Effect of Copper Addition on Corrosion Resistance of Commercial Al-Zn-Mg Alloy Welds[†]

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Abstract

An investigation has been made on the effect of copper addition of 0.17wt% on the corrosion resistance of commercial Al-Zn-Mg alloy welds by means of electrochemical measurement and transmission electron microscopy.

The weld cracking was hardly observed in the welds with 0.17wt% copper, and weldability was good. Distributions of hardness in the heat affected zone of welds with copper was similar to that without copper. The corrosion resistance of base metal (T5) was not affected by the copper addition.

The corrosion resistance of the bond area of the welds was improved by the copper addition, for the reason of the improvement of microstructure such as grain boundary precipitates, the width of precipitation free zone, and improvement of electrochemical characteristics.

KEY WORDS: (Pitting Potential) (Corrosion Resistance) (Transmission Electron Microscopy) (Al-Zn-Mg Alloy) (Al-Zn-Mg-Cu Alloy)

1. Introduction

Commercial Al-Zn-Mg alloys, which are extensively used in aircraft structures and vehicles, are susceptible to stress corrosion cracking. Considerable effort has been directed towards determining the causes of such failures by examining the microstructure, composition, aging treatment, minor alloy additions and dislocation arrangements[1),2),3)].

Addition of copper to the Al-Zn-Mg alloys has been found to simultaneously improve the yield strength and stress corrosion cracking resistance up to 2%Cu[1),4)]. An overaging treatment may be also used to greatly inhibit the stress corrosion cracking.

As copper bearing alloys are welded, the weld cracking such as solidification cracking often occurs. Then, it is necessary to decide the suitable content of copper addition. According to schoer et al.[5)], the weld cracking markedly takes place at 0.6wt% copper addition, but the cracking hardly occurs up to 0.3wt% copper. Gibbs[6)] showed that the cracking hardly occurred up to 0.03wt% copper.

For the weld cracking, the addition of copper to the Al-Zn-Mg alloy is desirable to be a little. Then, minor copper addition up to 0.2wt% to the commercial Al-Zn-

Mg alloy was made in this investigation.

The purpose of this paper is to present beneficial effects of minor copper addition on the corrosion resistance of the weld bond using transmission electron microscopy and electrochemical measurement.

2. Experimental Procedures

The materials used in this investigation are two kinds of commercial Al-Zn-Mg alloys (T5), and their chemical compositions are shown in **Table 1**. An alloy A without

Table 1 Chemical compositions of base metals (wt%).

	Zn	Mg	Cu	Si	Fe	Mn	Cr	Ti	V	Zr	Al
A	4.47	1.15	Tr	0.07	0.19	0.37	0.21	0.07	0.01	0.13	Bal.
B	4.52	1.10	0.17	0.08	0.18	0.37	0.21	0.06	0.01	0.13	Bal.

copper, and an alloy B with copper, they have almost same chemical compositions except copper.

The plates have been cut into 150mm wide and 200mm long, and the thickness was 6mm. The weld test was used single Vee groove. The welding was carried out by MIG

welding procedure. The filler metal was 1.6mm welding wire of Al-Mg system 5356. Three pass welding was made using the heat input at 7000J/cm. The interpass temperature was 50°C.

After welding, all the welded samples were artificially aged at 90°C for 20 days.

The electrochemical measurement was made in order to evaluate the corrosion resistances of welded samples. Anodic polarization curves showing the relation of potential to current density, were developed for each specimen, which was cut off from the welded samples.

Each curve was developed by anodically polarizing a specimen from its free corrosion potential to a potential above its breakdown potential. Potential/current curves were recorded at potential scan rates of 20mV/min.

The electrolyte used was 1M NaCl solution which was deaerated by bubbling argon through the solution for at least 30 min. before immersing the specimen.

Each specimen was abraded with 1500 grit emery paper, rinsed in deionized water, degreased in acetone, and then masked along its edges with stop-off lacquer prior to testing.

Each specimen was exposed to the solution for 5 min. before measurements which were begun to permit the developments of a steady-state free corrosion potential.

The microstructures of each part in the welded samples were observed using transmission electron microscope. The foils for transmission electron microscopy were prepared using a jet polishing technique, in a solution consisted of perchloric acid and ethanol below −30°C.

3. Results and Discussion

3.1 Hardness distributions of welded samples

Figure 1 shows hardness distributions of welded samples, as the samples were welded and then artificially aged at 90°C for 20 days.
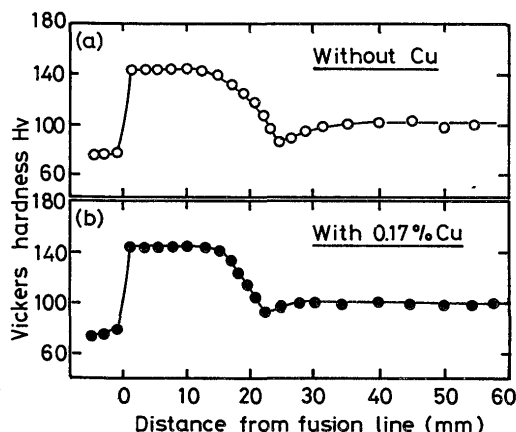

Fig. 1 Hardness distributions of the welded sample with and without copper.

Generally, the stress corrosion cracking of welds occurs at the root region. Then, the hardness was measured along the area near the root region.

As shown in Fig. 1-(a), the hardness of weld metal is about Hv72. In the weld heat affected zone, the hardness of the region from fusion line to the area of 15mm is Hv140. This region is heated at the solid solution temperature, and then the hardness increases by artificial aging after welding, and is higher than that of base metal (T5).

In the region of 15-25mm from the fusion line, the hardness decreases with increasing the distance from fusion line. This region is that G.P. zones and η' precipitates were partially solutionized.

In the region of 25-40mm from the fusion line, the hardness increases with increasing the distance from fusion line. This region is generally called as overaged region[7].

The hardness distributions of welded samples in both copper bearing sample and sample without copper are very similar.

Consequently, each part of the hardness of the welded samples hardly depend on the minor copper addition of 0.17wt%.

3.2 Microstructures of welded samples

Figure 2 shows the optical micrograph of the welded sample with 0.17wt% copper.

Generally, copper addition above 0.5wt% causes the weld cracking such as solidification cracking[6]. But, in this investigation, as shown in Fig. 2, the weld cracking is hardly observed for copper addition up to 0.2wt%.

Figure 3 shows transmission electron micrographs of base metal (T5) without copper addition.

Figure 3-(a) shows the micrograph which incident electron beam is parallel to the grain boundary plane, and Fig. 3-(b) shows the incident beam is vertical to the grain boundary plane. The relatively insoluble compounds such as $Al_{18}Cr_2Mg_3$, $Al_{12}Fe_3Si$ so on are observed as large dark particles[1]. The fine precipitates present within the grain. This is considered that G.P. zones and η' precipitates occurred by T5 treatment. Many gross precipitates such as η phase are observed at the grain boundary.

As shown in Fig. 3-(a), the precipitation free zone (PEZ), where the precipitate hardly occurs is present near the grain boundary, and the width in about 0.15μm. As shown in Fig. 3-(b), the grain boundary precipitates are larger than that of the precipitates in grain. The PFZ also occurs around the relatively insoluble compounds.

Fig. 4 shows transmission electron micrographs of the foils of base metal (T5) of 0.17wt% copper addition. Fig. 4-(a) shows the micrograph which incident electron
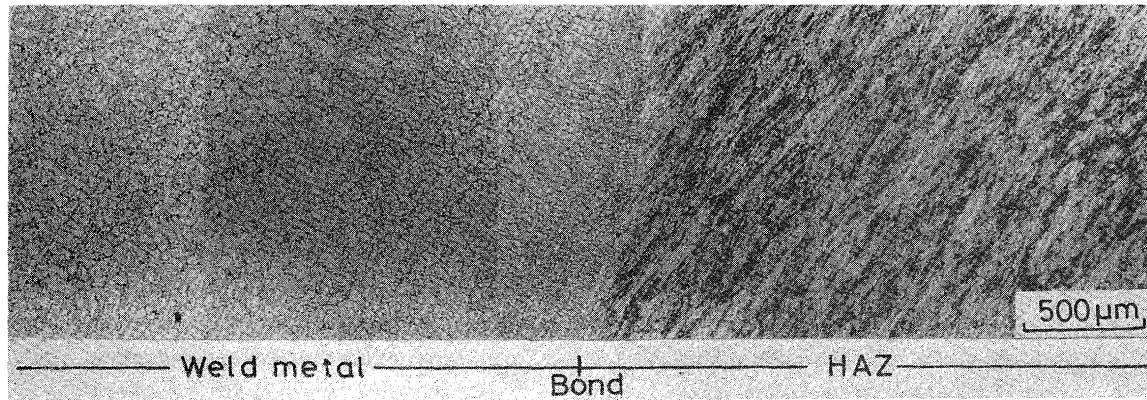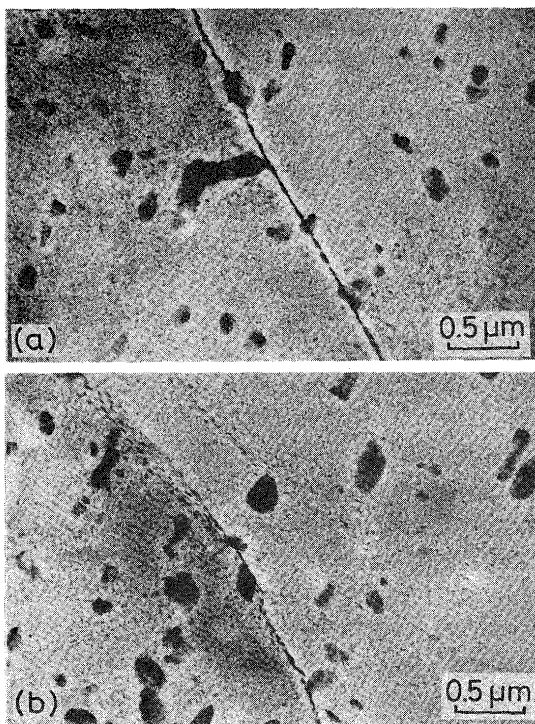
Fig. 2 Microstructure of welds with copper.

Fig. 3 Transmission electron micrographs of the base metal without copper.

Fig. 4 Transmission electron micrographs of the base metal with copper.

beam is parallel to the grain boundary plane, and Fig. 4-(b) shows that incident beam is vertical to the grain boundary plane.

As shown in Fig. 4-(a), many large precipitates occur at the grain boundary, and fine precipitates such as η' precipitates occur in the grain. Large relatively insoluble compounds are also observed as dark particles. The width of the PFZ near the grain boundary is a little larger than that without copper shown in Fig. 3.

As shown in Fig. 4-(b), the grain boundary precipitates are larger than that within grain. Consequently, the copper addition of 0.17wt% hardly affects the microstructure of the base metal treated T5. The results support that
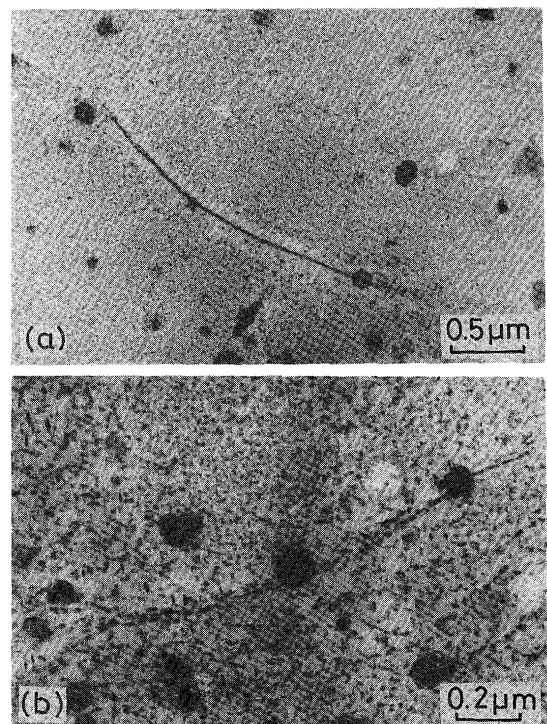
the hardness of base metal (T5) with or without copper is very similar as shown in Fig. 1.

Figure 5 shows transmission electron micrographs of the thin foils of weld bond area in the specimen without copper. Fig. 5-(a) shows the micrograph which incident electron beam is parallel to the grain boundary plane, and Fig. 5-(b) shows that incident beam is vertical to the grain boundary plane.

The grain boundary precipitates are small, as shown in Fig. 5-(a), or a little observed as shown in Fig. 5-(b). But the size of precipitates is very small. Many fine precipitates in the grain seem to be G.P. zones. The PFZ occurs around the relatively insoluble compounds of large black particles.
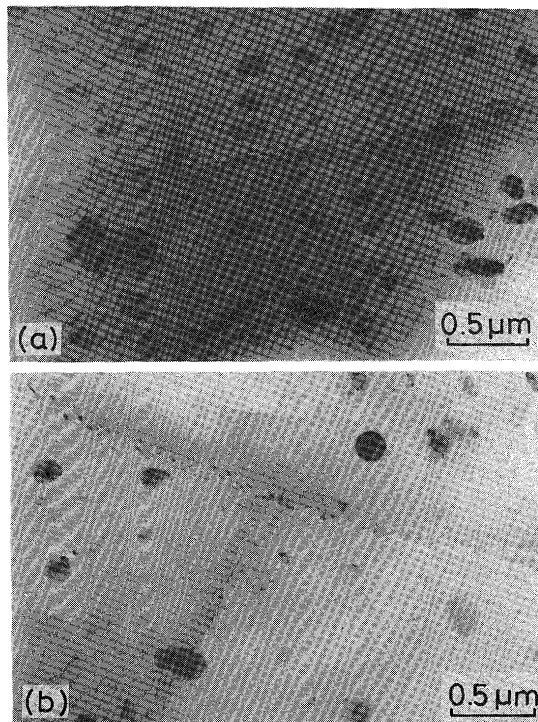
Fig. 5 Transmission electron micrographs of the bond area of welded sample without copper.
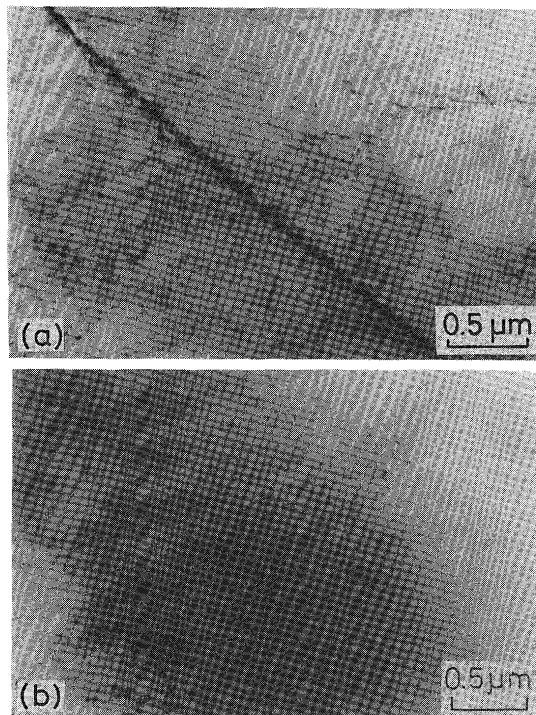

Fig. 6 Transmission electron micrographs of the bond area of welded sample with copper.

Figure 6 shows transmission electron micrographs of the bond area of the welded sample with 0.17wt% copper. Fig. 6-(a) shows the micrograph which incident electron

beam is parallel to the grain boundary plane, and Fig. 6-(b) is that incident beam is vertical to the grain boundary plane.

As shown in Fig. 6-(a), large grain boundary precipitates are observed. PFZ is hardly observed near the grain boundary. Large relatively insoluble compounds is hardly observed.

As shown in Fig. 6-(b), the grain boundary precipitates are divided two kinds of precipitates. Namely, fine precipitates seem to be $MgZn_2$, and other larger precipitates seem to be Al_2Cu[8] or $MgZn_2$ contained copper.

According to Tohomas and Nutting[9], 0.5% copper addition to the Al-Zn-Mg alloy affects the aging characteristics at 160°C, namely G.P. zones were larger and the onset of precipitation of η' was delayed, and the grain boundary changes were little affected except that the precipitates tended to be larger.

But, in this study, the size of G.P. zones is smaller by 0.17wt% Cu addition, because of the difference of aging temperature, and the onset of precipitation of η' was delayed as same as the result of Tohomas[9]. Smith and Grant[10] reported that the width of PFZ decreased by 0.5wt% copper addition, and copper additions to Al-Zn-Mg alloy increased the rate of homogeneous precipitation at lower aging temperature such as 20°C-90°C. In this investigation, as shown in Fig. 6-(a), G.P. zones is very fine and homogeneously precipitates.

Consequently, the age hardenable characteristics are hardly affected by the 0.17wt% copper addition. But, on the basis of the microstructure, it is clear that the copper addition of 0.17wt% caused the homogeneous precipitation of G.P. zones and η' precipitates, and increased the size and the number of grain boundary precipitates, and decreased the width of PFZ at the bond area of welded samples.

3.4 Anodic polarization characteristics of welded samples

Generally, the stress corrosion cracking starts at the grain boundary by the localized corrosion. The corrosion mechanism is based on the development of a preferential anodic path along grain boundaries resulting from localized precipitation.

The susceptibility was attributed to differences in corrosion potentials between matrix and grain boundary regions. The existence of an active region is the vicinity of grain boundaries has been attributed either to anodic precipitates or to solute-depleted regions resulting from precipitation.

Recently, investigators have shown the effects on the electrochemical properties of the grain boundary regions arising from solid solution composition fluctuations brought about by precipitation, and attribute the anodic

nature of the grain boundary region to a high concentration of solute atoms in these regions are compared to grain interiors[11].

Such corrosion potential's measurement is important to be clear the stress corrosion cracking. It is apparent that significant changes occur in the anodic polarization curves as a result of copper addition is the welded sample artificially aged.

The most appropriate way of distinguishing between the anodic polarization curves is to define each of these curves in terms of initial and final breakdown potentials and the values of these potentials.
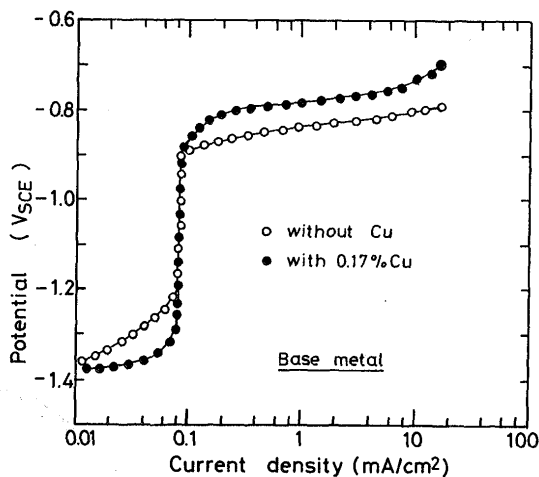

Fig. 7 Anodic polarization curves of the base metals with and without copper.

Figure 7 shows anodic polarization curves of base metals (T5) with and without copper. The corrosion potential of copper bearing sample is -1370mV_{SCE}, and that of sample without copper is -1350mV_{SCE}. In both specimens, a single breakdown is formed, occurring at -900mV_{SCE} followed by a rapid rise in current density. The region between the corrosion potentials (-1350mV_{SCE} or -1370mV_{SCE}) and the breakdown potential (-900mV_{SCE}) is a region of passivity.

Consequently, copper addition of 0.17wt% hardly affects on the breakdown potential in the case of base metal (T5).

Figure 8 shows anodic polarization curves of the welded sample without copper. The breakdown potential of weld metal is -900mV_{SCE}, the result is same that of base metal (T5) shown in Fig. 7. But the breakdown potential of weld bond area is -1000mV_{SCE}, and it is more active than that of base metal (T5). Consequently, it is clear that the corrosion resistance of the bond area is lower in the welded sample.

Figure 9 shows the anodic polarization curves of the welded sample with copper. The breakdown potential of weld metal is -900mV_{SCE}, and is same that of base metal
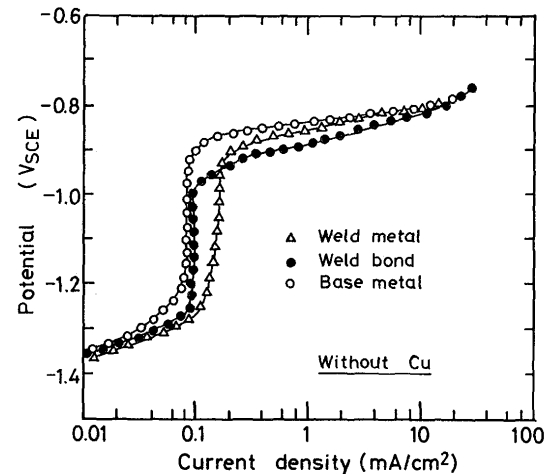

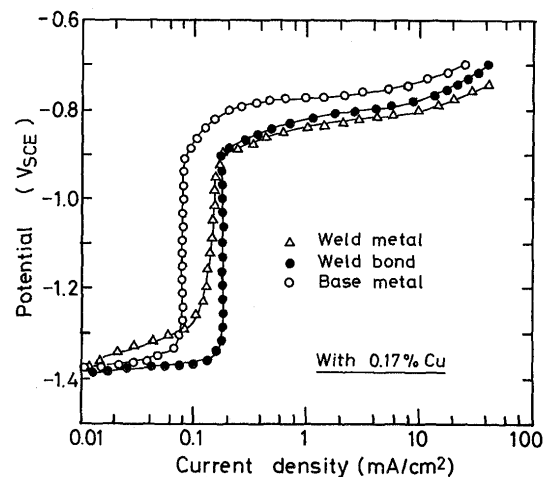Fig. 8 Anodic polarization curves of the welded samples without copper.

Fig. 9 Anodic polarization curves of the welded samples with copper.

(T5). The breakdown potential of the weld bond area is also -900mV_{SCE}.

Consequently, the breakdown potential of base metal is hardly affected by the copper addition of 0.17wt%, but that of weld bond area with copper is more noble than that without copper.

Generally, metallurgical phase has a unique breakdown potential in a given aqueous environment and given testing procedure, and this potential can be used, in principle, to indirectly characterize the composition of the phase.

In a microstructure containing more than one phase, and each in significant volume fractions, the anodic polarization curve may indicate the breakdown potentials of each of these phase.

If these breakdown potentials differ distinguishably from each other, the polarization curve will consist of a number of plateous joined together by regions of relatively constant current density. And the rate of dissolution of

a phase below its breakdown potential is generally low, but it increases rapidly just above the breakdown potential.

Maitra and English[11] found two kinds of breakdown potentials for Al-Zn-Mg-Cu system 7075 alloy (T7351). The first breakdown potential could be caused by the preferential dissolution of $MgZn_2$ at the grain boundary, the second breakdown potential could be caused by the pitting of the solid solution matrix, which now contained less Zn and Mg, because of the precipitation of $MgZn_2$. The active breakdown is caused by the large amount of Zn and Mg retained in solid solution, the value is same as that of $MgZn_2$[12].

Copper is generally noble element if the copper in solution present in the vicinity of the grain boundary, the breakdown potential becomes more noble, but as grain boundary precipitates such as Al_2Cu or $MgZn_2$ contained copper occurs, the breakdown potential becomes more active, because of the decrease of copper in solution in the vicinity of the grain boundary.

In the case of the base metal (T5), a number of grain boundary precipitates such as η phase, and η' precipitates and G.P. zones take place, and minor addition of copper is contained in the precipitates, and then copper in solution in matrix decrease. Consequently, the minor copper addition hardly give rise to occur beneficial effect in the microstructure consisting of a number of G.P. zones and η' precipitates, η phase such as the base metal (T5).

But, in the case of the microstructure consisting of G.P. zones (+ η' precipitates) such as weld bond area, copper retains in the matrix, and copper addition gives rise to the beneficial effect to corrosion resistance. Consequently, the minor copper addition plays an important role of corrosion resistance for bond area of welded sample.

4. Conclusion

An investigation has been made on the effect of copper addition of 0.17wt% on the corrosion resistance of commercial Al-Zn-Mg alloy welds by means of electrochemical measurement and transmission electron microscopy.

The results obtained in this investigation are summarized as follows.

(1) The weld cracking was hardly observed in the welds with 0.17wt% copper.

(2) Distributions of hardness in the heat affected zone of welded sample with copper was same that without copper. The copper addition of 0.17wt% could not give rise to beneficial effect.

(3) The microstructure of the bond area of the welded sample consisted of G.P. zones and fine η' precipitates in both with and without copper. The grain boundary precipitates of the welded sample bearing copper was larger than that of the sample without copper. The width of precipitation free zone decreased by copper addition. But, the microstructure of base metal didn't change by copper addition.

(4) On the basis of anodic polarization curves, the breakdown potentials in both copper bearing base metal and the base metal without copper were $-900mV_{SCE}$. The corrosion resistance of base metal (T5) was not affected by the 0.17wt% copper addition.

(5) In the case of bond area of welded samples, the breakdown potential of the sample with copper was $-900mV_{SCE}$, and that of the sample without copper was $-1000mV_{SCE}$. The corrosion resistance of the bond area of the welded sample was improved by the copper addition.

References

1) M.O. Speidel: Metall. Trans. A., 6A (1975), 631.

2) R.J. Gest and A.R. Troiano: Corrosion, 30 (1974), 274.

3) H.A. Holl: Corrosion, 23 (1967), 274.

4) B. Sarkar, M. Marek and E.A. Starke: Metall. Trans. A., 12A (1981), 1939.

5) H. Schoer and W. Gruhl: Metall. 20 (1966), 221.

6) F.E. Gibbs: Weld. J. 45 (1966), 445s.

7) M. Pirner and H. Bichsel: IIW/IIs-Doc. IX-1127-80.

8) K. Tohma, N. Takahashi and Y. Takeuchi: Keikinzoku, 33 (1983), 377. (In Japanese)

9) G. Thomas and J. Nutting: J. Inst. Metals, 88 (1959-60), 81.

10) W.F. Smith and N.J. Grant: Metall. Trans., 2 (1971), 1333.

11) S. Maitra and G.C. English: Metall. Trans. A., 12A (1981), 535.

12) D.O. Sprowls and B.W. Lifka: ASTM STP 516, 120.