NaCl on the surface of AISI 304 stainless steel after a corrosion test in wet salt chamber. The longitudinal pit is present on the bent edge

Slika 1: Ostanki rje in NaCl na površini AISI 304 nerjavnega jekla po korozijskem preskusu v vlažni slani komori. Na upognjenem robu se opazi vzdolžno jamičasto izjedo

Table 1: Chemical composition of the AISI 304 steel

Tabela 1: Kemična sestava jekla AISI 304

Composition	Element in mass fractions wt/%								
	C	Si	Mn	Cr	Ni	Mo	N	Cu	S
AISI 304	0.053	0.48	1.42	17.4	8.3	0.39	0.04	0.14	0.024

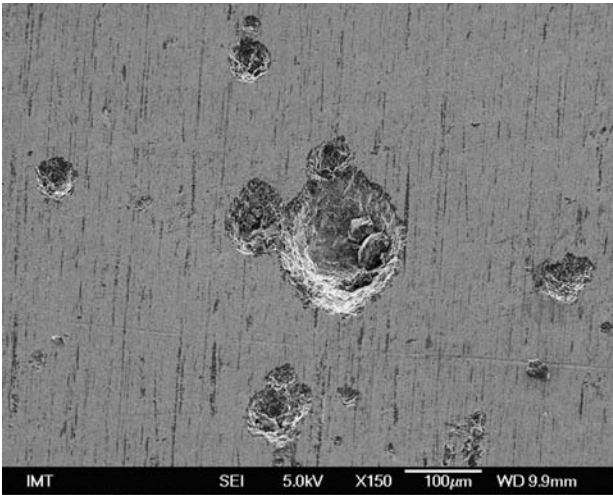


Figure 2: Corrosion pits on the brushed surface after the corrosion test. SEM

Slika 2: Jamičasta korozija na krtačeni površini po korozijskem preskusu. SEM

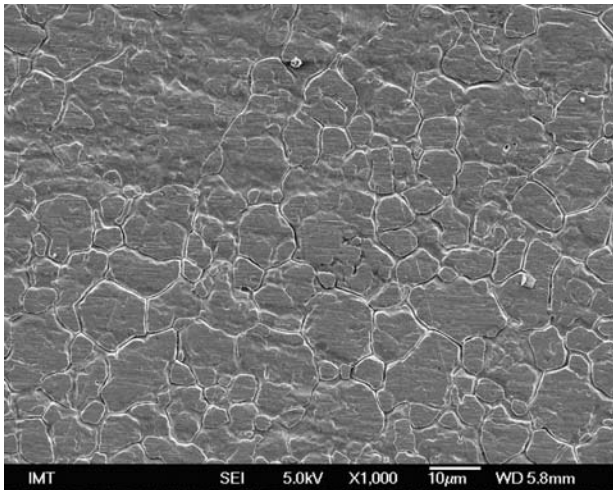


Figure 3: Untreated surface after the corrosion test. SEM

Slika 3: Neobdelana površina po korozijskem preskusu. SEM

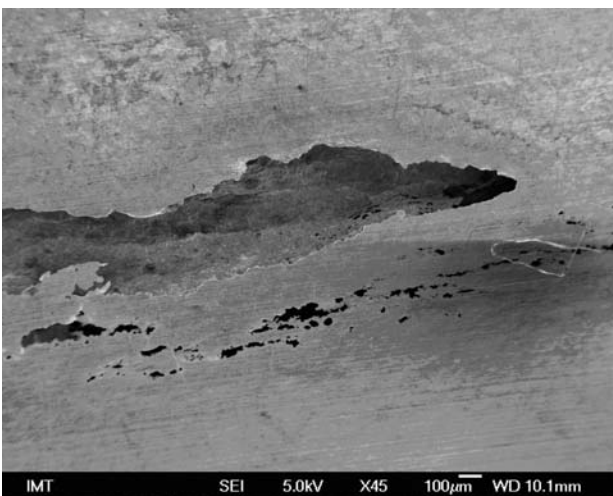


Figure 4: Longitudinal corrosion pit on the bent edge. SEM

Slika 4: Vzdolžne korozijske jamice na upognjenem robu. SEM



Figure 5: Micrograph of cross-section of the corrosion pit on the bent edge. Local corrosion advanced deep into the material of the case wall
Slika 5: Posnetek preseka korozijske jamice na upognjenem robu. Lokalno je korozija prodrla globoko v material stene ohišja

of the sheet and the non-brushed surface revealed equiaxed grains with clearly defined grain boundaries (**Figure 3**). Only the brushed surface and the bent edge of the sheet were damaged by corrosion, and on the curved edge longitudinal pits were observed (**Figure 4**). In corrosion-damaged regions we observed either the aggregation of shallow pits or individual deep pits (**Figures 2 and 5**).

The metallography revealed martensite in the deformed regions in the austenitic matrix. Also, elongated delta ferrite (**Figure 6**) was present in the matrix. Both phases were a possible source of the corrosion, when in contact with the corrosion medium.

Because of the wet environment and the presence of chloride ions in the salt chamber, the local pitting corrosion process started and advanced to the middle of the sheet, as revealed by the optical microscopy in the cross-section (**Figure 5**). The corrosion process was also accelerated by the presence of deformation-induced martensite. To transform the martensite into austenite, it is necessary to anneal the stainless steel after cold deformation.

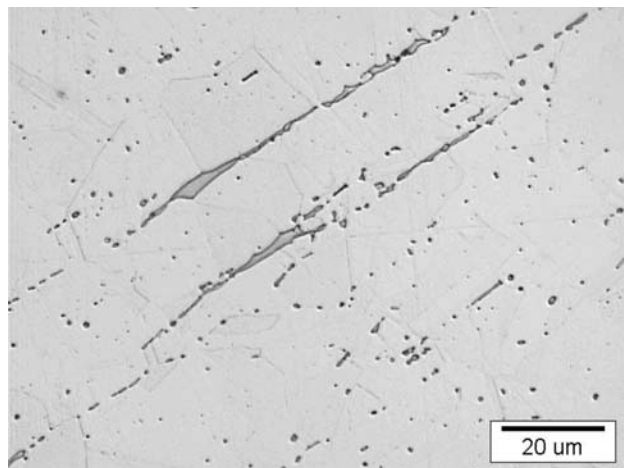


Figure 6: Microstructure of austenitic stainless steel AISI 304 with elongated delta ferrite. In deformed regions the deformation-induced martensite was also present. Etched with aqua regia.

Slika 6: Mikrostruktura avstenitnega nerjavnega jekla AISI 304 z razpotegnjenim delta feritom. V deformiranih področjih je bil prisoten tudi deformacijski martenzit. Jedkano v zlatotopki.

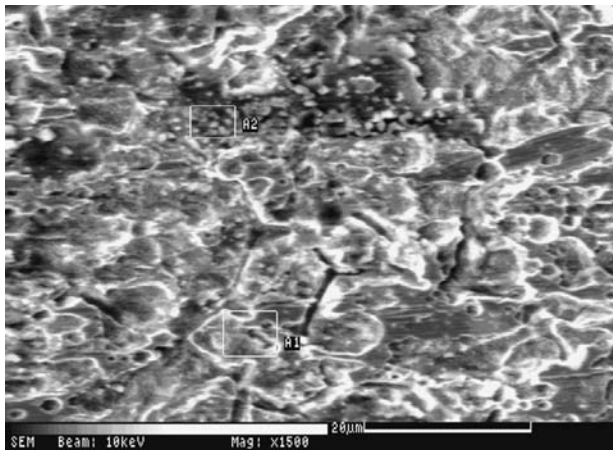


Figure 7: Surface damaged by corrosion (SEM). A1 and A2 mark the areas analysed with AES. Before the analyses the surface was ion etched for 45 minutes.

Slika 7: Površina poškodovana s korozijo (SEM). A1 in A2 sta področji, ki sta bili analizirani z AES. Pred analizo je bila površina 45 minut ionsko jedkana.

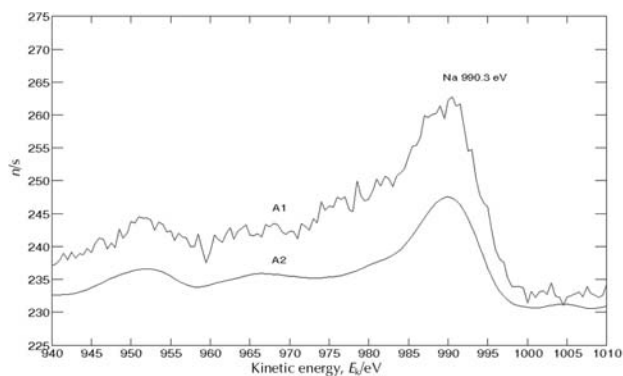


Figure 8: AES spectrum on the corroded places A1 and A2 marked in **Figure 7**. Presented peak for Na KLL at 990.3 eV in non-differentiated spectrum of AES corresponds to Na in NaCl⁹

Slika 8: AES-spekter na področjih korozije A1 in A2 označenih na sliki 7. Predstavljen vrh za Na KLL pri 990,3 eV v nediferenciranem spektru AES ustreza Na v NaCl⁹

The AES analysis of the corroded steel surface (**Figures 7 and 9**) after the wet salt chamber test revealed that in the corrosion pits either sodium and chlorine or only chlorine were present (**Figure 8 and 10**). The binding energy of the analyzed element sodium corresponded to NaCl (**Figure 8**). The source of the NaCl was the wet salt chamber. No traces of sodium or chlorine were detected on the non-corroded surface (**Figure 10, P2**). But in typical use a possible source of chloride ions is from the environment (sprayed brine, the salt in food, cleaners).

The investigation of the prototype case for use in domestic and outdoor activities, e.g., a barbecue, revealed several deficiencies. The AISI 304 stainless steel is less appropriate for a wet environment where chloride ions are present. The brushing of the surface, due to aesthetic reasons, damaged the passive film on the



Figure 9: Surface with corrosion pit. At the points P1 and P2 the AES analyses were performed. The presence of Cl was detected only in the pit. SEM

Slika 9: Površina z jamičasto korozijo. Točki P1 in P2 sta bili analizirani z AES. Samo v jamiči je bil prisoten Cl

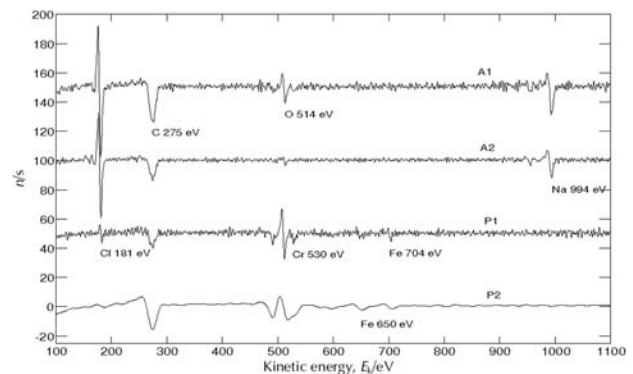


Figure 10: AES spectrum in the areas A1 and A2 (**Figure 7**), and at the points P1 and P2 (**Figure 9**) Only in the corroded areas A1 and A2 was the presence of Na and Cl detected. In the pit P1 only Cl was detected. Out of the pit no Na or Cl was detected.

Slika 10: AES spekter s področja A1, A2 (**slika 7**) in v točkah P1, P2 (**slika 9**). Samo na korodiranih področjih A1 in A2 je bila odkrita prisotnost Na in Cl, v jamiči P1 pa samo prisotnost klora. Izven jamiče ni bilo Na ali Cl.

steel's surface. A possible accelerator of the corrosion was the presence of deformation-induced martensite and delta ferrite in the microstructure of the steel, as well as unremoved iron particles on the steel's surface.

4 CONCLUSIONS

The corrosion test in the wet salt chamber revealed that the brushed surface was sensitive to pitting corrosion, but the unbrushed surface was corrosion resistant. From this we concluded that the corrosion of the prototype stainless-steel casing is very probably due to the smoothing that damaged the passive layer on the steel's surface. The re-passivation was too weak and the pitting corrosion appeared during the corrosion test due to the presence of iron particles and chloride ions in the

wet environment. The appearance of pitting corrosion is also to be expected during use.

The investigation of the prototype casing revealed that the wrong type of stainless steel had been selected for the proposed application.

Compared to AISI 304 the AISI 316 stainless steel should be more suited to the application in a wet environment where chloride ions are also present. Alloying with 2–3 wt% of molybdenum reduces the sensitivity of the steel to pitting corrosion.

It is also advisable to passivate the surface of the stainless steel with diluted nitric acid to remove the iron particles from the surface. Later, during the use of the casing, it is important to clean thoroughly and to rinse with clean water all surfaces that may come into contact with chloride ions.

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