JMEPEG (1992) 1:831-838

Intergranular Corrosion Resistance of Microstructure-Modified Type 316 Austenitic Stainless Steel

U.Kamachi Mudali, N. Vinod, M. Sundar, and R.K. Dayal

Cold working and a double aging treatment was used to produce a microstructure with fine nuclei of carbides distributed throughout the grains to improve the intergranular corrosion (IGC) resistance of austenitic stainless steel. The treatment was carried out on type 316 stainless steel as follows: cold working (20, 30, and 40% reductions in thickness), sensitization (923 K/5 h), and aging each for 1173, 1223, 1273, and 1323 K/1 h, respectively. Specimens in the solution annealed condition (0% cold work) were also given the above treatment. All of the specimens were resensitized at 923 K/5 h and tested for IGC resistance as per ASTM A262, Practice A(oxalic acid etch test) and Practice E (24 h immersion in boiling Cu-$CuSO_4$-H_2SO_4 and the U-bend test). Microhardness measurements were also carried out on all specimens. The results indicated that at an optimum treatment (30% cold work + sensitization + aging) all the specimens showed improved IGC resistance. The 0 and 20% cold worked specimens showed improvement at higher aging temperatures only. Specimens undergoing 40% cold work exhibited a decrease in IGC resistance. Compared to as-cold-worked specimens, an improvement in IGC resistance was obtained with 30% cold working.

1. Introduction

INTERGRANULAR corrosion (IGC) refers to a preferential attack along the grain boundaries in certain corrosive environments, which results in the loss of engineering properties. This type of corrosion is particularly severe when stainless steel is either heat treated or slowly cooled at 773 to 1073 K, which is referred to as sensitization.[1,2] This can be attributed to the formation of chromium-rich $M_{23}C_6$ carbides, with chromium-depleted zones adjacent to them, along the grain boundaries. Numerous investigations have shown that the sensitization kinetics can depend on the following aspects: (1) prior deformation,[3,11] (2) variations in grain size,[12,13] (3) addition of alloying elements,[2,14-16] and (4) changes in the corrosive environment.[2] Cold work has been found to produce increased susceptibility to sensitization in case of moderately cold worked (15%) austenitic stainless steels and to have a beneficial effect for higher levels of cold work (above 20%).

These results have been explained in terms of the rapid diffusion of chromium, shorter diffusion paths for carbon due to matrix precipitation, and the formation of martensite phase during cold working. Bain *et al.*[1] reported that cold working of austenitic stainless steels prior to sensitization significantly reduced the region of susceptibility in the time-temperature-sensitization (TTS) diagram. They attributed this to the nucleation and precipitation of intragranular carbides, which was also subsequently reported by Tedmon *et al.*[3] Briant *et al.*[4] established TTS diagrams for type 316 stainless steel in the annealed (0% cold work) and deformed states and have shown that the nose of these diagrams is at 1025 K. Dayal *et al.*[5,9] produced TTS diagrams for austenitic stainless steels with various levels of cold work. Mannan *et al.*[6] reported TTS diagrams for various levels of cold work (5 to 25%) and also studied the role of deformation on the morphology of grain boundary carbides and their influence on intergranular corrosion resistance. Briant and Ritter[7] reported the deleterious effect of martensite phase formed during higher cold working levels on the degree of sensitization and also noted that martensite favored extensive carbide precipitation. The effect of aging treatment after cold working and sensitization has not been studied to date.

Advani *et al.*[17] studied the sensitization behavior of type 316 stainless steel in the mill-processed condition to understand the influence of solution annealing effects. Weiss and Stickler[18] reported that higher solution annealing temperatures accelerated carbide precipitation and increased the degree of sensitization. In general, sensitization after cold working to a higher level will produce a high density of carbides throughout the matrix.[2,3,6] Aging of the above specimens to around the solution annealing temperatures of austenitic stainless steels can be expected to dissolve the carbide precipitates, leaving behind fine nuclei of carbides within the grains. This microstructure would increase the strength due to the precipitation hardening effect. Also, the nonavailability of carbon along the grain boundary during resensitization for the precipitation of carbides would decrease the probability of sensitization and favor maximum intragranular precipitation. Such a wide distribution of intragranular carbide precipitates was found to be beneficial in improving the IGC resistance of warm worked

---

U. Kamachi Mudali, Metallurgy Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India; **N. Vinod**, Department of Metallurgical Engineering, P.S.G. College of Technology, Coimbatore, India; presently at the University of Maryland; **M. Sundar**, Department of Metallurgical Engineering, P.S.G. College of Technology, Coimbatore, India; and **R.K. Dayal**, Metallurgy Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India.

Table 1 Chemical Composition of Type 316 Stainless Steel

Element	Composition, wt%
Chromium	16.46
Nickel	12.43
Molybdenum	2.28
Carbon	0.054
Manganese	1.69
Silicon	0.64
Sulfur	0.006
Phosphorus	0.025
Nitrogen	0.056
Titanium	0.01
Iron	bal

type 316 stainless steel, as reported by Kamachi Mudali *et al.*[19] Therefore, an attempt has been made in the present work to produce a similar microstructure in type 316 stainless steel comprising fine nuclei of carbides distributed uniformly over the grains to decrease sensitization and intergranular corrosion.

2. Experimental Work

The austenitic stainless steel chosen for this work was AISI type 316 stainless steel (a proprietary steel known as VIRGO 14SB), the chemical composition of which is given in Table 1. The material used for the present work was in sheet form of 100 by 25 by 3 mm dimensions, which were cut from a larger sheet.

Material in the as-received mill-annealed condition was cut to the above dimensions and solution annealed at 1323 K/0.5 h in a Granville Company of America make high temperature high vacuum (HTHV) furnace operating at 10^{-6} torr and rapidly quenched. The sheet was cold rolled to various reductions in thickness of 20% (2.4 mm), 30% (2.1 mm), and 40% (1.8 mm) by using a Carl-Wezel 2-high/4-high instrumented laboratory rolling mill. The solution annealed condition was used as a reference corresponding to a cold work level of 0%. All of the above materials were sensitized at 923 K/5 h, which corresponds to the nose region of the respective TTS diagrams published in the literature.[5,6] These samples were further aged at 1173, 1223, 1273, and 1323 K/1 h, respectively. Resensitization heat treatment was carried out at 923 K/5 h to assess the resistance to intergranular corrosion.

ASTM standard A262, Practices A and E, were used to detect the extent of intergranular corrosion.[20] Practice A test was carried out at each stage of the experiments, whereas Practice E test was conducted after aging and also after resensitization. The Practice A test consists of electrolytically etching in 10% oxalic acid or 10% ammonium persulfate solution (in the case of molybdenum-bearing alloys, 10% ammonium persulfate solution is preferred) and classifying the microstructure as step, dual, or ditch structures. The Practice E test consists of exposing the specimens embedded in copper turnings in boiling $CuSO_4$-16% H_2SO_4 solution for 24 h and then subjecting them to a 180 ° bend test. The presence of cracks/fissures on the bend region indicates susceptibility to intergranular attack.

Hardness measurements were carried out on all specimens using a Zwick hardness tester for the Vickers hardness to evaluate the change in hardness and hence strength.

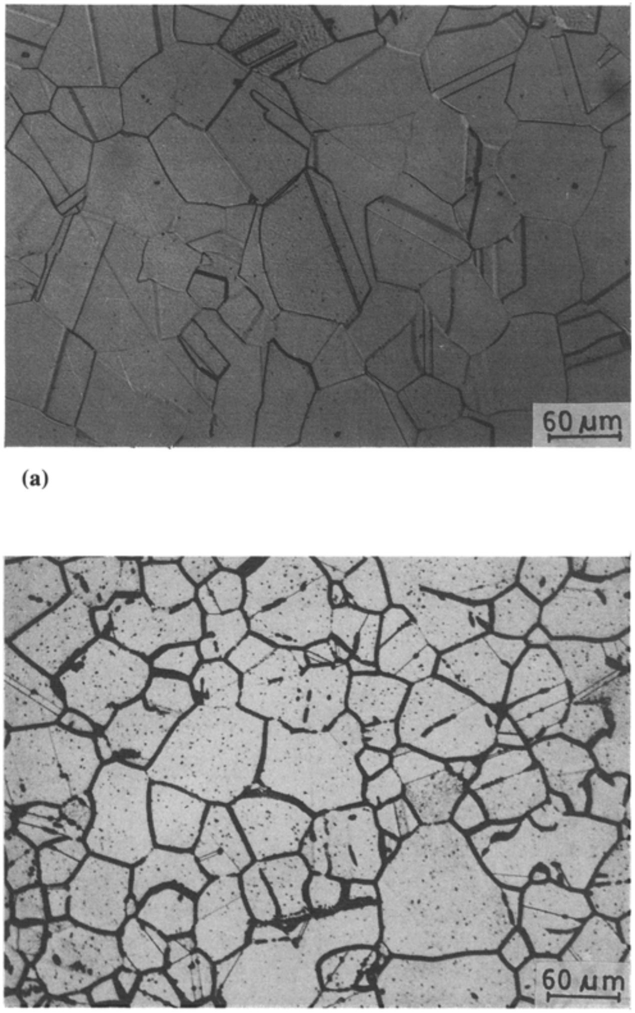
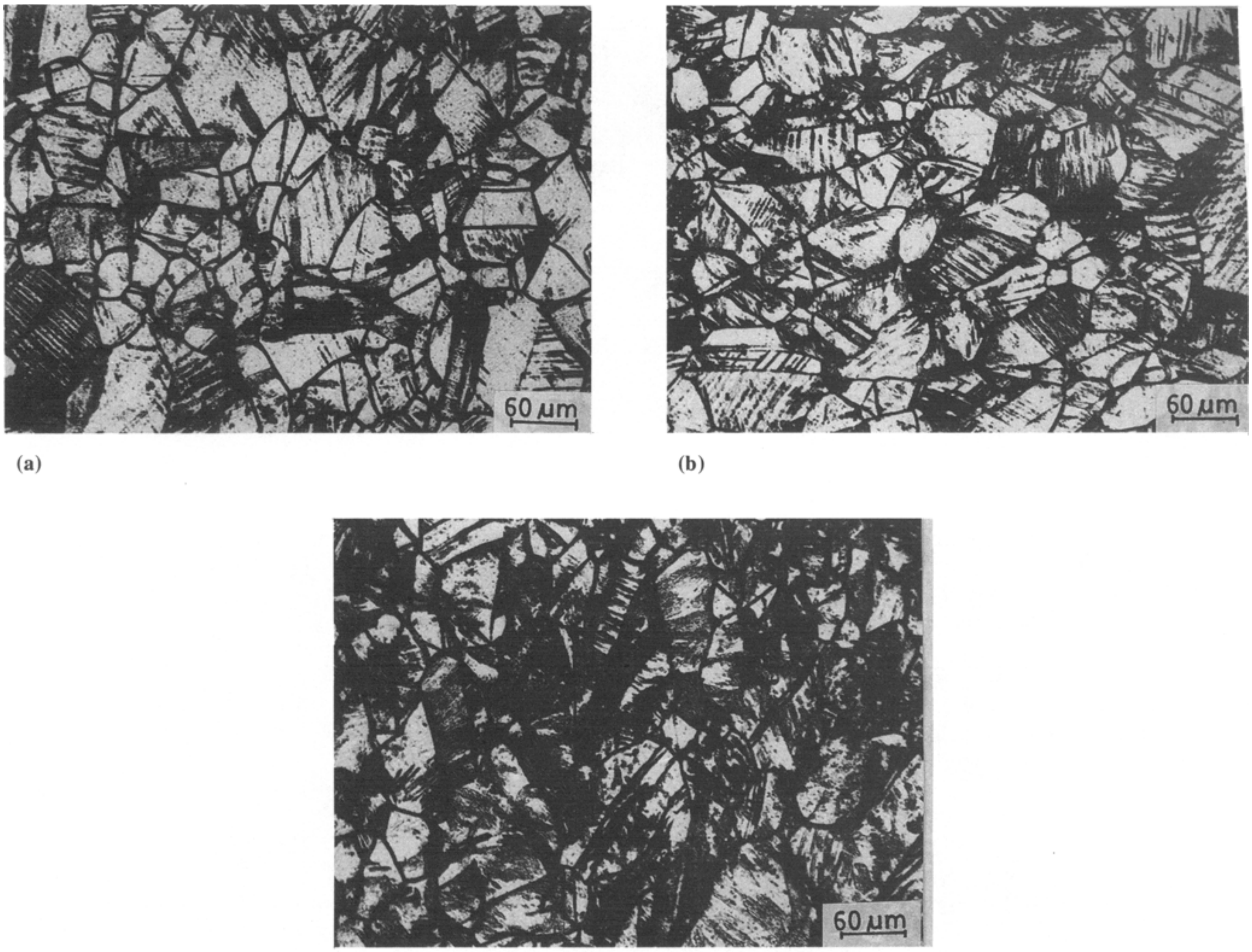


Fig. 1 Optical micrographs showing the microstructure obtained for the as-received material in the **(a)** solution annealed condition (0% cold work) and **(b)** sensitized condition (923 K/5 h).

3. Results and Discussion

3.1 *Microstructural Changes*

The microstructure of the solution annealed (0% cold working) specimen showed a typical step structure, and when sensitized at 923 K/5 h, it exhibited a ditch structure, indicating the formation of a continuous network of $M_{23}C_6$ carbides along the grain boundary (Fig. 1). Cold working of the specimens to 20, 30, and 40% reductions in thickness revealed elongated grains in an increasing order of density as the cold working level was increased. Sensitization of the above cold worked specimens at 923 K for 5 h showed the presence of a high density of carbide precipitates throughout the matrix, the density increasing with the level of cold work, as shown in Fig. 2.



(a) (b) (c)

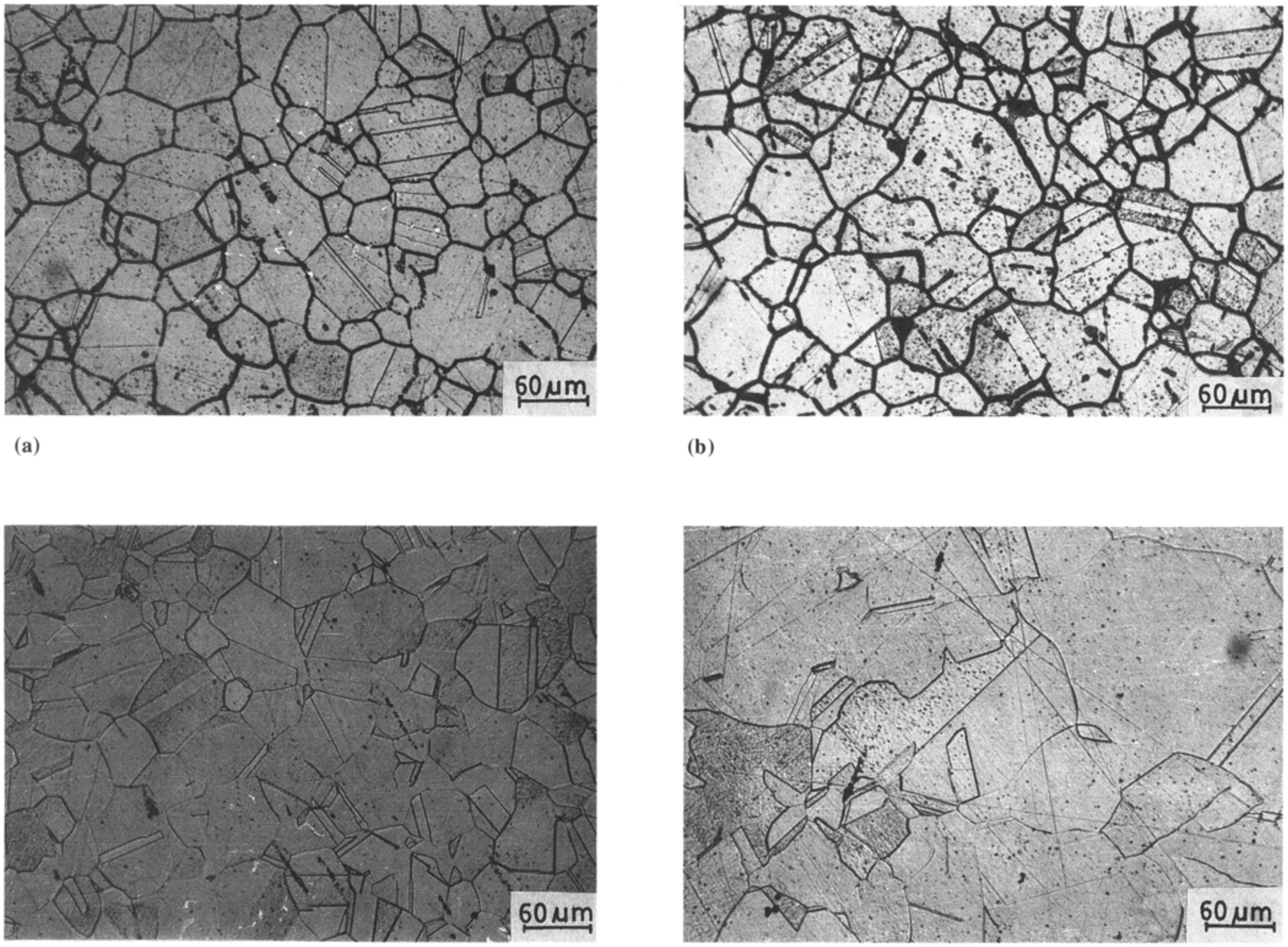
Fig. 2 Optical micrographs of specimens cold worked and sensitized (923 K/5 h). **(a)** 20% cold worked. **(b)** 30% cold worked. **(c)** 40% cold worked.

Aging of 0% cold worked and sensitized specimens produced a ditch structure at 1173 and 1223 K/1 h and a step structure at 1273 and 1323 K/1 h, as shown in Fig. 3. Coarsening of the grains can be observed at higher aging temperatures. Aging of 20, 30, and 40% cold worked and sensitized specimens produced a similar trend at 1273 and 1323 K/1 h. However, lower aging temperatures revealed only some recovery, with the presence of a high density of carbides throughout the matrix (Fig. 4). This aging treatment was given to partially dissolve the carbide precipitates such that a significant amount of carbide nuclei was present in the structure.

Resensitization was carried out to test the effectiveness of the preceding treatment on intergranular corrosion resistance. Optical microscopic observation of the 0% cold worked material showed ditch structures with the presence of smaller grains decreasing at higher aging temperatures, as shown in Fig. 5. In the case of 20, 30, and 40% cold worked specimens, a lower aging temperature showed that the resensitized microstructure had heavy carbide precipitates, but at higher aging temperatures they revealed the ditch structures (Fig. 6).

3.2 *ASTM Standard A262 Practice E Test*

Specimens that were cold worked, sensitized, and aged at different temperatures did not fail in the Practice E test. These specimens were further sensitized at 923 K for 5 h and tested according to Practice E to evaluate for their IGC resistance. The results of the bend test carried out on specimens exposed up to 24 h in boiling copper-copper sulfate-sulfuric acid solution are given in Table 2. It was found that all the specimens failed in the IGC test when they were only cold worked (0, 20, 30, and 40%) and sensitized at 923 K/5 h. The specimens that underwent 0 and 20% cold work and were sensitized and aged at 1173 and 1223 K showed a susceptibility to IGC attack when resensitized at 923 K for 5 h. However, they passed the IGC test at higher aging temperatures, namely 1273 and 1323 K/1 h, indi-



(a) (b) (c) (d)

Fig. 3 Optical micrographs of specimens cold worked 0%, sensitized (923 K/5 h), and aged for 1 h each at **(a)** 1173 K, **(b)** 1223 K, **(c)** 1273 K, and **(d)** 1323 K.

cating their resistance to IGC. Specimens undergoing 30% cold work that were given the above treatment passed the IGC test for all aging temperatures.

This improvement in IGC resistance can be attributed to the formation of a high density of fine intragranular carbide precipitates, as well as recrystallized smaller grains, as observed in the etch test. At the 40% cold work level with similar treatment, only specimens aged at the lowest aging temperature of 1173 K/1 h passed the IGC test, and the remainder of the specimens failed the IGC test.

3.3 *Microhardness Measurements*

Microhardness measurements were taken for all specimens prepared in this study. Figure 7 shows the variations in Vickers hardness obtained for different conditions. As the cold work level was increased, the microhardness values increased from 284 HV for 20% cold work to 306 HV for 30% cold work and to 347 HV for 40% cold work. Sensitization of these specimens reduced hardness. When the above specimens were aged for 1 h at different temperatures, namely 1173, 1223, 1273, and 1323 K, they showed significant reduction in hardness, as shown in Fig. 7. However, specimens undergoing 30 and 40% cold work had microhardness levels compared to those of solution annealed specimens aged for 1 h at 1173 and 1223 K, indicating the balance in strength and ductility upon aging.

3.4 *Influence of Microstructural Changes on IGC Resistance*

It has been well established that prior cold working induces sensitization up to 20% cold work, and above that level, resistance was provided for sensitization. At lower levels of cold working, diffusion of alloying elements was enhanced, which indirectly shortens the time required for sensitization. Healing

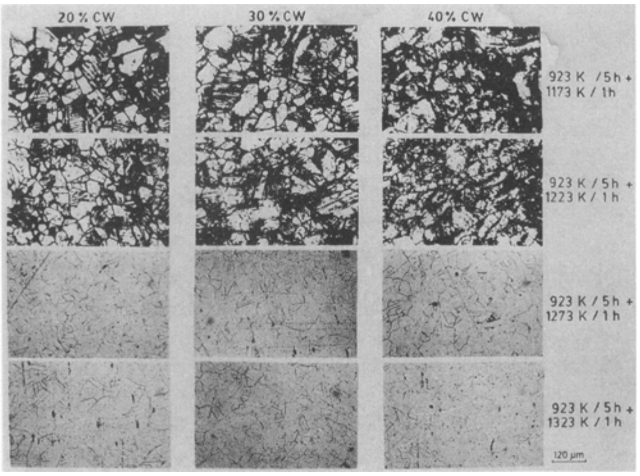


Fig. 4 Optical micrographs of specimens cold worked (20, 30, and 40%), sensitized (923 K/ 5 h) and aged each for 1 h at 1173, 1223, 1273, and 1323 K.

was also observed much earlier. In the case of cold working above 20%, sensitization susceptibility was reduced considerably due to additional precipitation sites at dislocations and deformation bands favoring intragranular matrix precipitates, because the diffusion path for carbon atoms are shortened. However, healing also occurred within shorter periods.

Bain *et al.*[1] and Tedmon *et al.*[2] observed the above phenomenon in their work. They also attribute the recrystallization effect observed during aging to be beneficial in improving IGC resistance in addition to matrix precipitation. It was also noticed that the strain-induced martensite formed during higher cold working levels significantly affected IGC resistance.[1-3,7,21,22]

In the present work, specimens cold worked to 20, 30, and 40% levels were sensitized at 923 K for 5 h to obtain a high density of matrix precipitates throughout the structure. The optical micrographs shown in Fig. 2 confirm the heavy intragranular precipitation as the cold working level was increased. Precipitation at deformation bands and twins can be clearly observed. Because austenitic stainless steels are low stacking fault energy materials, dislocations are generally distributed in planar ar-

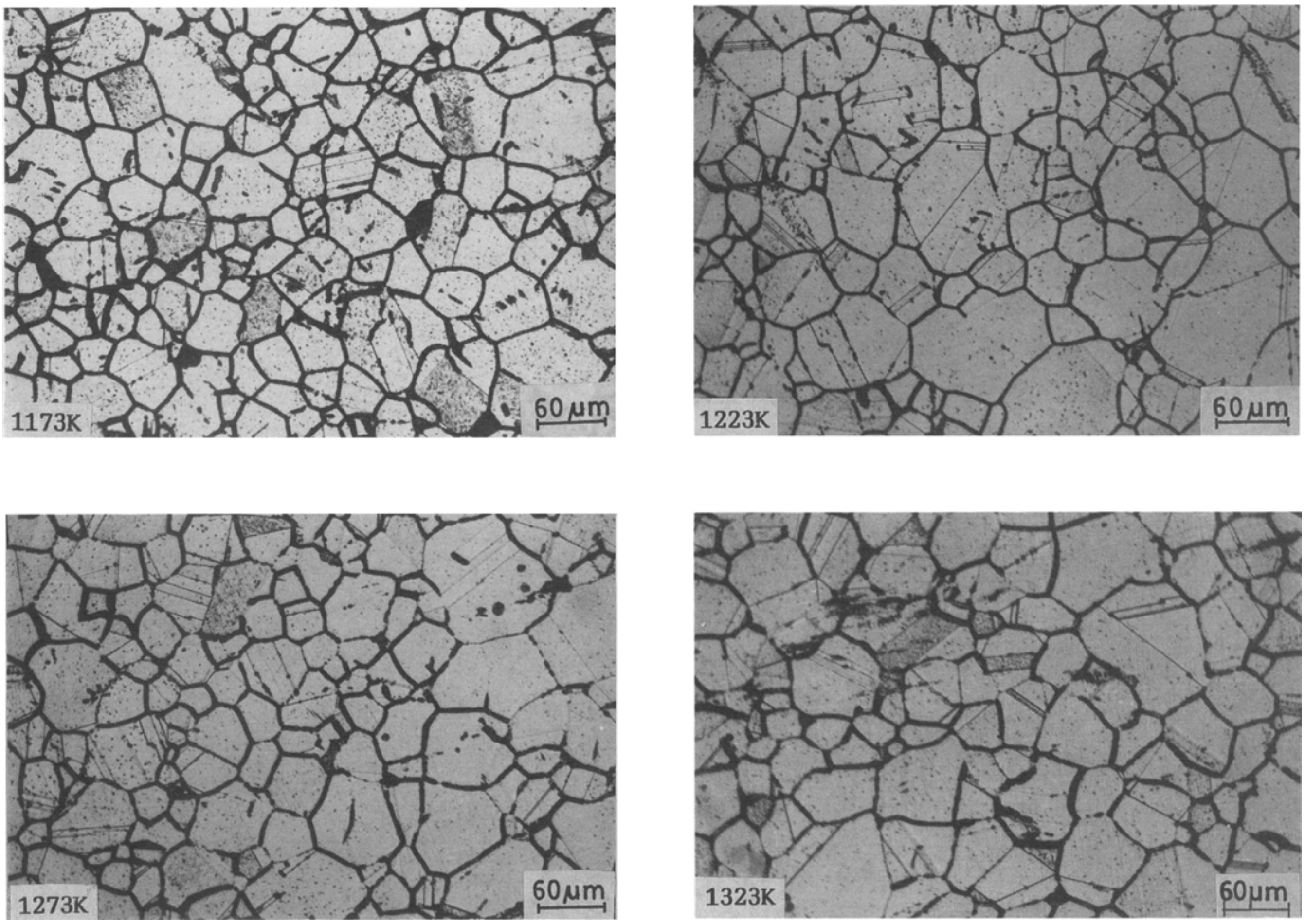


Fig. 5 Optical micrographs of the specimens cold worked 0%, sensitized (923 K/5 h), aged each for 1 h at 1173, 1223, 1273, and 1323 K, and resensitized at 923 K for 5 h.

rays. However, on cold working to higher levels beyond 30%, dislocations tend to form cells and deformation bands throughout the structure.[22] Thus, precipitation becomes easier at these sites during sensitization.[23] Aging of these specimens at various temperatures in the solution annealing range was carried out in the present work to dissolve the precipitates. However, dissolution should not be complete so that a large number of carbide nuclei remain in the matrix. In general solution annealing has been reported[17,18] to increase the grain size, which caused a higher degree of sensitization and longer times were required to complete desensitization than the fine-grained materials.

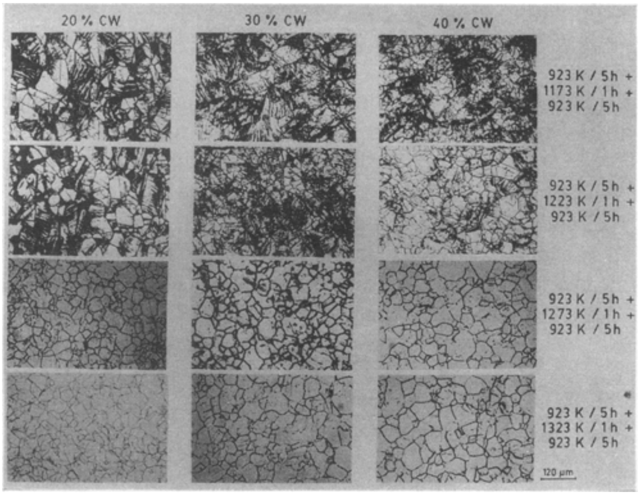


Fig. 6 Optical micrographs of specimens cold worked (20, 30, and 40%), sensitized (923 K/ 5 h), aged each for 1 h at 1173, 1223, 1273, and 1323 K, and resensitized at 923 K for 5 h.

Weiss and Stickler[18] reported that higher solution annealing temperatures accelerated carbide precipitation during subsequent aging of type 316 stainless steel and suggested that the effect was due to a higher quenched-in vacancy concentration and solute segregation on grain boundaries with increasing solution annealing temperatures. Recently, Advani *et al.*[17] reported that solution annealing at 1273 and 1323 K produced accelerated carbide precipitation and sensitization development, and this was attributed to the prenucleated carbides and other grain boundary chemistry changes. However, the specimens were in the mill-processed condition, and so the nuclei and precipitation were concentrated only along the grain boundary region.

In the present work, the materials were cold worked and sensitized to produce a heavy density of carbides throughout the structure. During the solution annealing treatment this would favor a high concentration of carbide nuclei left undissolved in the matrix compared to the grain boundary regions depending on the solution annealing temperature and time. Such behavior was noticed for all the specimens aged at 1273 and 1323 K in the present work, as shown in Fig. 5. When these specimens were resensitized at 923 K for 5 h to assess IGC susceptibility, it was found that all had the ditch structure in the etch test (Fig. 6). Also, the formation of a large number of smaller grains due to recrystallization effects were noticed, as shown in Fig. 6. The

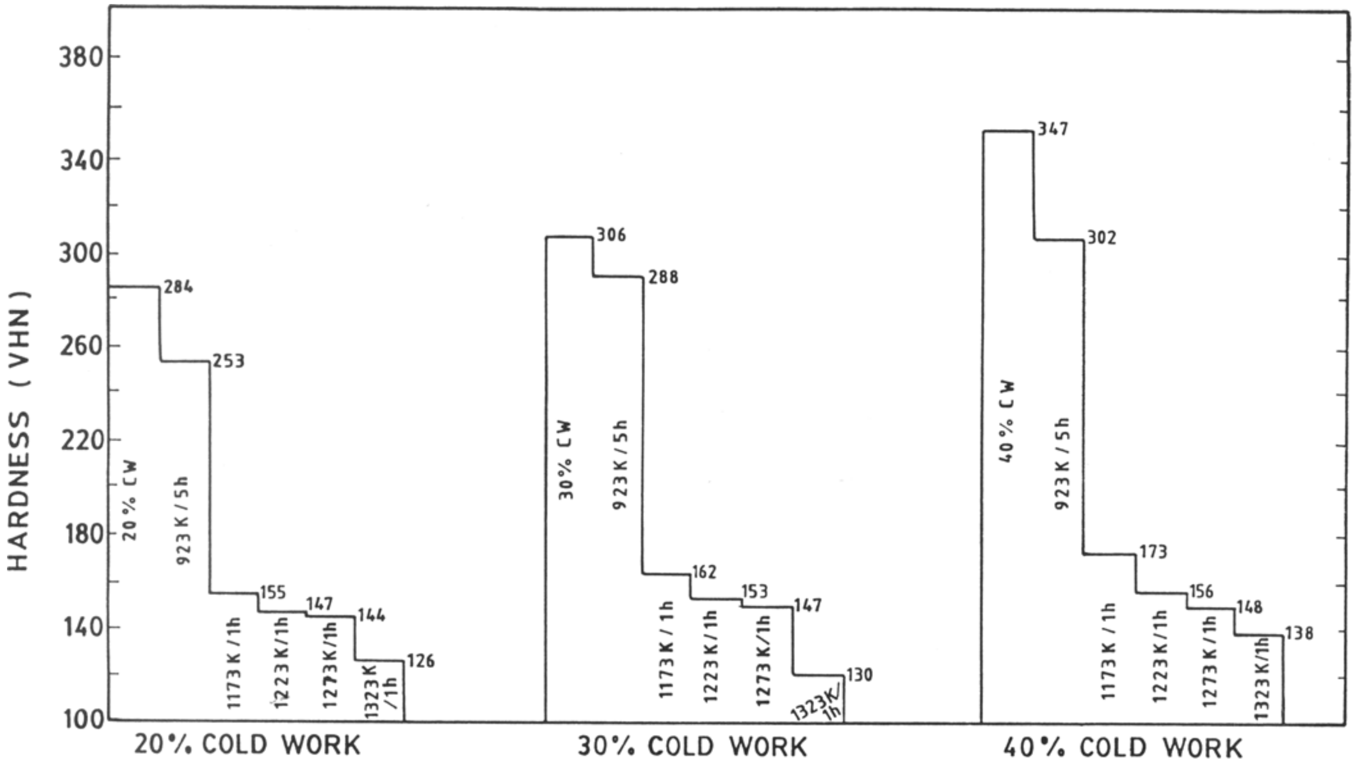


Fig. 7 Variations in microhardness of specimens at each stage of microstructure modification.

Table 2 Results of IGC Testing after Resensitization Heat Treatments

			Heat treatment:		
Cold work, %	923 K/5 h	923 K/5 h 1173 K/1 h 923 K/5 h	923 K/5 h 1223 K/1 h 923 K/5 h	923 K/5 h 1273 K/1 h 923 K/5 h	923 K/5 h 1323 K/1 h 923 K/5 h
0%	Failed	Failed	Failed	Passed	Passed
20%	Failed	Failed	Failed	Passed	Passed
30%	Failed	Passed	Passed	Passed	Passed
40%	Failed	Passed	Failed	Failed	Failed

smaller grains would increase the total grain boundary area and thus improve IGC resistance.

Specimens aged at 1173 and 1223 K were also found to exhibit incomplete dissolution of precipitates (Fig. 5) and did not show a clearly relieved structure after the resensitization treatment, as shown in Fig. 6. When all specimens were subjected to the Practice E test, interesting results were obtained, as shown in Table 2. Specimens cold worked to 30%, sensitized at 923 K for 5 h, and subjected to aging treatments at 1173, 1223, 1273, and 1323 K for 1 h passed the IGC test without showing cracks in the U-bend test. Also, specimens at 0 and 20% cold work, sensitized at 923 K for 5 h, and aged at 1273 and 1323 K for 1 h showed resistance to IGC attack. Specimens undergoing 40% cold worked failed at all conditions, except for those aged at 1173 K for 1 h. This could be attributed to the brittleness and the formation of fine martensites during cold working of austenitic stainless steels.[1-3,7,21,22]

Thus, the results of the present work confirmed the hypothesis that the formation of nuclei of carbide precipitates throughout the structure by the present methodology of cold working, sensitization; and aging at 30% cold work would decrease the susceptibility to sensitization and IGC during service or any resensitization treatment.

Although cold working increases strength and decreases ductility, subsequent sensitization and aging treatments were found to decrease strength by showing a decrease in microhardness. Samuel *et al.*[24] reported that carbide precipitation during sensitization treatment had two opposite effects on room-temperature strength properties, namely strengthening due to precipitation and weakening of the austenite matrix as it was depleted of carbon, chromium, and molybdenum. In the present work, because a microstructure with intragranular nuclei and precipitation was produced, the weakening effect was not foreseen, whereas strengthening would be considerably higher due to the intragranular precipitation compared to grain boundary precipitation. Thus, material at 30% cold work undergoing the present treatment would offer improved IGC resistance and moderate strength when used in service.

4. Conclusions

The following conclusions were obtained from this investigation: Aging of 30% cold worked and sensitized specimens between 1173 to 1323 K/1 h showed improved IGC resistance when specimens were resensitized. The improvement in IGC resistance can be attributed to the formation of numerous intragranular $M_{23}C_6$ carbide precipitates and the recrystallized smaller grains, resulting in an increased grain boundary area. Specimens undergoing 0 and 20% cold work showed an improvement in IGC resistance only at higher aging temperatures, namely at 1273 and 1323 K. Specimens at the 40% cold work level failed the IGC test, probably due to brittleness and the formation of martensite during cold working.

Acknowledgments

The authors thank Mr. J.B. Gnanamoorthy, Head, Metallurgy Division, and Dr. Placid Rodriguez, Head, Metallurgy and Materials Programme of IGCAR, Kalpakkam, for their constant support and encouragement.

References

1. E.C. Bain, R.H. Aborn, and J.J.B. Rutherford, *Trans. Am. Soc. Steel Treating*, Vol 21, 1933, p 481-509.
2. V. Cihal, *Intergranular Corrosion of Steels and Alloys*, Elsevier Science, Amsterdam, 1984.
3. C.S. Tedmon, Jr., D.A. Vermilyea, and D.E. Broecker, *Corrosion*, Vol 27, 1971, p 104-106.
4. C.L. Briant and A.M. Ritter, *Scr. Metall.*, Vol 13, 1979, p 177-181.
5. R.K. Dayal, N. Parvathavarthini, S. Venkadesan, S.K. Mannan, and J.B. Gnanamoorthy, "Proc. Workshop on Experience in the Fabrication and Use of Stainless Steel Equipment in the Department of Atomic Energy Projects," Paper No. C.66, Kalpakkam, India, 1981.
6. S.K. Mannan, R.K. Dayal, M. Vijayalakshmi, and N. Parvathavarthini, *J. Nucl. Mat.*, Vol 126, 1984, p 1-8.
7. C.L. Briant and A.M. Ritter, *Metall. Trans.*, Vol 11A, 1980, p 2009-2017.
8. S. Pednekar and S. Smialowska, *Corrosion*, Vol 36, 1980, p 565-577.
9. N. Parvathavarthini, R.K. Dayal, S.K. Seshadri, and J.B. Gnanamoorthy, *J. Nucl. Mater.*, Vol 168, 1989, p 83-96.
10. W.L. Clarke and G.M. Gordon, *Corrosion*, Vol 29, 1973, p 1.
11. L.E. Murr, A. Advani, S. Shankar, and D.G. Atteridge, *Mater. Characterization*, Vol 24, 1990, p 135-158.
12. R. Pascali, A. Benvenuti, and D. Wenger, *Corrosion*, Vol 40, 1984, p 21.
13. S.M. Bruemmer, *Mater. Sci. Forum*, Vol 1989, 1989, p 309-334.
14. S.M. Bruemmer, L.A. Charlot, and D.G. Atteridge, "Composition Effects on the Sensitization of Austenitic Stainless Steels," Report NUREG/CR-3918, US Nuclear Regulatory Commission, Washington, DC, 1984; Pacific Northwest Laboratory, 1984.
15. R.A. Mulford, E.L. Hall, and C.L. Briant, *Corrosion*, Vol 39, 1983, p 132-143.
16. A.J. Sedriks, *Corrosion of Stainless Steels*, John Wiley & Sons, 1979.

17. A.H. Advani, D.G. Atteridge, and L.E. Murr, *Scr. Metall. Mater.*, Vol 25, 1991, p 2221-2226.
18. B. Weiss and R. Stickler, *Metall. Trans.*, Vol 3A, 1972, p 851.
19. U. Kamachi Mudali, S. Venkadesan, and J.B. Gnanamoorthy, *J. Mater. Eng.*, Vol 12, 1990, p 227-234.
20. "Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels," A262-81, in *1981 Annual Book of ASTM Standards*, Section 3.1, ASTM, 1984, p 66.
21. D.C. Cook, *Metall. Trans. A*, Vol 18, 1987, p 201-210.
22. S.W. Yang and J.E. Spruiell, *J. Mater. Sci.*, Vol 17, 1982, p 677-690.
23. N. Terao and B. Sasmal, *Metallography*, Vol 13, 1980, p 117-133.
24. K.G. Samuel, P. Rodriguez, and K.A. Padmanabhan, *Trans. Ind. Inst. Met.*, Vol 39, 1986, p 421-425.