Nickel Diffusion Coating on Austenitic Stainless Steels & Its Effect on Stress Corrosion Cracking

By B. Ögel & I.A. Sapci

The effect of electrolytic and electroless nickel diffusion coatings was studied on stress corrosion cracking (SCC) behavior of AISI 304 austenitic stainless steel. The nickel coating was diffused at the annealing temperature range of AISI 304 steel. It was observed that the diffusion process improves adhesion of the coating to the substrate. The electrolytic Ni-coated and diffused 304 samples showed better resistance to SCC (ASTM G 36-87), when compared to plain AISI 304, 316 and 321 stainless steels. No failure was observed in coated and diffused samples even after a 180° bending prior to the SCC test, whereas the electroless Ni coating became brittle after the high-temperature diffusion process.

Austenitic stainless steels are among the materials susceptible to stress corrosion cracking (SCC).[1-4] In Cl- ion-containing environments, especially, and stress, their life is reduced with unexpected SCC failure.

There are several ways of minimizing the risk of SCC. Among these, stress relief annealing, shot peening and increasing the nickel content of austenitic stainless steels can be considered. Stress-relieving treatments do not completely eliminate the risk of SCC, however, because the stresses associated with assembly and thermal cycling are often responsible for SCC.[5] In the case of shot peening, the surface peened must be exposed to the blast. Moreover, if there is a possibility of pitting corrosion (especially for austenitic stainless steels), pits may penetrate through a compression layer up to layers of high residual stresses, accelerating SCC.[6,7]

A nickel content of 40-45 percent makes the austenitic stainless steel practically immune to SCC.[4,8,9] The use of high-Ni austenitic steels is an expensive solution to the problem, however. A more practical solution can be to coat stainless steel substrates with Ni, which would lower the cost of the operation, providing that adhesion between the coating and substrate is good. Despite the general belief that most electroplated deposits contain high residual stresses and that their adhesion is poor,[10,11] a recent study has indicated that excellent adhesion to stainless steel substrates can be obtained if necessary precautions are taken.[12] The only disadvantage with Ni coatings seems to be exposure of the substrate to a harmful environment, once the coating is damaged.

This paper recounts investigation of the effect of Ni diffusion coatings on SCC behavior of austenitic stainless steel substrates. It has been reported that adhesion between the coating and the substrate is further improved after a high-temperature diffusion process.[13,14] Also, a diffusion process is expected to increase the Ni content of the substrate just below the coating, which can impart extra protection against coating damage. This approach can be employed as an economical solution for substrates such as heat exchangers and electrical heater shielding tubes, where periodic heating and cooling cycles impart residual stresses to the substrate and often initiate a failure at the protective coating and substrate interface.

Experimental Procedure

Three different types of austenitic stainless steels were used in SCC experiments: AISI 304, 316 and 321. The Ni coating was applied only to the cheapest grade, AISI 304 specimens.

The electrolytic Ni coating was applied using a Watts bath, which consisted of nickel sulfate 300 g/L, nickel chloride 45 g/L, boric acid 35 g/L at pH 3.0. The plating was carried out at 60 °C with a current density of 5 A/

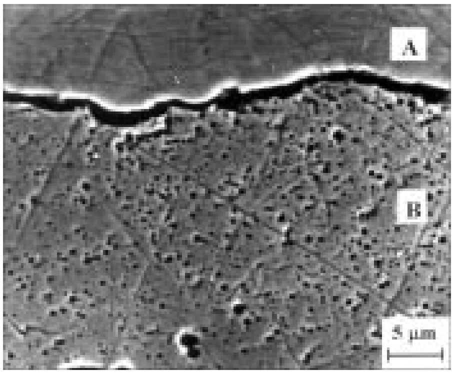

Fig. 1—Electroless Ni coating on AISI 304 substrate, as-coated: (A) coating; (B) substrate.

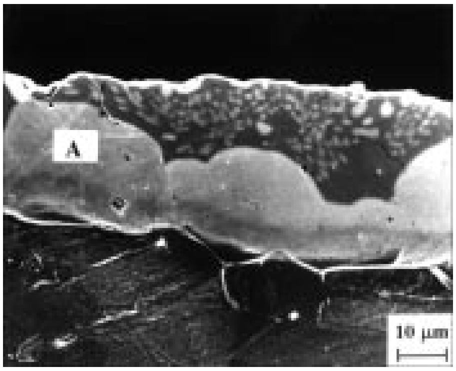

Fig. 2—Micrograph of the electroless Ni coating after a diffusion process at 1000 °C for 1 hr: (A) diffusion front of Fe.

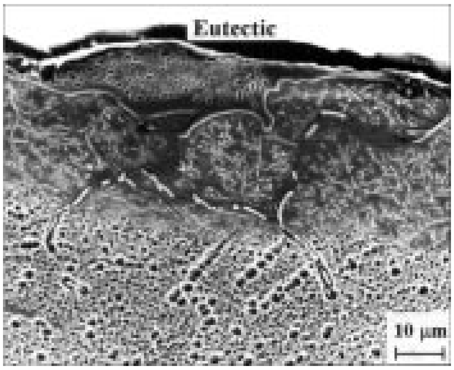

Fig. 3—Ni3P eutectic in electroless Ni coating after a diffusion process at 1000 °C for 1 hr. Specimen is overetched.

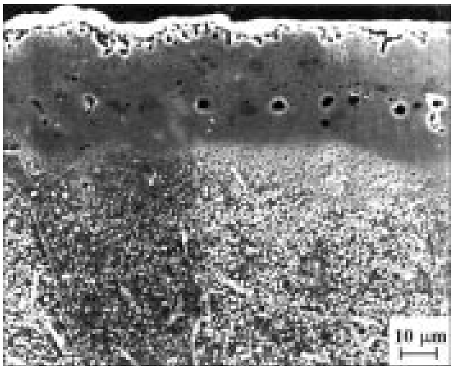

Fig. 4—Electrolytic Ni coating after a diffusion process at 1000 °C for 1 hr. Small voids are present at the original interface.

Stress Corrosion Test Results

Specimen #	Substrate	Type of Coating	Diffusion	Result
1	304	—	—	3.5 hr
2	316	—	—	18 hr
3	321	—	—	48 hr
4	304	Electrolytic Ni	—	OK
5	304	Electroless Ni	—	OK
6a	304	Electrolytic Ni	✓	OK
6b	304	Electrolytic Ni	✓	OK

6a: For this specimen, the U-bending (ASTM G 36-87) was done after the coating, but before the diffusion step.
6b: For this specimen, the U-bending (ASTM G 36-87) was done after both coating and diffusion steps.

dm². Before Ni plating, the surface of the 304 grade steel was treated with a nickel strike in a bath having nickel chloride 240 g/L, HCl 72.5 mL/L and at a current density of 1.2 A/dm² and at room temperature. For electroless Ni plating, an acidic commercial bath was used, yielding 8-9 percent phosphorus. For both Ni coating methods, the thickness was approx. 40 µm.

The diffusion experiments of Ni-coated specimens were carried out in a horizontal tube furnace under an argon atmosphere for periods of 15-60 min and at a temperature range of 1000-1100 °C. The heat treatment temperatures were close to the annealing temperature of commercial 304 grade steel, which is in the range of 1000-1050 °C.

For SCC tests, U-bend specimens were prepared in accordance with ASTM G 30-90. The specimens were cut and bent such that the length L was 100 mm, thickness T was 3 mm and bend radius R was 8 mm. The SCC susceptibility of the specimens was evaluated in 42-percent boiling $MgCl_2$ solution, using the ASTM G 36-87 standard. The tests were continued for a total of 168 hr (7 days) or until a crack was detected with the naked eye. For each test, three specimens were used and the results were averaged.

Results and Discussion

Microstructural Observations

Figure 1 shows a section through the electroless Ni-coated 304 substrate. A well-defined boundary can be observed between the coating and the stainless steel. When this specimen was heated to 1000 °C for one hr, a fast diffusion of Fe from the substrate into the coating was observed. The diffusion front of Fe can be seen in Fig. 2 as an irregular and lightly contrasted region. On the other hand, the diffusion of Ni in the opposite direction was not as fast as that of Fe. The EDS point analysis from the diffusion layer indicates that it is rich in Fe (20%) and Ni (80%). The amount of P detected in this region was negligible. It appears that P is rejected and rises to the surface of the coating. A similar observation was also reported by Schenzel and Kreye.[15] More significantly, local melting took place in the electroless Ni coating at 1000 °C. The Ni + Ni_3P eutectic is also marked in Fig. 2. This is in agreement with the Ni-P equilibrium phase diagram, in which the Ni+Ni_3P eutectic invariant lies at 880 °C and in the range 0-15 percent Ni. Overetching the specimen reveals the Ni_3P eutectic more clearly (Fig. 3). Using EDS point analysis, it was found that the small islands within the eutectic are nearly pure Ni, whereas the eutectic phase is rich in Ni (78%) and P (22%). A further increase in temperature to 1100 °C does not alter the general form of the microstructure, but the diffusion layer becomes thicker and the eutectic precipitates become coarser as well. In a recent relevant study,[16] it was reported that the electroless Ni coatings become brittle at temperatures as low as 750 °C.

As far as the electrolytic Ni coating is concerned, a diffusion process at 1000 °C caused mutual diffusion of Fe in the substrate and Ni in the coating. After the diffusion treatment, the original coating/substrate interface can be distinguished easily by small voids present at the interface (Fig. 4). Heating to 1000 °C for one hr is seen to form a Ni-rich layer on the stainless steel substrate having approximately 5-10 µm thickness. When compared to an electroless Ni coating, the slower diffusion rate of Fe may be a result of the absence of a liquid phase in the Fe-Ni system at this temperature; also in comparison to that of the Fe-Ni-P system. As far as the small voids at the interface are concerned, these can result from either the Kirkendall effect or residual defects at the coating/substrate interface. It is well known that porosities are formed at the site of a faster diffusing element, when the rates of diffusion are not equal. Several other studies on Fe-Ni diffusion couples have reported the formation of Kirkendall voids.[17-19] On the other hand, electrolytic and electroless coatings are inherently defective at the substrate/coating interface. The voids, therefore, can also result from the insufficient healing effect of the diffusion process. In this study, it was observed that an increase in diffusion temperature and/or time seems not to affect the size and amount of the voids; nevertheless, a sound explanation for void formation needs further investigation.

A simple test method was applied to the diffused specimens to determine the behavior of coatings under tensile stresses. For this purpose, the Ni-coated and diffused 304 sheets were sectioned and prepared metallographically. The

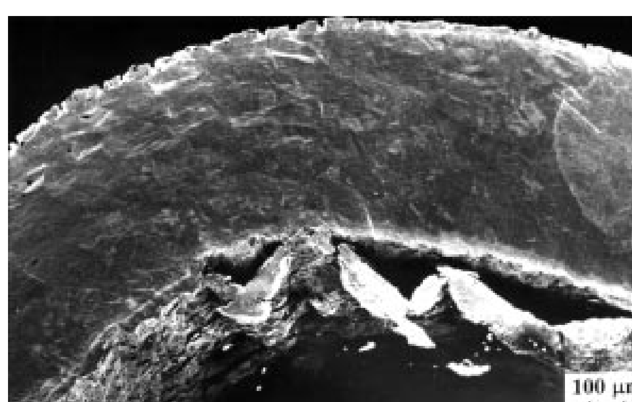

Fig. 5—Electroless Ni-coated 304 specimen after a bending operation that caused extensive damage.

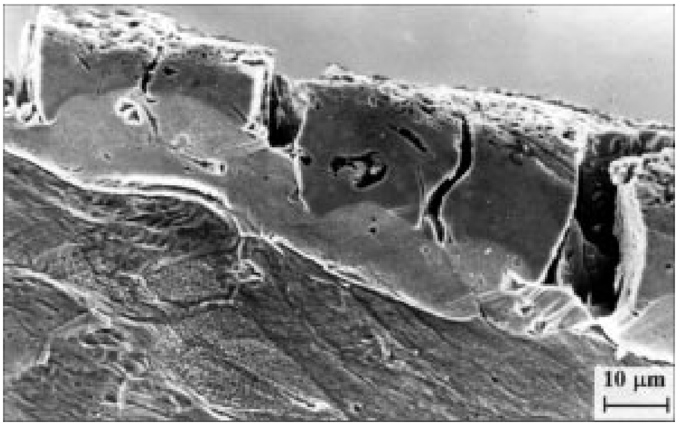

Fig. 6—Cracks initiating from brittle Ni3P phase after a bending operation.

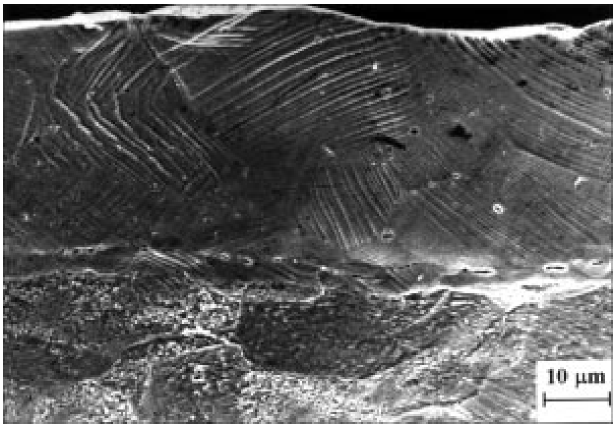

Fig. 7—Slip lines formed within electrolytic Ni coating, showing ductility retained after the diffusion process.

specimens were then bent into U-shape, such that the bend radius was around 2 mm—much more severe than that proposed in the ASTM G 36-87 standard. The coating/substrate interface at the tip of the bend was observed under a scanning electron microscope for possible failures, which would correspond to the region of largest tensile stresses. Figure 5 shows the micrograph of the electroless Ni-coated 304 specimen after such a bending operation. It is seen that bending has damaged the coating and caused peeling, especially at the compression side. Observations at higher magnifications have revealed that the Ni_3P phase precipitated within the coating renders it brittle. The initiation of cracks from the brittle Ni_3P phase can be seen in Fig. 6. A bending operation applied to diffusion-treated electrolytic Ni deposits does not cause a failure when compared to that of electroless Ni coatings. Figure 7 shows the behavior of an electrolytic Ni coating under tensile stresses. A deformation at the tension side of the bent specimen causes formation of slip lines on the Ni coating. Because of high ductility of the coating, however, no cracks are initiated at the coating surface. Not only ductility, but also the coating adhesion seems improved.

SCC Test Results

The specimens used in SCC tests and the processing details are given in the table. The uncoated AISI grades 304, 316 and 321 were tested just for comparison purposes (Specimen Nos. 1, 2 and 3 in the table). Thus, the relative resistance of coated specimens to SCC could be found.

As seen in the table, the 304 grade specimen without any coating could not resist cracking in the boiling solution after more than 3.5 hr. On the other hand, the 316 and 321 grades cracked in 18 and 48 hr, respectively. This was an expected result, inasmuch as the resistance of stainless steels to SCC increases in the same order: The 304 grade is weakest and the 321 grade is the most resistant.

To test the effect of Ni coating on stressed substrates, the specimens were bent in accordance with ASTM G 36-87, then coated with either electrolytic or electroless Ni (Specimens No. 4 and 5 in the table). In this case, the coated 304 grade specimens resisted cracking and survived the 168-hr (7 days) test (see table). Besides naked eye observation, these specimens were also investigated for hidden cracks. Specimens were sectioned after the SCC test and examined for cracks below the coating. No cracks were detected in the substrate. This indicated that both electroless and electrolytic Ni coatings were sound and no part of the substrate was exposed to the boiling solution.

The response of the stressed electrolytic Ni coating to the SCC test was also studied by changing the sequence of the bending operation (Specimen No. 6a in the table). The 304 grade specimens were first coated with electrolytic Ni and diffusion treated at 1000 °C. These diffusion-treated specimens were then bent 180° in accordance with ASTM G 36-87. Thus, the coating as well as the substrate could be stressed to the nearly same magnitude as with uncoated specimens. These stressed specimens survived the test without failure in 168 hr (7 days). This procedure was not applied to electroless Ni coatings because the Ni3P eutectics would render the coating brittle, creating cracks and exposing the substrate to the test solution.

For electrolytic Ni-coated 304 U-bend specimens, when the SCC test is applied after a diffusion process, no failure was observed (Specimen No. 6b in the table). This was an expected result and done for only comparison purposes. A diffusion process at such high temperatures would definitely relieve the stresses introduced in the specimen.

In view of these results, it seems that a nickel coating on a stressed part, either electrolytic or electroless, is very effective in avoiding SCC. As seen in the table, the life of coated specimens is increased nearly fourfold, even without a diffusion process. This is most probably a result of the isolation of the stressed substrate by the coating, preventing initiation of an SCC crack.

In the second more critical stage of the study, an attempt was made to investigate the effect of Ni diffusion coating on SCC. As mentioned above, both electroless and electrolytic Ni coatings were used for diffusion. Although electroless Ni coatings are not widely used and are relatively more expensive, some advantages, such as its perfect coverage to every part of components, even to blind holes, makes it attractive for use. For these reasons, electroless Ni coating was also examined for diffusion coating. In this case, however, the phosphorus caused precipitation of brittle intermetallics within the coating and rendered it brittle. On the other hand, the stressed electrolytic Ni coating yielded identical results with that of specimens without diffusion; no cracks were detected after a 168-hr test.

In diffusion treated specimens, diffusion of Fe from the substrate to the surface of the coating was observed. Because this might affect the surface composition, the diffusion time at a given temperature seems to be the most critical parameter. An insufficient diffusion time would yield a weak bond between substrate and coating. In contrast, a longer diffusion time would increase the Fe content of the Ni coating surface, by which the coating might become susceptible to SCC.

In light of the above results, it can be suggested that a Ni coating applied to the 304 stainless steel substrates, either with or without a diffusion treatment, makes them immune to SCC. For applications where there is cyclic thermal loading, however, and where possibilities of failure initiation from the coating/substrate interface is high, a diffusion coating process can bring an extra advantage, by improving the coating adhesion, and by creating a Ni-rich intermediate layer between the substrate and coating.

Summary

In the present study, the experiments carried out on U-bend specimens have indicated that Ni coating on AISI grade 304 improves the SCC resistance. The life of 304 grade steel is improved at least fourfold, when compared to that of plain (uncoated) AISI 304, 316 and 321 grade steels. In the case of electrolytic Ni coatings, a diffusion process improves adhesion of the coating to the substrate, whereas electroless Ni coatings become brittle because of precipitation of the Ni_3P phase.

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References

1. H.L. Logan, *The Stress Corrosion of Metals*, John Wiley and Sons, New York, NY, 1966; p. 124.
2. J.E. Trumann, *SCC and Hydrogen Embrittlement of Iron-Base Alloys*, 5, National Association of Corrosion Engineers, Houston, TX 1973, p. 111.
3. *ASM Metals Handbook*. Vol. 13., 9th ed., American Society for Metals, Metals Park, OH, 1986; p. 145.
4. R. Rimbert & J. Pagetti, *Corrosion Science*, 27, 189, (1987).
5. *ASM Metals Handbook*. Vol. 13., 9th ed., American Society for Metals, Metals Park, OH, 1986; p. 554.
6. W.H. Friske, *Shot Peening to Prevent the Corrosion of Austenitic Stainless Steels*, A1-75-52. Rockwell International (1975).
7. D.R. McIntyre & C.P. Dillon, *Guidelines for Preventing Stress Corrosion Cracking in the Chemical Process Industries*. Publication 15, Materials Technology Institute of the Chemical Process Industries, p. 164 (1985).
8. H.H. Uhlig, *Corrosion and Corrosion Control: An Introduction to Corrosion Science*. Wiley-Interscience Publ., 3rd ed., New York, NY, 1985.
9. H.R. Copson, *1st Int. Conf. on Metallic Corrosion*, 3, (1961).
10. G.M.C. Lee, *Canadian Metallurgical Quart.*, **25**, 327 (1986).
11. H. Speckhardt, *Industrie Anzeiger*, **92**, 849 (1970).
12. J.W. Dini & H.R. Johnson, *Plat. and Surf. Fin.*, **69**, 63 (Nov. 1982).
13. W. Riedel, *Electroless Nickel Plating*, ASM Finishing Publications, NY (1991).
14. E. Raup & K. Muller, *Fundamentals of Metal Deposition*, Elsevier Publ. Co., New York, NY, 1967.
15. H.G. Schenzel & H. Kreye, *Plat. and Surf. Fin.*, **77**, 50 (Oct. 1990).
16. B. Ögel and M. Yanar, *Proc. 14th Int'l. Cong. on Electron Microscopy*, Cancun, Mexico, 2, 221 (1998).
17. R.W. Ballufi & J.W. Cahn, *Acta Metall.*, **19**, 493 (1981).
18. D.A. Smith & A.H. King, *Phil. Mag.*, **A44**, 333, (1981).
19. C.M. Li, C. Chaturvedi & K.N. Tandon, *Materials Characterization*, **30**, 89 (1993).

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