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Understanding the effect of uniaxial tensile strain on the early stages of sensitization in AISI 304 austenitic stainless steel

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HIGHLIGHTS

- Interplay of various dynamic processes (four) in the early sensitization.
- Deformation induced martensite (α') playing major role at low temperature.
- α (Tempered martensite) induced processes plays a vital role at higher temperatures.
- Results in non monotonous variation in degree of sensitisation (DOS).

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ABSTRACT

In the present study, an attempt has been made to understand the effect of different competing mechanisms controlling the overall degree of sensitization (DOS) of deformed austenitic stainless steel at the early stage of sensitization. The Double Loop Electrochemical Potentiokinetic Reactivation (DL-EPR) studies were performed to characterize the Degree of Sensitization (DOS) as a function of both pre-defined strain and sensitization temperature. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to explain the phenomena qualitatively. A non monotonous behaviour in the variation of DOS has been observed with deformation and sensitization temperature. The presence of Deformation Induced Martensites (DIM) and their transformation into tempered martensites ($\alpha + M_{23}C_6$) at higher temperatures was found to play major roles in controlling the overall sensitization and desensitization processes.

1. Introduction

Austenitic stainless steels are widely used for different industrial purposes due to a combination of good mechanical properties and excellent corrosion resistance over a large temperature range [1–3]. The high chromium content in these alloys plays a vital role in achieving remarkable resistant properties against different types of uniform corrosions. However, there are also different types of localised corrosions which are observed in austenitic stainless steels [1–4]. Sensitization is caused by the formation of precipitates along the grain boundaries, resulting in the depletion of Cr at near grain boundary regions. Intergranular corrosion is a type of localised corrosion frequently observed in different types of austenitic stainless steels, solely due to the process of sensitization.

Since sensitization is a diffusion assisted process, it is effectively influenced by the microstructure which is the result of different thermo mechanical processes experienced by the materials. In the work performed by L. E. Murr et al. [5], it was observed that the uniaxial tensile strain prior to aging of solution annealed AISI 316 stainless steel pipes resulted in a dramatic change in the degree of sensitization (DOS) of those materials. It was first observed by Povich and Rao [6] that AISI 304 stainless steel pipings in boiling water reactors experience significant sensitization after 10 years even at the operating temperature of 573 K. Trillo et al. [7] have shown that not only the microstructure has significant influence on precipitation and sensitization kinetics, but also the deformation particularly the amount of straining may accelerate these kinetics processes [5,8,9]. The influence of deformation induced martensite (α') and γ austenite serve as nucleation sites for carbide precipitation and provide an effective grain refinement which accelerates

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both sensitization and desensitization [10]. However, in most of the recent works [11,12], the phenomenon of low temperature sensitization have been studied at relatively higher temperature (>773 K) and with longer ageing time. In the present study, the main objective is to understand the early sensitization process of 304 grade austenitic stainless steel due to prior straining of the as received as well as heat treated samples at a temperature regime of 473–873 K with soaking time of 1 h. The soaking time of 1 h was chosen to understand the interplay of the various dynamic processes (namely classical sensitisation and desensitisation and also α and α' induced sensitisation and desensitisation) involved in the overall sensitisation process before the equilibrium is reached. The microstructure of the samples has been characterised by Scanning electron microscope (SEM) and X-ray diffraction technique (XRD). The degree of sensitization (DOS) has been measured by double loop electrochemical potentiokinetic reactivation (DL-EPR) test [13–15]. The EPR test for measuring the DOS is known to have certain advantages over to the conventional corrosion tests, it is much quicker, more accurate and more sensitive, particularly for less sensitized specimens [15–19]. Since the main objective of this study is to understand the dynamics involved in the sensitisation process before equilibrium is reached, the EPR technique has been used to measure the DOS of the samples.

2. Experimental

The composition of the AISI 304 stainless steel used in the present study is given in Table 1. The steel was obtained in the form of rolled sheet of 3 mm thickness. Tensile samples of gauge length 30 mm were machined and these were deformed at different uniaxial strains (10%, 20%, 30%, 40%, 50%) using the Instron™ tensile testing machine at a strain rate of 10^{-3} per second. The gauge length portion of each sample was then cut into four rectangular pieces and three of them were heat treated at temperature 473 K, 673 K and 873 K. The heat treatment was performed under vacuum (air pressure ~ 10^{-3} mbar) and the soaking time was maintained at 1 h followed by furnace cooling. A set of 24 samples were thus prepared from 5 set of tensile samples.

The XRD patterns were obtained from a Rigaku Ultima III X-ray Diffractometer using Cu-K_α radiation in the 2θ range of 30° to 100°.

The DL-EPR studies were carried out on all the 24 samples to measure their DOS. The specimens were finely polished and then ultrasonically degreased in soap solution. Then the samples were washed thoroughly with distilled water and dried. DL-EPR test were conducted in a polarization cell containing 0.5 M H_2SO_4+0.01 M KSCN solution. The mounted sample were immersed in the solution and the open circuit potential (OCP) of the specimen were noted. Inside the cell, the polarization of the specimen with respect to a saturated calomel electrode (SCE) was maintained to −500 mV for 2 min to dissolve the air formed oxide film. Then the specimen was polarized anodically from −500 mV (SCE) to +300 mV (SCE) and then cathodically polarized from +300 mV (SCE) to OCP at a scan rate of 1.67 mV/s using Gamry 600TM model electrochemical interface. The electrode potential vs. Log current was then recorded with the help of the interface. From the variation of current density with electrode potential (the DL-EPR curve), the peak current during reactivation (Ir) and the peak current during activation (Ia) was noted and the percentage ratio of them (Ir/Ia × 100%) were measured as DOS.

The JEOL JSM-6360 Scanning Electron Microscope (SEM) was used to obtain the micrographs of all the samples. Before taking the micrographs, the samples were finely polished and then etched using 10% HNO3 + 30% HCl +60% distilled water solution.

Table 1
Chemical composition in wt% of AISI 304 austenitic stainless steel.

C	Mn	Ni	Cr	P	S	Si	Fe
0.039	1.490	8.620	18.890	0.031	0.009	0.560	Balance

3. Results

XRD pattern has been collected in as received and heat treated condition. Fig. 1a shows the XRD peaks of as received sample and deformed sample as a function of strain. Split in (111) γ peaks reveals the presence of martensite in a small quantity within the matrix. A change is observed at 20% strain where a single peak of (111) γ is only observed with the suppression of adjacent (110) α′ peak due to preferred orientation. The split in the peak is again observed at 30% strain and the intensity of this peak increases as a function of deformation. The similar phenomena were observed for the sample heat treated and aged at 473 K (Fig. 1b), where strain induced martensite formation is seen at a relatively lower strain (i.e. at 20%). The martensite is found to exist up to 50% strain without decomposition and its intensity increased with deformation due to preferred orientation. However at 673 K the α′ martensites present in the sample start transforming into tempered martensite having carbide precipitation in the form of $M_{23}C_6$ [7,11,20] which results in the phase mixture of α and α'. As a result the intensity of XRD peaks corresponding to α' phases substantially decreased which is evident from Fig. 1c. The transformation becomes more predominant at higher temperature, resulting in the formation of substantial amount of α phases in γ austenite matrix at the temperature of 873 K. Hence at that temperature a measurable increase in the intensity of the XRD peaks adjacent to the (111) γ peaks is observed in Fig. 1d due to the presence of α phase in the sample.

A typical DL-EPR curve for the highest strained as deformed sample is represented in Fig. 2. From this figure, it is clear that the height of the reactivation peak (I_r) is significantly smaller than the height of the activation peak (I_a), resulting in a measurable value of DOS for this sample.

The variation of DOS with respect to percentage strain for all the deformed and heat treated samples along with the as received one is shown in Fig. 3. No significant variation in the DOS was observed at the room temperature. However, at higher temperatures, the variation of DOS with strain becomes significant and changes with increasing temperature. A systematic increase in DOS with increasing strain is observed after 20% pre-strain, especially at the temperature of 873 K. However, the nature of variation of DOS with strain is almost similar at temperatures 473 K and 673 K.

Fig. 4 represents the variation of DOS with respect to temperature. It was observed that, though the DOS values at room temperature for all the samples are almost same, their nature of variation with temperature changes drastically depending upon their extent of deformation.

The Scanning Electron Microscopy (SEM) was done on all the samples to study the microstructural change with respect to strain and sensitization temperature. Some typical Scanning Electron Micrographs of the as received and of the deformed samples are shown in Fig. 5. A small amount of deformation bands is observed (Fig. 5) even in the as received samples. From Fig. 5, significant change in the microstructure of the sample was observed with increasing degrees of deformation. However, there is an increase in the population of deformation bands which initiates significantly from the sample with 20% strain. Different scanning electron micrographs obtained from the selected samples after the heat treatment at different temperature is shown in Fig. 6. The micrographs in Fig. 6 reveal the presence of deformation bands at all the