INFLUENCE OF SIGMA PHASE PRECIPITATION ON THE INTERGRANULAR CORROSION RESISTANCE OF X2CRNIMON25-7-4 SUPER DUPLEX STAINLESS STEEL

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Abstract

Secondary phase’s precipitation is dangerous for stainless steels. Most important secondary phases for stainless steels with carbon amount higher than 0.2% are carbides (especially M23C6). Most dangerous secondary phase for stainless steels with smaller amount of carbon and high chromium content (for example 25% of Cr) is sigma phase (\(\sigma\)). Secondary phases absorb chromium from neighbouring areas. This mechanism is very danger for technological treatment of stainless steels (welding, heating above 300\(^\circ\)C). Fundamental property of stainless steel is corrosion resistance for working conditions. Aim of the work was to analyse influence of sigma phase precipitation on the intergranular corrosion resistance for X2CrNiMoN25-7-4 super duplex stainless steel. High chromium amount induce precipitation of high chromium sigma phase and it cause changes of the material intergranular corrosion resistance. Very low carbon amount (about 0.02%) prevents carbides precipitation and well described sensitization caused with carbides do not occurs in this case. Heat treatment parameters for performed analysis have to initiate different amount of sigma phase precipitation. Results of performed analysis confirm conservative opinion about sigma phase influence on the intergranular corrosion resistance. Some additional and not described jet results concerning influence of sigma phase precipitation on the intergranular corrosion achieved. On the basis of achieved results, specific case, when sigma phase increase intergranular corrosion of X2CrNiMoN25-7-4 super duplex stainless steel was revealed. The paper describe mechanism of intergranular corrosion resistance improve for X2CrNiMoN25-7-4.

Keywords: Intergranular corrosion, sigma phase, sensitization, Huey test

1. INTRODUCTION

Austenitic and duplex stainless steels are designed for use in aggressive environments and at temperatures below 300-320\(^{\circ}\)C. Typically, they are used to manufacture pipelines and other components operating at temperatures below 320\(^{\circ}\)C. Usually, stainless steels work with aggressive environments (acids, oil and other). Stainless steel corrosion poses a significant threat because it can lead to the release of potentially harmful or toxic circulating substances. In Nuclear Power Plants (NPP), stainless steels are used for primary cooling system with possible radioactive substances. During installation made of stainless steel operation, intergranular corrosion exists. Mechanical properties of super duplex stainless steels are two times higher than for typical austenitic stainless steels. Tow phase (ferritic – austenitic) stainless steels has ferrite – austenite interface, which can be danger in case of intergranular corrosion. Corrosion rate (mm/year) increase during operation as result of grain boundary etching and contact area increase. Literature describes secondary phase precipitation (sigma phase, carbides) as reason of corrosion rate increase and intergranular corrosion resistance decrease [1,2,5,6]. Main subject of the paper was to describe mechanism of super duplex stainless steel X2CrNiMoN25-7-4 microstructure evolution to achieve negative corrosion rate (corrosion rate decreasing) after sigma phase precipitation.
2. MATERIALS AND METHODS

Experimental specimens were collected from a 5-mm thick sheet of X2CrNiMoN25-7-4 super duplex stainless steel. The geometry and positioning of samples on the steel sheet were consistent with standard PN-EN ISO 3651-1, the key norm for intergranular corrosion analysis. Reference microstructure achieved as solutioning heat treatment at 1100°C for 30 minutes. All specimens were solution heat treated at 1100°C for 30 minutes to remove stresses from manufacturing process. To achieve the aim of the work, three sets of heat treatment parameters were analyzed. First, reference microstructure achieved as result of solution heat treatment. Second microstructure was achieved after solution heat treatment and aging at 1000°C for 30 minutes. Third set of heat treatment was defined as solution heat treatment and aging at 900°C for 30 minutes. Microstructure for above heat treatment parameters described in the paper [5].

Formula (1) was used to calculate the corrosion rate for X2CrNiMoN25-7-4 steel [mm/year] in boiling nitric acid V 65% in accordance with standard PN EN ISO 3651-1 [3].

\[ r_{corr} = \frac{87600 \cdot m}{S \cdot t \cdot \rho} \]

where:
- \( t \) – time of treatment in a corrosive solution of boiling nitric acid, in hours,
- \( S \) – surface area of the sample, in cm\(^2\),
- \( m \) – average mass loss in boiling solution, in grams,
- \( \rho \) - sample density (8 g/cm\(^3\) for X2CrNiMoN25-7-4 steel according to the applied standard).

According to the standard [3], investigated material was immersed 5 times for 48 hours in boiling nitric acid V 65%. Corrosion rate was analyzed for each immersion and as sum of immersion time and mass loss sum. Corrosion rate change was analyzed for both cases. The cross section of studied material was subjected to a metallographic (light microscopy) analysis to observe the progression of corrosion during microstructural changes in X2CrNiMoN25-7-4 steel caused by sigma phase precipitation.

3. RESULTS AND DISCUSSION

Fig. 1 presents influence of immersion time in boiling nitric acid on the corrosion rate for solution heat treated X2CrNiMoN25-7-4 super duplex stainless steel. Corrosion rate calculated for each immersion is higher than corrosion rate calculated for cumulated weight loss and immersion time. Difference between summarized and single immersion analysis reach 50% of summarized value for 5x48h immersion time. Increasing difference between summarized and single immersion corrosion rate shows corrosion rate acceleration connected with acid contact area (grain boundaries). Fig. 2a shows cross section of the specimen after solution heat treatment and 5x48h immersion in boiling nitric acid. Grain boundary etching was observed and grains loss from the surface. Picture achieved after observation in polarized light (Fig. 2b) better shows surface degradation and grain boundary etching. Taking into account high corrosion resistance of solutioned X2CrNiMoN25-7-4 super duplex stainless steel, strongly oxidizing environment induce corrosion rate equal 0.18 mm/year after 5x48h of immersion time. Taking into account results presented in the paper [5], in the microstructure, secondary phases were not observed.
Fig. 1 Influence of immersion time in boiling nitric acid on the corrosion rate of X2CrNiMoN25-7-4 after solution heat treatment (1100°C/30 min.).

Second analyzed heat treatment set, solution heat treatment and aging at 1000°C for 30 minutes influences significantly on the corrosion rate evolution. Fig. 3 presents influence of immersion time in boiling nitric acid on the corrosion rate for solution heat treated aged at 1000°C for 30 minutes X2CrNiMoN25-7-4 super duplex stainless steel. In this case, summarized corrosion rate is almost stable in the rang 0.1 – 0.12 mm/year during immersion in boiling nitric acid. Second and third immersion induce corrosion rate decrease but fourth immersion cycle induce high increase of corrosion rate up to 0.15 mm/year for on immersion cycle. Fig. 4a presents cross section of solution heat treated and aged (1000°C/30 min.) X2CrNiMoN25-7-4 super duplex stainless steel after 5x48h immersion in boiling nitric acid. White grains in precipitated in ferrite area are sigma phase precipitations. Interface between sigma phase with high chromium amount and austenite is more difficult for intergranular corrosion propagation. If corrosive solution will reach surface without ferrite (especially Cr depleted), intergranular corrosion propagate easily. Taking into account paper [5], 4.83% of sigma phase precipitation induce stabilization and decrease of corrosion rate during immersion time. Fig. 4c presents zoom of surface shown in the Fig. 4a. Fig. 4b. presents cross section shown in Fig. 4a. observed with polarized. Polarized light shows surface degradation after 5x48h immersion. Corrosion rate peak after fourth immersion cycle can be results of depleted ferrite zone (near sigma phase precipitation) achievement.
with corrosion solution. Accelerated corrosion rate can be decreased with small amount of sigma phase precipitation between austenite grains (Fig. 4c).

Fig. 3 Influence of immersion time in boiling nitric acid on the corrosion rate of X2CrNiMoN25-7-4 after solution heat treatment and aging (1000°C/30 min.).

Fig. 4 Cross section of solution heat treated and aged (1000°C/30 min.) X2CrNiMoN25-7-4 super duplex stainless steel after 5x48h immersion in boiling nitric acid observed in a. white light microscopy, b. polarized light and c. magnified Fig. 4a.
Third set of heat treatment parameters of analyzed material was solution heat treatment and aging at 900°C for 30 minutes. Fig. 5 presents influence of immersion time in boiling nitric acid on the corrosion rate for solution heat treated aged at 900°C for 30 minutes X2CrNiMoN25-7-4 super duplex stainless steel. In this
case, corrosion rate decrease with immersion time. Behavior of corrosion rate is similar to microstructure with 4.83% of sigma phase (aging 1000°C/30 min.). Aging at 900°C for 30 minutes induce precipitation 28.83% sigma phase [5]. Decreasing corrosion rate can be correlated with small amount of depleted ferrite and bi amount of austenite – sigma phase interfaces. Corrosion rate peak after fourth immersion cycle can be connected with depleted ferrite etching between sigma phase grains.

4. CONCLUSIONS

As shown in the previous paragraph, sigma phase precipitation can increase corrosion resistance of X2CrNiMoN25-7-4 super duplex stainless steel. Small amount of sigma phase (about 5%) stabilize corrosion rate and prevent for increase of this value, what was observed for solution heat treated microstructure (product available in the market). Precipitation of 28.83% sigma phase induce corrosion rate decrease with immersion time. Depleted ferrite around sigma phase induces corrosion rate peaks for single immersion cycles. Interface austenite – sigma phase do not dissolve during nitric acid immersion. Small work hardening observed after aging (1000°C/30min.) [4] and corrosion rate stabilization can be better solution for most applications than typical solution heat treatment.

LITERATURE