Effect of Cold Work on Intergranular Corrosion Cracking of Sensitized Stainless Steel†

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Abstract

In this paper, it is clarified that the resistance of AISI304 stainless steel to intergranular corrosion cracking in acid copper sulfate solution (Strauss solution) increased with cold working before or after sensitizing heat treatment. To discuss the effect of martensite induced by cold working, the temperature of cold working is chosen two levels: 100°C and – 196°C. The susceptibility for the intergranular corrosion cracking is scarcely affected only by the presence of martensite in austenite matrix, but is greatly affected by the martensite in which the precipitation of carbides is occured.

Moreover, the correlation of the susceptibility for corrosion cracking and the rate of ordinary intergranular corrosion is also discussed.

1. Introduction

The corrosion cracking of stainless steels due to polythionic acid is one of the most important cracking experienced in oil refining apparatus. Most of these cracking are intergranular corrosion cracking due to the precipitation of chromium carbides occured at the grain boundary during the heat cycle of welding or heat treatment.

In constructing the apparatus, forming and welding are indispensable process. Then there may be the place at which the stainless steel is sensitized (for example, due to the heat cycle of welding) after cold working in forming process. In this place, the susceptibility for intergranular corrosion cracking probably differs from that of the material only sensitized, because of the different distribution of precipitated carbides. Moreover, in the case of AISI304 stainless steel, martensite transformation occurs during the cold working at low temperature, and the susceptibility of corrosion cracking may also be affected by the transformed martensite.

On the other hand, Somas reported that the test in acid copper sulfate solution was able to show the same properties as those in polythionic acid solution.[1]

Then, in this paper, the effect of cold work and sensitization on the resistance of AISI304 stainless steel to intergranular corrosion cracking in the acid copper sufate solution is discussed. Especially, the effect of martensite transformed during cold working is discussed.

2. Experimental Procedure

The chemical composition and mechanical properties of tested material are shown in Table 1.

Table 1 Chemical composition and mechanical properties of tested material.

Chemical composition (wt%)							Mechanical properties			
C	Si	Mn	P	S	Ni	Cr	0.2% Proof stress (kg/mm²)	Tensile strength (kg/mm²)	Elongation (%) G.L=20	Reduction of area (%)
0.06	0.40	1.04	0.028	0.010	8.92	18.25	24.5	67.5	65.0	50.0

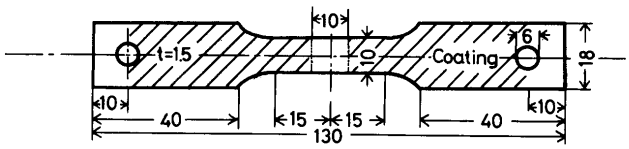

Fig. 1 Dimensions of test specimen. (mm)

Test specimens, of which dimensions were shown in Fig. 1, were solutionized 30 minutes at 1050°C and were prepared as follows:

Specimen I : Stretched at –196°C and next sensitized

Specimen II : Sensitized and next stretched at –196°C

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Specimen III : Stretched at 100°C and next sensitized
Specimen IV : Sensitized and next stretched at 100°C

The sensitization heat treatment was 2 hours at 660°C. The cold stretching was performed in the liquid nitrogen (– 196°C) or in the boiling water (100°C), and the amount of cold working was shown by the elongation of specimen. All the specimens were polished by buff before the corrosion cracking test.

The amount of martensite contained in the specimens was measured by the ferite indicator.

The test of susceptibility for intergranular corrosion cracking were conducted by placing specimens in boiling aqueous solution containing 16% of H_2SO_4 and 8.7% of $CuSO_4$ $5H_2O$ under the constant tensile load and obtained the time to failure. The value of applied load were settled two kinds: one was 15Kg/mm by initial stress and another was three quarters of the yielding stress (σ_y) of the tested specimen at 100°C.

The ordinary intergranular corrosion test was performed for the specimen I. The specimens were immersed in the same solution as that for the cracking atest for 48 hours, and the weight loss and the decrease of tensile strength due to corrosion were measured.

3. Results and Discussion

3.1 Metallurgical structure of cold worked and sensitized stainless steel

AISI304 stainless steel transforms into martensite during the cold working at low temperature.[2]

Figure 2 shows the relation between the amount of transformed martensite and the rate of cold working for the specimens stretched after sensitizing (Specimen II and IV). In the case of stretching at – 196°C (Specimen II), large amount of martensire beyond 10% was measured in the specimen stretched about 20% in elogation. But, in the case of stretching at 100°C (Specimen IV), martensite below about 1% was hardly detected in the specimen stretched heavily such as 40% in elongation, and martensite transformation scarcely occured during the stretching in this temperature.

Figure 3 shows the relation between the abount of transformed martensite and the rate of cold working for the specimens sensitized after stretching (Specimen I and III). Large amount of martensite was transformed on the process of stretching at – 196°C (Specimen I), but some part of that was resolved on the following sensitizing process. In the stretching at 100°C (Specimen III), the amount of martensite was little, and the amount became less in the following sensitization heat treatment.

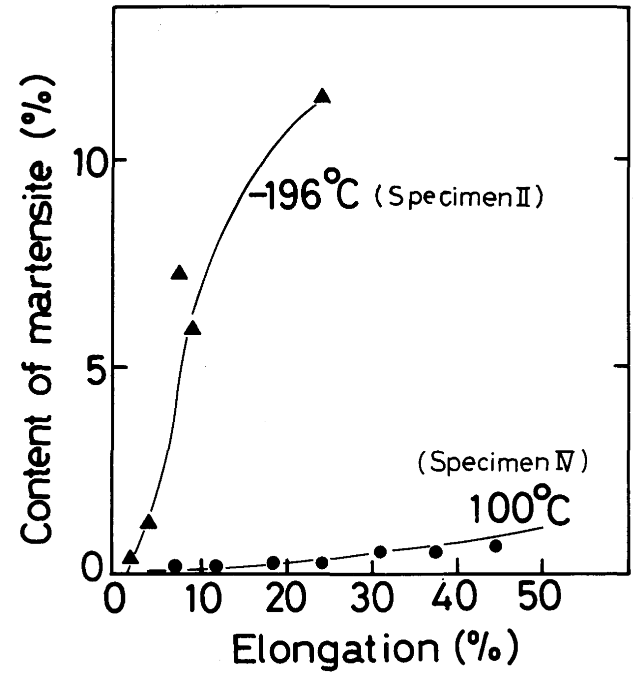

Fig. 2 Effect of cold work on content of , martensite for specimen I and IV.

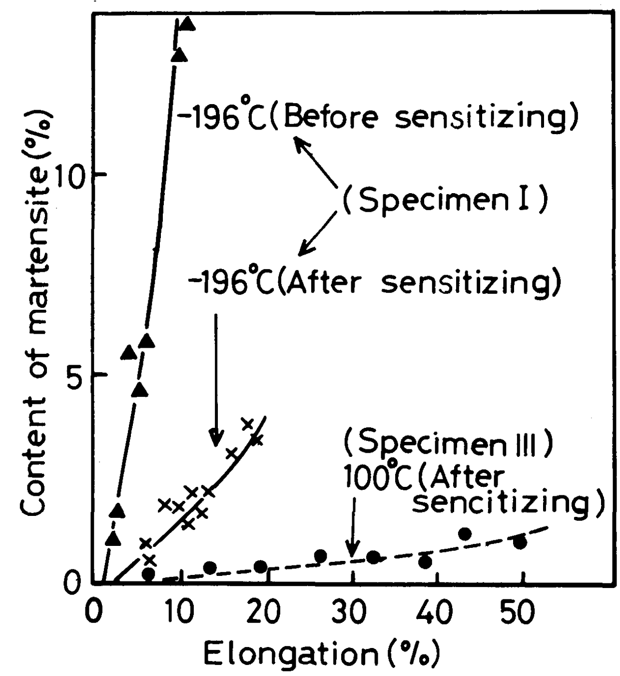

Fig. 3 Effect of cold work on content of martensite for specimen I and III.

It is generally known that when AISI304 stainless steel is heat treated for sensitization, it becomes weak in intergranular corrosion because of the precipitation of carbides at the grain boundary. In the sensitization of the cold worked stainless steel, precipitation of carbides occured at the defects produced by the slip deformation and martensite transformation during the cold working as same at the grain boundary.

Figure 4 shows the typical distribution of carbides

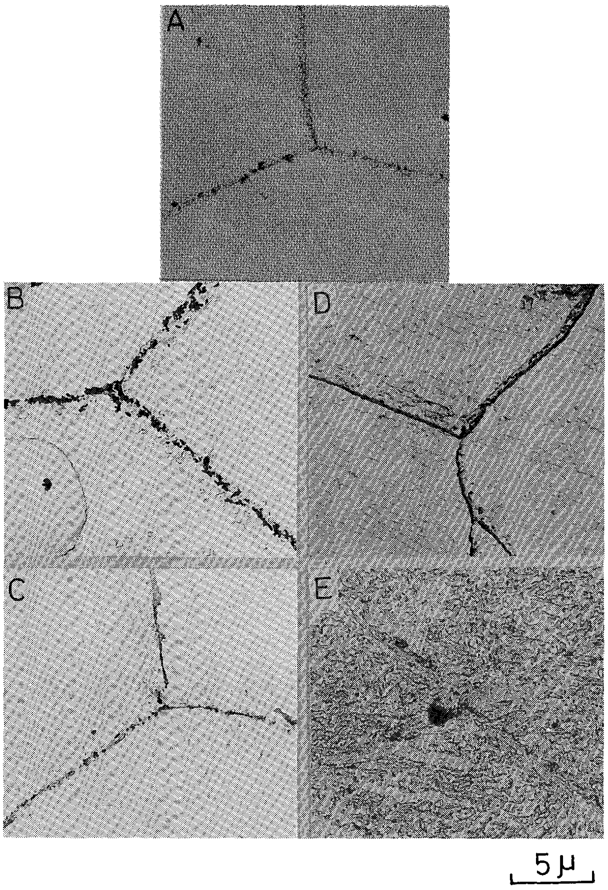

Fig. 4 Typical distribution of carbides for each specimen by the extraction replica method.

A; Only sensitization heat treatment
B; Specimen IV, C; Specimen II,
D; Specimen III, E; Specimen I.

for each treated specimen (I, II, III and IV). In the case of only sensitizing, carbides precipitates mainly at the grain boundary as shown in Fig. 4A. Fig. 4B and C are the case of stretching after sensitizing. So the specimen did not jet cold worked, when it was heat treated, that carbides precipitated at the same part as the part in Fig. 4A. But, in the case of sensitizing after stretching, carbides precipitates both in matrix and grain boundary as shown in Fig. 4D and E. Fig. 4D shows the case of specimen after stretching at 100°C, carbides precipitated in grain may perhaps precent at the defects occured by the shipping deformation, because the martensite transformation does not occur at this temperature. Figs. 4E shows the case of specimen sensitized after stretching at − 196°C, carbides precipitates at the boundary of martensite lath transformed by the cold stretching at − 196°C.

Large parts of these precipitated carbides were confirmed as the $M_{23}C_6$ type compound by the electorn disfraction method as shown in Fig. 5.

3.2 Sensitivity of intergranular corrosion cracking

Figure 6 shows the relationship between cold work and time to failure of intergranular corrosion cracking for specimen II and IV. When the rate of cold work is below approximately 20%, the more the cold work, the less the time to failure. It is estimated that when the

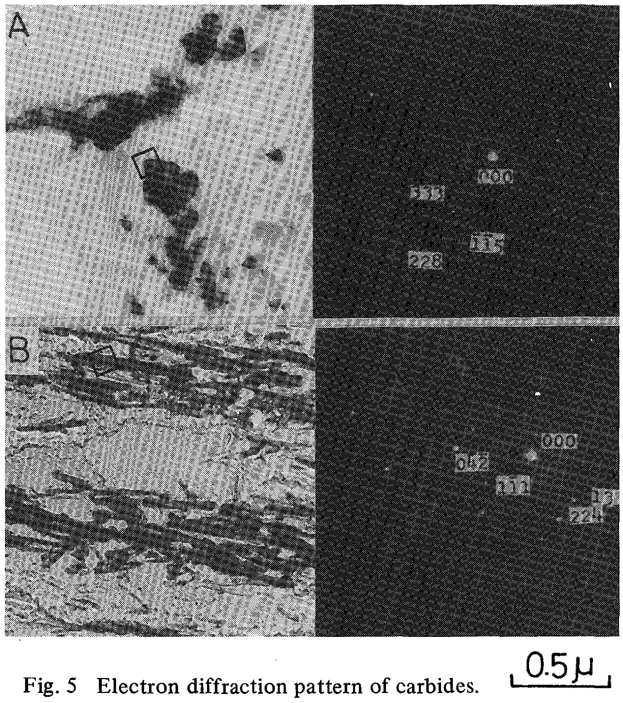

Fig. 5 Electron diffraction pattern of carbides. A; Specimen IV, B; Specimen I.

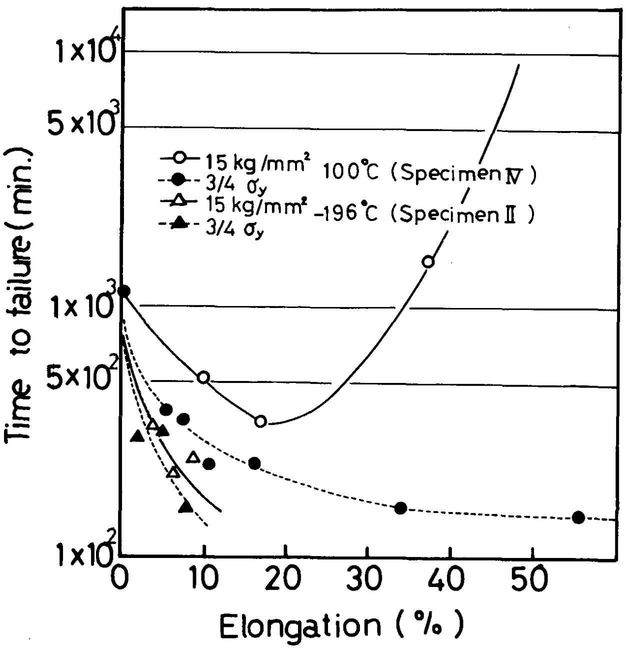

Fig. 6 Effect of cold work on time to failure of corrosion cracking for specimen II and I.

cold work is small, strain hardening occures at only beside grain boundary, and this part becomes weak for general corrosion. But, when cold work increases more, strain hardening extended to the whole part of grain, and it is safely said that the difference of corrosion between grain and grain boundary decreases. So we would conclude that the above mentioned effect disappears. When the cold work is above 20%, time to failure increases with increase of cold work. This fact occurs because yielding stress increases with increase of cold work. If the applied stress is set as $3\sigma_y/4$, the time to failure does not increase. In another word, increase of the resistance to cracking is due to the increase of yielding strength. From the metallurgical point of view, the grain of specimen cold worked strongly is ingthened, and the pass of crack tends to take a zigzag course as shown in Figs. 7B. It shows the aspect that it may hardely break.

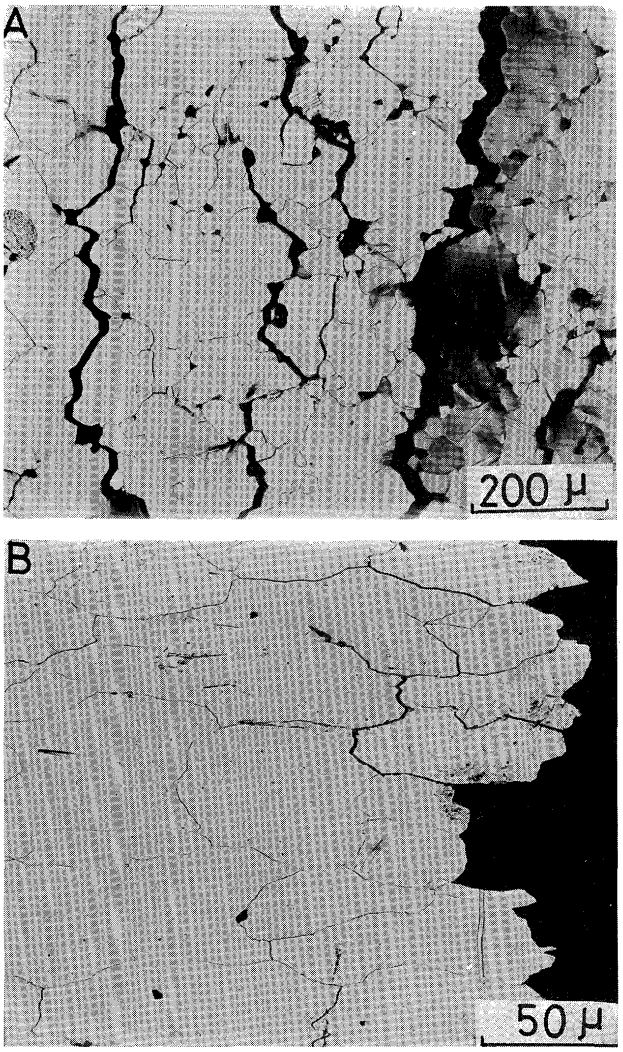

Fig. 7 Surface features of tested specimens near to fractured part.
A; Only sensitization heat treatment,
B; Specimen IV (elongation 55%)
Applied stress : 15Kg/mm^2

Figure 8 shows the major example of surface features of specimen after test. The specimen, which is strongly stretched at 100°C as shown in Fig. 8B, is deformed largely by slip. The specimen, which is stretched at − 196°C as shown in Fig. 8D, is expected to have large amount of martensite induced by cold work.

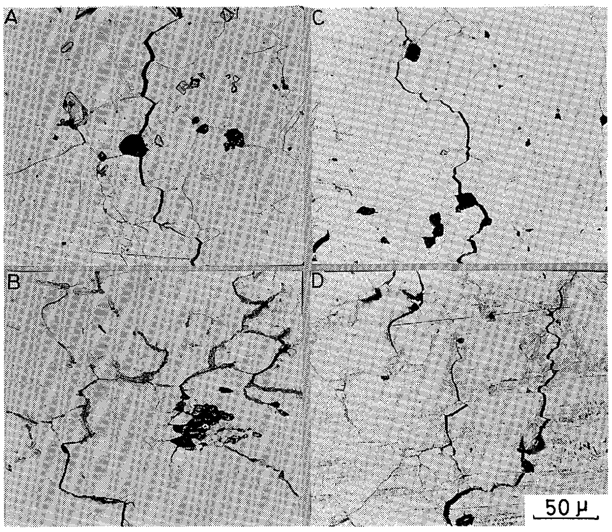

Fig. 8 Surface feature of specimen after corrosion cracking test.
A; Specimen IV (elongation 17%)
B; Specimen IV (elongation 55%)
C; Specimen II (elongation 4%)
D; Specimen II (elongation 9%)
Applied stress ; 15Kg/mm^2

However, it is interesting to observe the fact that the slip lines and martensite were not attacked by corrosion, and these surfaces of grains were clean. Only intergranular cracks were observed.

Figure 9 shows the relationship between cold work

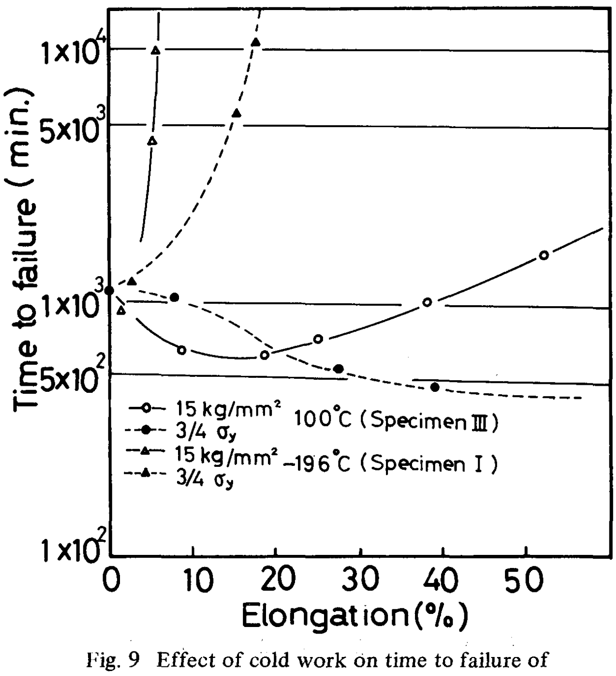

Fig. 9 Effect of cold work on time to failure of corrosion cracking for specimen I and III.

and time to failure of corrosion cracking for specimen I and III. The specimen stretched at 100°C, of which applied stress was 15Kg/mm^2, tended to have a shorter time to failure till the elongation exceeded beyond 20%, time to failure tended to be longer as cold work increased. In the case when the applied stress was set as $3\sigma_y/4$, the time to failure did not become long with increase of cold work. We suppose that this tendency is leaded by the same cause as we have observed in Fig. 6. When specimen was stretched at 100°C, martensite did not transform, but slip deformation occured and some carbides has been precipitated on the dislocation piled up on slip plain on the process of the sensitizing heat treatment after cold working. Consequently, as to be observed on the Figs. 10A and B, not only the grain

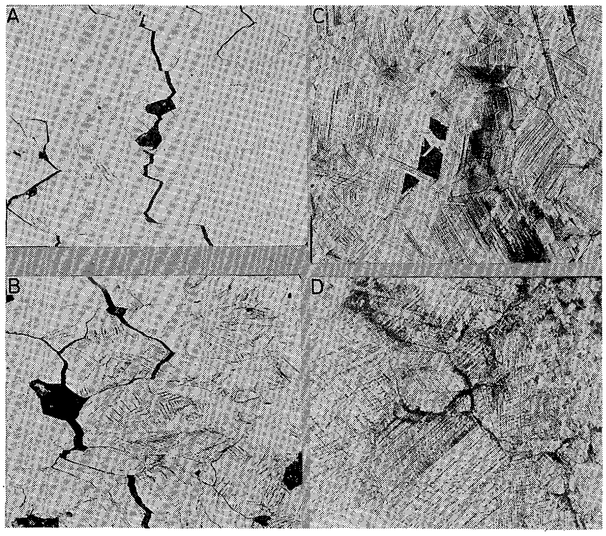

Fig. 10 Surface features of specimen after corrosion cracking test.
A; Specimen III (elongation 28%)
B; Specimen III (elongation 52%)
C; Specimen I (elongation 6%)
D; Specimen I (elongation 10%)
Applied stress ; 15kg/mm^2

boundary but also the slip line tend to be attached on the way of the corrosion cracking test. However we do not think this tendency greatly affects the sensitivity of cracking. In Fig. 9, the specimen stretched at − 196°C, and tested by 15Kg/mm^2 of applied stress, showed the interesting phenomenon that the time to failure has been prolonged significantly by only a little cold work of 10% or so. Also, when the applied stress was set as $3\sigma_y/4$, the time to failure did not become constant against the amount of cold work, and it increased as the cold work increased. This means that the prolong of time to failure, when the cold work increases on the specimen I, does not depend upon the more increasing of yielding stress. This case makes contrast with the three types of specimen II, III and IV. The surface of specimen I after cracking test has many attached lines inside the grain as shown in Figs. 10C and D. We would believe, as described before, that some carbides were precipitated by the sensitizing heat treatment on the lath boundary of martensite, and the boundary part was attacked during the cracking test. We may have two possible causes for the large prolongation of time to failure for specimen I. One is that the carbides precipitated at grain boundary decreases because the carbides are precipitated on the lath boundary of martensite inside the grain. The other possible cause is that the electro-chemical accelerating effect of grain surface to the local attack of grain boundary decreases because the passivity of grain surface decreases.

Figure 11 shows a typical examples of fractured

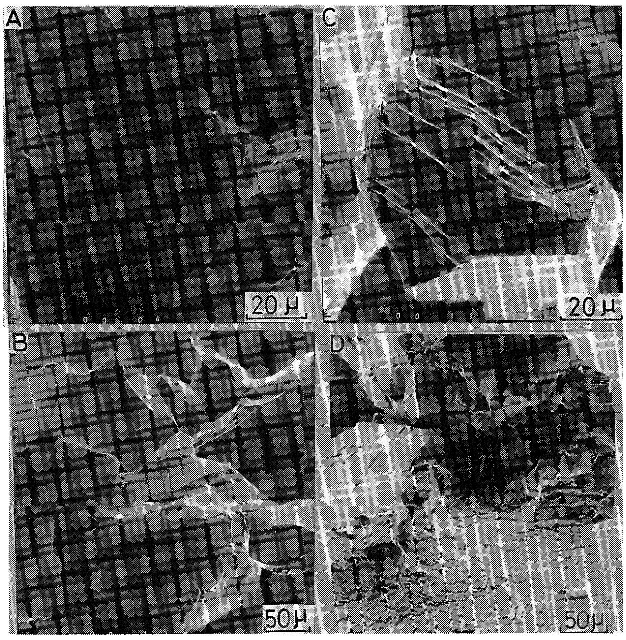

Fig. 11 Fractgrafic photographs of fractured surfaces of specimens.
A; Specimen IV (elongation 55%)
B; Specimen II (elongation 9%)
C; Specimen III (elongation 52%)
D; Specimen I (elongation 9%)
Applied stress ; 15Kg/mm^2

surfaces by SEM. Fig. 11A is the case of specimen IV. In this case we can see the rock candy pattern having the wavy slip. Fig. 11B is the case of specimen II. In this case we can recognize the rock candy pattern and many parallel lines which may be considered as martensite. In the case of specimen III (Fig. 11C), we can see the similar aspect as Fig. 11A. The evidence in this case is that we can recognize the pitting corrosion at the crossing points of weavy slip lines. In the case of specimen I (Fig. 11D), we can a different feature from the previous three specimens II, III and IV. It is estimated that this complex feature of fractured surface is created by the corrosion of martensite-lath boundary.

3.3 Correlation between the susceptibility for cracking and the ordinary intergranular corrosion in the specimen I

As we find the peculiar properties on the fracture of specimen I, we must discuss the correlation between the time to failure and the property of ordinary intergranular corrosion in this specimen.

Figure 12 shows the effect of cold work on the weight loss of intergranular corrosion after immersion in the same solution as that for the cracking test for 48 hours. Till the elongation reached about 10%, the weight loss is not change, and the elongation exceeds beyond 10%, the weight loss decreases to a considerable point. Because the corrosion in this solution is mainly intergranular type, there are some dropping of grains themselves in addition to the dissolution of grain boundary in this measured value. It may be said that the grain boundary is made a zigzag and tied up the cold working, and then it becomes hard to drop off.

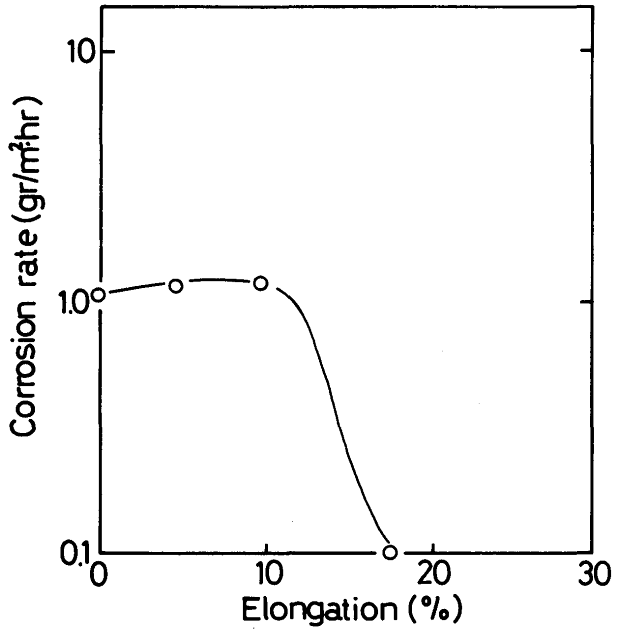

Fig. 12 Relation between corrosion rate and amount of cold work. (Specimen I)

To evaluate the attacked value in grain boundary more clearly, we obtain the tensile strength of specimen after the immersion. The result is shown in Fig. 13. We clearly see a similar tendency like the result of specimen I in Fig. 10. This means that the susceptibility of the corrosion cracking is controlled by the intergranular corrosion, even in the case of specimen I where abnormal phenomenon has been occured.

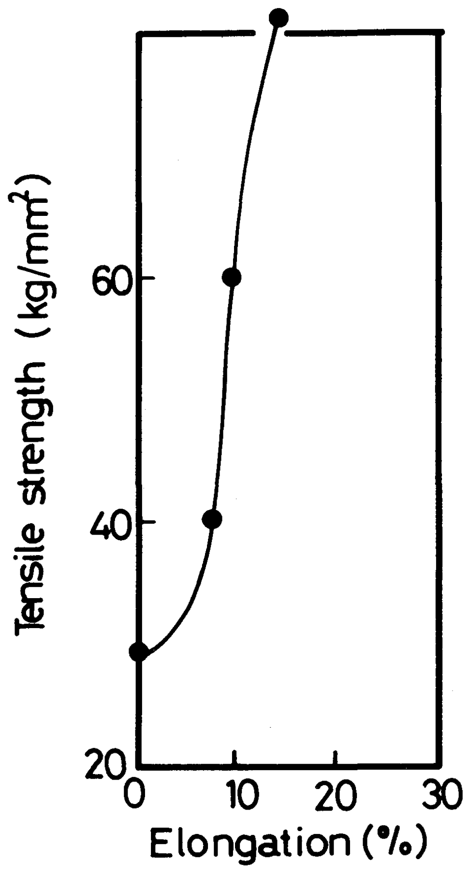

Fig. 13 Effect of cold work on tensile strength after immersion in acid copper sulfate solution for 48 hrs. (specimen I)

4. Conclusion

The effect of cold work and sensitization heat treatment on the resistance of AISI304 stainless steel to intergranular corrosion cracking in acid copper sulfate solution is discussed. The results are summarized as follows:

1) Some amounts of martensite are transformed by the cold working at $-196°C$. But, the cold working after the sensitization heat treatment does not change the distribution of carbides largely.

2) The resistance of the stainless steel, which is cold worked after sensitizing, to corrosion cracking increases with increase of cold work. This is mainly due to the increase of yielding stress of specimen.

3) In the specimen sensitized after cold worked, precipitation of carbides occurs at the defects produced by the slip deformation (at 100°C) or martensite transformation (at $-196°C$).

4) The specimen, which is sensitized after cold worked at $-196°C$, has a large resistance to the corrosion cracking.

Reference

1) C. H. Samans : Corrosion (1964) vol. 20, p256t.
2) M. Watanabe and Y. Mukai : Proceedings of the 4th ICMC, (1969)