# Evaluation of the sensitization process in 304 stainless steel strained 50% by cold-rolling

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A suitable selection of stainless steels is based on their corrosion resistance, characteristics of manufacture, availability, mechanical properties, cost, etc. Nevertheless, the mechanical properties and corrosion resistance are, generally, the most important factors in the selection of the stainless steel (especially 304 SS). This material has broad applications in commercial industry which includes transportation and storage of toxic and corrosive waste, and piping for the petroleum, nuclear, and chemical industries [1]. However, when 304 stainless steel is subjected to a temperature range of 450–850 °C the phenomenon known as sensitization occurs. It consists of the development of carbide precipitates ($Cr_{23}C_6$) in the grain boundaries, principally. The material then becomes susceptible to intergranular corrosion and intergranular stress corrosion cracking in certain aqueous environments [2]. Drastic changes due to thermomechanical processing and fabrication can have a serious effect on the microstructures of the material. Such microstructural characteristics include grain size, strain, and chemical composition. Changing any of these variables generates a wide variety of material properties, and as a consequence these parameters are extremely crucial in austenitic stainless steels since they are susceptible to intergranular corrosion [3–5].

The main goal of this work was to evaluate the effect of the sensitization in 304 stainless steel strained to 50% by cold-rolling at 625 and 670 °C for 0.1 to 10 hr of aging time, since no work has been done at these conditions. In addition, the evolution of the microstructure was examined by using transmission electron microscopy (TEM) in order to have a better understanding of the effect of strain on the sensitization process.

TABLE I Chemical composition of 304 stainless steel

| %C | %S | %Cr | %Ni | %Mo | %Mn |
|---|---|---|---|---|---|
| 0.067 | 0.010 | 18.78 | 7.78 | 0.23 | 1.73 |

The chemical composition of the 304 stainless steel used in this investigation is shown in Table 1.

The material was received in plate form. Strips of material measuring 7 cm in length × 1.5 cm in wide × 0.6 cm in thickness were cut. The strips of the material were first solution annealed at 1200 °C for 1 hr and water quenched to eliminate any carbide precipitate formation during mill processing. The grain size was determined by the Abrams three-circle method (ASTM E 112- 85) [6]. Then, strips were cold-rolled to 50%. The strained and non-strained samples were heat treated at 625 and 670 °C for 0.1,0.4, 1,2, 10 hr of aging times. Unstrained samples were used t6 compare the effect of the strained samples on the sensitization process.

In order to measure the degree of sensitization (DOS), the electrochemical potentiokinetic reactivation (EPR) technique was used, which represents the relationship between the potential and the current for a corrosion system [7]. The sample preparation for TEM consisted of cutting plates of the strain and no-strained

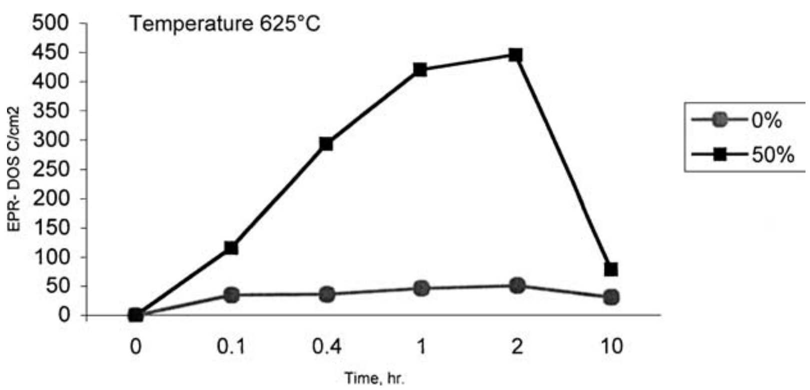


*Figure 1* Degree of sensitization (DOS) plotted as a function of aging time for the 304 stainless steel strained (50%) and un-strained samples at 625 °C.

 

samples and polished until obtaining a final thickness of 200 pm. Standard techniques for jet polishing were employed using a Struers Tenupol-3 jet polishing system and a methanol/perchloric acid solution. The TEM was operated at an accelerating potential of 200 kV; utilizing a goniometer-tilt stage.

Grain size measurements of samples with and without heat treatment were 82 and 190 $\mu$m, respectively.

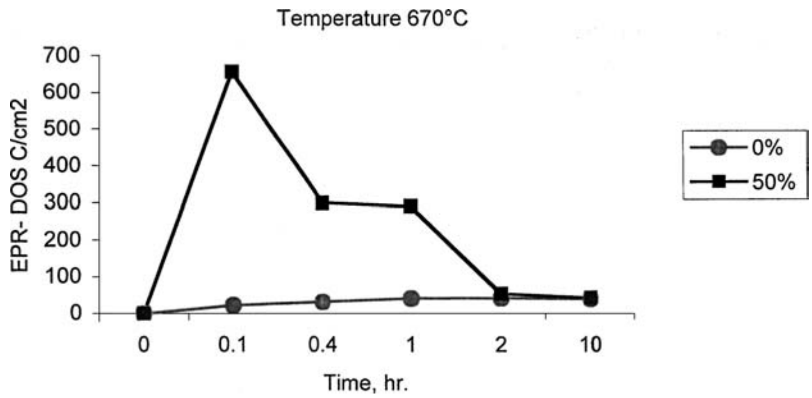


*Figure 2* Degree of sensitization (DOS) plotted as a function of aging time for the 304 stainless steel strained (50%) and unstrained samples; at 670 °C.

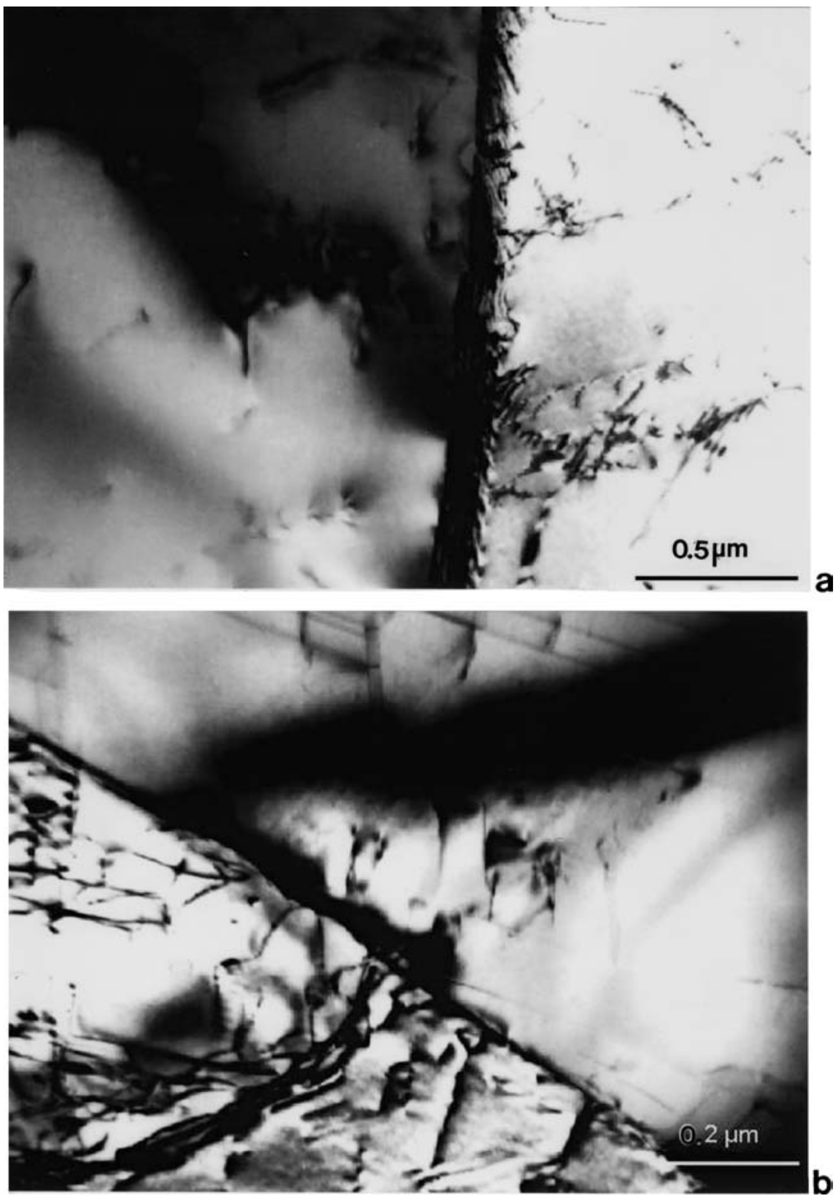


*Figure 3* TEM micrograph of 304 SS non-strained samples heat treated at 625 °C. (a) 0.1 hr showing the grain boundary without the presence of carbide precipitates and, (b) 2 hr of aging time showing carbide precipitates at the grain boundary.

The effect of cold-rolling samples at 50% and non-strained samples at 625 °C on the sensitization process is shown in Fig. 1. An increase in the DOS is observed in the strained samples as well as the desensitization (or healing) after 2 hr of aging time, while in the unstrained samples these effects did not occur even up to 10 hr. These differences can be explained by an increase in the dislocation pipe density for the strained sample [8], which in turn increased the diffusion of species to form precipitates. Also it is well known that strain of 304 stainless steel will produce an increasing number of planar defects which can intersect and form preferred sites for both $\alpha'$-martensite and carbide nucleation [9–11].

The kinetics of sensitization are quite different at 670 °C (see Fig. 2) in comparison to 625 °C, especially in the strained samples. As can be observed in Fig. 2, the onset of the desensitization process starts in a shorter period of time (0.1 hr) at 670 °C than at 625 °C (2 hr), where a complete healing of the material is reached up to 10 hr of aging time.

Almanza *et al.* [12] found that the most rapid sensitization-desensitization behavior in 304 stainless steel strained by cold-rolling to 40%, and heat treated at 670 °C, occurred at about 1 hr of aging time. Therefore, the results obtained in this work showed a considerably reduced time for the onse of sensitization-desensitization process (0.1 hr). This difference can be attributed in part to increasing dislocations density, which acts as an enhanced diffusion pipe as noted above, and an increase in the volume fraction of $\alpha'$-martensite present in the 304 SS which contributed to a pseudo-recrystallization; creating numerous, small-grain regions which promote rapid sensitization-desensitization kinetics and precipitation.

By means of the analysis made in the TEM, it was possible to observe the evolution of the microstructure for strained and non-strained samples (see Fig. 3). For

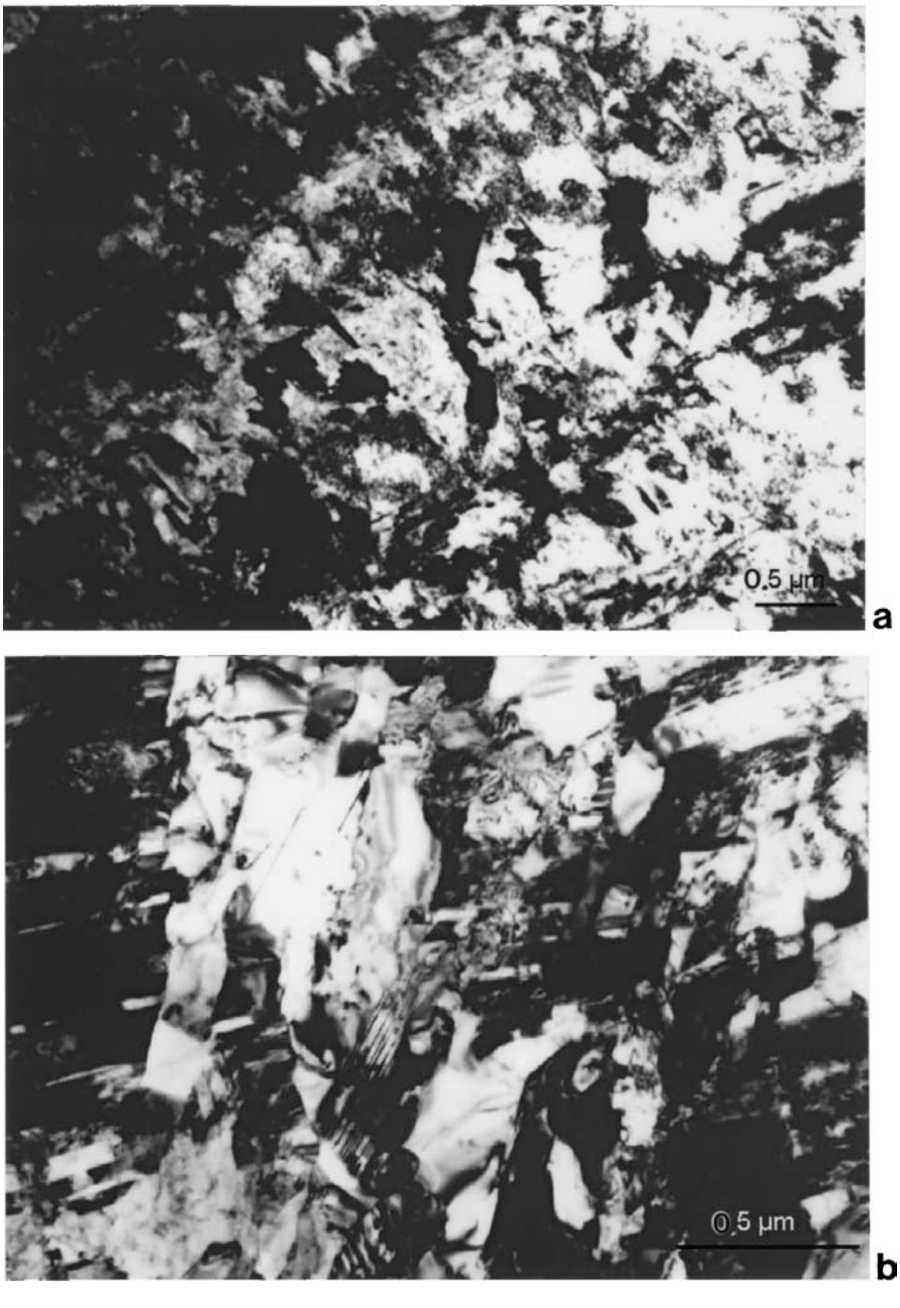


*Figure 4* TEM bright-field image showing some austenite and $\alpha'$-martensite after (a) 0.1 hr and (b) 2 hr at of 625 °C in strained samples (50% rolled).

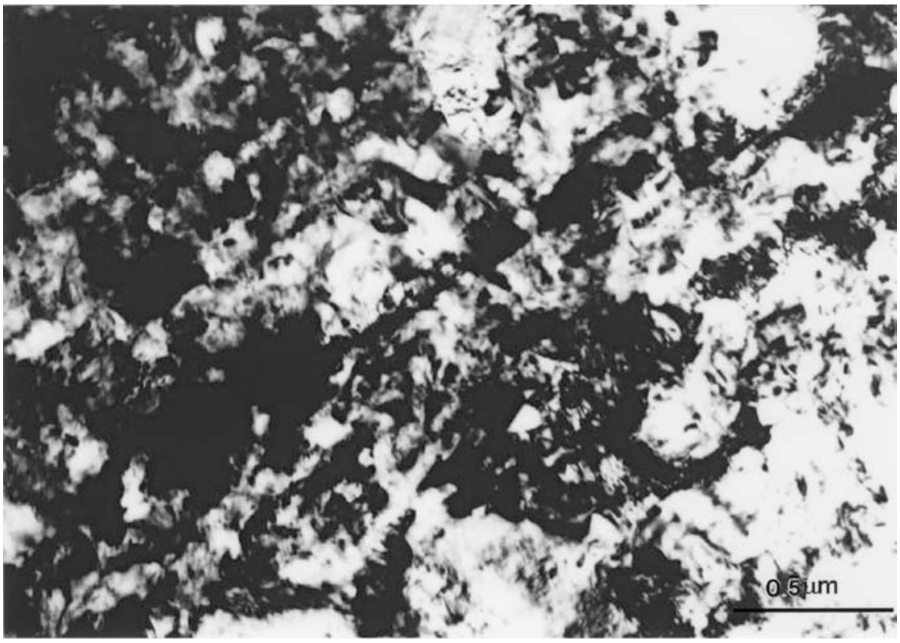


*Figure 5* Sensitization sample to 670 °C at time 0.1 hr, deformed 50% by rolling.

non-strained samples heat treated at 625 °C for 0.1 hr (Fig. 3a) and 2 hr (Fig. 3b), gradual changes in the microstructure, principally carbide precipitates CrZ3C6, can be observed since there was not a significant increases on the DOS. Following with the same treatment of sensitization (625 °C), but in this case in strained samples by cold rolling to 50%, a very noticeable difference in the microstructural evolution is observed as shown in Fig. 4. Making a comparison with non-strained samples, the strained samples exhibit a more complex microstructure, probably a mixture of austenite, $\alpha'$-martensite, as well as an increase in the precipitation of carbides ($Cr_{23}C_6$) as the aging time increases from 0.1 hr (Fig. 4a) to 2 hr (Fig. 4b).

The most important changes correspond to temperatures at 670 °C and they appear in the samples strained 50% by cold-rolling. At times of 0.1 hr, where the DOS value is the highest, we observed a microstructure characterized by an austenite/$\alpha'$-martensite interphase interface or phase/grain refinement shown in Fig. 5. These interfaces act as nucleation sites for carbide precipitates leading to an increased DOS ($Cr_{23}C_6$ precipitates) [13]. The recovery of the depleted zones of chromium, is due to microstructural changes such as recrystallization that can be observed at various times at temperature (Fig. 4b).

In Conclusions:

1. For the samples strained 50% by rolling, the effect on the sensitization/desensitization process was more drastic at 670 °C than at 625 °C. At 670 °C the healing or desensitization occurred after 0.1 hr of aging time while at 625 °C this phenomenon occurred after 2 hr of aging time. Therefore, the cold-rolling strain accelerates the sensitization-desensitization process due to a greater dislocation density which acts to promote pipe diffusion of Cr atoms.

2. A complex microstructure was observed in the strained samples both at 625 °C and 670 °C. This microstructure could also influence the high amount of $Cr_{23}C_6$ carbide precipitates since the interface of $\gamma/\alpha'$ acts as a preferential site for nucleation of such carbide precipitates.

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## References

1. ASM Specialty Handbook, Stainless Steels. J. R. Davis and Davis & Associates., (ASM International Materials Park, OH, 1994) p. 181.
2. N. PARVATHAVARTHINI, R. K. DAYAL, S. K. SESHDRI and J. B. GNANMOORTHY, *J. Nucl. Mater.* **168** (1989) 83.
3. C. GARCIA, F. MARTIN, P. DE TIEDRA, J. A. HEREDERO and M. L. APARICIO, *Corrosion* **56**(3) (1999) 317.
4. REYNALDA BELTRAN, J. G. MALDONADO, L. E. MURR and W. W. FISHER, *Acta Mater.* **45**(10) (1997) 4351.
5. J. G. MALDONADO, L. E. MURR and W. W. FISHER, "Mechanical Properties and Fracture Mode Characteristics of Liquid-Nitrogen-Deformed and Sensitized 304 Stainless Steel, in Microstructural Science," edited by D. Alman, J. A. Hawks and J. W. Simmons, (ASM International, Metals Park, OH, 1998) Vol. 25, p. 445.
6. "Standard Test Method for Determining Average Grain Size, Annual Book of Standards, 3.01 (E112-88)" (American Society for Testing Materials, Philadelphia, PA, 1988).
7. W. L. CLARKE, R. L. COWAN and W. L. WALKER, *ASTM-STP* **656** (1978) 99.
8. A. H. ADV ANI, D. G. A TIERIDGE, L. E. MURR and R. CHELAKARA, *Scripta Metall.* **25** (1991) 343.
9. L. E. MURR and S. H. WANG, *Res Mechan.* **4** (1982) 297.

10. L. E. MURR, A. ADV ANI, S. SHANKAR and D. G. ATIERIDGE, *Mater. Character.* **24** (1990) 135.
11. C. L. BRIANT and A. M. RITIER, *Scripta Metall.* **13** (1979) 170.
12. E. ALMANZA, L. E. MURR, J. G. MALDONADO, D. E. ALMAN, J. A. HANK and J. W. SIMONS (eds.), "Characterization and Comparison of the Effects of Grain Size and Uniaxial and Rolling Strain on Carbide Precipitation and Sensitization of 304 and 316 Stainless Steels," Microstructural Science, (ASM International, Metals Park, OH, 1997) Vol. 25, p. 437.
13. J. G. MALDONADO, L. E. MURR and W. W. FISHER, in ISS International Symposium on Recovery and Recrystallization in Steels Proceeding, 1996, Vol. XXXIII, p. 849.

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