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Study of corrosion behavior of a 22% Cr duplex stainless steel: Influence of nano-sized chromium nitrides and exposure temperature

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ABSTRACT

Chromium nitrides may precipitate in duplex stainless steels during processing and their influence on the corrosion behavior is of great importance for the steel performance. In this study, the influence of nano-sized quenched-in chromium nitrides on the corrosion behavior of a heat treated 2205 duplex stainless steel was investigated at room temperature and 50 °C (just above critical pitting temperature). The microstructure was characterized by SEM/EDS and AFM analyses, and quenched-in nitrides precipitated in the ferrite phase were identified by TEM analysis. Volta potential mapping at room temperature suggests lower relative nobility of the ferrite matrix. Electrochemical polarization and in-situ AFM measurements in 1 M NaCl solution at room temperature show a passive behavior of the steel despite the presence of the quenched-in nitrides in the ferrite phase, and preferential dissolution of ferrite phase occurred only at transpassive conditions. At 50 °C, selective dissolution of the austenite phase was observed, while the ferrite phase with the quenched-in nitrides remained to be stable. It can be concluded that the finely dispersed quenched-in nitrides do not cause localized corrosion, whereas the exposure temperature has a strong influence on the corrosion behavior of the duplex stainless steel.

1. Introduction

Duplex stainless steels (DSSs), with austenite (γ) and ferrite (α) phases in almost equal amount, are widely used in marine environment, petrochemical, oil and gas, chemical and desalination industries, because of their greater corrosion and mechanical properties when compared to most of the austenitic stainless steels [1,2]. Products made of DSSs may require welding of different parts and/or exposure to high temperature during the processing of the material. Upon heating the material to high temperature for a sufficient time, undesirable secondary phases will precipitate in different areas and different amounts, with the risk of being detrimental for the mechanical and corrosion properties of the material. In order to minimize their nucleation and growth, particular procedures must be followed, i.e., by selecting the optimal welding temperature and by ensuring a fast cooling process after the heat treatment. However, even in this case the precipitation of secondary phases may occur [2]. The most common secondary phases in duplex stainless steels are the intermetallic sigma phase (σ), chromium nitrides (Cr_2N), chi phase (χ), carbides ($M_{23}C_6$) and secondary austenite (γ_2). Thermodynamic calculations by using Thermo-Calc software [3] are commonly used to predict the fraction of equilibrium phases obtained during heat treatment, e.g., annealing. However, short annealing times do not allow the steels to reach the thermodynamic equilibrium, and in this case secondary phases may precipitate in different ways and at different locations [4]. This should be kept in mind when comparing the thermodynamic calculation and the experimental results.

The chromium nitrides formed in DSSs are mostly present in the form of Cr_2N. Two types of Cr_2N have been observed after welding procedures and heat treatments: quenched-in Cr_2N particles that are finely dispersed in the ferrite phase, and isothermal Cr_2N particles that precipitate along phase and/or grain boundaries [5–9]. Quenched-in Cr_2N particles are formed during the cooling process from high annealing temperature. At properly chosen annealing temperature ferrite and austenite are the only stable phases, so the material should be free from chromium nitrides. However, during the water quench process the temperature drops at a very high rate, passing through the equilibrium temperature for the formation of chromium nitrides. Due to the fast cooling process the solubility of N in ferrite decreases greatly. At this point the N present in the ferrite phase does not have enough time to diffuse toward the austenite phase, which has higher solubility of N, and consequently small quenched-in Cr_2N particles are formed and finely dispersed in the ferrite phase. On the other hand, at lower annealing temperatures, chromium nitrides become thermodynamically stable

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and N diffusion from the ferrite toward the austenite phase leads to the formation of isothermal Cr_2N particles, which precipitate along phase and/or grain boundaries. In this case the time at the annealing temperature has a crucial influence on the amount and the size of the precipitated isothermal Cr_2N particles.

The presence of chromium nitrides in DSSs is often observed in practice [5,10–12], especially for highly alloyed DSSs because of higher N and Cr contents. In some cases, nitrides may be detrimental for the corrosion resistance of the material when exposed to aggressive environments. However, the risk for the nitride particles to cause initiation of localized corrosion depends on their amount, size and distribution, as well as their location and their surrounding region. The corrosion behavior of the material also depends on the exposure environment and temperature, and the research focus on chloride containing solution is natural due to its presence in many of the media (e.g., sea water) in which duplex stainless steels are used [13]. The achievement of a deep understanding of the influence of chromium nitrides on the corrosion behavior of the material is of great importance, not only from a fundamental prospective but also for industrial applications of the DSSs. In an attempt to reach such understanding, we have prepared the DSS samples with chromium nitride particles through heat treatments, characterized the nitrides in detail, and then performed in-situ local probing studies of the dissolution behavior of the samples in a NaCl solution under electrochemical potential control. To investigate the effect of exposure temperature, the corrosion experiments were also performed at 50 °C, temperature just above the critical pitting temperature (CPT), and the corrosion attack was examined by post-analysis.

In this communication, we report the study of the corrosion behavior of a heat treated 2205 grade of DSS in a NaCl solution at different exposure temperatures, aiming at clarifying the effect of nano-sized quenched-in chromium nitride particles. The phases and the precipitated chromium nitrides were characterized by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED). An evaluation of corrosion tendency of the phases and precipitated particles in the tested material was done at room temperature by using atomic force microscopy-based Kelvin force microscopy (AFM/KFM), to examine the relative nobility difference between the ferrite, austenite and precipitated nitrides. In order to study the corrosion behavior of the heat treated 2205 DSS, potentiodynamic polarization measurements of the samples were carried out in 1 M NaCl at room temperature (T_{room}) and 50 °C. In-situ electrochemical atomic force microscopy (EC-AFM) measurements of the samples were performed in 1 M NaCl solution at T_{room} to examine whether or not the chromium nitride particles lead to localized corrosion initiation for the heat treated 2205 DSS. Furthermore, in order to verify the selectively dissolved phase at temperature just above the CPT, magnetic force microscopy (MFM) was used in combination with SEM/EDS for post-polarization analysis.

2. Experimental

2.1. Material and sample preparation

Samples of a Sandvik SAF 2205 duplex stainless steel (UNS S32205) in dimension of 20 × 20 × 2 mm were supplied by AB Sandvik Materials Technology, Sweden. The main elemental composition of this DSS is shown in Table 1.

The samples were subjected to an experimental heat treatment where the material was first annealed at 1250 °C (1 min), followed by air cooling down to 950 °C at which it was water quenched. This heat treated material will, from now on, be called 2205 HT.

Table 1
Chemical composition of the tested material (wt%).

C	Si	Mn	Cu	Cr	Ni	Mo	N	Fe
< 0.030	0.61	0.76	0.17	22.2	5.22	3.13	0.19	Bal.

The quenching temperature of 950 °C was selected after the thermodynamic calculation (Fig. 1) by means of Thermo-Calc [3] and TCFE6 database. The diagram in Fig. 1 was obtained by the calculation using the exact composition of this batch of the material. At this temperature the expected equilibrium phases are shown to be ferrite, austenite and a small fraction of chromium nitrides.

For general microstructure characterization by SEM, the 2205 HT sample was first embedded in bakelite, wet ground with SiC paper up to 1200 grit, polished with diamond paste successively up to 0.25 μm, and followed by final polishing with 0.04 μm silica suspension. The sample was then gently etched in diluted aqua regia (15 mL HCl, 5 mL HNO_3, 100 mL H_2O) at 40 °C. Note that this gentle etching was done only for the sample used for this preliminary SEM characterization.

Prior to the potentiodynamic polarization, the 2205 HT samples were wet ground with SiC paper up to 1200 grit, and then polished using diamond paste successively up to 0.25 μm. The samples used for the KFM measurements were also polished up to 0.25 μm in order to have a smooth surface and minimize the influence of roughness on the Volta potential signal.

For the in-situ EC-AFM measurements, the small 2205 HT sample was cut from a received material and mounted on a brass disc by conductive glue. It was then fixed in a plastic mold by epoxy, leaving an exposed area of 0.2 cm^2. Also in this case the sample was polished up to 0.25 μm with diamond paste. All the samples, including those used for post-polarization analysis, were ultrasonically cleaned in ethanol and dried in a N_2 gas stream prior to the experiments.

2.2. Solution

The solution containing 1 M NaCl was prepared from analytical grade NaCl and ultrapure water (Milli-Q, 18 MΩ cm).

2.3. SEM analysis

The SEM instrument used was a ZEISS Ultra 55 FE-SEM (FE-SEM). The secondary electron SEM mode imaging was performed on the gently etched 2205 HT sample to find areas with precipitated

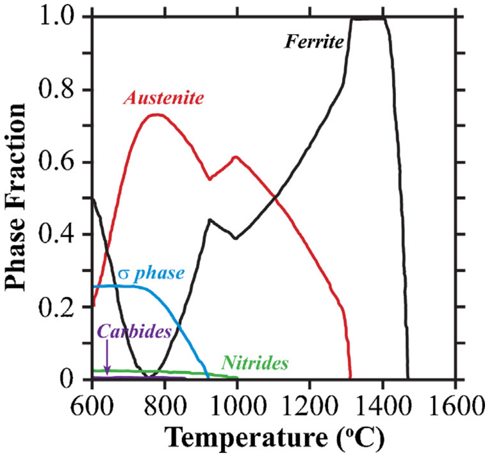

Fig. 1. Thermodynamic calculation of equilibrium phase fractions for the tested SAF 2205 as a function of temperature.