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INTERGRANULAR CORROSION OF WELDED JOINTS. FORMING CONDITIONS AND PROCEDURES FOR PREVENTION

INTERKRISTALNA KOROZIJA ZAVARENIH SPOJEVA. USLOVI NASTANKA I POSTUPCI SPREČAVANJA

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Ključne reči
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- senzibilizacija

Abstract

The paper describes structural changes in the welded joints, leading to the emergence of intergranular corrosion (IGC) during exploitation. The occurrence of intergranular corrosion in welded joints of austenitic, ferritic and duplex stainless steels and in welded joints of aluminium alloys and nickel alloys is analysed. Special attention was paid to austenitic stainless steels, due to their wide application in practice. In addition to sensitization in the weld heat-affected zone (HAZ), which results in degradation of the welded joint ("weld decay"), also considered is the sensitization that occurs close to the weld metal in the stabilized steel, which leads to a "knife line attack". Considerable attention is devoted to describing the various procedures in order to prevent the sensitization of the welded joints.

Izvod

U radu su opisane strukturne promene u zavarenom spoju, koje dovode do pojave interkristalne korozije (IKK) tokom eksploatacije. Analizirana je pojava interkristalne korozije u zavarenim spojevima austenitnih, feritnih i dupleks nerđajućih čelika, kao i u zavarenim spojevima aluminijumskih legura i legura nikla. Posebna pažnja posvećena je austenitnim nerđajućim čelicima, s obzirom na njihovu široku primenu u praksi. Pored senzibilizacije zavarenog spoja u zoni uticaja toplote (ZUT), koja za posledicu ima propadanje zavarenog spoja ('weld decay'), razmotrena je i senzibilizacija koja se javlja neposredno uz metal šava kod stabilizovanih čelika, koja dovodi do nožaste korozije ('knife line attack'). Značajna pažnja posvećena je opisu različitih postupaka u cilju sprečavanja senzibilizacije zavarenog spoja.

INTRODUCTION

In addition to structural changes, stress and a thermal gradient, there often occurs chemical inhomogeneity in the welded joints. Chemical inhomogeneity significantly affects the corrosion behaviour of welded joints. Throughout the heating and cooling during welding, in the HAZ, different phases and structural transformations occur. Thus, in stainless steels, aluminium alloys and nickel alloys, there is often precipitation of certain phases at the grain boundaries and the appearance of a structure that is susceptible to intergranular corrosion. Intergranular corrosion is a form of localized corrosion, which is manifested by dissolving the area of grain boundaries, /1-12/. This type of corrosion leads to a large deterioration in the mechanical properties of metals.

INTERGRANULAR CORROSION

Intergranular corrosion most commonly occurs in austenitic stainless steels, /1-5/. At high temperatures ($T > 1030$°C) chromium carbides are completely dissolved. However, due to the slow cooling and annealing in the temperature range of 420 to 820°C, chromium carbides are precipitated by the grain boundaries (Figs. 1 and 2). The rate of diffusion of chromium in austenite is low at the indicated temperatures. As a result, grain boundary areas become poorer in chrome. If the chromium content is reduced below 12%, which is necessary for the maintenance of the protective passive film, grain boundary areas become sensitized and prone to intergranular corrosion. In the corrosive environment, this area dissolves faster than other grain fields.

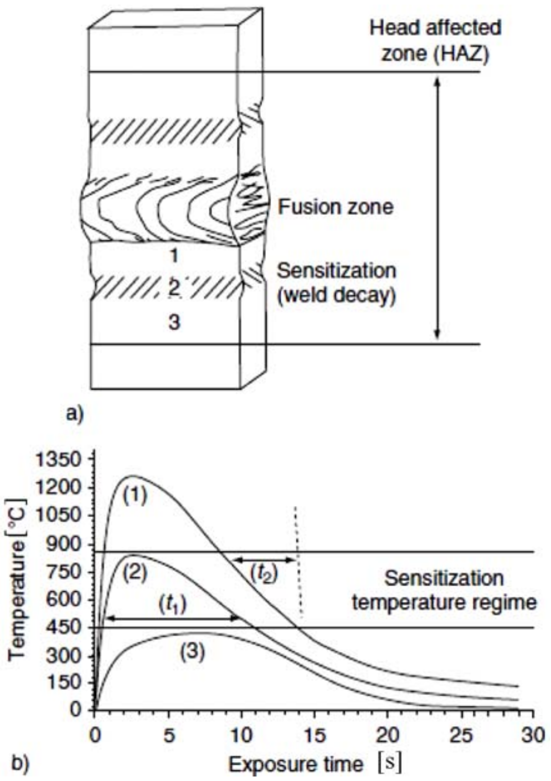

Figure 1. Formation structure that is prone to intergranular corrosion due to sensitization in the HAZ, on stainless steel: a) welded joint, with three designated locations in the HAZ, b) typical temp.-time profiles for indicated location in HAZ /4/.
Slika 1. Obrazovanje strukture koja je sklona interkristalnoj koroziji usled senzibilizacije u ZUT, na nerđajućem čeliku: a) zavareni spoj sa tri označena mesta u ZUT, b) tipčni profili temperatura–vreme za označena mesta u ZUT /4/.

The sensitization of the HAZ usually occurs during welding or during annealing to remove residual stresses. Intergranular corrosion occurs in a region that is parallel to the weld metal. This type of intergranular corrosion, which leads to degradation of the welded joint, is known as weld decay.

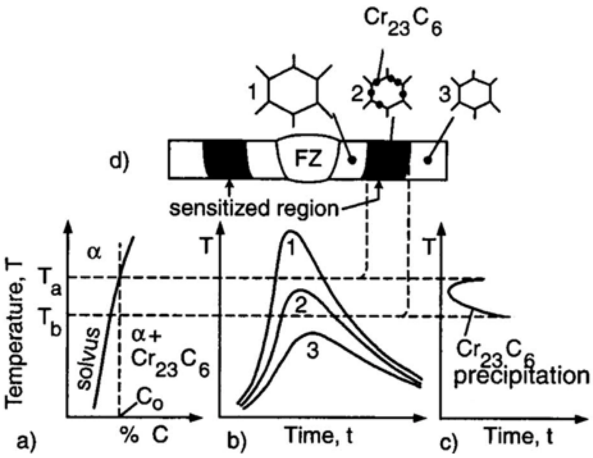

Figure 2. Sensitization of austenitic stainless steel: a) phase diagram, b) thermal cycle, c) curve of precipitation of chromium carbide, d) scheme with sensitization weldment zone /2/.
Slika 2. Senzibilizacija austenitnog nerđajućeg čelika: a) fazni dijagram, b) termički ciklus, c) kriva izdvajanja karbida hroma, d) shema zavarenog spoja sa senzibilizovanom zonom /2/.

The metallurgical aspect of the formation of sensitized structure is shown in Fig. 2. Figure 3 shows a pipe made of stainless steel, where intergranular corrosion in the welded joints has occurred.

The sensitivity to the described form of intergranular corrosion can be reduced by annealing the steel at a temperature at which chromium carbides are completely soluble, with the rapid cooling across the critical temperature interval. Also, sensitization can be avoided by reducing the carbon content in stainless steel (typically below 0.03% C, Fig. 4), or if there are added elements that form a more stable carbide than chromium. These are usually Ti or Nb.

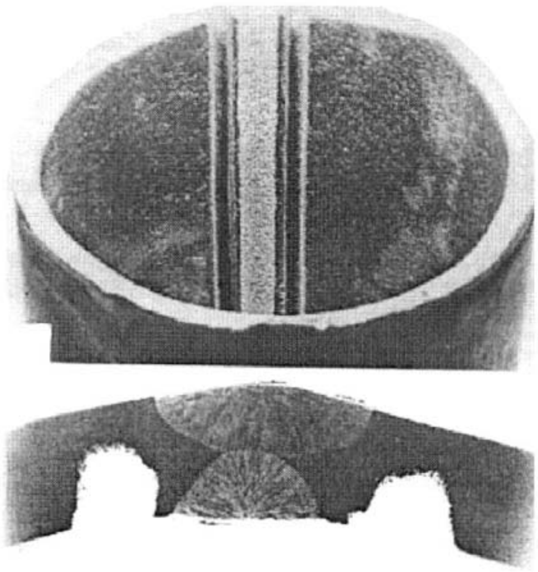

Figure 3. Intergranular corrosion in welded joints of pipes of austenitic stainless steels /2/.
Slika 3. Interkristalna korozija u zavarenom spoju cevi od austenitnog nerđajućeg čelika /2/.

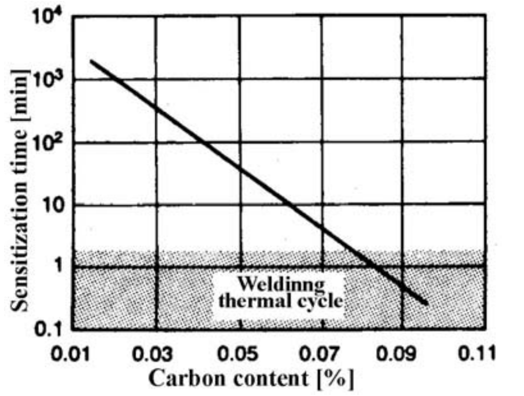

Figure 4. Minimum time of sensitization depending on the carbon content, for the 300 series stainless steels /1/.
Slika 4. Minimalno vreme senzibilizacije u zavisnosti od sadržaja ugljenika, za nerđajuće čelike serije 300 /1/

The influence of the welding procedure on the occurrence of intergranular corrosion depends on the welding process and the thickness of the plates that are welded, so it can not give unambiguous recommendations for each plate thickness. The degree of risk of developing this form of corrosion is directly related to the time of sensitization.

Structural transformations in HAZ, i.e. formation of σ and χ phases, are described in detail in /8/. The addition of nitrogen slows the formation of these phases and increases the resistance of austenitic stainless steels to localized forms of corrosion in acidic oxidizing environments containing chloride ions.

Stabilized stainless steels (with the addition of Ti or Nb) may become prone to the localized corrosion form of intergranular corrosion known as knife-line attack. This type of intergranular corrosion occurs close to the weld metal and is shaped like a groove blade, when exposed to steel in hot concentrated HNO_3, which is why this corrosion is named knife-line attack.

Metallurgical conditions, which are necessary for the formation of the structure prone to this form of intergranular corrosion, are shown in Fig. 5. Stabilized stainless steels with Nb are more resistant to this form of corrosion than steel stabilized with Ti, because the decomposition temperature of Nb carbides is higher than the temperature of decomposition of Ti carbides. The risk of knife-line attack can be minimized if we limit the carbon content in stainless steel /1, 2/.

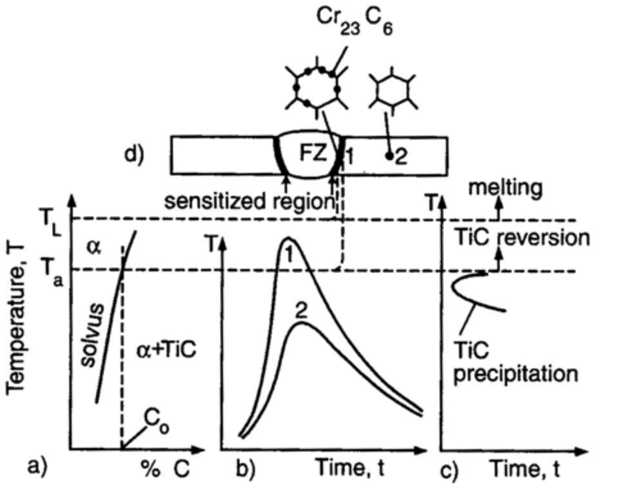

Figure 5. Sensitization of stabilized austenitic stainless steels: a) phase diagram, b) thermal cycle, c) curve separation TiC, d) scheme of the sensitization weld zone, /2/.
Slika 5. Senzibilizacija stabilizovanih austenitnih nerđajućih čelika: a) fazni dijagram, b) termički ciklus, c) kriva izdvajanja TiC, d) shema zavarenog spoja sa senzibilizovanom zonom /2/

During welding, at a certain distance from the weld, a metal microstructure is established, prone to a knife-line attack. The base metal, close to the melting zone, was heated almost to the melting point (Fig. 5), and the carbides of chromium and the carbides of Nb or Ti are completely dissolved. At rapid cooling of welded joints, particularly in the case of thin elements, there is not enough time for the formation of Cr carbide or carbides of Nb or Ti. If the weld is annealed (to remove residual stresses) or is heated during multipass welding, there is a rapid precipitation of chromium carbides, but the temperature is too low to lead to the formation of Nb and Ti carbides. The narrow zone of metal, which during welding reaches a temperature sufficient to dissolve carbides of Nb or Ti ($T >$ 1230°C), becomes sensitized to a knife-line attack. This can be avoided by subsequent heating of the welding parts, after welding, to a temperature of 1070°C, during which dissolved chromium carbides and carbides Ti or Nb are formed. In this case the cooling rate is not important.

As stated above, it is clear that the knife-line attack occurs close to the weld metal and weld decay at some distance from the weld metal (Figs. 3 and 6).

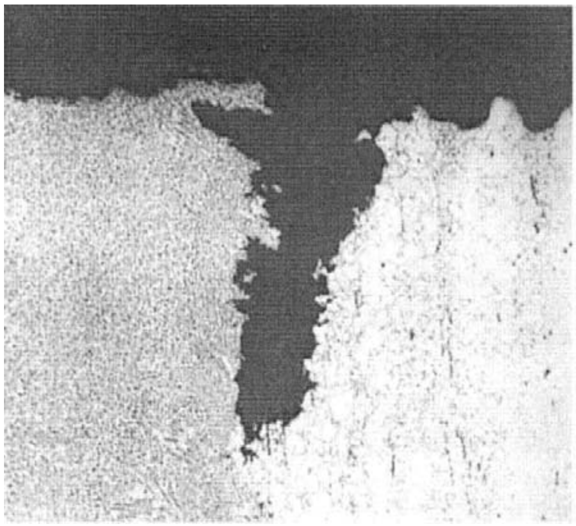

Figure 6. Knife-line attacks of stabilized austenitic stainless steel in the vicinity the weld metal, /2/.
Slika 6. Nožasta korozija stabilizovanog austenitnog nerđajućeg čelika u blizini metala šava /2/.

In ferritic stainless steels one can have intergranular corrosion due to the formation of chromium carbides at grain boundaries, /8/. Sensitization occurs at lower temperatures than in austenitic stainless steels, and its rate is so great that it can be prevented only by very rapid cooling, which is practically impossible. Thus, during exploitation intergranular corrosion may occur if appropriate heat treatment (annealing at ~ 800°C) is not applied after welding. In contrast to austenitic stainless steels, in ferritic stainless steels intergranular corrosion occurs in a wide area and includes the HAZ, melting zone and the zone close to the melting zone. Fast sensitization is a consequence of the lower solubility of carbon and higher rate of its diffusion in ferrite. C-curves exist for ferritic steels but, in contrast to austenitic steels, sensitization (knee at the C-curve) is achieved in a shorter time and at a lower temperature (400 to 550°C). Sensitization during welding can be prevented by using ferritic stainless steel with an extremely low content of carbon (and nitrogen), which is not practically possible. It can also be made of steel with the stabilization of Nb or Ti, but requires higher concentrations of these elements than in the case of austenitic stainless steels. In order to prevent intergranular corrosion, ferritic steels are most commonly used with a combination of low carbon content and the addition of Ti, /8/.

Figure 7 illustrates the two typical mechanisms of intergranular corrosion. The first mechanism: dissolution of the area in the vicinity of precipitates at grain boundaries that are poor in alloying elements (stainless steel, nickel alloys, aluminium alloys of 2000 series, etc.). The second mechanism: dissolution of precipitates isolated at grain boundaries (aluminium alloy series 5000, 7000, etc.).

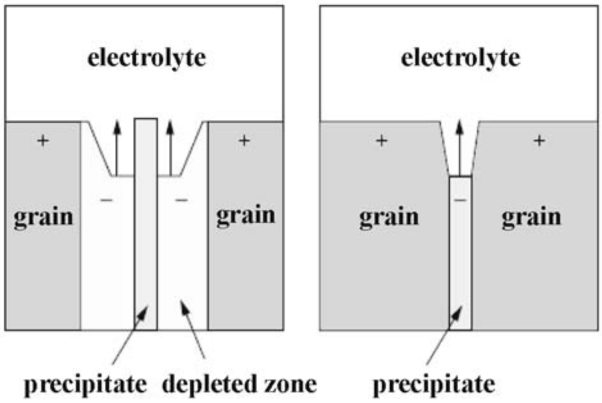

Figure 7. Two mechanisms of IGC: a) dissolution of anodic grain boundary area, poor with alloying elements, b) dissolution of the anodic precipitate at grain boundary, /13/.
Slika 7. Dva mehanizma odvijanja IKK: a) rastvaranje anodne oblasti uz granicu zrna, siromašnu legirajućim elementima, b) rastvaranje izdvojenih anodnih taloga na granici zrna /13/

Improper heat treatment of aluminium alloys (2000 series, 5000, 6000, 7000 and 8000) can also lead to the precipitation of certain phases in grain boundaries and the formation of a sensitized structure, which under a service condition is subject to rapid intergranular corrosion. As a result of intergranular corrosion there is large deterioration in the mechanical properties of aluminium alloys. On several occasions it has been shown that applying two-stage precipitation hardening improves the resistance to intergranular corrosion of aluminium alloys which are strengthened by aging, /12/.

The resistance to intergranular corrosion of welds of nickel and its alloys depends on the microstructural and chemical changes that occur during welding. These changes are similar to findings in austenitic stainless steels. For example, in alloys with Mo (Hastelloy B), and the Ni-Mo-Cr alloys (Hasteloy C), there is intergranular corrosion (knife-line attack and weld decay), as a result of sensitization. Methods to prevent these types of corrosion are similar to the procedures applicable in austenitic stainless steels. The structural changes that lead to the emergence of these forms of corrosion, and methods for their prevention in detail are given in /3/. Weldability, welding defects and their effect on corrosion resistance of various alloys are described in /14/.

METHODS FOR PREVENTING INTERGRANULAR CORROSION OF WELDED JOINTS

To prevent IGC, weldments are treated by using different procedures. A welded structure of stainless steel is heat treated in order to dissolve chromium carbide, furthermore, chromium concentration in the equalization structure is often impractical for larger structures, and may be applied to local heat treatment. However, the local heat treatment may lead to a sensitization zone located near the area that has been heat treated.

Application of steel with low carbon steel or stabilized steel (i.e., austenitic stainless steel containing Ti or Nb) is more suitable than heat treatment. In addition, the weld filler material should also be stabilized, especially at multi-pass welding, where in previous layers, due to heating, there is already heat treatment. Often it is necessary that the contents of Ni and Cr increase in the additional material, so to reduce their losses during welding.

Additional materials that contain Ti should not be used during arc welding in argon, because Ti will evaporate, and its effectiveness as a stabilizer diminishes. Carbonisation (increase in carbon content) in the weld, due to surface contamination by carbon from the atmosphere or coating the electrode arc, increases the risk of intergranular corrosion, /15/.

Figure 8 shows the 4 plates of austenitic stainless steel, joined by welding, after exposure to hot HNO_3 + HF. It can be seen that only panel 304 of stainless steel is prone to intergranular corrosion, while in plates of stainless steel type 304L, 321 and 347, intergranular corrosion is not observed. Steel 304L has a very small amount of carbon, and steel 321 is stabilized with titanium, and the steel 347 is stabilized with niobium.

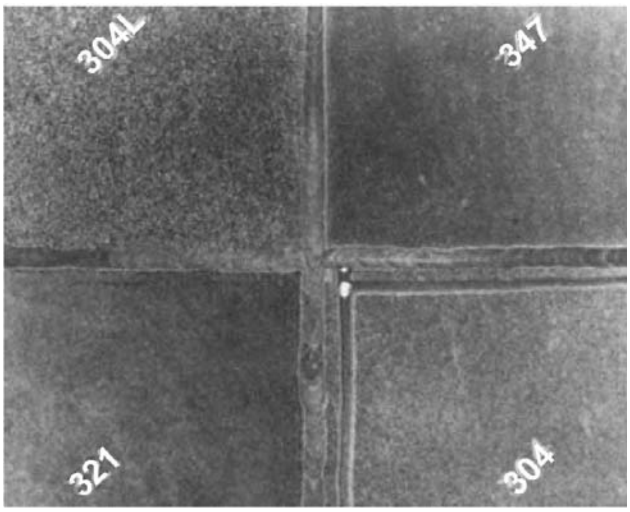

Figure 8. Proceedings of prevention of intergranular corrosion of austenitic stainless steel 304L (low in C), 321 - stabilized with Ti, 347 - stabilized with Nb, 304 - occurrence of IGC, /16/.
Slika 8. Postupci sprečavanja interkristalne korozije austenitnog nerđajućeg čelika: 304L (nizak sadržaj C), 321 – stabilizovan sa Ti, 347 – stabilizovan sa Nb, 304 – pojava IKK, /16/

Knife-line attack can be prevented by using stainless steel with low content of C, which reduces the risk of chromium carbide precipitation. The risk of a knife-line attack significantly reduces by alloying stainless steel with the REM (Rare Earth Metals), such as La and Ce (Fig. 9). These elements favour the formation of chromium carbides in the grains and thus reduce the carbon content for the separation of carbides at grain boundaries. In some cases the risk of a knife-line attack can be eliminated by modifying the welding process (Fig. 10).

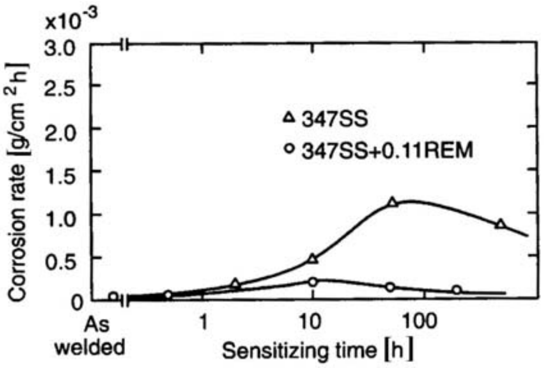

Figure 9 The influence of REM (La and Ce) on the occurrence of knife-line attack of stabilized stainless steels, /2/.
Slika 9. Uticaj REM (La i Ce) na pojavu nožaste interkristalne korozije stabilizovanih nerđajućih čelika /2/.

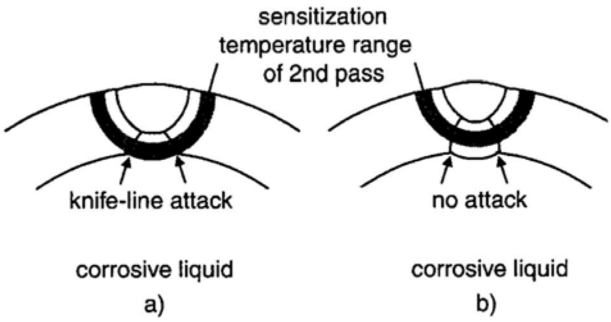

Figure 10. Prevention of knife-line attack by modifying the welding process: a) the emergence of knife-line attack, b) absence of knife-line attack, /2/.
Slika10. Sprečavanje nožaste interkristalne korozije modifikacijom postupka zavarivanja: a) pojava nožaste korozije, b) odsustvo nožaste korozije, /2/

Modern methods of testing IGC are described and applied in /17/. Various aspects of corrosion welded joints of different metals and alloys are discussed in /18/. While /19, 20/ goes into the details, significance and applicability of the structural integrity assessment, as well as risk analysis in structural integrity, which is often applied in corrosion testing.

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