Sacrificial Anode Type Al-10Si-1Mg Brazing Filler Metals for Suppression of Corrosion of Brazed 3003 Aluminum Alloy†

Tadashi TAKEMOTO *, Ikuo OKAMOTO ** and Kazuhiko KUROSHIMA ***

Abstract

Corrosion of brazed 3003 aluminum base metal was studied in an aqueous sodium chloride solution to clarify the effect of zinc and tin addition to Al-10%Si-1Mg filler metals on the protection ability of corrosion of aluminum base metal.

The addition of zinc and tin to filler metal lowered the corrosion potential of filler metals and were proved to be effective to reduce the pit depth of brazed 3003 base metal. The improvement effect of zinc addition was clear in N_2 gas brazing (760 torr), however, the effect was not exerted by vacuum brazing due to zinc vaporization during brazing. Iron as an impurity element in the sacrificial anode type filler metals had no detrimental effect on the pit depth of base metals.

KEY WORDS: (Corrosion) (Pitting) (Brazing) (Brazing Filler Metals) (Aluminum) (Sacrificial Anode) (Corrosion Protection) (Additional Elements)

1. Introduction

Heat exchangers such as radiator, condenser and evaporator employed in automobiles are required to be highly corrosion resistant. The pitting corrosion of tube materials is critical because if the pit penetrate through the tube materials, the contents in heat exchangers leaks out. The main protection method is zinc diffusion from the brazing flux and the use of zinc bearing tube materials with high resistance to pitting corrosion. However, these methods is not effective in a vacuum brazing process because of sublimation of zinc due to high vapor pressure of zinc. New sacrificial alloys for fin and tube materials[1)–5)] and brazing methods have been investigated.[6)]

Since the potential of silicon in filler metal is very high than base metals,[7)] the corrosion resistance of brazed base metal is lower than the base metal alone.[4)] Therefore in the heat exchangers with brazing sheet fin and bare tube material, the use of fin material with filler metal of low electrode potential would be effective to protect tube materials by the sacrificial anodic effect of filler metal cladding. The addition of tin and zinc has been known to lower the electrode potential of aluminum.[8)–10)] In this study, the effect of tin and zinc on the corrosion resistance of brazed 3003 aluminum alloy was investigated.

2. Materials and Experimental Procedures

2.1 Materials

The base metal was 3003-H14 (1.08%Mn, 0.57%Fe, 0.23%Si, 0.14%Cu, wt%) aluminum alloy. The composition of filler metals used for corrosion test are listed in **Table 1**. The filler metals were melted in a graphite crucible in argon gas atmosphere and cast, homogenized, hot rolled and cold roled to 1 mm. The shape and size of brazing specimens were shown in the previous paper.[11)]

Brazing were performed in a vacuum (vacuum brazing: 2×10^{-5} torr) or in purified nitrogen atmosphere (N_2 gas brazing: 760 torr, $-70°C$ dewpoint). The surface treatment was emery paper polishing for filler metals and was ultrasonic degreasing of as received surface in an acetone bath for 3003 base metal. Brazing condition was 600°C for 3 min. The brazed specimens were immersed in 0.4M NaCl + 0.1M H_2O_2 aqueous solution at 30°C. The other experimental methods were same as the previous paper.[11)]

Table 1 Nominal chemical compositions of filler metals (wt%).

System of filler metal	Element					
	Si	Fe	Mg	Zn	Sn	Al
Al-10Si-1Mg-Zn	10	—	1	1	—	Bal.
	10	—	1	2	—	Bal.
	10	0.5	1	1	—	Bal.
	10	0.5	1	2	—	Bal.
Al-10Si-1Mg-Sn	10	—	1	—	0.06	Bal.
	10	—	1	—	0.15	Bal.
	10	0.5	1	—	0.06	Bal.
	10	0.5	1	—	0.15	Bal.

† Received on Nov. 4, 1986

* Research Instructor
** Professor
*** Graduate student, present address: Daihatsu Motor Co., Ltd. (Ikeda)

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

3. Experimental Results

3.1 Effect of zinc addition of Al-Si filler metal

The addition of zinc, tin and indium has been known to lower the electrode potential of aluminum.[8)–10),12)] The effect of zinc addition to Al-10%Si filler metal on the electrode potential is shown in **Fig. 1**. The potential remarkably decreased with zinc addition up to 2%, and slightly decreased by further zinc addition.

Figure 2 shows the anodic polarization curves of the above mentioned filler metals. The degree of anodic polarization was very small, accordingly anodic current shows sharp increase with small rise in anodic potential. **Figure 3** shows the contact polarization curves between 3003 base metal and zinc bearing Al-10%Si filler metals. The 3003 base metal with higher electrode potential was cathode and the filler metal with lower electrode potential was anode. The contact current increased with the increase of zinc content up to 2%Zn, however, the increase was small in further zinc content. From the results all filler metals are expected to act as an sacrificial anode to protect the corrosion of 3003 base metal. On the practical point of view of brazing, the addition of zinc enhances the erosion of base metal. Consequently the addition of more than 2%Zn is not significant. The small addition of tin also lowered the electrode potential of filler metals **(Fig. 4)** and the filler metals also expected to protect 3003 base metals acting as effective sacrificial anodes.

3.2 Effect of sacrificial anode type filler metals

The additional elements that lowers the electrode potential of aluminum also lowered those of Al-10Si alloys. The corrosion resistance of 3003 aluminum brazed by Al-10Si-1Mg filler metals with zinc were tested. The effect of iron in filler metals were also investigated. Iron is

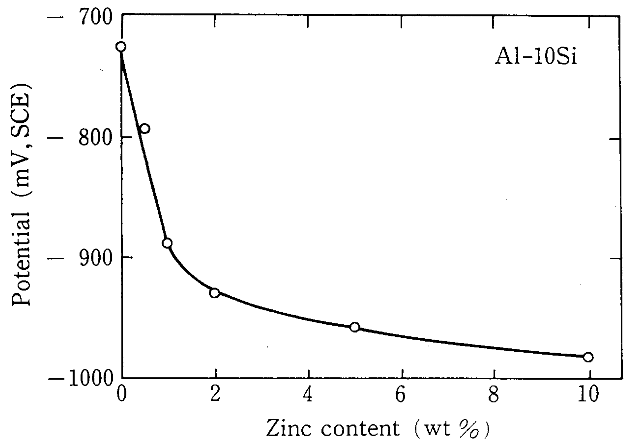

Fig. 1 Effect of zinc content on electrode potentials of Al-10Si alloys in 0.4 M NaCl.

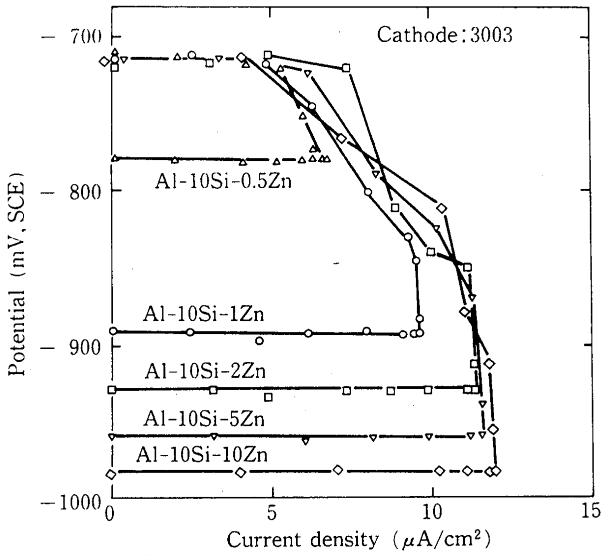

Fig. 3 Contact polarization curves between 3003 and Al-10Si-0~10Zn filler metals.

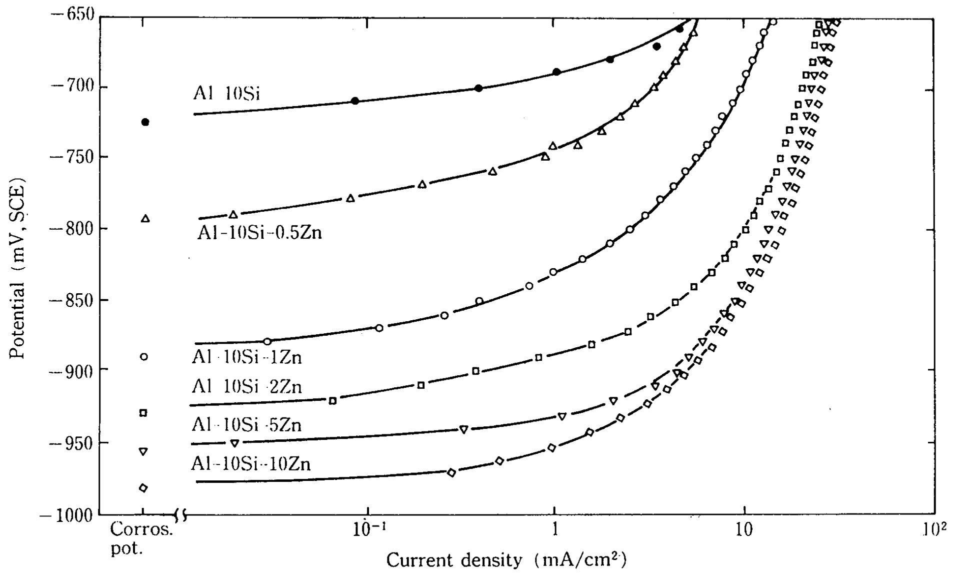

Fig. 2 Anodic polarization curves of Al-10Si-(Zn) alloys in 0.4 M NaCl.

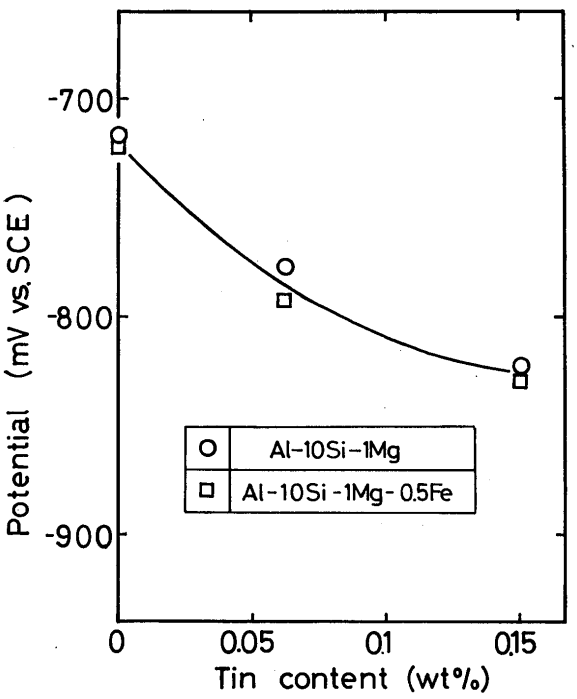

Fig. 4 Changes of electrode potential of Al-10Si-1Mg filler metals with addition of tin, in 0.4 M NaCl.

fixed to 0 and 0.5% by considering the JIS specification Z 3263 (1980) and the results of previous paper.[11]

Figure 5 shows the effect of zinc content on the pit depth of 3003 base metal. The effect of zinc addition is not recognized clearly in vacuum brazing. On the other hand, in N_2 gas brazing, the pit depth decreased with increasing the zinc content in filler metals, which confirmed the effectiveness of sacrificial anode type filler metals to protect 3003 base metal. The iron in filler metal had little influence on the pitting of base metals.

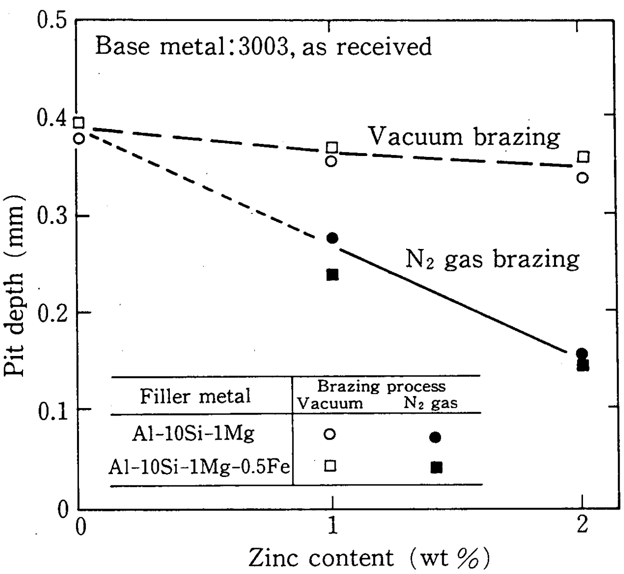

Fig. 5 Effect of zinc content in Al-10Si-1Mg filler metals and brazing process on pit depth of 3003 base metal.

Figure 6 shows the electrode potentials of filler metals of brazed specimens. After vacuum brazing, the added zinc almost completely vaporized as will be mentioned in the following section. Accordingly the electrode potential of filler metal was not lowered. In N_2 gas brazing the potential lowered with the zinc content. The potentials in Fig. 6 were lower than in Fig. 5 because the potentials of filler metals on brazed specimens were measured at the brazed part. Therefore zinc was diluted by the dissolution of 3003 aluminum base metal and the diffusion loss of zinc into base metal.

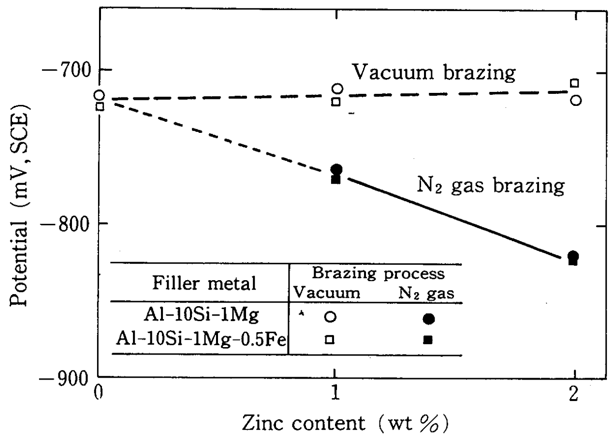

Fig. 6 Effect of zinc content and brazing process on electrode potential of filler metals in 0.4 M NaCl.

4. Discussion

Figure 7 shows the EPMA line analysis on cross section of brazed specimens. Almost whole added zinc vaporized after vacuum brazing irrespective of zinc content in filler metals. The maximum residual amount of zinc was 0.1% and the mean values were ranging between 0.04 to 0.07% (**Table 2**).

The decrease of electrode potential of filler metal was inhibited by vaporization of zinc, which extinguished the effectiveness for the suppression of pitting corrosion of 3003 base metal. On the other hand, zinc remained in the filler metal after N_2 gas brazing. The maximum and mean values of residual zinc were listed in Table 2. In N_2 gas brazing, the zinc diffused layer was found at filler metal/base metal interface (Fig. 7). The concentration gradient was also found at the surface due to dezincification.

The plots between the maximum or mean residual zinc concentration and pit depth of 3003 base metal are shown in **Fig. 8**. The pit depth decreased with increasing the residual zinc after brazing, which confirmed the effective protection by zinc bearing sacrificial anode type filler metals. In Al-Zn sacrificial anode, it was reported that the protection effect was still remained after the sublimation of zinc because pure aluminum with low electrode potential remains after sublimation of zinc,[13] however, in the

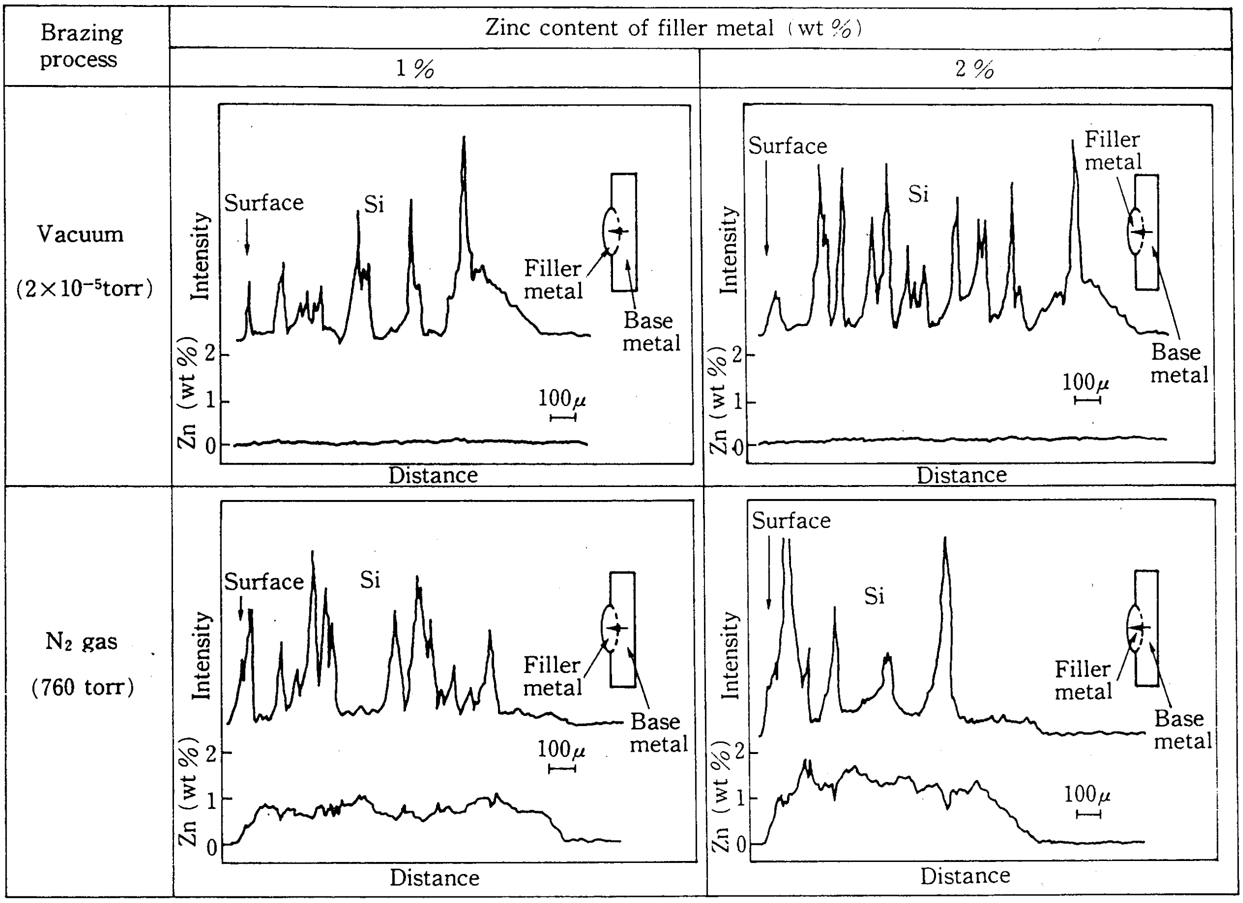

Fig. 7 EPMA line analysis of zinc and silicon at cross section of brazed specimen.

present study, zinc was added to Al-10Si filler metal, the potential was relatively high. Consequently the sacrificial anodic effect disappeared after vaporization of zinc. (Fig. 8).

Figure 9 is the results of corrosion tests on tin bearing filler metals. Brazing was carried out in a vacuum. The effect of tin addition was cleary observed. The pit depths

Table 2 Results of EPMA analysis of zinc concentration in filler metals after brazing.

Brazing process		Zinc concentration (wt%) Al-Si-Mg-1Zn	Al-Si-Mg-2Zn
N_2 gas (760 torr)	Max.	1.0	1.8
	(Mean)	(0.8)	(1.4)
Vacuum (2×10^{-5} torr)	Max.	0.1	0.1
	(Mean)	(0.04)	(0.07)

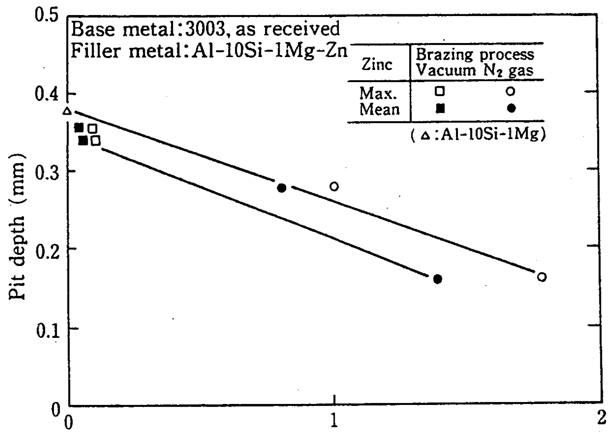

Fig. 8 Relations between residual zinc concentration in filler metals after brazing and pit depth of 3003 base metal.

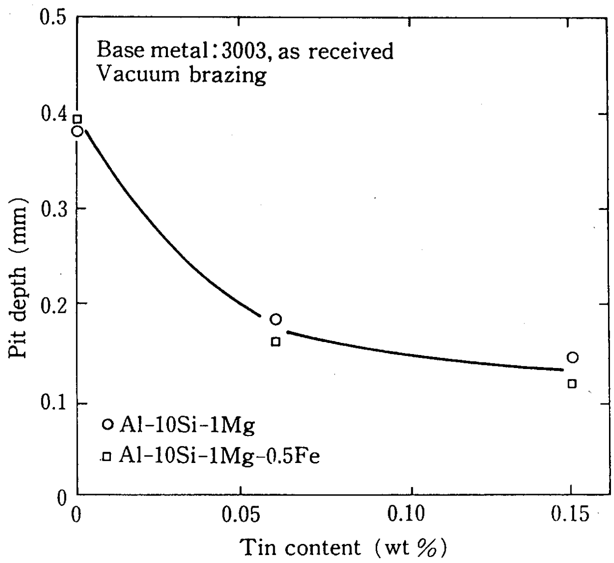

Fig. 9 Effect of tin addition in filler metals on pit depth of 3003 base metals.

were slightly small in iron bearing filler metals. Commercial filler metals usually contain 0.2~0.6%Fe, the iron in filler metals of sacrificial anode type would not enhance the pitting of base metals.

5. Conclusions

The effect of zinc or tin addition to Al-10Si filler metals on the protection ability of pitting corrosion of 3003 base metals was studied. The obtained results are summarized as follows.

(1) The addition of zinc or tin decreased the electrode potential of Al-10Si filler metals, and showed large anodic current by applying the small anodic potential. These filler metals became anode when combined with 3003 alloy.

(2) These filler metals were found to be effective for protection of pitting corrosion of 3003 base metals, because of their sacrificial anodic effect. The pit depth of brazed 3003 base metals decreased with increasing the content of additional elements (~ 2%Zn, ~ 0.15%Sn).

(3) Zinc bearing filler metals should be brazed in N_2 gas at atmospheric pressure, because the zinc almost completely vaporized during vacuum brazing and no improvement was obtained in vacuum brazed specimens.

(4) The iron in filler metals showed no acceleration on pit depth of base metals.

Acknowledgement

The studies were conducted with the financial support of the Grant-in-Aid for Scientific Research (B), The Ministry of Education, Science and Culture, in 1983 and 1984. The authors would greatly appreciate this financial support.

References

1) H. Kawase, M. Yamaguchi and K. Ishikawa: J. Japan Inst. Light Metals, Vol. 29 (1979), No. 11, 505 (in Japanese).
2) T. Ishimaru and T. Miura: *ibid.*, Vol. 33 (1983), No. 3, 157 (in Japanese).
3) K. Yamada: Altopia, Vol. 9 (1979), No. 4, 49 (in Japanese).
4) K. Yamada: J. Light Metal Weld. & Construction, Vol. 17 (1979), No. 11, 491 (in Japanese).
5) H. Kawase and K. Ishikawa: *ibid.*, Vol. 21 (1983), No. 1, 13 (in Japanese).
6) T. Fukui, H. Irie, S. Kimura and Z. Tanabe: J. Japan Inst. Light Metals, Vol. 29 (1979), No. 5, 410 (in Japanese).
7) E. H. Dix, Jr., R. H. Brown and W. W. Binger: Metals Handbook (8th ed.), Vol. 1 (1972), ASM, Ohio, 917.
8) J. T. Reding and J. J. Newport: Materials Protection, (1966), No. 12, 15.
9) N. Sudo, T. Abe, K. Aizawa and M. Hasegawa: J. Japan Inst. Light Metals, Vol. 20 (1970), No. 3, 129 (in Japanese).
10) Y. Hisamatsu and T. Kodama: *ibid.*, Vol. 19 (1969), No. 8, 356 (in Japanese).
11) T. Takemoto and I. Okamoto: Trans. JWRI, Vol. 15 (1986), No. 2, 273.
12) Y. Hisamatsu and T. Kodama: J. Japan Inst. Light Metals, Vol. 19 (1969), No. 8, 352 (in Japanese).
13) Y. Hattori and A. Sakamoto: Weld. J., Vol. 61 (1982) No. 10, 339-s.