INTERGRANULAR CORROSION OF DEFORMED SS304

Raghuvir Singh*, P.K.Dey, A. Kumar, S.K. Das, Ravi Kumar and I.Chattoraj

National Metallurgical Laboratory, Jamshedpur-831007

**rsr@csnml.ren.nic.in*

ABSTRACT

Intergranuular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) of commercial stainless steels e.g. type 304 and 316 are frequently observed in several process environments. These localized attacks are normally attributed to the carbide precipitation and concomitant depletion of chromium near grain boundary due to alloy exposure to sensitization temperature. Such undesirable microchemistry is expected to be changed further if the material undergoes deformation prior to sensitization.

Present paper deals with the influence of a wide range of cold rolling on the sensitization kinetics and consequently on intergranular corrosion. The plates of SS3O4 were cold rolled and coupons cut from these were sensitized at various temperatures for different periods. The consequences of deformation on IGC have been investigated by using ASTM A262 methods. Intergranular corrosion of solution-annealed samples was found to increase with sensitization temperature and time. Introducing deformation to the stainless steel seems to change the kinetics and thereby changes its resistance to IGC. Low level of cold rolling increases the IGC while severe rolling enhances the resistance. This critical level of rolling may depends upon the time and temperature of sensitization. Overall, effect of deformation is found to reduce the aggressiveness of IGC.

Key words : Sensitization, intergranular corrosion, cold working.

INTRODUCTION

Stainless steels are common material of construction as these offer a wide range of corrosion resistance alongwith good fabrication and mechanical properties to many industrial environments e.g. chemical, nuclear etc. At the same time, these alloys are prone to microstructural changes alongwith changes in chemistry when exposed to sensitization temperatures possibly due to faulty heat treatment or welding operation. In the case of SS304/316, precipitation of chromium carbides takes place along the grain boundary region in the temperature range of 580-815°C. This results in chromium depletion near the grain boundary and makes the region more susceptible to corrosion attack (1-3). In certain environments, sensitized steels corrode preferentially along the grain boundary leaving the matrix unattacked, termed as intergranular corrosion (IGC). This causes frequent catastrophic failure of engineering components. These sensitized stainless steels when subjected under load in certain corrosive atmospheres, experience crack propagation through the boundary leading to even faster failures.

Before shaping the component into a desired geometry, steels often undergoes a thermo-mechanical processing during which materials change certain properties. By such interaction of temperature and strain, a material's micro-chemistry may be altered so that its functional properties are changed. Cold deformations are assumed to alter the properties of steels through increasing dislocation density which apart from its effect on mechanical properties, may help in accelerating the diffusion mechanism, phase transformation, lowering the activation energy and free energy for faster nucleation, etc. It is reported that the prior deformation influences the sensitization process and as a result change in intergranular corrosion and IGSCC of stainless steels. There have been contradictory remarks in the literature about the net influence of deformation on the sensitization kinetics of stainless steels. It was first studied by Bain and Tedmon (2, 3) who reported the lower corrosion of strained material compared to that of annealed. On the other hand Briant (4) observed higher resistance of the unstrained material. One reason of such conflicting results could be the consideration of low level of deformations only. Consequently, the need was felt to investigate the sensitization and intergranular corrosion behavior of SS304 with wide range of deformation in order to understand the mechanism. The present paper reports the results of various deformation levels on IGC and the attempt has been made to establish the kinetics by correlating corrosion rates with microstructures.

Experimental Techniques

Stainless steel 304, obtained from Salem steel plant, Vishakhapattanam, were solution annealed at 110°C for 1hr and cut into various plate sizes for cold rolling operation. The original thickness of the material was 0.8 cm. The stainless steel plates were processed for uniaxial cold rolling at 20, 40, 60 & 80% reduction in thickness. The samples were cut with an average size of 2.0 cm x 3.0 cm from each cold rolled plate. These samples were then subjected to ageing at 500, 600 & 700°C for various periods. The surface cleaning of the samples were made as per the standard for intergranular corrosion test (ASTM-A262-practice A & F) which are discussed below.

Oxalic acid etch test (Practice A) : Electrochemical etching was made in oxalic acid solutions as described in the ASTM -A262 practice. This test helps in defining the rate and location of the precipitation of chromium carbide in the grains. The different degrees of IGC was identified as step, dual, and ditch structures.

Modified Strauss test (Practice F) : The test solution was made by adding AR grade sulfuric acid and copper sulfate to distilled water. Before immersing the test specimens, they were well degreased with acetone solution and weighed to the fourth point of decimal (grams). The solution was then put in an Erlenmeyer flask which was connected to a glass condenser and heated to boiling point of the solutions. Specimens were then slid into the flask. The test period was reduced to 36 hours from 120 hours as the latter is extremely corrosive (5). The reduced level of test solution noted after 36 hours was found to be insignificant; therefore it would have negligible affect on the test. The specimens were cleaned and weighed after the test was over. The corrosion rates were obtained by using the formula given elsewhere (5) and are reported in mm/month.

Result and Discussion

Deformation at ambient temperature : Enhanced cold working is known to increase the dislocation density. It was observed earlier that the 25% strained SS304 contains 6×10^{10} dislocations/cm^2 and may increase further to the order of 10^{12}/cm^2 with severe strain level (6, 7). These dislocation tangles may pile up on the slip plane at grain boundary regions and so become nucleation sites for precipitation. Another fact is that the energy expanded in the plastic deformation partly remains in the lattices as internal stored energy, which makes the material's structure unstable. Such distortion of equilibrium may increase the reactivity of the stainless steels to the exposed environment and may cause the corrosion resistance to reduce.

Modified Strauss test : The results of the IGC test of various sensitized and rolled SS304 specimens are shown in the Fig 1-3.

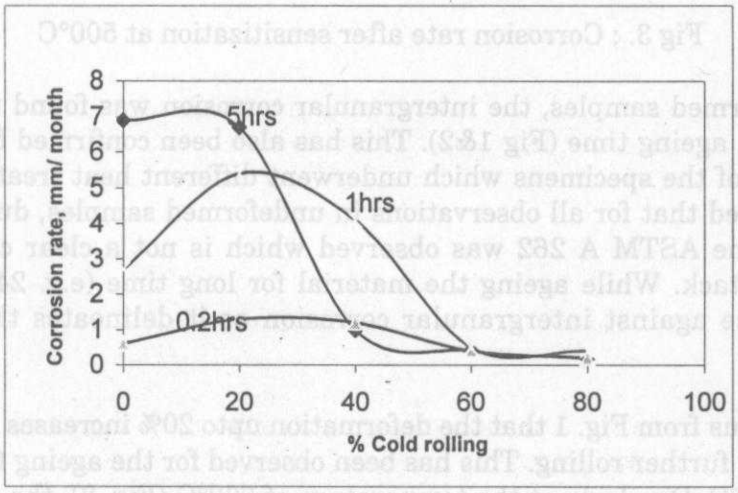

Fig 1. : Corrosion rate after sensitization at 700°C for different post-deformation aging times

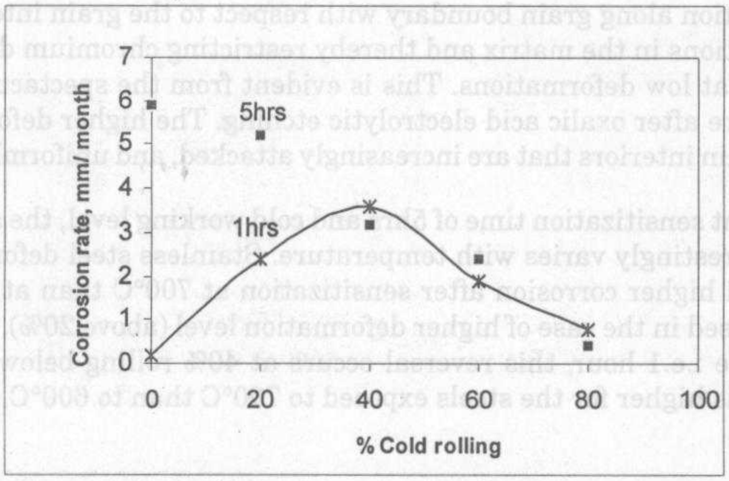

Fig 2. : Corrosion rate after sensitization at 600°C for different aging times

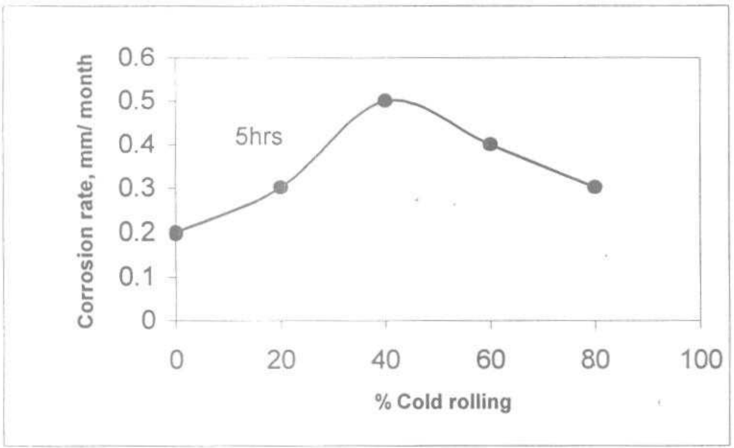

Fig 3. : Corrosion rate after sensitization at 500°C

In undeformed samples, the intergranular corrosion was found to increase with temperature and ageing time (Fig 1&2). This has also been confirmed by observing the microstructures of the specimens which underwent different heat treatment history. It should be qualified that for all observations in undeformed samples, dual structures as categorized in the ASTM A 262 was observed which is not a clear cut indication of intergranular attack. While ageing the material for long time (e.g. 24 hrs) cannot be acceptable to use against intergranular corrosion as it delineates the ditch type of microstructure.

It is obvious from Fig. 1 that the deformation upto 20% increases IG corrosion but it decreases with further rolling. This has been observed for the ageing time of 0.2 and 1 hour only at 700°C. Similarly at the temperature of 600°C (Fig. 2), the corrosion rate is observed to be maximum at the deformation of 40% and reduces thereafter in the case of 1 hour of sensitization treatment. Also the specimens sensitized at 500°C-1hour, showed maximum IGC when rolled to 40%, though the rates were quite low. Overall, the modified Strauss test indicates a decreasing trend of IGC with high deformations, with a maximum at 20 to 40% deformation. The initial increase in IG attack is possibly due to increased dislocation density resulting in increased chromium diffusivity which helps in carbide precipitation. However, vigorous rolling seems to reduce the ratio of nucleation sites for carbide precipitation along grain boundary with respect to the grain interior by inducing favorable dislocations in the matrix and thereby restricting chromium depletion at grain boundary unlike at low deformations. This is evident from the spectacular difference in the microstructure after oxalic acid electrolytic etching. The higher deformation induced samples show grain interiors that are increasingly attacked, and uniformly, with % rolling.

At constant sensitization time of 5hrs and cold working level, the alloy's resistance to IG attack interestingly varies with temperature. Stainless steel deformed below or at 20%, experienced higher corrosion after sensitization at 700°C than at 600°C while the situation is reversed in the case of higher deformation level (above 20%). Similarly at still lower ageing time i.e.1 hour, this reversal occurs at 40% rolling below or at which the corrosion attack is higher for the steels exposed to 700°C than to 600°C.

Conclusions

Intergranular corrosion of undeformed specimens increases with sensitization temperature and time of exposure. High deformations reduces IGC while low amounts of deformations tend to accelerate IGC. The transition point with regards to deformation is found to be dependent on the sensitizing conditions (time and temperature). At low levels of deformation, grain boundaries were found to be attacked while uniform corrosion prevailed for high deformation levels. This is possibly due to a change in the chromium carbide precipitation location and kinetics, influenced by the change in density and distribution of dislocation on deformation. So that, the chromium depletion instead of localization at the grain boundaries occurs throughout the matrix with resultant lower local depletion.

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