Stress Corrosion Cracking Mechanism of Cu-4%Ti Alloy[†]

Tadashi TAKEMOTO*, Shigenori HORI** and Ikuo OKAMOTO***

Abstract

Stress corrosion cracking (SCC) mechanism of an aged Cu-4%Ti alloy has been investigated with respect to the effect of modulated structure on dissolution reactions. SCC tests were carried out in 6N aqueous ammonia containing 10.2/ℓ copper under the applied tensile load of 80% of 0.2% proof stress. The depth of cracks and the number of transgranular cracks were measured after various testing times. Both inter- and transgranular cracks were formed during SCC test, but the depth of intergranular cracks was larger than that of transgranular ones irrespective of aging condition and testing time.

The mechanism of the influence of aging at 450°C on transgranular cracking susceptibility has been also investigated in relations to corrosion reaction and modulated structure. The increase of concentration difference of zone complex within the modulated structure was found to be responsible to the increase of the number of transgranular cracks in definite periods of modulated structure. The increase of the ratio of cathode area to anode area increased the depth of cracks. The increase of cathode area enhanced the dissolution reaction that was considered to be a main SCC process of this system since the dissolution reaction of the alloy proceeded under concentration polarization and was controlled by cathodic reaction.

KEY WORDS: (Stress Corrosion) (Copper Alloys) (Cracking) (Heat Treatment) (Mechanisms)

1. Introduction

Various copper alloys have been known to be susceptible to stress corrosion cracking (SCC). Above all, many studies have been carried out on α -brass in relations to the pH of corrosive solution,[1]~[4] deformation substructure[5],[6] and dezincification.[7] The inhomogenious concentration distribution of solute atoms such as segregration at grain boundaries and stacking faults was also attracted attention.[8] Our earlier work on α -brass[9] pointed out that the local segregation of solute atom concentration was important for SCC. Then the authors found that aged Cu-Ti alloy, in which the periodical fluctuation of solute atom concentration (modulated structure) exists, was susceptible to SCC[9]~[11]. The time to failure of Cu-4%Ti alloy was mainly controlled by propagation of intergranular cracks, however, many fine transgranular cracks were also found in aged specimens.

In previous works,[10],[11] SCC susceptibility was compared by the time to failure which was determined by the propagation of intergranular cracks. Therefore, little discussions were attempt for the transgranular cracks. This article is scheduled to investigate the effect of aging on the transgranular cracking susceptibility and then to clear the SCC mechanism of Cu—Ti alloy. For the first time, the progress of SCC was examined by measuring the depth and the number of intergranular and transgranular cracks after various stress corrosion testing times.

The purpose of this article is to clear the cause of transgranular cracks and the effect of modulated structure on the corrosive reaction and SCC susceptibility.

2. Experimental Procedures

The laboratory cast Cu—4%Ti alloy was made from high purity copper and sponge titanium. The cast ingot (40 × 40 × 150, mm) was then forged, hot rolled, and cold rolled to 0.8 mm thickness. The chemical composition of the alloy was as follows: 3.7%Ti, 0.006%Fe, 0.002%Pb and balanced Cu. The alloy sheet was machined to a size of 15 mm gage length and 4 mm width as shown in **Fig. 1**, solution treated at 900 °C in vacuum and aged at 450 °C up to 48 hr.

SCC tests were carried out by applying the constant load on specimen. The applied stress was 80% of the 0.2% proof stress of each specimen. Illustration of the test apparatus is shown in **Fig.2**. Corrosive solution for SCC test was 6N aqueous ammonia containing 10.2g/ℓ copper added as $CuSO_4 \cdot 5H_2O$. The solution was prepared from special reagent grade chemicals and doubly distilled water. Prior to the SCC test, specimens were sanded by emery paper followed by electropolishing. Test
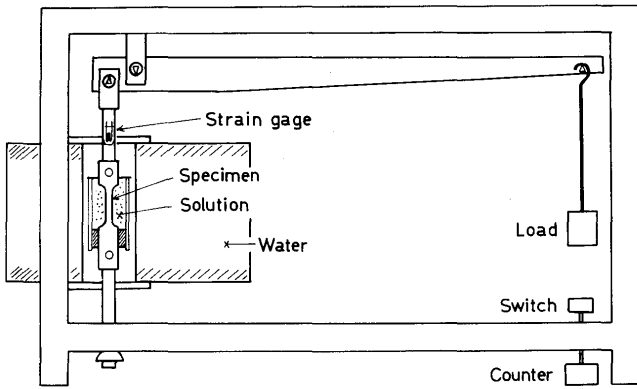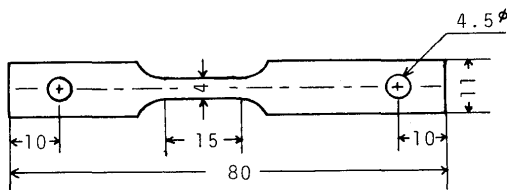
Fig. 1 Schematic illustration of SCC test apparatus

Fig. 2 Shape and size of SCC test specimen

temperature was maintained at 25 ~ 28 ℃.

SCC tests were stopped after certain periods, then the depth and the number of cracks were measured at longitudinal section by optical micrographs. Corrosive solutions after the tests were analyzed by atomic absorption analysis. Corrosion products on specimen surface were analyzed by chemical analysis and electron diffraction.

3. Results

3.1 Progress of stress corrosion

The time to failure of Cu–4%Ti alloy was strongly dependent on aging time at 450℃ and the minimum time to failure was obtained in the specimen aged for 54 min[10]. **Figure 3** shows the changes of the depth of stress corrosin cracks and the number of transgranular cracks during stress corrosion tests for the specimen aged at 450°C for 54 min. After testing for 11 min, a few transgranular cracks were found per 1mm longituditional section, and the depth of intergranular cracks was about 10 μ. The number of transgranular cracks increased after 17 min, and remakably increased after 25 min, but it scarsely changed until failure. Both inter- and transgranular cracks grew with the testing time, but intergranular cracks were always deeper than transgranular ones. And the difference of crack depth between intergranular cracks and transgranular ones becomes larger with testing time, as a result, the time to failure is mainly controlled by the propagation of intergranular cracks[10]. **Figure 4** shows the cracks in 54 min aged

Fig. 3 Changes of the depth of inter- and transgranular cracks and the number of transgranular cracks during SCC tests of Cu-4%Ti alloy aged at 450°C for 54 min

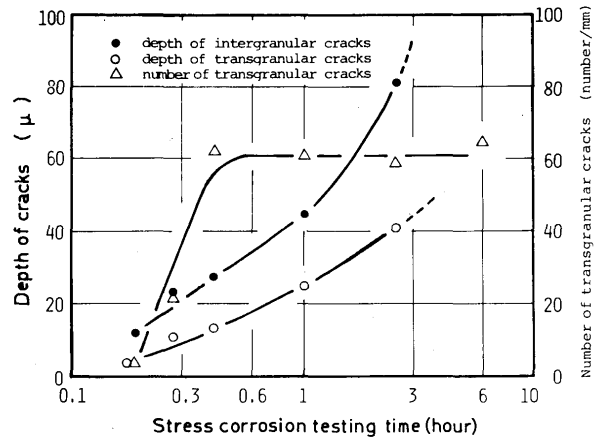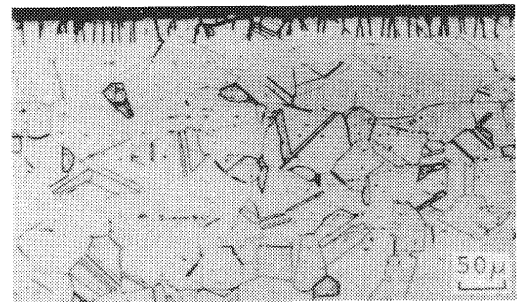Fig. 4 Crosssectional stress corrosion cracks after 1 hr SCC test of Cu-4%Ti alloy aged at 450°C for 54 min

Fig. 5 Changes of the depth of inter- and transgranular cracks and the number of transgranular crack during SCC tests of Cu-4%Ti alloy aged at 450°C for 12 min

specimens after 1 hr SCC test where the number of cracks reached a constant value.

The growth of cracks during stress corrosion tests of the specimens aged for 12 min at 450°C is shown in **Fig. 5.** Similar process of growth observed in 54 min aging is shown. But the time that the number of transgranular cracks reached a plateau was prolonged to 40 min and the number of transgranular cracks was lower than that of the specimens aged for 54 min.

3.2 Effect of aging

In the 12 min aged and 54 min aged specimens, the number of transgranular cracks reached a plateau after tested for 1 hr. To investigate the effect of aging on the depth and the number of cracks, specimens were aged for various periods at 450°C and then stress corrosion tested for 1 hr. **Figure 6** shows the effect of aging on the stress crrosion susceptibility. The depth of cracks rised with aging time and reached a maximum depth when aged for about 1 hr. Further aging reduced the depth of cracks. Changes of the crack depth with aging time are similar irrespective to cracking path such as intergranular or transgranular. The results indicate that aging for about 1 hr caused the maximum crack depth, i.e., the highest SCC susceptibility. This result coincides well with the previous work[10] that investigated the effect of aging on the time to failure.

As already mentioned in 3.1., intergranular cracks were always deeper than transgranular ones at any aging times. Consequently, the fracture proceeded mainly intergranularly. **Figure 7** represents the intergranular failure of 54 min and 48 hr aged specimens. Typical configuration of intergranular fracture is shown, but the morphology of fracture is somewhat intricated near the grain boundary triple points according to the cellular precipitation. Cellular precipitates increased with the aging time,[12] therefore,

the area of typical intergranular cracking was decreased by aging for 48 hr (Fig. 7 (b)). Figure 7 (C) shows the slip lines or deformation twins on intergranular fractographs showing the evidence of plastic flow during SCC process. At the interior of specimen or fracture surface in air condition, dimple pattern which indicates the ductile fracture is shown (Fig. 7 (d)), reprepenting that the alloy is ductile in nature.

The change of the number of transgranular cracks with aging time is also shown in Fig. 6. Transgranular cracks appeared in the specimens aged for more than 2 min after 1 hr SCC test. The number of cracks
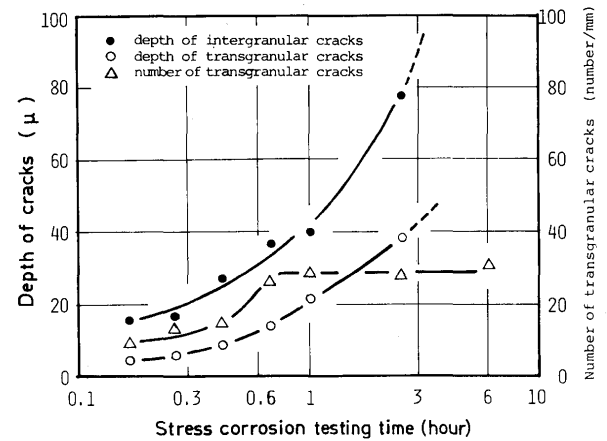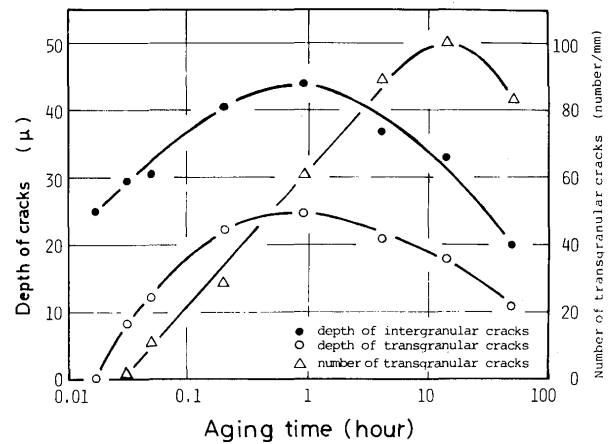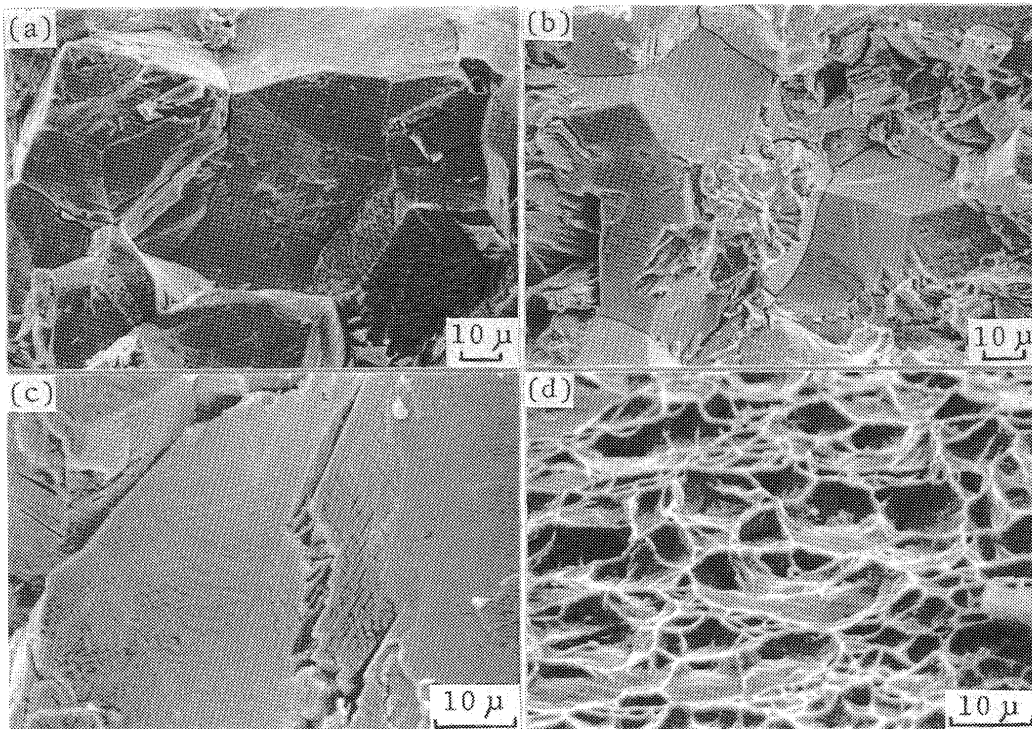

Fig. 6 Variations in the depth of inter— and transgranular cracks and the number of transgranular cracks after SCC tests for 1 hr on Cu–4%Ti alloy aged at 450 °C for various times

Fig. 7 Fractographs of Cu-4%Ti alloy by SCC, (a)(c)(d) aged at 450 °C for 54 min, (b) aged at 450 °C for 48 hr, (c) deformation pattern on intergranular cracks, (d) dimple pattern at interior of specimen (final fractured area)
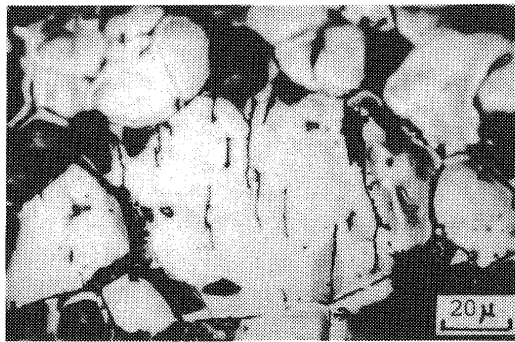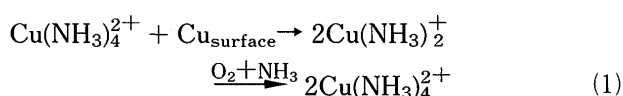
Fig. 8 Transgranular cracks at the surface of specimen aged at 450 °C for 1 min, after SCC test for 4 hr

Table 1 Increase of copper and titanium in 6N aqueous ammonia containing 10,2g/ ℓ of copper after stress corrosion tests

Heat treatment	$\sigma_A/\sigma_{0.2}$	Increase in Cu content (g/ℓ)	Ti content (mg/ℓ)
As-quenched	0.8	9.40	1
	1.0	6.30	1
Quenched and aged at 450°C for 54 min	0.3	5.00	1
	0.6	5.50	1
	0.8	4.00	1
	0.9	5.50	1
Quenched and aged at 450°C for 170 hr	0.4	6.00	1
	0.6	6.35	1
	1.0	5.85	1
	1.15	5.35	1
	1.3	3.75	1

σ_A : applied stress
$\sigma_{0.2}$: 0.2% proof stress of specimen

Table 2 Chemical compositions of copper and titanium in corrosion products of unstressed specimens immersed in 6N aqueous ammonia containing 10.2g/ ℓ of copper

Heat treatment	Cu (%)	Ti (%)
As quenched	30.9	27.9
Quenched and aged at 450°C for 54 min	37.0	18.9

remarkably increased with aging and reached a maximum at aging for 16 hr, prolonged aging reduced the number of cracks. After stress corrosion for 1 hr, transgrnular cracks were not found in the specimens aged for 1 min, however, further stress corrosion test produced fine transgranular cracks. **Figure 8** shows transgranular cracks in the specimen aged for 1 min after testing for 4 hr.

3.3 Corrosion reaction

To clarify the corrosion reacton of this alloy, copper and titanium in corrosive solutions were analyzed after SCC tests for the specimens of various aging conditions. The results are shown in **Table 1**. Copper is dissolved into the solution for all aging conditions however, titannium is found only as a trace element. Therefore, titanium is difficult to dissolve independent of the aging coadition such as supersaturated solid solution, modulated structure, intermediate phase and equilibrium phase.

On the other hand, corrosion products attached to the specimen surface contained much titanium as shown in **Table 2**. From the above mentioned results, it is clear that the corrosion of the alloy is proceeded mainly by dissolution of copper. The corrosion reaction of Cu-4%Ti alloy in the solution containing cupric complex ions is supposed as follows, which is originally proposed by Pugh et al.[13] for Cu—Zn alloys.

$$Cu(NH_3)_4^{2+} + Cu_{surface} \rightarrow 2Cu(NH_3)_2^+$$
$$\xrightarrow{O_2+NH_3} 2Cu(NH_3)_4^{2+} \qquad (1)$$

Anodic and cathodic reactions are supposed as equations (2) and (3) respectively, presented by our another work[11] and Pugh et al.[14]
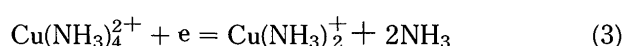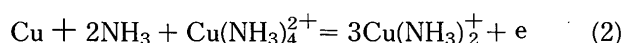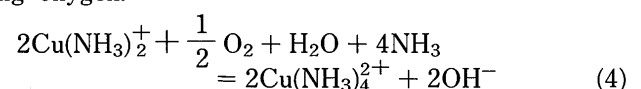
$$Cu + 2NH_3 + Cu(NH_3)_4^{2+} = 3Cu(NH_3)_2^+ + e \qquad (2)$$

$$Cu(NH_3)_4^{2+} + e = Cu(NH_3)_2^+ + 2NH_3 \qquad (3)$$

$Cu(NH_3)_2^+$ is changed into $Cu(NH_2)_4^{2+}$ by the following reaction because it is unstable in the solution containing oxygen.

$$2Cu(NH_3)_2^+ + \frac{1}{2}O_2 + H_2O + 4NH_3$$
$$= 2Cu(NH_3)_4^{2+} + 2OH^- \qquad (4)$$

Aging at 450°C causes the periodical concentration fluctuation of Ti atoms, therefore it makes a possibility that the preferential dissolution of copper may occur in the region of either lower titanium concentration martix or higher titannium concentration zone. To investigate the preferential site for copper dissolution, the weight loss of equilibrium phase Cu₃Ti in corrosive solution is investigated. Stoichiometric Cu-25at%Ti cast alloy was fully homogenized. After confirmation that the alloy phase is Cu₃Ti (h.c.p.) by diffractometer, specimens were immersed in stress corrosion test solution. The weight loss is only 0.3 mg/cm² after immersion for 3 hr. The value is extremely lower than that of 54 min aged Cu-4%Ti alloy (11.1 mg/cm²). Corrosion of overaged specimens, in which the discontinuous precipitates covered almost grains, ocurred at low titanium concentration
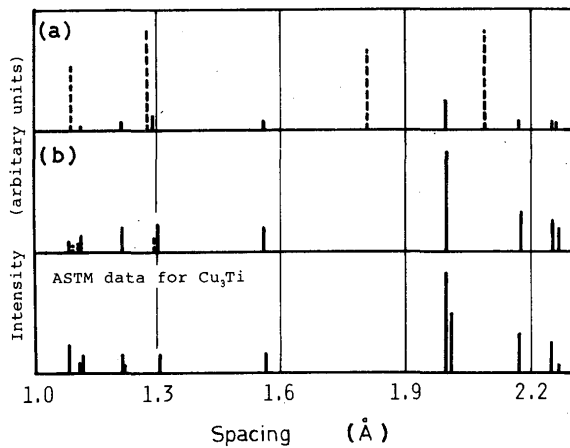
Fig. 9 X-ray diffraction diagram of Cu-4%Ti alloy aged at 450°C for 500 hr, (a) as electropolished specimen, (b) specimen immersed in 6N aqueous ammonia containing 10.2g/ℓ of copper for 24 hr, solid lines represent the diffractions of Cu_3Ti and broken ones represent those of matrix

matrix and equilibrium Cu_3Ti phase was stable in corrosive solution. **Figure 9** shows the X-ray diffraction intensity of overaged specimens. After immersion in stress corrosion test solution, the diffraction lines from matrix was scarcely observed, but the diffraction lines from Cu_3Ti was clearly observed. As mentioned above, the corrosion of this alloy proceeded by the preferential dissolution of copper, terefore it may be

believed that the dissolution of copper of aged Cu-Ti alloy is predominant in the region of low titanium concentration matrix than in high titanium concentration zone.

3.4 Corrosion products

During SCC tests, the corrosion products are formed on the specimen surface. To investigate the relations among the dissolution reactions, formation of corrosion products, and the SCC mechanism, identification of the corrosion products was carried out. The analysis of corrosion products were done only for the 54 min aged specimen. Because the dependence of the corrosion potential on the aging condition is rather slight (less than 25 mV), the kind of corrosion products might not be different with aging condition. **Figure 10** shows the scattering rings obtained by electron diffraction. Figure 10(a) is the diffraction from standard sample (Au) and corrosion products, and Fig.10 (b) is that of Au only. The results are settled in **Table 3.** The number of diffraction rings are rather scarce, however, all obtained lines coincide well the ASTM date for $Cu_4(OH)_6SO_4$, which corresponds the corrosion products formed in the Mattsson's solution (pH12.4)[11].

Table 3 Results of electron diffraction analysis of corrosion product formed by SCC test of Cu-4%Ti alloy aged at 450°C for 54 min

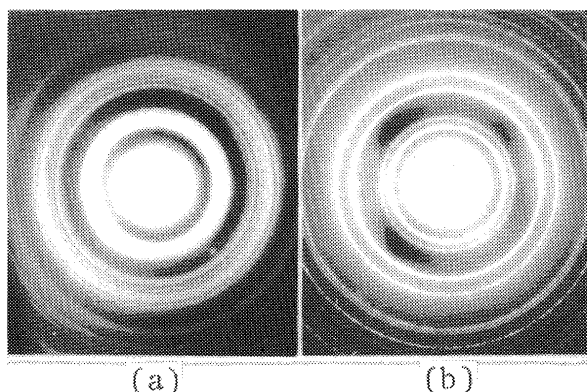| Data for Au (Calculation)		Observation		Data for $Cu_4(OH)_6SO_4$		Data for $Cu_3(SO_4)_2(OH)_4 \cdot H_2O$	
(hkl)	d Å	d Å	I	d Å	I/I₀	d Å	I/I₀
111	2.3546	2.254	S	2.29	13	2.27	50
				2 19	13	2.18	10
				2.12	3	2.15	10
200	2.039	2.100	S	2.07	10		
				2.01	7	2.00	60
		1.940	M	1.96	13		
				1.89	3	1.88	10
		1.824	M	1.82	17	1.83	30
				1.74) 6 *lines*) *1.46*	10~33	*1.76*) 4 *lines*) *1.56*	10~20
220	1.442	1.428	W	1.44	17	1.43	30
				1.40	17		
		1.356	M	1.37	10	1.38	10
				1.34	7	1.36	10
		1.296	M	1.31	20	1.30	10
				1.28	13	1.27	10
311	1.230	1.223	W	1.23	3	1.21	10
222	1.177	1.167	M	1.19	10		
		1.108	W	1.14	20	1.14	10

(a)   (b)

Fig. 10 Electron diffraction rings, (a) diffraction of both corrosion products and standard sample (Au), (b) diffraction of Au only

4. Discussions

4.1 Possible SCC mecanism for Cu-4%Ti alloy

Forty et al[15]., Bond et al.[16] and Pugh et al.[17] stated that SCC of α —brass can be proceeded by the alterndtive formation and brittle rupture of surface film Cu_2O. In this film rupture mechanism, the propagation rate of cracks depends on the formation rate of surface films (Cu_2O). On the other hand, corrosion products of Cu—4%Ti alloy were not Cu_2O but basic copper sulfate. Moreover, corrosion potential of Cu—4%Ti alloy changed only less than 10 mV during the immersion for 24 hr. Therefore, formation of basic copper sulfate dose not influence the corrosion potential. However, the formation of Cu_2O shifts the potential toward noble direction[2]. In addition to this, considering that no transgranular cracks has been found in as quenched specimens[9],it may be concluded that such alternative process as the rupture of surface film and following preferential localized corrosion at a newly produced surface cannot form the transgranular cracks of this alloy.Therefore,activated dissoulution at the crack tips may be believed a most important cracking process.

Generally, chemical reactivity of metals and alloys is high under large stress concentration or yielding. Hoar et al.[18]~[21]considered that the SCC was an electrochemical dissolution process accelarated by stress. Ohtani et al.[22] tried to explain the SCC using mechanochemical mechanism. They showed that the relation between the logarithm of the time to failure and the applied stress was represented by a curve with two points of inflections when the mechanchemical process was operated. Similar curves were obtained in our previous work[10] and the evidence of deformation was observed in fracture surface (Fig.7(C)), so the activated dissolution at the crack tips was suggested in this system. Therefore, the SCC of this alloy may

be proceeded under the mechanism similar to the mechanochmical theory.

Mechanochemical theroy is consisted on the basis of such hypothesis as (a) activated dissolution at a crack tip and (b) retardation of corrosion in the region of crack wall. Then the dissolution rate at crack tips controles the SCC susceptibility. The following discussions inquire into the retardation of corrosion in the region of crack wall, and lead the reasonableness that the SCC of the alloy is controlled by the dissolution rate at crack tips.

4.2 Retardation of corrosion at crack walls

Anodic and cathodic reaction of this system is represented by equation (2) and (3) respectively. In the interior of stress corrosion cracks, concentration of $Cu(NH_3)_4^{2+}$ is enriched by the oxidation reaction of cuprous complex ions, on the other hand, ammonia is consumed and then its concentration is reduced. As the dissolution reaction is proceeded under concentration plarization,[11] diffusion of those species in crack interior is retarded compared in bulk solution. Therefore, dissaperance of enriched $Cu(NH_3)_4^{2+}$ and supply of consumed NH_3 is required for the continuous dissolution of copper. Precipitation of $Cu_4(OH)_6SO_4$ is adequet for this requirement because the precipitation of basic copper sulfate consumes the $Cu(NH_3)_4^{2+}$ and produce NH_3. After Mattsson's designation[1], basic copper sulfate is reprepented as $Cu(SO_4)_{0.25}(OH)_{1.5}$. Possible precipitation reaction is as follows:

$$Cu(NH_3)_4^{2+} + \frac{3}{2}OH^- + \frac{1}{4}SO_4^{2-}$$
$$= Cu\ (SO_4)_{0.25}\ (OH)_{1.5} + 4NH_3 \qquad (5)$$
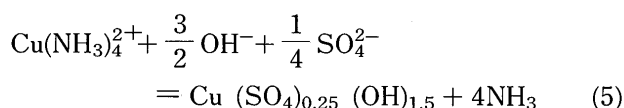
Equilibrium constant $K_{(5)}$ is

$$K_{(5)} = \frac{[Cu(SO_4)_{0.25}(OH)_{1.5}]\,[NH_3]^4}{[Cu(NH_3)_4^{2+}]\,[OH^-]^{1.5}[SO_4]^{0.25}} \qquad (6)$$

After Mattsson[1],

$$\frac{[Cu^{2+}]\,[NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 2.35 \times 10^{-13} \qquad (7)$$

$$[Cu^{2+}]\,[SO_4^{2-}]^{0.25}[OH]^{1.5} = 1.30 \times 10^{-16} \qquad (8)$$

Determining $[Cu(SO_4)_{0.25}(OH)_{1.5}] = 1$, put (7) and (8) into (6),

$$K_{(5)} = 1.81 \times 10^3$$

Of course, it may not be adequate to estimate the transient reaction in crack interior by the equilibriun constant, however, it offers an criterion that the

reaction (5) is possible to occur theoretically. The precipitation in the crack wall reduces the dissolution of copper cofining it only at the crack tips. Then, it may be concluded that the dissolution rate at crack tips is believed to be a main process which controles the SCC susceptibility of this system.

In our experiment, cupric sulfate is added to ammonical solution in which SO_4^{2-} ions exist. The calculated equilibrium constant of the precipitation reaction of $Cu(OH)_2$ in the solution of no SO_4^{2-} ions is 1.55×10^7. Therefore, the precipitation of $Cu(OH)_2$ is possible and the existence of SO_4^{2-} ion may not substantially influence the dissolution reaction.

4.3 Influence of the Modulated Structure on dissolution reaction and SCC Susceptibility

4.3.1. Number of transgranular cracks

From the discussions in 4.2, the dissolution reaction at crack tips was believed to be a main process that controlled the SCC susceptibility. Following discussions deal with the effect of modulated structure on dissolution reaction and SCC susceptibility. The modulated stucture has periodic solute concentration distribution. The titanium concentration distribution in grain matrix of Cu-4%Ti alloys aged at 450 °C has been investigated by means of X-ray diffraction[23),24)], transmission electron microscope[23)] and X-ray small angle scattering[25)~27)]. The obtained results were not always concordant in details, however, by combining together with the results of

Fig. 11 Changes of solute concentration distribution during aging at 450 °C , aging time increases from (a) to (c), (R_1 : radius of central zone, C_0 : alloying concentration, C_{matrix} : solute concentration in matrix, C_1 : solute concentration in central zone)

Tsujimoto[27)] and Saji et al[23)]., the change of titanium concentration profile is supposed to be the angular distribution as shown in **Fig. 11**. At relatively early stage of aging, tiatanium rich particle (titanium concentration: C_1) with rather clear interface is precipitated, and surrounding area is slightly less in titanuim than matrix. The structure is so called zone complex. With the progress of aging, increase in the radius of central zone (R_1) and the amount of precipitation and the decrease in titanium concentration are proceeded. The stable phase is appeared and coalesence of particle is followed by further aging. In view of the above mentioned discussions on corrosion reaction, it would seem reasonable to suppose that the titamium rich central zones are stable in corrosive solution and the matrix with low titanium content is the site for preferential dissolution.

The period of modulated structure of Cu-4%ti alloy grew proportional to $t^{1/3}$ (t: aging time)[28),29)]. **Table 4** shows the change of the period of modulated structure in Cu-4%Ti alloy during aging at 450°C. The data from 1 to 12 min are extrapolated values. Table 4 also shows the radius of central zone (R_1) measured by Tsujimoto[27)] by means of X-ray small angle scattering. On the basis that the formation of transgranular cracks is responsible to the modulated structure, the plots of the number of transgranular cracks in 10^4 periods of modulation against the aging time is represented in **Fig. 12**. The number of cracks in 10^4 periods of modulation is similar to the probability of cracking. The probability of transgranular cracking increased with aging time but it slightly increased beyond aging time of 16 hr. Saji et al.[23)] has shown that the lattice parameter decreased continuously
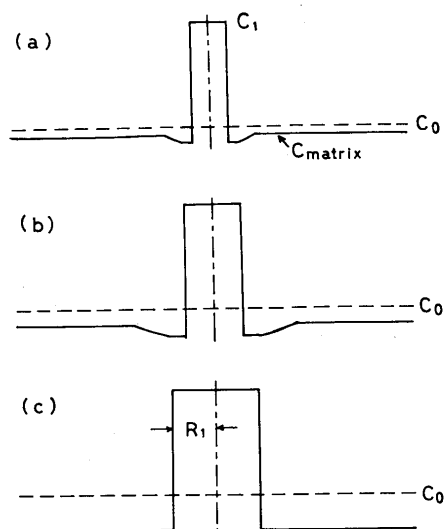
Table 4 Variation in the period of modulated structure, the radius of central zone and the number of transgranular cracks with aging time at 450°C, the values put in parentheses are extrapolated

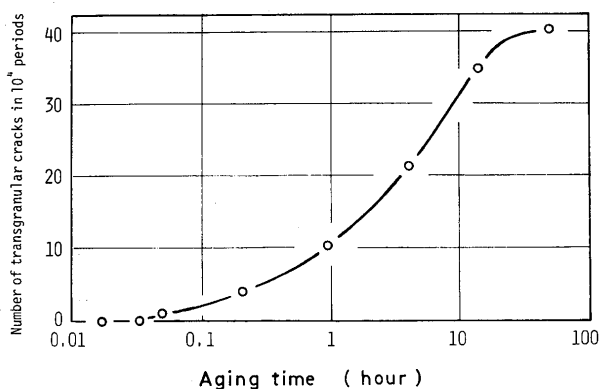| Aging time (min)	Period of[30)] modulated structure (Å)	Radius of[27)] central zone (Å)	Number of transgranular cracks (number/mm)
1	(85)	12	0
1.83	(93)	16	1.5
3	(100)	20	11
12	(125)	35	28.5
54	170	50	60.5
240	240	65	89
960	350	(80)	100
2880	490	(91)	82.5

Fig. 12 Relationship between the number of transgranular cracks in
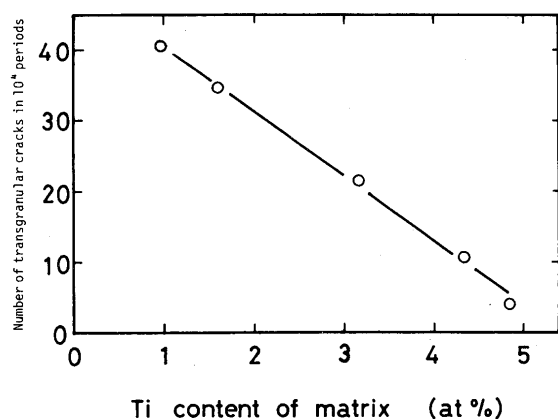10^4 periods of modulated structure and the aging time at
450°C.

Fig. 13 Relationship between the number of transgranular cracks in
10^4 periods of modulated structure and the titanium content
of matrix.

during aging at 450°C up to about 50 hr, but further
aging to several hundred hours had a slight influence
on the decreasing rate in lattice parameter. The
decrease in lattice parameter has been considered to
correspond the decrease in the titanium concentration
of matrix[23]. Consequently it is possible to obtain the
titamiun concenration of matrix from the data after
Saji et al[23]. **Figure 13** represents the relation
between the transgranular cracking probability (the
number of transgranular cracks in 10^4 periods) and
the titanium content in matrix. The plots reveals the
negative liner relationship between the transgranular
cracking probability and the titanium content of
matrix. Since the titanium concentration of central
zone has been seemed to be constant from the early
stage of aging[27], it is clear that the the difference in
titannium cotent between central zone and matrix
increased with aging time. In other words, the
concentration difference in zone complex increased
with the decrease in titanium content of matrix, and
this increase of concentration difference raised the
transgranular cracking probability. Conequently, it is

concluded that the existence of local difference in
solute atom cocentration is important for the occur-
ence of transgranular cracking.

4.3.2. Depth of transgranular cracks

In succesion, the influence of the modulated struc-
ture on the change of the depth of transgranular crack
with aging is considered. The radii of central zones
(R_1) after Tsujimoto[27] were shown in Table 4. As
mentioned above, the corrosion proceeded preferen-
tially at the marix with low titanium content and the
central zones with high titanium content were believed
to be stable in the corrosive solution. Therefore, it
would be reasonable to consider that the low titanium
content matrix act as anodes and high titanium content
central zone act as effective cathodes. As shown in
Fig.11, the matrix adjacent to the central zone is
thought to have the least titanium content, however,
since the difference of titanuim concentration in
matrix is small and the area has been unknown, the
whole matrix except the central zones are considred to
be anodes.

The crosssectional area fraction of central zone can
be calculated as follows. The number of zone in a
square with a definite side length (a) could be
represented by using the period of modulated struc-
ture (λ), $(a/\lambda)^2$. Supposing that the crosssection at
diameter for each central zone, the total crosssection-
al area of central zone with diameter R_1 existing in a
square with a side length a is $2\pi R_1^2 \cdot (a/\lambda)^2$. On the
other hand, the area of matrix can be represented as
$a^2 - 2\pi R_1^2 \cdot (a/\lambda)^2$. The ratio of cathode area to
anode area is expressed by the ratio of central zone
area to matrix area, i.e.,

$$R_{C/A} = S_C/S_A = (2\pi R_1^2/\lambda^2)/(1 - 2\pi R_1^2/\lambda^2)$$

where, $R_{C/A}$: cathode area ratio, S_C : cathode area, S_A
: anode area.
All zone complexes are , of course, not always cut at
the center (i.e., diameter) of central zone, however,
$R_{C/A}$ is efficient for relative comparison of the change
of cathode area ratio with aging time. **Table 5** shows
the caliculated values of $R_{C/A}$ using the values of λ
and R_1 represented in Table 4. $R_{C/A}$ increased with
aging time at 450°C up to 54 min, where the maximum
value of 1.19, and then decreased with the progress of
aging. **Figure 14** shows the plots of $R_{C/A}$ $(= S_C/S_A)$
at each aging time and the depth of transgranular
cracks of corresponding aging time. The depth of
transgranular cracks remarkably increased with the
increase of $R_{C/A}$ up to 0.5, that means cathode area is
just half of the anode area. Further increase in $R_{C/A}$
also increased the crack depth, consequently the

Table 5 Changes of cathode area ratio during aging at 450°C

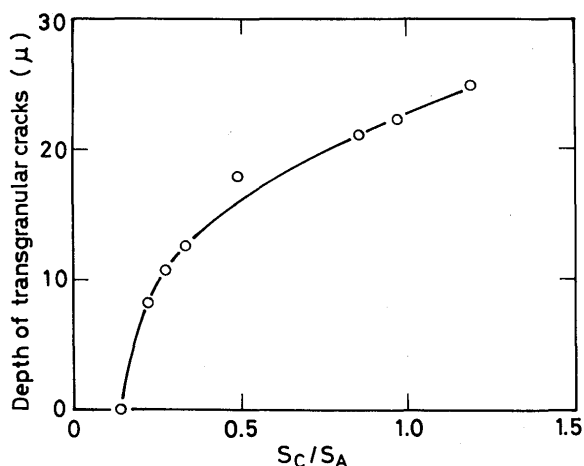| Aging time (min)	1	1.83	3	12	54	240	960	2880
Cathode area ratio	0.14	0.23	0.34	0.97	1.19	0.85	0.49	0.28

Fig. 14 Plots of cathode area ratio ($R_{C/A} = S_C/S_A$, S_C : cathode area, S_A : anode area) and the depth of transgranular cracks

transgranular cracking is easy to propagate with the increase of $R_{C/A}$.

Corrosion of this alloy proceeds by the preferencial dissolution of copper, and the matrix (low titanium concentration) is expected as anodic site and the zone (high titanium concentration) is an effective cathode. Increase in the amount of pricipitates at the early stage of aging bring the rise of cathode area and relatively decreases the anode area. On the other hand, further aging beyond 80~100 min decreases cathode area by coalescence of the zone and relatively increases anode area.

Previous work[11] revealed that the corrosion process of this system was proceeded under diffusion control i.e., concentration polarization showing the limiting current desity (i_L) in cathodic polarization curve. i_L is closely ralated to the diffusion of cupric complex ions and defines the amount of corrosion. Therefore, the corrosion rate is increased by promoting anodic dissolution through accelaration of cathodic reaction. On the contrary, decrease in cathodic area suppresses the cathodic reaction and lowers the corrosion current. **Figure 15** shows this schematically. Decrease in cathode area relatively increases anode area, and it relieves the anodic polarization. but it suppresses the cathodic reaction. This change is drawn in Fig.15 (a) by arrows. As indicated by broken lines, corrosion current is reduced to i_2 from i_1. In addition to this, anodic current density is reduced owing to increased anode area, which relieves the local
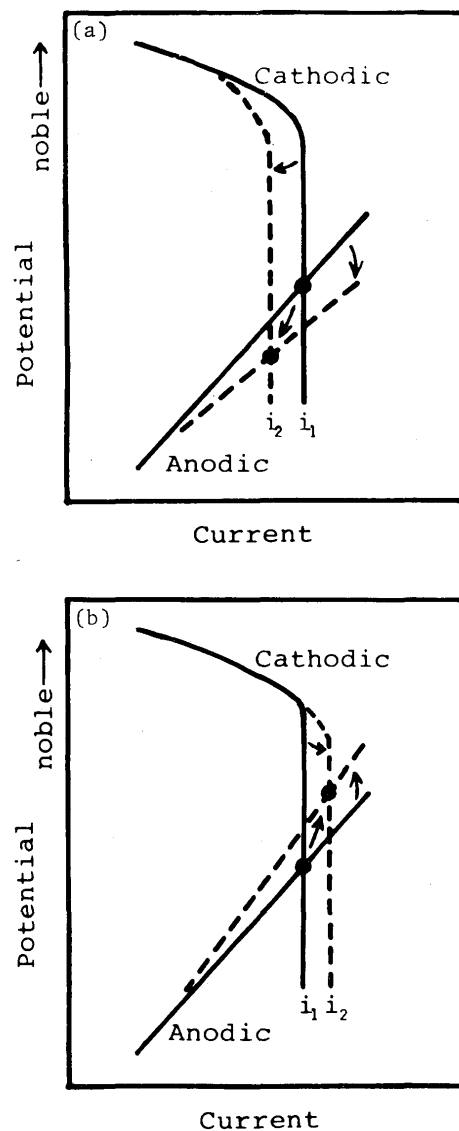

Fig. 15 Schematic illustration of the change of polarization curves with aging, (a) changes when the cathode area ratio is decreased by aging beyond 4 hr. (b) changes when the cathode area ratio is increased by aging up to to 1 hr

corrosion. The above metioned reduction of anodic current desity is considered to be a main factor for the relief of the susceptibility by more than aging for 4 hr. On the other hand, as drawn in Fig.15(b), increase in cathode area promotes cathodic reaction and corrosion current is increased to i_2 from i_1. Anodic polarization is relieved, however, the corrosion current is controlled by cathodic reaction. Local corrosion becames severe owing to the increase in anodic

current density due to the decrease in anode area. This is the cause of the rise in susceptibility when aged up to about 1 hr. Interior of cracks especially at crack tips, the diffusion of chemical species were more difficult than in bulk solution, the concentration polarization is thought to be a main rate controlling factor. Therefore the increase of cathode area ratio $(R_{C/A})$ is supposed to be important for the enhancement of dissolution rate especially at crack tips. Thus the change of SCC susceptibility with aging is well described by the mechanochmical mechanism under consideration of activated dissolution at the crack tips.

5. Conclusions

SCC tests have been carried out in 6N aqueous ammonia with $10.2g/\ell$ copper in order to investigate the SCC mechanism of an aged Cu–4%Ti alloy. The results were discussed with respect to the effect of aging at 450°C ,changes of the titanium concentration within the modulated structure and rate controlling mechanism of dissolution reaction. Obtained results are sammarized as follows.

(1) The depth of inter- and transgranular cracks increased with SCC testing time but the number of transgranular cracks reached a plateau within a testing time of 1 hr.

(2) The depth of cracks showed a maximum value at aging time for about 1 hr.

(3) The transgranular cracking probability increased with the increase of concentration difference in zone complex.

(4) Retardation of dissolution reaction at crack walls could be well interpretable by precipitation of basic copper sulfate and the mechanochemical dissolution process was believed to be a main rate controlling mechanism of the system.

(5) Corrosion proceeded preferentially at the low titanium matrix by selective dissolution of copper and high titanium central zones were considered to be stable in corrosive solution and to act as effective cathodes.

(6) Changes of the depth of cracks with aging time at 450°C was well explainable by change of the ratio of cathode area to anode area. The increase of crack depth by aging up to 1 hr was corresponded to the increase in cathode area and the decrease in crack depth by aging beyond 1 hr was corresponded to the decrease in cathode area. The plots of the ratio of cathode area to anode area and the depth of cracks showed a positive relationship.

(7) Since the dissolution reaction of the alloy proceeded under concentration polarization and was controlled by cathodic reaction, the increase of cathode area enhanced the dissolution at crack tips that was considered to be a main SCC process of this system.

References

1) E. Mattsson : Electronchimica Acta,3(1961), 279.
2) T. P. Hoar and C. J. L. Booker: Corros. Sci., 5(1965), 821.
3) H. E. Johnson and J. Leja: Corrosion, 22(1966),178.
4) G. M. Sparkes and J. C. Scully: Corros. Sci., 14(1974), 619.
5) A. Howie and P. R. Swann: Phil. Mag., 6(1961), 1215.
6) S. Hori and T. Takemoto: J. Japan Inst. Metals, 37(1973), 257.
7) A. J. Forty: *Physical Metallurgy of Stress Corrosion Fracture*, Ed. by T. N. Rhodin, Inter Sci., (1959), 99.
8) P. R. Swann and J. Nutting: J. Inst. Metals, 88(1959–60), 478.
9) S. Hori and T. Takemoto: Trans. JIM, 17(1976), 191.
10) T. Takemoto and S. Hori: J. Japan Inst. Metals, 38(1974), 743.
11) T. Takemoto and S. Hori: Corros. Sci., 18(1978), 323.
12) S. Ikeno, S. Saji and S. Hori: J. Japan Inst. Metals, 38(1974), 1186.
13) E.N. Pugh, J.V. Craig and A.J.Sedriks: *Proceedings of Conf. on Fundamental Aspects of Stress Corrosion Cracking*, Ohio State Univ., (1967), 118.
14) E.N.pugh and J.A.S. Green: Met. Trans., 2(1971), 3129.
15) A.J.Forty and P. Humble: Phil. Mag., 8(1963), 247., *Environment Sensitive Mechanical Behaviour*, ed. by A.R.C. Westwood et al., New York, (1966), 403.
16) A.J.McEvily, Jr., and A.P. Bond: J. Electrochem. Soc., 112(1963), 131.
17) E.N.Pugh and A.R.C. Westwood: Phil. Mag., 13(1966), 167.
18) J.G. Hines and T.P. Hoar: J. Iron Steel Inst., 184(1956), 166.
19) T.P. Hoar: Corrosion, 19(1963), 33t.
20) T.P. Hoar and J.C. Scully: J. Electrochem. Soc., 111(1964), 348.
21) T.P. Hoar and J.M. West: Proc. Roy. Soc., 268(1962), 304.
22) N. Ohtani and Y. Hayashi: J. Japan Inst. Metals, 38(1974), 1103.
23) S. Saji, S. Ikeno and S. Hori: J. Japan Inst. Metals., 42(1978), 63.
24) T. Miyazaki, E. Yajima and H. Suga: J. Japan Inst. Metals, 34(1970), 1184.
25) T. Tsujimoto, K. Saito and T. Hashimoto: J. Japan Inst Metals, 37(1973), 61, 67.
26) T. Tsujimoto, K. Saito and T. Hashimoto: Trans. JIM, 16(1975), 445.

27) T. Tsujimoto: J. Japan Inst Metals, **39**(1975), 285., Trans. JIM, **18**(1977), 393.

28) W.E. Krull, E.A.Starke, Jr. and R.W. Newman: Mater. Sci. Eng., **9**(1972), 211.

29) J.A. Cornie, A Datta and W.A. Soffa: Met. Trans., **41**(1963),727.

30) S. Ikeno: Doctorial thesis, Osaka Univ., (1978), p58.