Peculiarities of stress corrosion fracture of sensitized and neutron irradiated chromium-nickel austenitic steel

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Abstract. The results of SEM studies of fracture surfaces for the 12Cr18Ni9 austenitic steel ruptured under a fixed tensile load in FeCl$_3$ water solution and in air are presented. The samples of austenized, sensitized at 650°C and irradiated with neutrons (to $10^{20}$n/cm$^2$) steel were examined. It was shown that irradiation hardening and sensitizing annealing increased the susceptibility of steel to intergranular cracking in corrosive solution. Structural features of formation of the strain-induced $\alpha'$-martensite and its reinforcing effect on fracture in various environments are discussed.

1. Introduction

The increased resistance to stress corrosion cracking (SCC) is one of the important requirements for structural stainless steel of nuclear reactors. The resistance to SCC depends on many factors, including the condition of reactor steels (a chemical composition and a structural-phase state), mechanical properties of materials, the susceptibility to corrosion damage, environments, temperature, etc. [1-3].

It is known that structure and properties of austenitic stainless steels can be significantly changed by impact of elevated temperatures and irradiation. The sensitizing aging during prolonged annealing or continuous cooling in the temperature range of 450 – 850°C leads to the formation of chromium rich carbides and the related chromium depletion of nearby grain boundary regions [4]. As a result, the sensitized steels are susceptible to intergranular corrosion and corrosion cracking. Neutron irradiation substantially influences on the structural-phase condition of steels due to complicated segregation processes and generation of radiation defects. Radiation damage significantly increases the susceptibility of austenitic steels to intergranular corrosion and SCC [5-6]. Except this, radiation hardening and embrittlement take place in steels under irradiation [7]. The formation of strain induced $\alpha'$-martensite with a bcc lattice in austenitic steels influences corrosion resistance [8], and gives an additional path for cracking development [9].

In a number of studies, it was concluded that the increase in a volume fraction of the $\alpha'$-phase in austenitic grains decreases in pitting and generalized corrosion resistance [10] as well as in resistance to intergranular corrosion [11]. The $\alpha'$-martensite acts as an effective reinforcing phase, as it supports a higher stress than the austenite under external loading [12]. The mechanisms of fracture in various environments for sensitized and neutron irradiated steel, containing $\alpha'$-phase, are not clear and require additional research.

This paper presents the analysis of fracture for samples of the 12Cr18Ni9 austenitic steel (AISI 304 analogue) ruptured under a fixed tensile load in air and in corrosive solution. This steel is metastable to formation of the strain-induced $\alpha'$-martensite. There were considered samples of austenitized, sensitized by annealing and neutron irradiated steel.
2. Materials and methods

Plane samples of the 12Cr18Ni9 austenitic steel were austenitized at 1050°C for 30 min, with further water quenching. The steel had a chemical composition (in wt.%) Fe (balance), C<0.12, 18.5Cr, 8.5Ni, 1.5Mn, 0.8Si, S<0.02, Ti<0.1. The microstructure of austenized steel was studied with an optical microscope Neophot-2. The grain sizes changed over the range of 17 - 60 µm, the average grain size was ~25 µm. Some of the samples were irradiated with neutrons up to a fluence of $10^{20}$ n/cm$^2$ at a temperature $\leq$80°C in the WWR-K research reactor (Almaty, Institute of Nuclear Physics). Other samples were sensitized by annealing at 650°C for 3 hours.

The shape and dimensions of steel samples are given in Figure 1. The samples had two symmetrically located triangular notches in the middle of a working part to localize strain and fracture in this narrow region. Experiments were carried out at room temperature in air and in a corrosive environment (a 30% FeCl$_3$ water solution). The samples were subjected to a fixed tensile load P. The critical fracture stresses $\sigma_f$ were determined as $P/S_0$, where $S_0$ is the initial cross-section in the region between the notches. The values of $\sigma_f$ were taken and increased stepwise to fracture in the interval of (0.2…1.1)$\times\sigma_{US}$, where the ultimate strength $\sigma_{US}$ were obtained from uniaxial tensile tests at a strain rate of $8.3\times10^{-4}$ sec$^{-1}$ at room temperature, using an Instron-1195 test machine, for appropriate steel samples without notches. Here $\sigma_{US}$ was 680 MPa for austenized steel, 720 MPa for sensitized steel and 725 MPa for neutron irradiated steel. The local ductility of steel in the region between the notches was characterized by a relative constriction $\psi$.

![Figure 1. A shape and dimensions (in mm) of steel samples. The thickness, $t$, equals 1 mm for non-irradiated samples and 0.3 mm for samples irradiated with neutrons.](image)

The analysis of fractured surfaces of steel samples was performed with a Hitachi TM4000 scanning electron microscope using a backscattered electron detector. Volume fraction ($M_f$) of a ferromagnetic martensitic $\alpha'$-phase induced by strain in steel was determined with a Fischer feritscope MP30E-S. Microstructure of the $\alpha'$-phase in steel samples was investigated with a JEOL-2100 transmission electron microscope.

3. Results and discussion

Table 1 data show the facilitated fracture of all types of steel samples in iron chloride solution as compared to the tests in air. The strain processes were accompanied by the formation of the strain-induced $\alpha'$-martensite. The volume fraction of the $\alpha'$-phase and the ductility were higher for samples loaded and ruptured in air compared to the samples ruptured in corrosive solution.

| Steel condition | Environment          | $\sigma_f$, MPa | $M_f$, %Fe | $\psi$, % |
|-----------------|----------------------|-----------------|------------|----------|
| Austenized      | Air                  | 619             | 8.7        | 11       |
| Austenized      | Iron chloride solution | 592             | 2.9        | 6        |
| Sensitized at 650°C | Air          | 757             | 15.0       | 39       |
| Sensitized at 650°C | Iron chloride solution | 632             | 9.6        | 20       |
| Irradiated to $10^{20}$ n/cm$^2$ | Air        | 359             | 1.3        | Low      |
| Irradiated to $10^{20}$ n/cm$^2$ | Iron chloride solution | 180             | 1.2        | Low      |

The sensitized steel showed a higher local ductility and martensite formation, when tested in both environments. The fracture stress for sensitized steel in air was found to be higher than the ultimate
strength. Neutron irradiated samples showed a high fragility of fracture in both environments and, as a result, small values of $M_f$ and $\psi$. The fracture stresses of the irradiated samples are several times lower than those of annealed steel samples.

Figure 2 shows fractographs for austenized steel samples ruptured in both environments. The fracture surfaces are typical for the dimpled rupture developing by the mechanism of nucleation, growth and coalescence of microvoids. The surface of fracture in air was characterized by the presence of equiaxed shallow and deep dimples with sizes of 2-17\(\mu\text{m}\) (Figure 2a). At fracture in corrosive solution, the dimples grew and merged with each other stretching along the direction of cracking.

**Figure 2.** The fracture surfaces of the 12Cr18Ni9 austenized steel ruptured in air (a) and in corrosive solution (b).

**Figure 3.** The fracture surfaces of the 12Cr18Ni9 steel sensitized at 650\(^\circ\text{C}\) and ruptured in air (a) and in corrosive solution (b, c).
On fracture surface, linear cracks with a length of 100 - 200 μm were observed, which nucleated at pitting corrosion defects on the lateral face of the sample and propagated through the sample by transgranular mechanism (Figure 2b).

The fracture surface of sensitized steel ruptured in air had an extended fibrous micromrelief (Figure 3a). Shear dimples and discontinuity flaws, up to 35μm in length, were formed at brittle secondary inclusions (as Me₂₃C₆ and residual TiC) being observed at the bottom of dimples.

The dimple micromrelief and narrow cleavage area near the corroded grains were observed at fracture surface for sensitized steel ruptured in corrosive solution (Figure 3b). There were observed many cracks (a river pattern) nucleating at corrosion defects and propagating normal to the tensile load direction, along grain boundaries and through grains (Figure 3b, c). The presence of multiple cracking seems to be responsible for decrease in ductility of sensitized steel in corrosive solution. The intergranular mode of fracture predominated for samples tested in corrosive solution as compared to samples tested in air.

TEM studies of sensitized steel, at a distance of 1.5 mm from the fracture surface, revealed the formation of α’-martensite with the length of 0.3 μm to 15 μm nucleating at intersections of stacking faults and twins. There were observed wedge and plate-shaped martensite inclusions adjoined grain boundaries (Figure 4a, c) and martensite lamels inside grains (Figure 4b, c). In accordance with the model of intergranular crack nucleation[13], the martensite inclusions act as strong barriers for dislocations and slip bands. The volume growth of martensite phase leads to increase in internal stresses acting on grain boundaries to a critical level, when the conditions for microcrack nucleation may be satisfied.

![Figure 4](image-url)

Figure 4. Strain-induced α’-martensite in the 12Cr18Ni9 sensitized steel near the fracture region. Wedge (a) and plate-shaped (b, c)martensite.(a) dark field image in the α’-phase reflex; (b, c) bright field image and dark field image, correspondingly, from the same site. The dotted line indicates the grain boundary position.

The influence of strain-induced martensite on fracture mode can be governed by size and distribution of α’-inclusions, which are nucleated in the neck region under load. When α’-inclusions are few and widely spaced, the dimple rupture is predominate. This was typical for steel in austenized and sensitized conditions. When inclusions nucleate and grow at the grain boundaries, intergranular dimple rupture results (Figure 3c). The growth of α’-inclusions can also contribute to the appearance of new planes of fracture. At large sizes or an increased local concentration of α’-inclusions, the formation of a cleavage surface is most likely. The latter is typical for steel irradiated with high neutron fluences.

Neutron-irradiated samples, ruptured both in air and in corrosive solution, showed the mixed type of fracture with the predominance (~70-80%) of brittle mode (Figure 5). The fracture surface consisted of a near-surface periphery region of cleavage fracture with numerous cracking (Figure 5 a,c) and an inner region of dimple fracture with separate cleavage facets and nuclei of microcracks (Figure 5 b, d).
The striation microrelief was revealed due to corrosive etching at the periphery regions of fracture surface for the sample ruptured in corrosive solution (Figure 5c). This area was situated directly behind the zone of corrosion damage of surface grains and has a length of ~80-100 μm. The pattern observed most likely corresponds to the packets of α’-phase lamels, mechanical twins and slip bands, as well. The most developed striations were observed in the immediate vicinity of deep intergranular cracks. It can be supposed that the cracks nucleated at martensitic packets and further propagated by intergranular mechanism. Except this, a number of cracks appeared at pitting corrosion defects, triple-point cracks, cracks on the etched twin-matrix interfaces and slip bands inside grains were observed.

The formation of a cleavage zone and deep intergranular cracking are responsible for the brittle fracture of irradiated steel in corrosive environment. Note that the irradiated sample ruptured in air is also characterized by a cleavage surface, deep cracks, which develop from the surface into the interior of the sample, but the structural mechanism of brittle fracture is not obvious.

![Figure 5](image_url)

**Figure 5.** The fracture surfaces of the 12Cr18Ni9 steel irradiated with neutrons, ruptured in air (a, b) and in corrosive solution (c, d). The fracture was predominantly intergranular with some transgranular contribution.

Radiation hardening cannot explain the change in fracture mode along the depth of irradiated steel samples. It is known that neutron irradiation increases the susceptibility of austenite steels to martensitic transformation and accelerates α’-phase nucleation and growth under stress [14-15]. Consequently, the formation of α’-phase can be expected to be peak in near-surface layers of the sample and relatively small in the internal area, where compressive stresses impede the growth of α’-phase. Thus, it is necessary to take into account non-uniform in depth hardening created by the non-uniform distribution of α’-inclusions. These events develop in a narrow region of a neutron irradiated sample between the notches and have little effect on the nearby volumes of the sample, in which the formation of the martensite phase is unlikely.
4. Conclusion
The experiments on fracture of the 12Cr18Ni9 austenitic steel under a fixed tensile load in FeCl₃ water solution as well as in air were carried out. There were considered samples of austenitized, sensitized by annealing at 650°C and irradiated with neutrons (to 10²⁰ n/cm²) steel. It was shown that fracture in corrosive solution occurred at lower stresses and strains in the structure containing a lower quantity of α’-martensite in comparison with fracture in air. Pitting and intergranular corrosion defects were additional centers of numerical cracking.

Austenitized steel exhibited ductile transgranular fracture surfaces in both environments. In sensitized steel, the mixed ductile transgranular and intergranular fracture took place in both environments, as well. The fracture surfaces of steel irradiated with neutrons and ruptured in both environments, had a layered structure, which included a peripheral region of cleavage fracture with numerous cracking and an internal region of dimple fracture with cleavage facets and nuclei of microcracks. The presence of two-layer fracture in irradiated steel is supposed to be connected with both the radiation hardening of steel and non-uniform spatial distribution of α’-inclusions formed under stress. It was shown that radiation hardening and sensitizing annealing increased the tendency of steel to intergranular cracking. The formation of packets of α’-martensite lamellae increases intergranular cracking, the presence of twins and slip bands can promote transgranular fracture in corrosive solution.

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