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Sensitization Evaluation of the Austenitic Stainless Steel AISI 310 used in Biomass Gasifier

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Abstract

Stainless steels are the most important family of passive materials. In addition to wide-range applications in corrosion services, some members of this family namely AISI 310 have been used in the structural components of biomass gasifiers operated at temperature as high as 850°C. The high temperature performance of these alloys depends largely on the stability of the microstructure, particularly the distribution of precipitates in the form of carbides and other intermetallic phases. On the other hand, the most widely encountered corrosion failures experienced with stainless steels are localized in their nature like intergranular corrosion. It is important to note, this type of corrosion are the results of the unavoidable changes in the microstructure during improper heating condition. The corrosion resistance of these alloys was degraded due to the depletion of chromium. In this paper, double loop electrochemical potentiokinetic reactivation (DLEPR) test was applied to the specimen taken from worn-out air nozzle and service exposed hearth portion of the bio-mass gasifier to detect the effect of intergranular corrosion in these alloys. The ratio of reactivation and anodic current densities (I_r /I_a) X 100 permit the evaluation of the degree of sensitization (DOS). The air nozzle worn out sample, which must be characterized by weak values ($I_r/I_a<1$) of the current density ratio (I_r /I_a = 1.02%). For both the samples the anodic and reactivation current densities must also be high enough to lead to peaks clearly perceptible. The effect of low amounts of chromium depletion is corresponding to the fine precipitations of carbides or high-chromium intermetallic phases at the interfaces.

Key words: DLEPR; Austenitic stainless steel; Corrosion; Sensitization; Bio-mass Gasifier

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1. Introduction

A biomass gasifier system in its traditional version of development had been fabricated using high quality AISI type 310 stainless steel (high temperature stainless steel), for its reactor section. A schematic diagram of the gasifier is given in Fig.1. Solid biomass fed from the top of the system is pyrolysed in the middle zone of the reactor after the biomass passes through a drying zone. The pyrolysed gas mixture undergoes further reduction reactions and the final gas agglomerates are taken from the bottom of the gasifier systems.

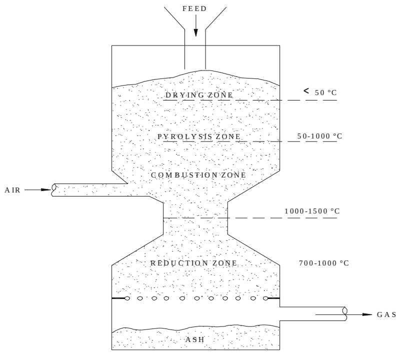

Fig.1. Schematic diagram of a down drought gasifier

In order to ascertain that the gas coming out from the bottom strata of the system has undergone the reduction reaction fairly compliably a 'throat' or restricted region is adopted in the design. In the earlier version of such reactors the throat region was exposed to high temperatures with fluctuations in the temperature profile. Due to intermittent operations after shut off and start on sequences of the systems around this region was experiencing cyclic thermal stress and hence after few hours of operation the throat portion gave way by developing cracks.

Even though the macroscopic reason for the failure was broadly known leading to improvement of throat portion with ceramic lining in subsequent versions of gasifier systems, no serious attempt was put to understand the microscopic details of the occurrence of such failures. Here an attempt is made to understand this problem using electrochemical potentiokinetic reactivation (EPR) tests on specimens taken from worn-out air nozzle and service exposed portion of the gasifier.

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A field study [1] indicates that all gasifier technologies available in India are based on induced downdraft gasification and designed primarily for woody biomass. The major reason for the failure in most cases of the gasifier part is because of the failure of the structural material used for gasifier construction. Materials failure can be because of imperfect design, selection of improper material, intrinsic material flaws, and poor maintenance and service. The austenitic steel has been used for the construction of the gasifier. Material failures occur mainly in the gasifier throat and air nozzle regions and mostly within 1500 hours of operation. This is mainly because of the material of construction experiencing severe high temperature oxidation and corrosion during operation [2].

The electrochemical potentiokinetic reactivation method has been developed for testing and evaluation of intergranular corrosion sensitivity as well as stability of passive state [3]. This technique for especially detecting sensitization of 304 stainless steels was developed by Majidi and Streicher [4].

In the double loop test, specimen is first polarized anodically through the active region then the reactivation scan in the reverse direction is carried out. When it is polarized anodically at a given rate from the corrosion potential to a potential in the passive area, this polarization leads to the formation of a passive layer on the whole surface. Then when scanning direction is reversed and the potential is decreased at the same rate to the corrosion potential, it leads to the breakdown of the passive film on chromium depleted areas. A ratio of maximum current generated in the double loop test (I_r/I_a) is used as a measure for the degree of sensitization.

2. Experimental

For Double loop EPR test, the specimens were mounted in epoxy resin (Araldite) using brass rod as electrical connection. The mounted specimens were polished up to fine diamond (1µm) finish. The specimens were ultrasonically washed in soap solution, degreased, rinsed in distilled water and finally dried. DL EPR tests were conducted in the polarization cell containing 0.5M H_2SO_4+ 0.01M NH_4SCN solution. The electrolytes were purged with purified argon gas to deaerate the electrolyte prior to experiment and purging was continued till the end of the experiment. The mounted specimen was immersed in the solution after polishing upto fine diamond finish. Open circuit potential (OCP) was noted. The specimen was polarized to -500 mV (SCE) and kept at that potential for 2 minutes, and then the specimen was anodically

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polarized from -500 mV (SCE) to +300 mV (SCE) and then cathodically polarized to OCP from +300 mV (SCE) at a scan rate of 100 mV/min using Solartron Model 1287 electrochemical interface. For each specimen, the activation and reactivation curves were recorded. From these curves reactivation current density (I_r) and activation current density (I_a) were measured and (I_r/I_a x100) % was calculated. This value represents the %DOS of the specimen. The chemical composition of this steel is given in Table 1.

Table1: Chemical composition of AISI 310 stainless steel

Carbon	0.25 max
Chromium	24 - 26
Nickel	19 - 22
Manganese	2 max
Silicon	1.5 max
Phosphorus	0.045 max
Sulphur	0.03 max
Iron	Balance

2.1 Double Loop Electrochemical Potentiokinetic Reactivation Tests

The tests were performed an active to a passive domain (activation or anodic scan), followed by a return to the initial potential (reverse or reactivation scan). The ratio of reactivation and anodic current densities (I_r /I_a) permits the evaluation of the degree of sensitization and are presented in Figures 2&3. The DL-EPR test efficiency is measured by means of a response test, which must be characterized by weak values of the current density ratio for two different materials namely the air nozzle worn out (I_r /I_a = 1.02% DOS) and the service exposed sample (I_r /I_a = 0.024% DOS).

For the air nozzle worn out and service exposed samples, the anodic and reactivation current densities must also be high enough to lead to peaks clearly perceptible. In addition, the test selectivity must be confirmed by the existence of the reactivation peaks related to inter-crystalline chromium depletion, followed by film formation on the passivation process. The effect of low amounts of chromium depletion is corresponding to the fine precipitations of carbides or high-chromium intermetallic phases at the interfaces.

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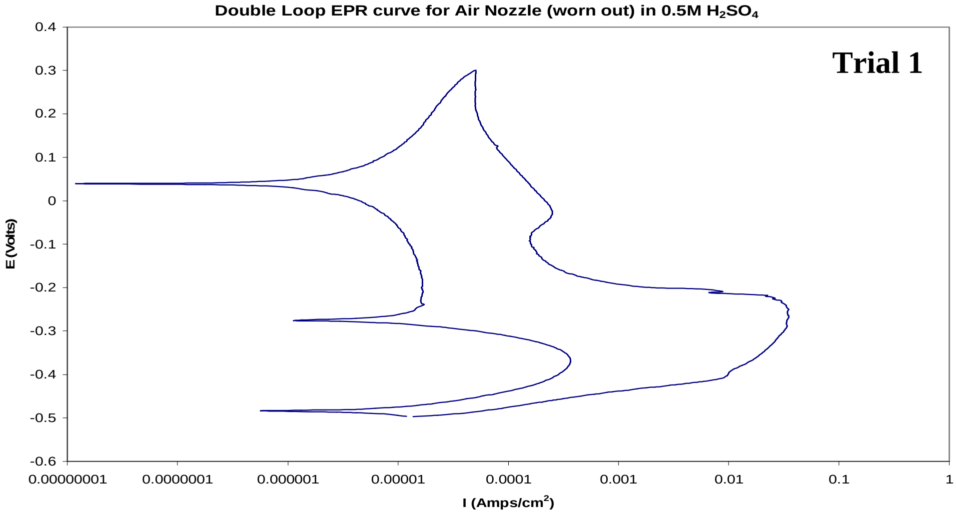

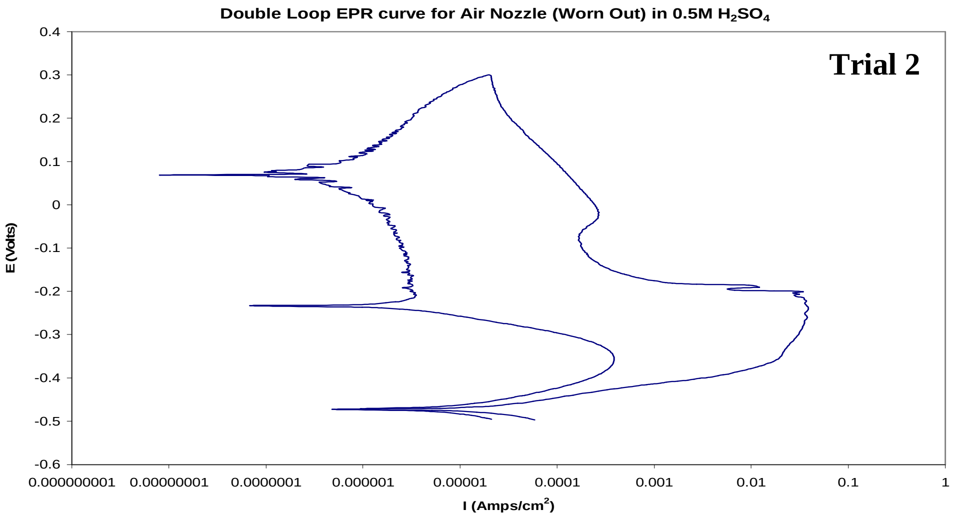

Fig.2.Double Loop EPR curve for Air Nozzle (worn out) in 0.5M H_2SO_4

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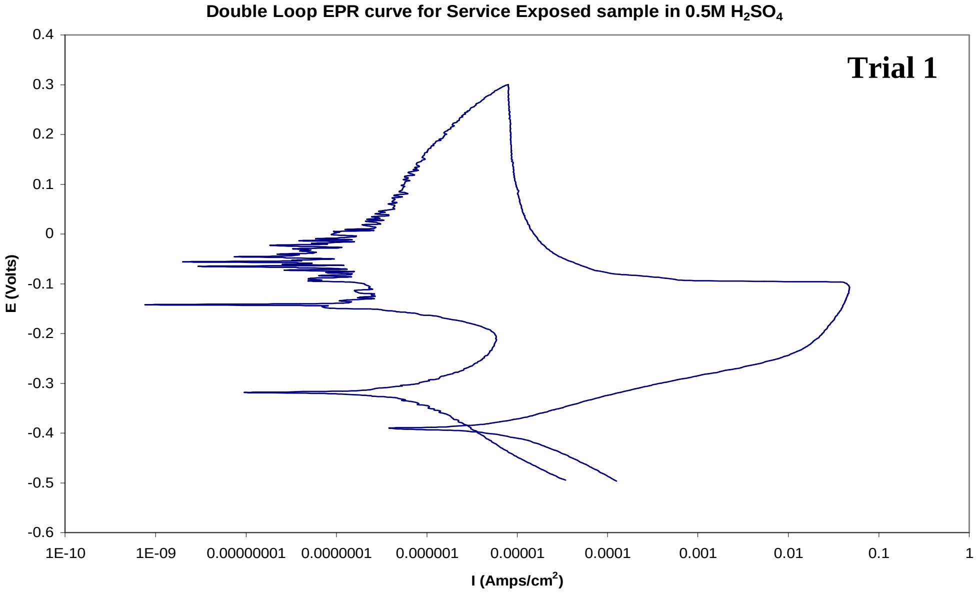

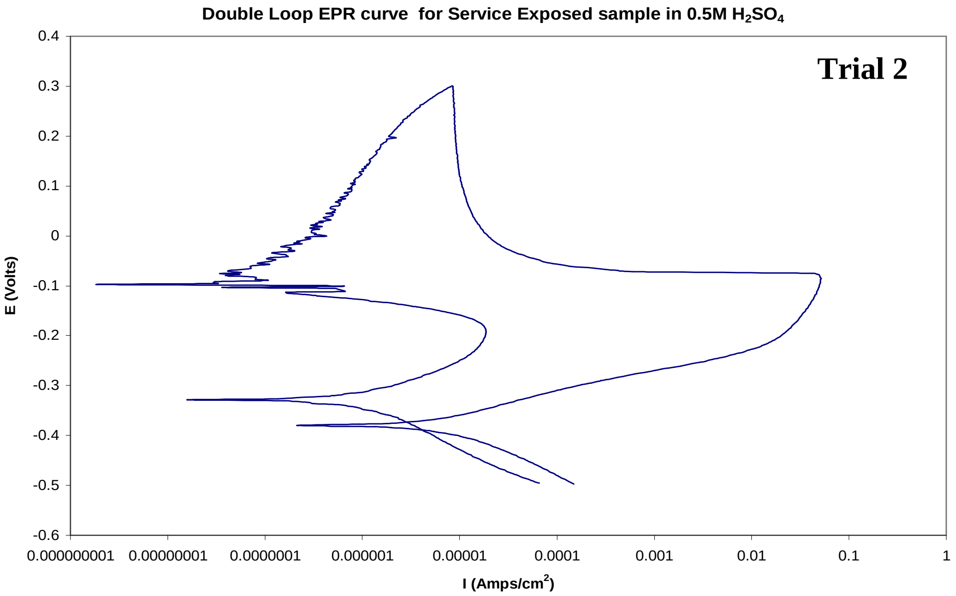

Fig.3. Double Loop EPR curve Service Exposed sample in 0.5M H_2SO_4

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2.2 Influence of the Potential Scan Rate

Anodic and reactivation current densities are high enough to yield a clearly perceptible reactivation peak (at - 250 mV/SCE). It corresponds to (IGC) Intergranular corrosion. A second peak relative to uniform corrosion appears at a potential of + 50 mV/SCE, for both materials, with a high density of pits localized in the austenitic phase.

2.3 Structure of Steel

The EPR microstructure will show the regions where etching taken place due to poor passive film which is a result of Cr/Mo depletion. The micro structure of the steels reveals the visible precipitation of chromium carbide at the grain boundaries as shown in Figures 4&5. The micro structure corresponding to an eutectoid decomposition of the austenite phase, which is transformed partially or totally into regenerated austenite (γ), chromium carbides, and intermetallic phases. This decomposition is very fast form negative potential region to more anodic region. The attained state of the austenite decomposition depends on the chemical composition of the steel. The precipitation of chromium carbides at the grain boundaries is due to the thermal and mechanical stresses in the material on elevated temperature exposure service conditions. Sensitization to Intergranular Corrosion (IGC) in stainless steels occur due to a thermal treatment as grain boundary carbides form leaving chromium depleted regions adjacent to the grain boundaries [5].

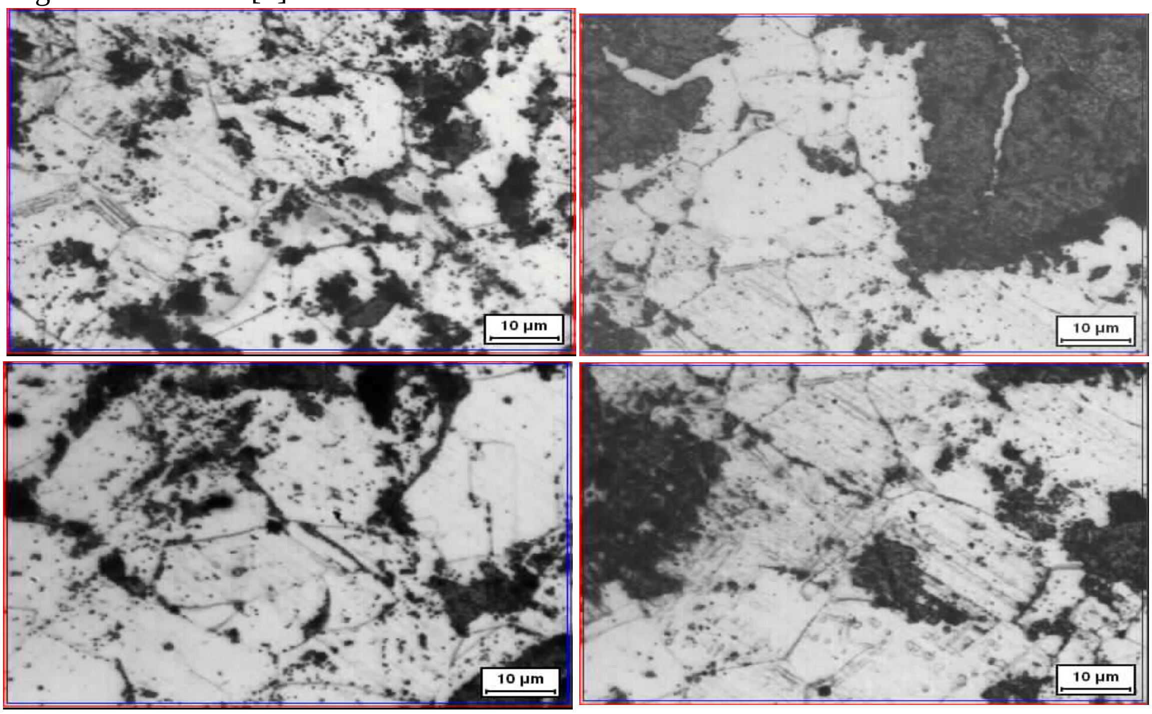

Fig.4. Microstructure obtained after DL EPR experiment for Air nozzle (worn out)

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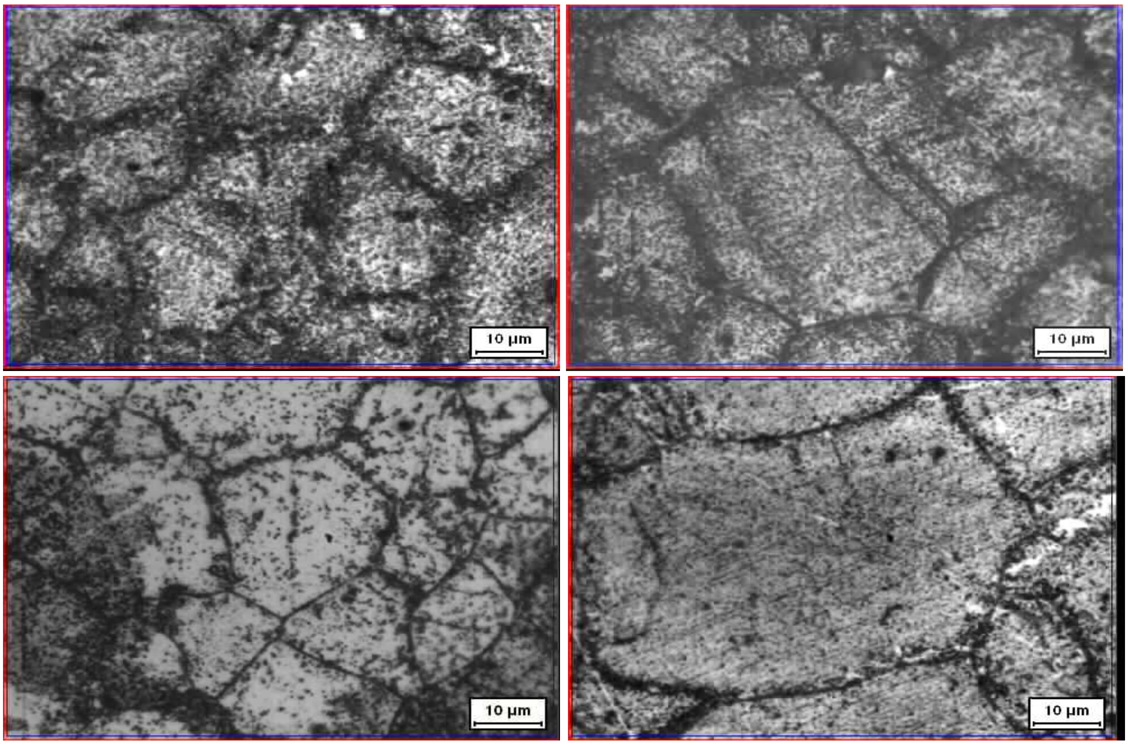

Fig.5.Microstructure obtained after DL EPR experiment for Service Exposed

3. Results and discussion

The results of this study confirm the usefulness of the DL-EPR method in evaluating quantitatively the sensitization of austenite phase. The DL-EPR method has the advantage of being a fast, quantitative, nondestructive test that can easily be incorporated into the monitoring of equipment exposed to localized corrosion risks in general and to IGC in particular. However, the sensitivity and the selectivity of the test in the detection of chromium depleted zones seem to depend markedly on the type and temperature of the electrolyte and the potential scan conditions of the test. Activation and reactivation current densities depend significantly on the kind atmosphere exposed.

The role of NH_4SCN modifies the stability of the passive layer generated in an H_2SO_4 medium. On increase in anodic polarisation leads to the cracking of the passive layer during the anodic scan and to the dissolution of chromium-depleted zones, this has a less resistant passive film, during the reactivation scanning. For this reason, the anodic (I_a) and reactivation (I_r) current

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densities increase noticeably on increase in potential. A second reactivation peak appears at + 50 mV/SCE. This corresponds to the high-density pitting in the initial austenite phase. However, the magnitude of the reactivation peak current varied significantly with the degree of sensitization and these values are summarized in Table.2. It is very small approximately in the order of 10^{-6}-10^{-4}A/cm^2 for non sensitized service exposed specimen but increased to values as high as 10^{-3} A/cm^2 for mildly sensitized worn out specimen, originating from the Cr depleted regions.

Table 2: Degree of sensitization (%)

Specimen	Trial 1		%DOS	Trial 2		%DOS	Average %DOS
	I_r(A)	I_a(A)		I_r(A)	I_a(A)		
Air Nozzle (Worn Out)	0.00035619	0.034451	1.03	0.00038062	0.037646	1.01	1.02
Service Exposed	5.9 X 10^{-6}	0.047447	0.012	1.86 X 10^{-5}	0.051398	0.036	0.024

The DL-EPR test selectivity through the appearance of a second reactivation peak, at + 0.50 mV/SCE in both materials, related to pitting or uniform corrosion as reported in many of the austenite stainless steels. The micro structural investigations reveal after DL-EPR tests a marked pitting in all austenitic grains is visualized. The second sample, i.e service exposed austenite stainless steel, the rate of chromium carbide precipitation is relatively low. It is due to the carbon solubility is higher in the austenite phase. It is known that the carbon solubility increases significantly with decreasing molybdenum and chromium content, resulting in the resolution of precipitated $M_{23}C_6$ carbides [6]. In addition, the intermetallic phases are less stable, in the material because of high temperature exposure on service. Here the chromium diffusion rate is high, which ensures a fast rechromization on eventual chromium-depleted zones. Consequently, for those reasons, the absence of the formation of chromium-depleted zones explains the very low values of ratios (I_r/I_a). This result confirms the close relation between both the chromium depletion and IGC sensitization and the rechromization and the desensitization to the IGC.

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4. Conclusions

The optimal condition of the DL-EPR tests for evaluation of IGC sensitization of the austenitic stainless steels namely 310 is manifested. A reproducible DL-EPR test method was developed to characterize the degree of sensitization in both materials. This method makes use of a solution of 0.5 M H_2SO_4 + 0.01M NH_4SCN and a scan rate of 100mV/min. The high selectivity and sensitivity of this test at a low degree of chromium depletion could lead to the future widespread use of this test as a fast, quantitative, and nondestructive technique for evaluating the IGC sensitization of service equipment or wrought products.

The IGC sensitization of austenitic stainless steels is imputed to the chromium depletion phenomenon resulting from the precipitation, forming the intermetallic phase (Fe-Cr- Mo) and $M_{23}C_6$ carbides on high temperature service. The chromium-depletion phenomenon resulting from the precipitation of chromium carbides was evaluated by EPR micro structural studies. The DL-EPR test enables the quantitative evaluation of the degree of the sensitization, which is useful in monitoring stainless steel structures in service. The interactions between precipitation and IGC sensitization have been well studied by this technique.

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