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CONTRIBUTION TO THE STUDY OF EFFECTS OF SURFACE STATE OF WELDED JOINTS IN STAINLESS STEEL UPON RESISTANCE TOWARDS PITTING CORROSION

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Successful corrosion resistance of stainless steels is based on their natural ability of passivation, i.e. formation of film of chromium oxides that prevents corrosion in many environments. Any nonuniformity of surface layers may be initial spot for corrosion processes and damages. In this contribution, beside real corrosion damages occurred in practice, results of testing of pitting corrosion resistance of weld beads made applying TIG process on AISI 316L steel grade are presented. SEM and EDX testing, as well as electrochemical corrosion testing confirmed adverse effects of heat tints zones upon corrosion resistance of stainless steels.

Key words: *stainless steel, weld joint, heat tints, pitting corrosion*

Prilog izučavanju utjecaja stanja površine zavarenih spojeva od nehrđajućih čelika na otpornost rupičastoj koroziji. Cjelokupna korozijska otpornost nehrđajućih čelika temelji na njihovom prirodnom svojstvu pasiviranja - nastanka filma kromovih oksida koji onemogućuje koroziju u mnogobrojnim sredinama, kao i to da svaka nehomogenost površinskih slojeva može biti inicijalno mjesto pokretanja procesa korozijskih razaranja. U radu su osim realnih korozijskih oštećenja na konstrukcijama iz eksploatacije, te ranije provedenih laboratorijskih ispitivanja, prikazani rezultati ispitivanja otpornosti navara izvedenog TIG postupkom zavarivanja na austenitnom čeliku oznake AISI 316L na pojavu rupičaste korozije. SEM i EDX ispitivanjima, kao i elektrokemijskim korozijskim ispitivanjima potvrđen je navedeni negativni utjecaj zona toplinskih obojenja na korozijsku postojanost nehrđajućeg čelika.

Ključne riječi: *nehrđajući čelici, zavareni spoj, zone toplinskih obojenja, rupičasta korozija*

INTRODUCTION

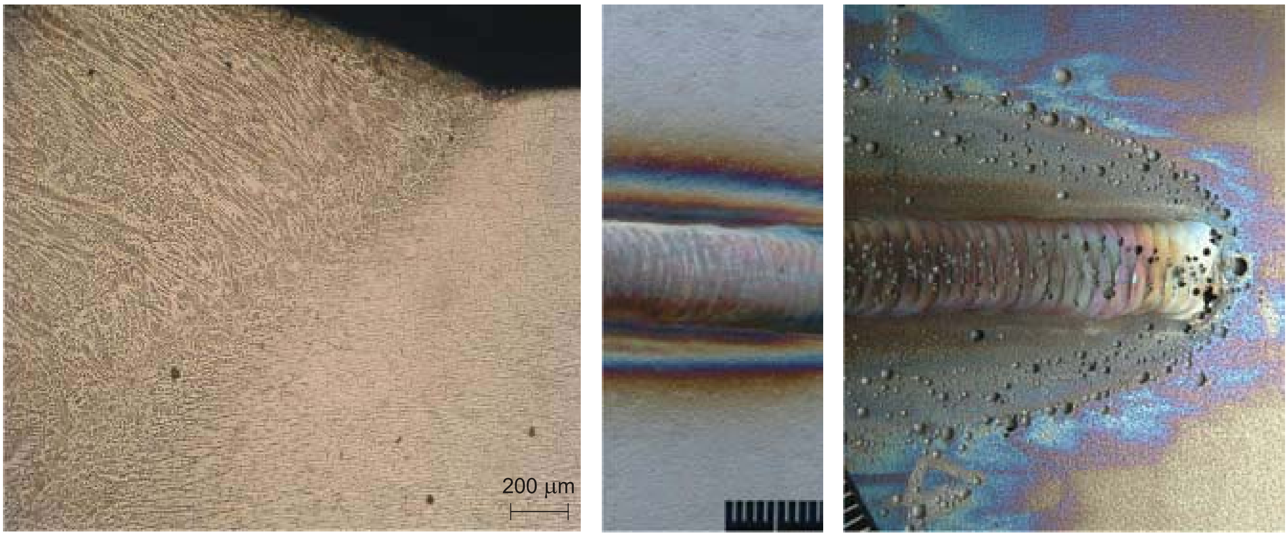
Corrosion resistant stainless steels are structural materials that meet very wide range of various requirements, from high corrosion resistance, mechanical properties or good processing characteristics. Because of their high resistance to general corrosion in various aggressive media which can be found e.g. in chemical, pharmaceutical, paper and petrochemical industry, shipbuilding, etc. they are used for production of vital components. Cr-Ni stainless steels gain their corrosion resistance through natural process of passivation - formation of passive oxide film with high Cr-content which forms on the surface in air, fresh water and in many oxidizing environments. Thickness of the Cr_2O_3 passive layer for CrNi steels is in range 1 to 10 nm. Being very thin, layer can be easily damaged. Any damage on the protective surface layer is seriously harmful to the corrosion resistance of the bulk of material. Thereby, reliability of stainless steel structures in aggressive media where stainless steel structures are often used depends mainly on few paramount factors: selected material (base and filler), applied joining technology and applied surface treatment of welded joint or whole structure.

However, under certain circumstances, even in media which are less corrosive, local depassivation takes place bringing about localized corrosion of stainless steels and causing serious accidents, especially on structures with thin walls, e. g. pipes and tanks.

Beside the structural changes occurring in the weld metal and heat affected zone caused by welding (Figure 1.a), on the surface heat tint zones are created (Figure 1.b). Considering the nature of corrosion resistance of such materials and mechanism of corrosion resistance based on the spontaneously created passive layer of chromium oxides, heat tint zones have significantly adverse effect upon the corrosion resistance of welded joint (Figure 1.c).

Pitting corrosion is the most frequent form of the electrochemical deterioration caused by local depassivation of metals that are usually in passive state like stainless

I. Juraga, V. Šimunović, Đ. Španiček, Faculty of Mechanical Engineering and Naval Architecture University of Zagreb, Zagreb, Croatia



a) Structural changes in the weld area - fusion line – right: base metal (AISI 304L), left – weld metal)

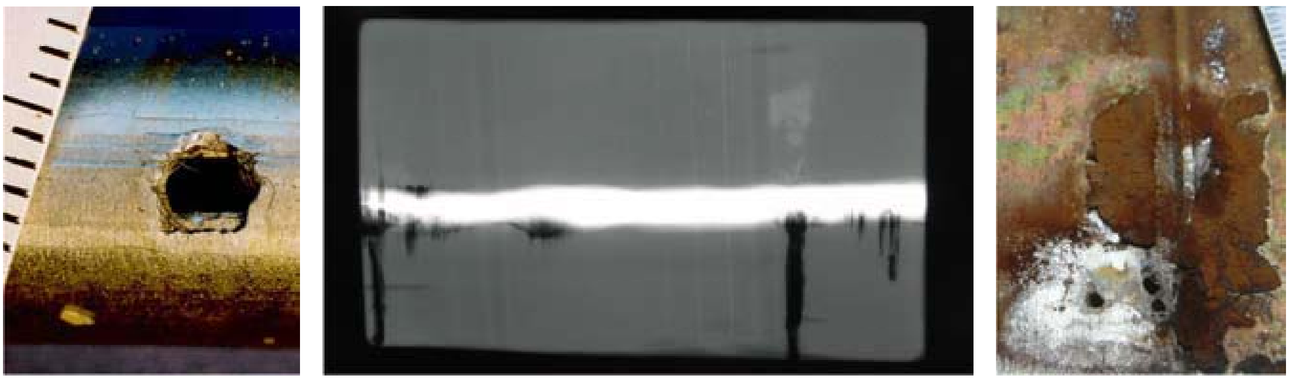
b) Formation of heat tints in the area of stainless steel welded joint

c) Appearance of the specimen in as welded condition (heat tints not removed) after corrosion testing according to ASTM G48, steel AISI 316Ti

Figure 1. **Presentation of structural and surface changes in the area of welded joint with influence of heat tints on corrosion resistance**
Slika 1. **Prikaz strukturnih i površinskih promjena u području zavarenog spoja s utjecajem zona toplinskih obojenja na korozijsku otpornost**

steels. Compact passive film on stainless steel contains chemically absorbed oxygen or epitaxial oxides (which merges with crystalline matrix - pseudomorphosis), and has thickness in range 1 to 10 nm. At the temperatures above 300 °C (i.e. at welding), if there is available oxygen (O_2) or its compounds (H_2O, CO_2), nuclei of oxide matrix $(Fe, Cr, Ni, Mo)_xO_y$ having ratio $y/x = 1 - 2$ are generated, i.e. initiation of defects in the passive film occurs. This phenomenon results in interference colors and finally in generation of opaque film with thickness in excess of 1 μm. Such films have not characteristics of natural passive film. Since the volume of generated oxide is larger than volume of metal, compression stresses occur resulting in breaking of oxide. In this way cracks are formed, exposing active stainless steel to aggressive electrolyte, such as $FeCl_3$ water solutions that is used in testing of liability to pitting corrosion. Pits are propagating, and corrosion products having volume up to 20 times larger than that of original metal, (like hydrated chlorides) are formed. Hydrolysis (i.e. $2MeCl_3 + 3H_2O \leftrightarrow 2Me(OH)_3 + 3HCl$) reduces pH values and strong acid is produced. That provides conditions for autocatalytic process of deterioration [5].

Chloride ions in water solutions are specific aggressive agents that often cause pitting corrosion on such materials.



Pitting damage formed within crevice, AISI 316L pipe, weld seam, exposed several months to sea water

X-ray radiograph of welded joint damaged by microbiologically influenced corrosion in which pitting is form of damage that occurs most frequently, AISI 304 L steel, tank of raw water, several months exposure

Pitting damages beneath biological and corrosion deposits, weld seam on pipe, AISI 304L, raw water, few months exposure

Figure 2. **Examples of various real corrosion damages in the form of pitting caused by different corrosion mechanisms**
Slika 2. **Primjeri različitih realnih korozijskih oštećenja u obliku rupičaste korozije uzrokovanih različitim mehanizmima korozije**

Similar adverse affects have other halide ions (Br^-, F^-), causing destruction of passive film.

Chlorides, considered by many authors as most important factor inducing local processes of destruction, are anions of a strong acids.

Many metal cations have large solubility in chloride solutions. Additionally, chlorides are rather small anions with considerable power of diffusion, largely handicapping passivation. Pitting corrosion is considered as an autocatalytic process; once a pit is formed and corrosion process is initiated closely located at the area of the pit, significant changes in media occur. Solution is depleted in cathodic reactants (such as dissolved oxygen) and enriched in metallic cations and chlorides. Also, as mentioned earlier pH value within pit is lowered. Thus created chloride media is highly aggressive, blocks repassivation and stimulates further propagation of pit [6]. Initial processes when depasivation occur, such as deterioration of passive oxide film and formation of initial flaws are topics of numerous research and are not fully understood till now [7].

It should be noted that welded joints in stainless steel may be a serious problem in a structure due to possible corrosion damages caused most frequently by pitting, but also other mechanisms such as crevice corrosion, stress corrosion, microbiologically influenced corrosion, intercrystalline corrosion may be encountered. Some of mentioned phenomena, despite the different mechanism of damaging, can have appearance that resembles to the pitting corrosion (Figure 2.).

EXPERIMENTAL WORK

Experimental work has been conducted on the samples made of AISI 316L steel grade on which a single layer weld bead has been done applying TIG process. Appropriate filler wire has been used (grade 19/12/3 Cr/Ni/Mo). In the report on the conducted testing also comparative review of tests results obtained on real corrosion cases from practice has been included.

Testing of chemical composition of base material

Quantitative chemical analysis applying spectrometric method has been used for the base material, from which samples were made (Table 1.). Results are revealing common chemical composition for austenitic steels of AISI 316L grade, additionally alloyed with molybdenum to improve corrosion resistance in comparison with ordinary AISI 304L grade.

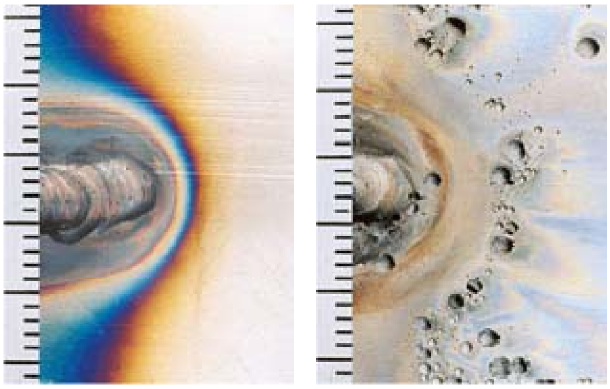
Table 1. **Chemical composition of base metal**
Tablica 1. **Kemijski sastav osnovnog materijala**

	Chemical composition / %						
Base metal	C	Si	Mn	Cr	Ni	Mo	Fe
	0,03	0,33	1,26	16,32	9,90	1,90	balance

RESULTS AND DISCUSSION

Testing of resistance to the pitting corrosion

Resistance to the pitting corrosion has been conducted according to ASTM G48 standard, applying $FeCl_3 \times 6H_20$ agent for 72 hours at temperature of 20 ± 2 °C.



a) Heat tints zone

b) After corrosion testing according ASTM G48 standard

Figure 3. **Presentation of of pitting test results**
Slika 3. **Prikaz rezultata ispitivanja otpornosti na rupičastu koroziju**

Visual inspection of test samples after the corrosion testing revealed two characteristic locations in which processes of damaging have been significantly more developed:

- area of transition from weld to base material, i.e. fusion line,
- area of tints at the largest distance from the weld, i.e. zone of colors of interference of 1st order.

Figure 4. **Results of field test of resistance towards microbiologically influenced corrosion on as welded joint**
Slika 4. **Rezultat terenskog korozijskog ispitivanja otpornosti na mikrobiološki poticanu koroziju na zavarenom spoju**

Selection of results of conducted pitting corrosion testing is shown in Figure 3. Comparison with results of field-testing of untreated welded joint to the microbiologically influenced corrosion in raw water is presented on Figure 4. It can be noted that even to the microbiological colonies inhomogeneity of surface is highly attractive as a location for their habitat and initial point of damaging that will develop as a product of their metabolism.

SEM and EDX testing

Electron scanning microscope testing (SEM) and Electron - X ray testing (EDX analysis) of chemical composition of sample that was not exposed to corrosion testing (Figure 3.a) and samples exposed to corrosion testing (Figure 3.b) have been done in laboratories of Materials Science & Corrosion Laboratories, California State University Northridge, California, USA.

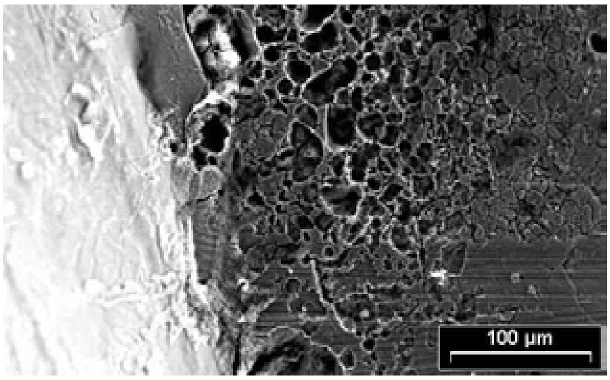


Figure 5. **SEM presentation of pitting damages closely to weld metal (conditions: AISI 316L base material, corrosion testing method according ASTM G48, agent 10 % FeCl3×6H20, for 72 h, at 20 ± 2 °C**

Slika 5. **RSEM prikaz rupičastih korozijskih oštećenja u blizini metala zavara (osnovni material AISI 316L, korozijsko ispitivanje prema ASTM G48 u 10 % otopini FeCl3×6H20, u trajanju od 72 h, pri 20 ± 2 °C**

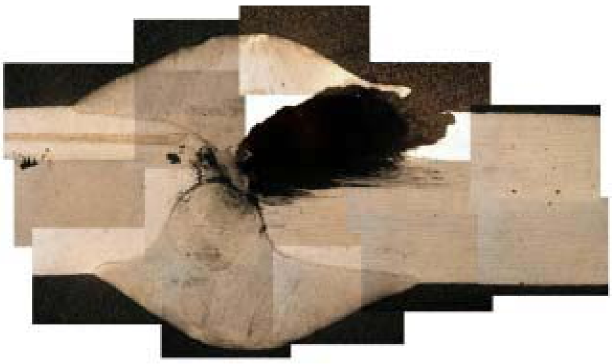


Figure 6. **Presentation of a real corrosion damage initiated at the fusion line of AISI 304L welded joint caused by microbiologically influenced corrosion in form of pitting (water tank, 3 months in use, thickness of the base material: 4 mm)**

Slika 6. **Prikaz realnog korozijskog oštećenja iniciranog u području linije staljivanja zavarenog spoja od čelika AISI 304L izazvanog mikrobiološki poticanom korozijom u obliku rupičaste korozije (spremnik vode, 3 mjeseca u upotrebi, debljina osnovnog materijala: 4 mm**

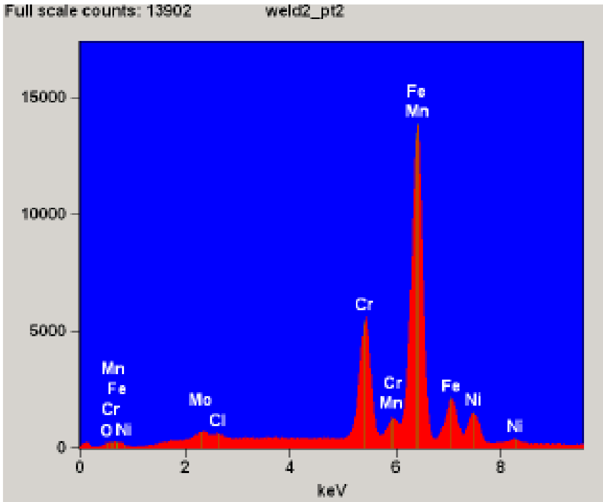


Figure 7. **Presentation of EDX analysis of non damaged metal - outside pit**

Slika 7. **Prikaz EDX analize neoštećenog metala - izvan jamice**

Testing has been done on characteristic surface areas, i.e. at the fusion line and heat tint zones on all samples. Testing results confirm that significant changes in content of major alloying elements which are necessary for corrosion resistance of stainless steels can be found on the "as welded" surface close to weld bead.

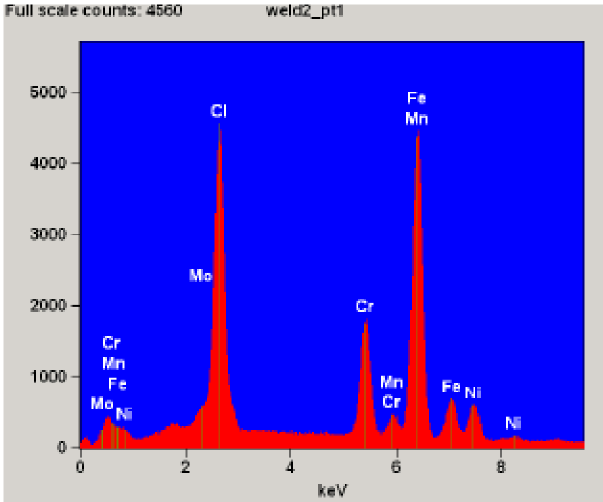


Figure 8. **Presentation of EDX analysis of deposits within pit**

Slika 8. **Prikaz EDX analize nakupina unutar jamice**

Moreover, numerous inhomogeneieties enhance initiation of corrosion deterioration. Additionally, accumulation of aggressive particles, mainly chlorides, within the pit has been established. Results of conducted tests and comparison with real corrosion damages are given in Figures 5. - 8.

Electrochemical corrosion testing - cyclic polarization

Conducted electrochemical corrosion testing applying cyclic polarization done on sample of base material and sample on which heat tints have been produced as a result of application of TIG welding and related heat input confirms essentially harmful effect of thermal oxides upon maintaining passive state, Figure 9. While the sample of base material without heat tints has characteristics expected for tested material grade, properties of identical material with heat tints are significantly deteriorated.

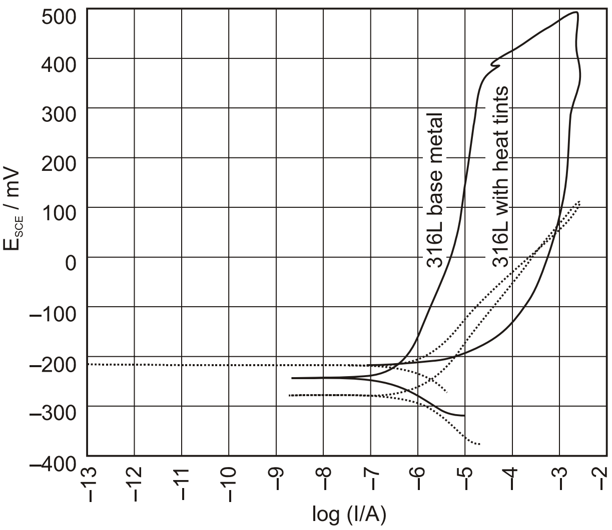


Figure 9. **Results of electrochemical testing applying cyclic polarization on sample of base material (AISI 316L steel grade) and sample on which heat tints zone has been produced as result of application of TIG process. Corrosive agent was artificial seawater. It can be seen that sample with heat tints zones even has no possibility to attain passive condition**

Slika 9. **Prikaz rezultata elektrokemijskog ispitivanja cikličkom polarizacijom uzorka osnovnog metala – čelika AISI 316L i uzorka na kojem su unosom topline TIG postupkom postignute zone toplinskih nijansi u umjetnoj morskoj vodi. Vidljivo je da uzorak s prisutnim područjima obojenja nema čak niti mogućnost postizanja pasivnosti**

CONCLUSION

Corrosion resistance of welded joints in high-alloyed CrNi stainless steels of austenitic structure depends on fulfillment of specific requirements for such structural materials during welding. To achieve appropriate corrosion resistance of welded joint, it is necessary to comply to specified requirements, starting with joint preparation, selection of welding process and appropriate welding conditions, selection of shielding and auxiliary gases, appropriate filler materials, surface treatment after welding, etc. If this is not a case, severe corrosion damages may occur in the area of welded joint, caused either by metallurgical or surface changes.

Corrosion damages are in most case localized, and very often in the form of pitting corrosion. Thereby various factors influence initiation and propagation of corrosion process, starting from those mentioned above, up to those regarding corrosive properties of the medium and even presence of various microorganisms or the design of the welded structure itself.

Conducted tests of resistance to pitting corrosion on AISI 316L steel grade, together with results of electrochemical corrosion tests of samples with different surface states (with and without heat tints produced by heat input), SEM and EDX analysis of tested samples confirm significant negative effects of heat tints zones upon the corrosion resistance. Additionally, results of research of corrosion damages encountered in practice, presented in comparison with laboratory tests, support the stated explanations, indicating the complexity of ensuring corrosion resistance of welded joints in stainless steels as well as other not fully understood processes and necessity of further research.

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