CORROSION CRACKING OF STAINLESS STEEL UNDER STRESS: THE PROBLEM AND ITS SOLUTION

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ABSTRACT

This study addresses the reasons behind stress corrosion cracking (SCC) of stainless steel and the lines of attack on this problem. The effects of different deposited oxide films on SCC were studied. These film coatings permitted the modeling of mechanical and chemical properties of the steel surface and surface layer. The understanding of the reasons behind SCC made it possible to suggest the ways of solving this problem. In particular, these films can increase the time-to-failure of steel under creep from 1 to 4575 h, while the average strain increases to 14–16%.

KEYWORDS

Stainless steel, deposited oxide films, chloride ion, corrosion cracking.

INTRODUCTION

Corrosion cracking of alloys depends on the level of mechanical stress [1]. In particular, corrosion tests of the SUS304 steel in a boiling (143°C) 42% $MgCl_2$ solution showed that (i) cracking did not take place at stresses below 110 MPa ($\sigma_{0.2}$= 244 MPa); (ii) at stresses 132–150 MPa, a crack issued from a corrosion center and propagated across a grain; (iii) at a stress of 180 MPa, cracking was of mixed character (intra- and intergranular); (iv) at stresses near the yield point, cracks formed at the junctions of three grains and rapidly propagated into the bulk along the grain boundaries. In the last case, the result was fatal, and brittle fracture proceeded rapidly, at virtually zero strains.

An abrupt increase in dislocation density in the surface layer accompanies the corrosion cracking of any alloy [2]. Brittle cracks propagate across dislocation pileups and twins and along grain boundaries loosened up (expanded) by dislocations.

As has been shown in [3], deposited oxide films can be used to control the dislocation density in the surface layer and the magnitude and sign of stress and to insulate the surface from an environment. In addition, film coatings permit the modeling of the stress–strain state of surface layers, with allowance for environmental effects, in SCC under virtually any conditions. This makes it possible to study all the processes that cause SCC and the reasons behind this phenomenon.

RESULTS

The tests were carried out with tubular pieces of 0.02C-16Cr-15Ni stainless steel under stress and creep in water with a chloride ion concentration of 100 mg /l and pH 3 at 340°C. The stress–strain state of the stainless steel surface was modified by deposited oxide films. This state was controlled by the following factors: (i) the sign of surface stresses (extension or compression); (ii) the intensity of surface stresses and relaxation effect; (iii) the surface energy barrier to dislocation egress; (iv) the lack of the surface energy barrier to dislocation egress; (v) insulation of the surface from environment. The testing cycle consisted of four stages. The first stage involved mechanical loading below the yield point; the second, third, and fourth stages involved creep at a rate of $1.06 \ 10^{-4}$, $4.2 \ 10^{-3}$, and $5.4 \ 10^{-3}$ % h^{-1}, respectively. These test conditions may be thought of as of the severest ones. They were used to reliably assess the efficiency of films for solving the problem of SCC and to study the influence of these films on the process of SCC itself.

The time to failure under given conditions depends on the composition of a deposited film and its thickness [4]. It is obvious that these two factors do not give a comprehensive idea of the mechanism and protective action of deposited films. Therefore, the following parameters were considered to study the effects of deposited films:

1. ***Oxide film material.*** Both amorphous and crystalline metal oxide films (Zr, Y, Zr–Y, Zr–Ni–Fe, Sn, Ce, Sc, Fe, Ni, U), as well as layered oxide compositions, were used. Employing different film materials made it possible to modify the properties of the films and the properties of steel–film systems and resulted in various degrees of insulation of the specimen surface against ambient chloride ions.

2. ***Film thickness.*** The thickness of films was varied from 0.01 to 6 μm.

3. ***The intensity and sign of internal stresses in as-deposited films.*** As has been shown in [3], virtually all deposited films are characterized by considerable internal stresses. Film properties, including the intensity and sign of internal stresses, are able to considerably change the kinetics of deformation, hardening, and failure of substrate materials.

4. ***Relaxation effects in films***. This parameter determines the sign and intensity of the mechanical stress induced by a film in the surface layer of a substrate, both before and in the course of corrosion treatment.

5. ***Film deformability and imperfectness.*** Defects were monitored with a scanning electron microscope both in the as-deposited films and at the moment of test termination.

The time to failure and average strain of specimens were used as criteria for their stability toward corrosion cracking. In addition, the surfaces and fractures of selected specimens were examined at different stages of test. The test results are listed in Table 1.

TABLE 1

FORMAL RESULTS OF SCC TESTS OF STEEL SPECIMENS

No.	Specimen	Time to failure, h	Average strain, %
1	Uncoated steel	1 – 3	3.6 – 3.7
2	With an urania film	< 1	1.0 – 3.0
3	With an iron oxide film	1 – 1020	1.2 – 5.6
4	With a nickel oxide film	1 – 1980	2.2 – 7.6
5	With a zirconia film	200 – 1820	3.9 – 7.4
6	With a ceria film	500 – 1920	5.7 – 7.7
7	With a tin oxide film	1660 – 1880	7.3 – 9.0
8	With a zirconia–yttria film	340 – 1820	4.4 – 6.7
9	With a zirconia–iron oxide–nickel oxide film	1820 – 1980	6.4 – 13.1
10	With layered films	From 920 to 4575 without failure	5.0 – 14.0
11	With an yttria film	From 2140 to 4575 without failure	8.2 – 16.8
12	With a scandia film	From 1660 to 3600	6.3 – 12.6

Noteworthy is a large scatter of time-to-failure and average-strain values for specimens of the same set. However, there is no conflict here, since the above characteristics depend on the properties of the film and steel–film system and on the varied protective function of the film against a corrosive environment. Comprehensively studying the film-coated specimens of the same set have shown that both time-to-failure and ultimate strain correlate well with several factors that determine the process. The influence of these factors was studied for each specimen set.

The effects of the sign of mechanical stresses induced by a deposited film in the surface layer of steel. This influence follows the rule: tensile stresses provoke SCC, and compressive stresses inhibit SCC. In particular, urania films (set 2) (over the entire range of varying other parameters) and iron and nickel oxide films (sets 3 and 4, respectively) (in a portion of the range) created tensile stresses in steel. This resulted in a decrease in time-to-failure and ultimate strain, against uncoated steel. The remaining films (sets 5 and 6) created compressive stresses. This led to an increase in time-to-failure and ultimate stress, against uncoated steel.

The effect of the intensity of stresses induced by a film. The effect of tensile stress is quite definite: the higher the stress, the stronger the corrosion cracking caused by a film. The effect of compressive stress depends on stress intensity more complexly. With an increase in compressive stress, the resistance to corrosion increases, goes through a maximum, and then decreases. Figure 1 shows the plot of time-to-failure of coated specimens versus stress created by different films.
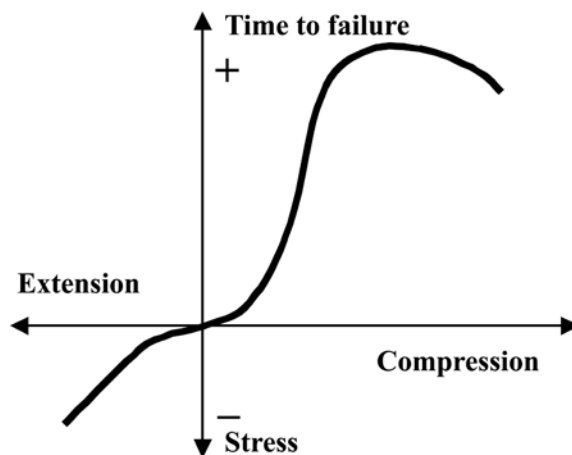

Fig. 1: Qualitative dependence of time-to-failure upon SCC on the magnitude of stresses created in the steel surface layer by a deposited film. Zero at the time coordinate axis corresponds to the time-to-failure of an uncoated steel specimen

We assume the following reason behind the effect of surface stresses on SCC: if a film, along with the external mechanical load, promotes the accumulation of deformation defects (for example, dislocations) in the surface layer of a steel specimen, this provokes brittle crack nucleation. In this case, the time-to-failure and ultimate-strain values decrease. Critical hardening of the steel surface layer can be realized even prior to corrosion tests (in the course of oxide film deposition). This is the case with a set of urania-coated specimens. If a film, due to compressive stresses, retards accumulation of deformation defects in the steel surface layer, a brittle crack forms at a later time, and the ultimate strain increases. However, given that a film creates large compressive stresses in the steel surface layer, the latter can be deformation-hardened by the film itself. Under external mechanical load and environment action, such a hardened layer can also be prone to brittle crack formation. However, the time-to-failure and ultimate strain values undoubtedly exceed those observed for tensile stresses.

The effect of the film thickness. It is quite reasonable to assume that an increase in the thickness of a deposited film should result in the buildup of its protective effect, for example, under the conditions of corrosion cracking tests. This general tendency was observed for some sets of specimens, but not for all of them. For specimens of the same set, the time-to-failure upon cracking is dominated by internal stresses in a film, which induce corresponding stresses in the steel surface layer, rather than by film thickness. This correlation is exemplified by an iron oxide film in Fig. 2a and by a zirconia film in Fig. 2b.
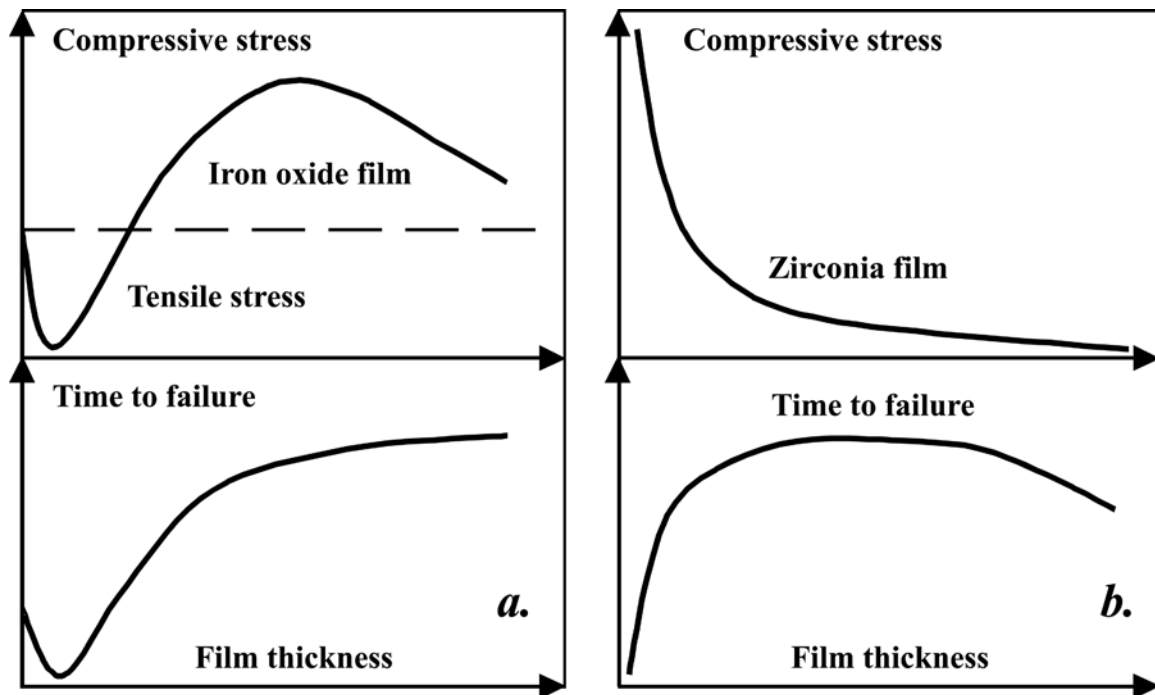
Fig. 2a: Correlation between internal stress in an iron oxide film and time-to-failure of film-coated steel specimens, depending on the thickness of the deposited film

Fig. 2b: Correlation between internal stress in a zirconia film and time-to-failure of film-coated steel specimens, depending on the thickness of the deposited film

Figure 2a shows that tensile stresses in iron oxide films up to 1 μm thick reduce the time to failure of the substrate. For compressive stresses, the time to failure abruptly increases for the film thickness ranging from 1 to 2 μm, and a further increase in film thickness has virtually no effect on the time to failure of the substrate.

Figure 2b shows that zirconia films with maximal compressive stresses considerably (hundredfold) increase the time-to-failure of film-coated steel specimens compared to the uncoated one. However, with an increase in film thickness and the corresponding decrease in internal stress, the time-to-failure increases still further, passes through a maximum, and then abruptly decreases.

Influence of relaxation in deposited films. Deposited films are characterized by structural relaxation [3]. Relaxation is a structural reconstruction, which changes stresses, continuity (imperfection), and many other film properties. In addition, relaxation effects in deposited films can considerably change the stress–strain state of the surface layer of substrates, their mechanical properties, and even the character of failure [3]. For the SCC problem under given test conditions, thermal, deformation, and adsorption relaxations are of crucial importance. Generally, relaxation can result in the decrease in internal stresses in films and in the enhancement of their influence on the steel surface layer; also, relaxation can lead to the crystallization of some films and to the formation of microcrack defects in these films. The most injurious effect is typical of adsorption relaxation. Adsorption relaxation, in the form of implantation of chloride ions in the film structure, usually results in additional tensile stresses in the film and, correspondingly, in the steel surface layer. This effect is most pronounced in iron, nickel, and uranium oxide films. Zirconia, tin oxide, and ceria films, as well as mixed Zr–Y and Zr–Fe–Ni oxide films, respond to the implantation of chloride ions to a lesser extent: tensile stresses in films decrease. For yttria and scandia films, adsorption relaxation does not manifest itself, at least, over a period of 1500 h.

Film deformability and imperfection. As shown by tests, all as-deposited films had no defects. In tests, crystalline films strained 1–1.5% cracked. In addition, crystalline films create a high barrier to dislocations, thus resulting in their concentration in the steel surface layer. Cracking these films promotes steel failure, regardless of the other properties of the surface and films. Therefore, crystalline films were not used in further tests.

In amorphous films, microcrack defects were observed in specimens coated by Zr, Zr–Y, Zr-Fe-Y, Ce, and Sn oxide films at an average strain of more than 5%. Noteworthy is that microcracks are uncommon in urania and nickel and iron oxide films, although the specimens coated by these films fractured rapidly at a

strain of less than 2.5%. Yttria and scandia films exhibit the highest deformability without defect formation. Examining the surface under the electron microscope indicates that these films are capable of deforming without failure up to strains of 8–12%. With an increase in test duration and deformation, these films crystallize and crack; however, hundreds of hours can elapse before failure.

Figure 3 shows a representative fracture. As a rule, the fracture section contains the region of brittle failure, in which cracks propagate along grain boundaries; the region of brittle–ductile failure, in which cracks propagate along the directions of stress localization; and the region of ductile failure, typical of ductile steel.
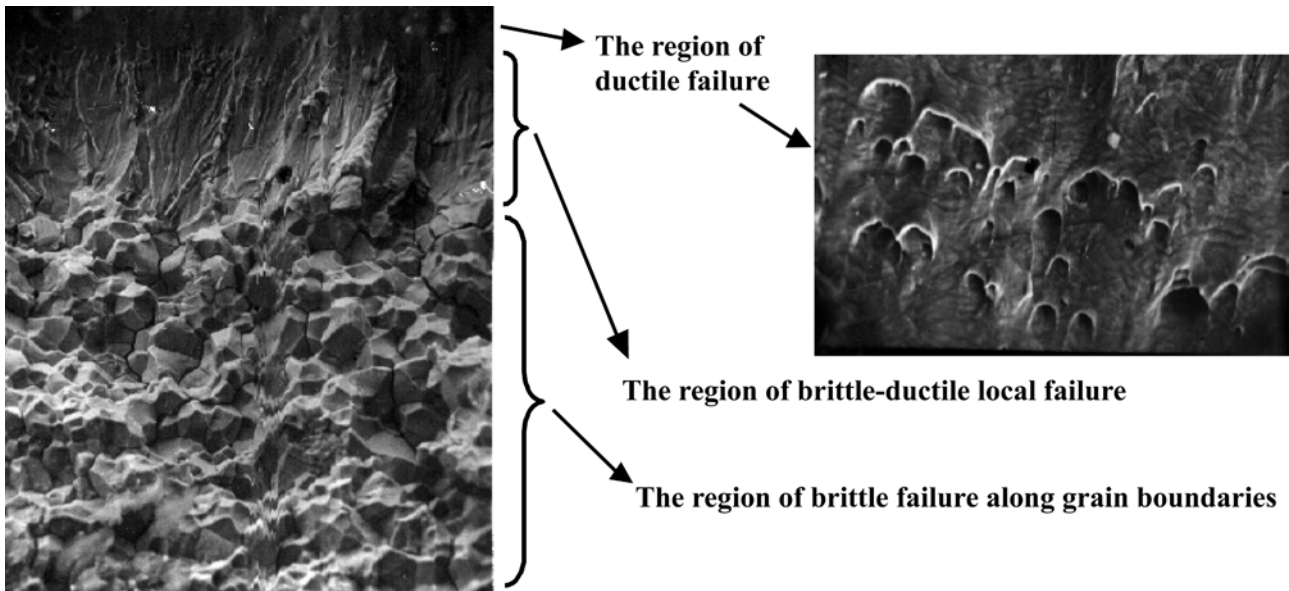

Fig. 3: Representative fracture of broken specimens

Reasons behind brittle failure upon SCC. Our findings and results reported in [3] allow us to argue that brittle failure is a result of the abnormal deformability of the surface layer, which accumulated deformation defects under an external mechanical load considerably lower than the yield strength of the bulk. The accumulated defects are localized in planes, and localization directions depend on the intensity of external mechanical stresses. This factor distinguishes intergranular brittle failure from intragranular one. The phase film that forms in water stimulates this process, since its formation is accompanied by an increase in volume, which results in additional tensile stresses in the surface layer. Chloride ions, being built into the structure of the phase film, induce even greater tensile stresses in the surface layer. The phase film and hardened surface layer represent an efficient barrier that prevents a "soft" drop of internal stresses and mechanical energy dissipation. Therefore, crack nucleation across dislocation pileups requires minimal energy consumptions. Brittle crack nucleation is a process of separation of a grain along the plane of dislocation pileups, or a process of separation of grains from one another along the grain boundaries. Embrittlement can propagate inward and can result in local deformation at stress concentrators upon stability loss of an entire specimen.

Ways of preventing SCC of steels.
To efficiently guard against SCC, the following measures are recommended:
1. To create internal compressive stresses, in the surface layer, which persist for a long time under material extension conditions;
2. To create conditions preventing accumulation of deformation defects in the surface layer, for example, by virtue of the dislocation and vacancy pump effect revealed and described in [3];
3. To insulate the surface against injurious environmental effects, in particular, against chloride ions.

Deposited oxide films can meet the above requirements. These films should have a complex of appropriate properties and characteristics, the most important being an amorphous layered structure, chemical stability in chloride-containing water, internal compressive stresses whose relaxation results in compression, and high adhesion and deformability.

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