

## The Attack of solid Copper by Liquid Tin

by

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(Received November 10, 1961)

### SYNOPSIS

A Study has been made of the kinetics of attack of solid copper by molten tin under nominally static and isothermal conditions in the temperature ranged from 252°C to 432°C. The effect of grits detached from solid-liquid interfacial alloy layer on the attacking-rate, was especially remarkable. We call this effect as "*Colonies effect*." The attack process is shown to conform a general expression of the form ;

$$\frac{l_t}{l_x} = \frac{1 - e^{[\log(1-x)]\sqrt{t/t_x}}}{x}$$

where  $l_t$  = attacking depth at time  $t$ ,  $l_x = xl_0$  = any fraction of the saturated attacking depth  $l_0$  at any given temperature, and  $t_x$  = time required to reach the value  $l_x$  for the attacking depth in solid.

### INTRODUCTION

In spite of the seriousness of the studies on the kinetics of the dissolution of solid metals in liquid metals, these studies just now became the recent subject. A. G. Ward and J. W. Taylor<sup>1)</sup> studied about the kinetics of the dissolution of solid copper in liquid lead and bismuth under nominally static and isothermal conditions, as a simplest case in which the solid metals did not form the intermetallic compounds with liquid metals, and found out the fact that the rate of solution was shown by the very same formula as in the case in which the inorganic salts dissolve into the water.

When the pure inorganic salts dissolve into the water, the rate of dissolution is, generally, determined by two processes in series, (1) the transition of individual atoms or molecules from the solid into the liquid phase and (2) diffusion of solute material from a laminar solid-liquid boundary layer toward the bulk liquid. They investigated an activation energy for the dissolution process and reached to

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A Part of this research was presented before the Meeting of the Physical Society of Japan, held in Tokyo, March 31, 1959, and the 45th Convention of Japan Institute of Metals, held in Osaka, November 5, 1959.

the conclusions that the process (2) was the rate-determining step and the slight discrepancy between the theory and experiment would be caused by the influence of natural convection accompanied inevitably with this experiment. Moreover, they extended their experiment to the case of dynamic conditions<sup>2)</sup> and they confirmed the correctness of the opinion above-mentioned, and they found out the solution rate under dynamic conditions was shown by the same formula as in the case under static conditions. The dissolution of solid alloys in molten metals is still more complex, because, in general, the solubilities of the components of the solid alloy in the liquid differ and may cause the pronounced localized attack. As a result of the precise researches following the example of the case of Au-Cu alloys immersed in liquid Bi and solid Cu-Ni alloys immersed in liquid Bi and liquid Ag, J. D. Harrison and C. Wagner<sup>3)</sup> found out the attack of solid alloys by liquid metals was controlled essentially by diffusion of more soluble component in the solid alloy.

The present paper is a report of a study of the kinetics of the dissolution of solid copper in liquid tin under nominally static and isothermal conditions, at temperatures ranged from 252°C to 432°C. This system was selected for the following reasons. The dissolutions are rather complex in the sense that the pure solid metal dissolves in the liquid with intermetallic compound formation, and that this intermetallic compounds may play special role. Furthermore, from the studies<sup>4)5)6)</sup> of hot-tining and soft soldering of copper, some information is available on the qualitative aspects in the attack of solid copper by liquid tin.

## EXPERIMENTAL

### *Procedures and Materials:*

To investigate the rate of attack of solid metal in liquid metal, chemical analysis of the liquid bath is desirable as reported by Taylor<sup>2)</sup>, but this procedure is rather time consuming and tedious to carry out. Moreover, there is naturally a definite limit in the exactness of measured values, because of the inevitability of natural convection of liquid, though it is a test under static conditions. By this reason, we searched more brief and suitable method. After many preliminary experiments, we knew that it was the most suitable method to measure directly the decreasing grade in the weight or volume of copper.

In the early stage of the experiments, we used the cylindrical rod of copper as a material (8mm  $\phi$   $\times$  40mm). Thereafter, to make the measurement simple, we covered the copper rod (12mm  $\phi$   $\times$  20mm), remaining one side of section uncovered and immersed this rod into molten tin, turning uncovered edge upward. After a definite period of time we took out the specimen from the liquid bath, eliminating the excessive tin thoroughly. Then we measured the change in the length of this cylindrical copper test piece to know the attacked volume. Of course, we should use covering material not attacked by molten tin. For this purpose, it is

desirable to use graphite<sup>7)</sup>, however, the working up is somewhat difficult. Iron shows the limited resistance to molten tin at the temperature below  $450^{\circ}\text{C}$ <sup>8)</sup>, but iron-tin compound formed at the boundary between iron and molten tin, grows with fixing in solid iron, and it is not broken<sup>5)</sup>. Crow<sup>4)</sup> also used the steel plug as the standard to recognize the original surface in the experiment concerning the attack of copper by soft solder. Moreover, it is known that the hot-tining is extremely difficult, if there is a oxide-films on the metal surface<sup>9)</sup>.

By this reason, we tried to investigate the possibility of using of mild-steel having oxide-films on its surface as the covering material above mentioned, and we recognized that the influence due to this procedure was within the experimental error by the results of our experiment.

Therefore, the large majority of experiments was performed as follows: we resolved 60g Sn in Tammann-Tube made of alumina (18mm I.D.  $\times$  100mm) and kept it at definite temperature. Then we inserted gently a test piece as shown in Fig. 1, turning uncovered section upward, and took out from a crucible after definite period, and eliminated quickly tin adhering on the uncovered surface. Then, we measured the quantity of retrogression by means of spherometer. The areas of sections of copper rod were circle having diameter of 12mm, 8.5mm, 6.9mm, and 6.0mm, and the ratios of areas were 1:1/2:1/3:1/4. Temperatures in the experiment were superheat  $20^{\circ}\text{C}$ ,  $60^{\circ}\text{C}$ ,  $100^{\circ}\text{C}$ ,  $150^{\circ}\text{C}$  and  $200^{\circ}\text{C}$  against melting point of tin. The general view of the apparatus was shown in Fig. 2, and the Tammann-Tube (3) was kept in the supporting apparatus (4) made of steel in order to maintain the temperature uniformly. Powder of graphite or charcoal was placed on the upper part of molten tin (2) to prevent the oxidation. Temperature was measured by  $1^{\circ}\text{C}$  by means of Chromel/Alumel thermometer (6). Temperature control was effected through a Hokushin E. W. Type 1036 regulator, and the maximum temperature differences through each test were  $\pm 2^{\circ}\text{C}$  at  $332^{\circ}\text{C}$  and  $\pm 4^{\circ}\text{C}$  at  $432^{\circ}\text{C}$ . The temperature within the supporting

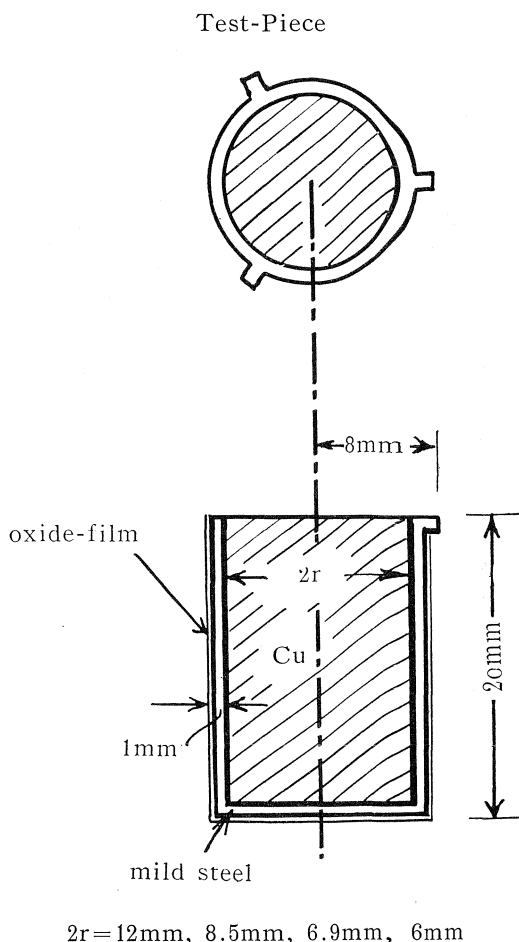
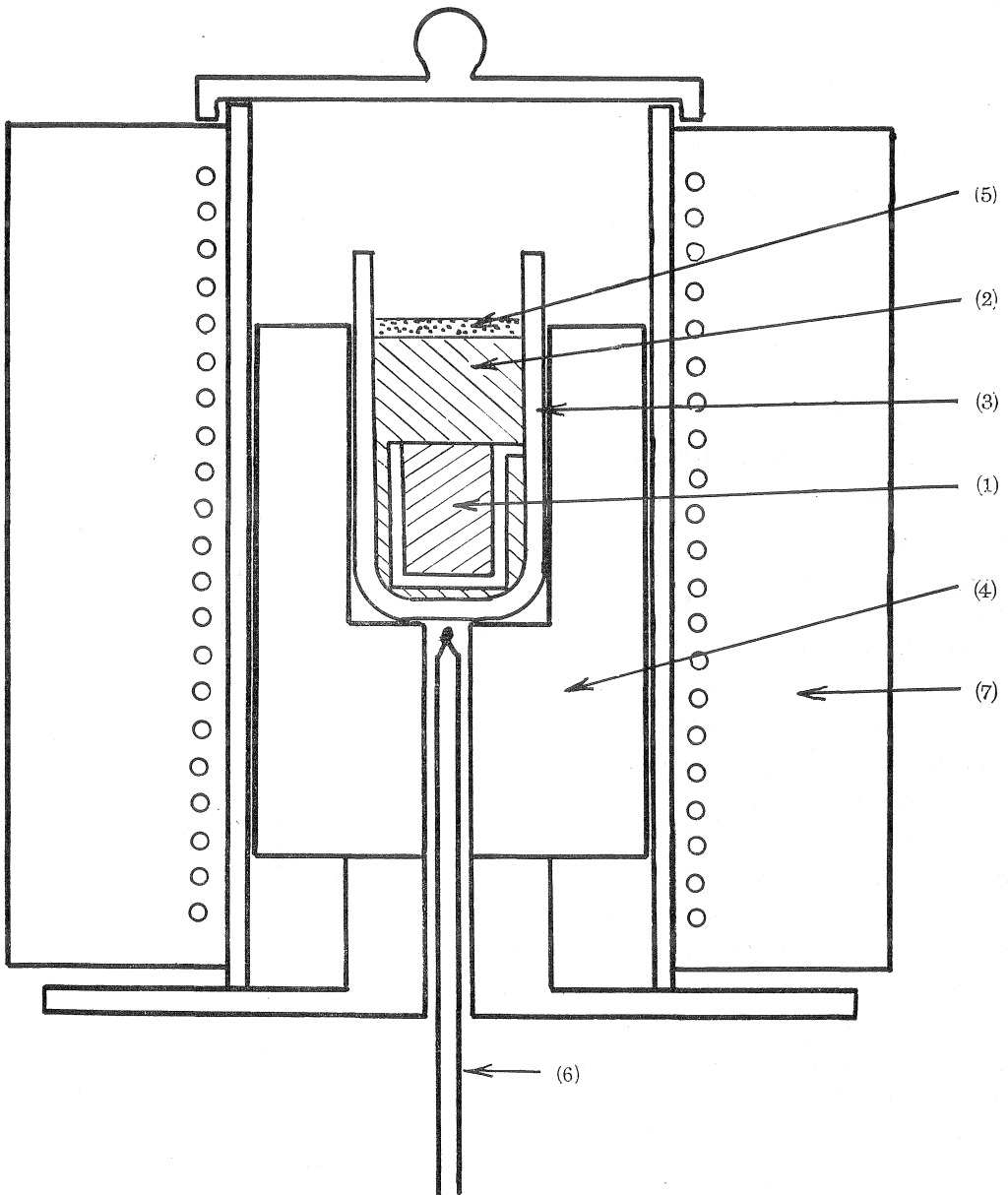


Fig. 1

## General View of Apparatus



- (1) Specimen    (2) Liq. Sn    (3) Tamman-Tube    (4) Container  
 (5) Graphite Powder    (6) Chromel-Alumel Thermo-couple    (7) Furnace

Fig. 2

apparatus (4) was completely uniform within the precision of the meter. Soaking period was ranged from 0.5hr. to 350 hrs.

Before test, any test piece was annealed for 5 hrs. at 450°C. The oxide-film was made by heating the outer side of material by means of gas-flame. The uncovered edge of copper rod was polished to 05 by emery paper directly before the experiment.

If the temperature is rather high and soaking period is not short, the result obtained by the method abovementioned has a precision within 5% at worst. When the experimental temperature was low and the soaking period was short, we checked by the method of weight measurement and chemical analysis.

In some experiments, after the process of a definite period, each crucible was cooled down at the condition of immersion of materials in the molten tin, and crucibles were broken after solidification as a whole, and the longitudinal sections were microscopically observed.

The identification of the intermetallic compounds formed between solid copper and liquid tin was done by the comparison of their diffraction pattern with that of the prepared samples of  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  and with the results described in A. S. T. M. Diffraction Data Cards by means of X-ray diffractometer.

As the material we used the electrolytic copper and commercial copper of high quality, however, the difference between the two was confined within the experimental error, and there was no recognizable difference. Therefore, a large majority of experiments was done by commercial copper and the electrolytic copper was used for checking purpose. Tin used in the experiments was virgin ingot supplied from OSAKA ASAHI METAL Co. and its chemical analysis is given in the Table I.

(Table I. Composition of the tin used.)

Composition, %					
Sn	Cu	Fe	Pb	Sb	As
99.89	0.032	0.002	0.034	0.003	0.032

### Results :

The rates of solution of solid copper in liquid tin were determined at 252°C, 292°C, 332°C, 382°C and 432°C. As a representative result, the attacked depth/time relationship obtained from Fig. 1. Type test-piece having  $2r=12\text{mm}$  are shown in Figs. 3 and 4. Fig. 4 is the enlarged short period portion in Fig. 3.

Metallographic observations showed that the intermediate compound layer existed in solid-liquid interface. The alloy layer was duplex, i.e. immediately adjacent to the copper, was a band of greyish blue alloy, separated from the tin by the band of white alloy, and their thickness was nearly constant in all specimens irrespective of the time and temperature of soaking. Occupying the portion which was previously liquid, the small isolated fragment of alloy existed here and

there, probably detached from the main layer during the solution test. Most of the fragments or grits existed near the solid-liquid interface, and the higher the immersion temperature was, the more plentiful they were.

The Attack of Cu by Liq. Sn

(Fig. 1 Type Test-Piece,  $2r=12\text{mm}$ )

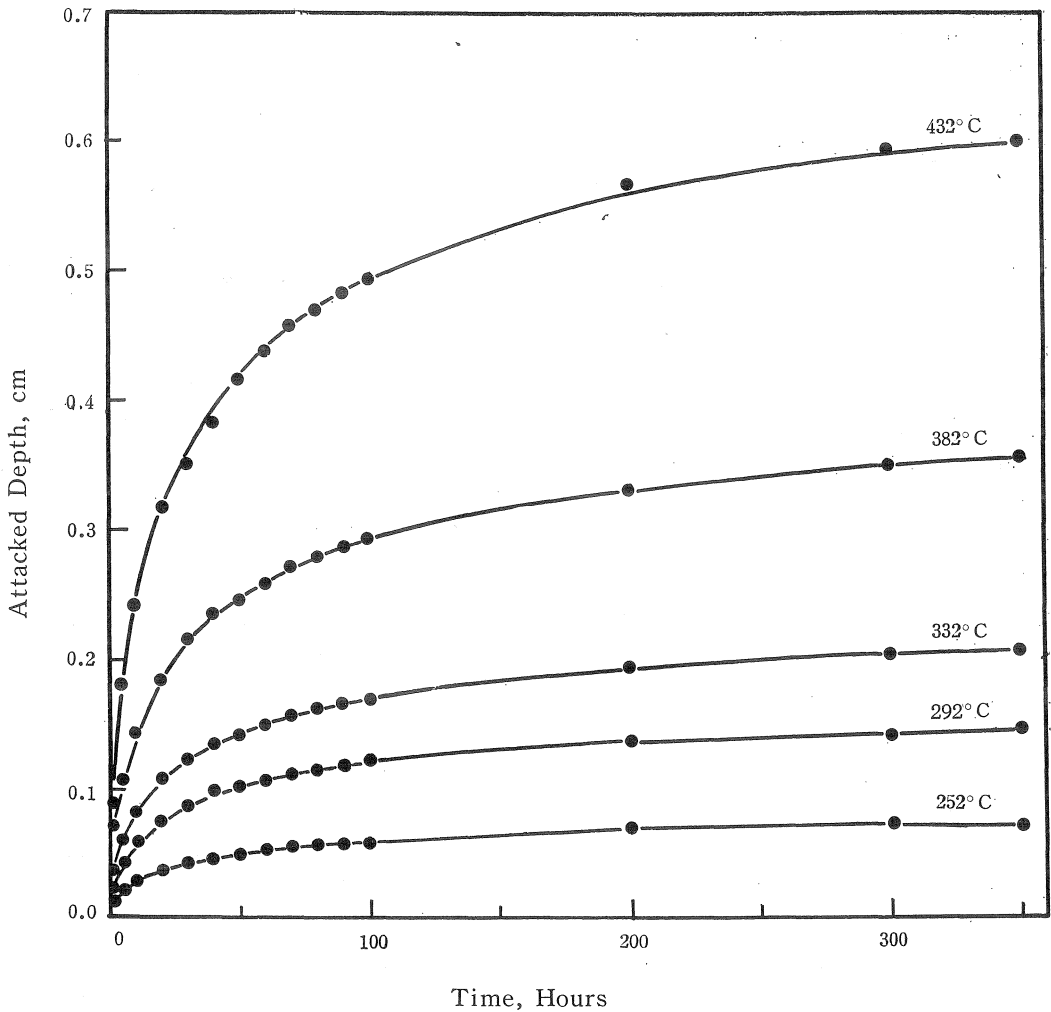


Fig. 3

The Attack of Cu by Liq. Sn  
(Fig. 1 Type Test-Piece,  $2r=12\text{mm}$ )

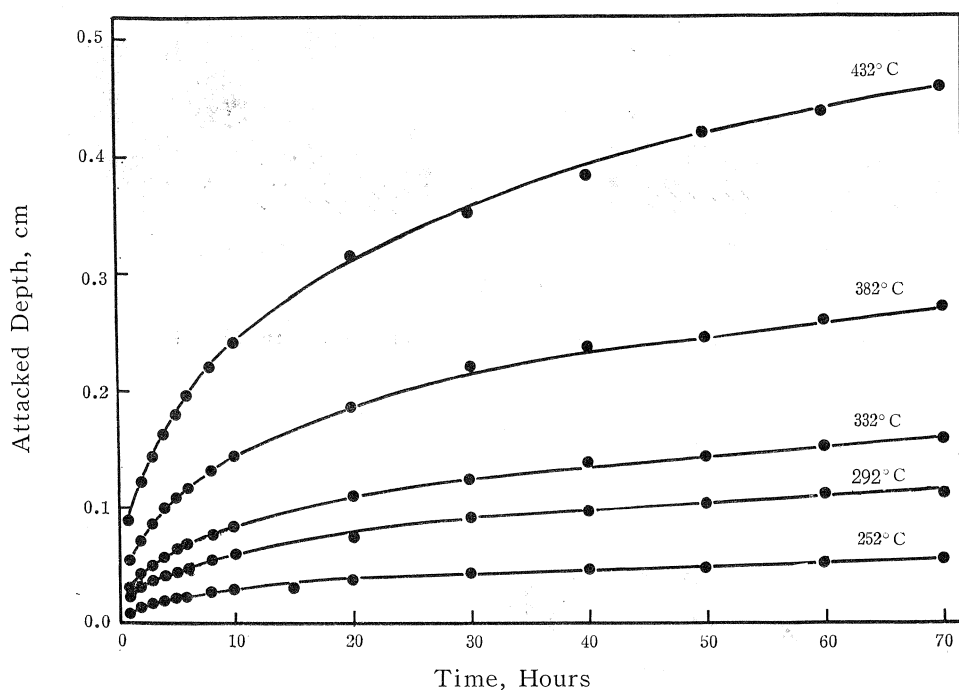
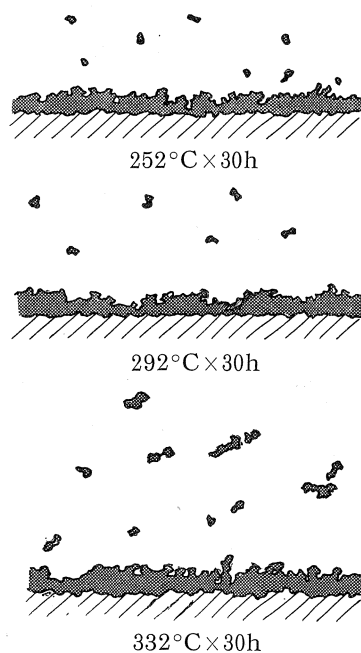


Fig. 4

Grits are generally made of white alloy. Among them existed many grits having grey-blue core. These phenomena are as has been referred to frequently in the previous investigations of tinned copper coatings and soft-soldered copper, and their schematic appearances are shown in Figs. 5 and 6. These grits were not precipitated from liquid phase at cooling period, but were intermediate compound layer breaking up and becoming detached from copper base. Moreover, we have no objection to conclude that the compound layer has not ever become liquid condition. In addition, this opinion corresponds to that of Daniels<sup>5)</sup>. According to the results of X-ray analysis, the greyish blue alloy layer is  $\epsilon$ -phase ( $\text{Cu}_3\text{Sn}$ ) and the white alloy layer is  $\eta$ -phase ( $\text{Cu}_6\text{Sn}_5$ ). These results corresponded to the results by Scratch-Hardness Test of Crow<sup>4)</sup>, and also corresponded to the conclusions by Daniels<sup>5)</sup>, Bailey and Watkins<sup>6)</sup>.

Schematic Appearances of  
"Grit-Collonies"

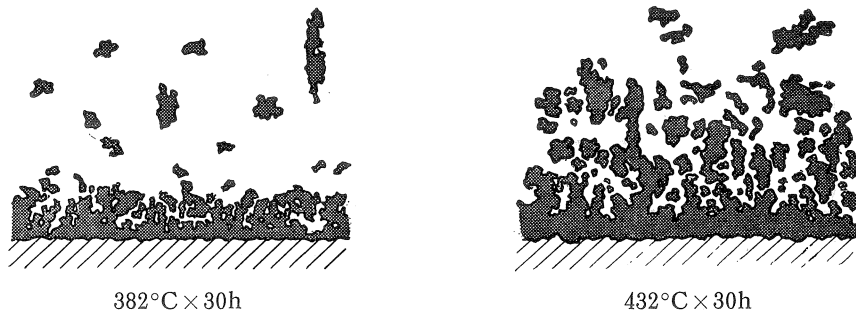


Fig. 5

Actually, the alloy layer is duplex, as shown in Fig. 6.

#### Schematic Appearances of Intermediate Compound Layer and Grits

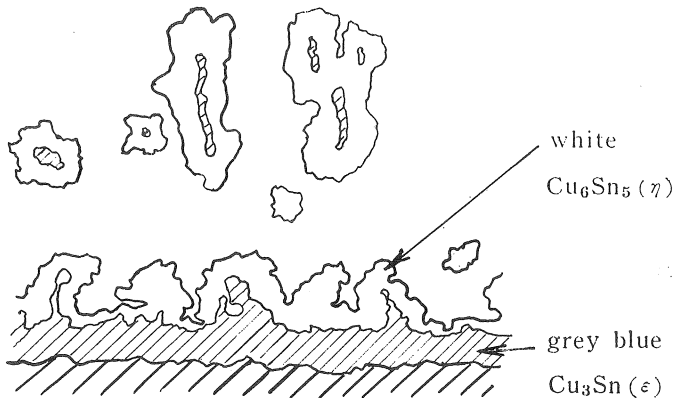


Fig. 6

### DISCUSSION OF RESULTS

A study has already been reported by J. W. Taylor et al<sup>1)</sup> of the kinetics of the solution of a solid metal in liquid metal with no intermediate compound formation under nominally static and isothermal conditions. According to their conclusion, the dissolution followed an expression of the form :

$$n_t = n_o (1 - e^{-kt}) \quad (1)$$

where  $n_t$  = solution concentration at time  $t$ ,  $n_o$  = saturation concentration at a fixed temperature,  $k = k_r (S/V)$ ,  $k_r$  = solution-rate constant for the process at a fixed temperature,  $S$  = area of solid exposed, and  $V$  = volume of solvent.



At the beginning of this study, we tried to investigate concerning the possibility to analyse the attacked depth/time relationship in terms of the expression (1), and we knew the attack of copper by liquid tin did not act on formula (1) and  $k$  became the function of time. It must be remembered that our results differ markedly from the experiments performed by Taylor et al. in the following points :

(i) The intermetallic compound layer exists on the interface.

(ii) Detached grits or "colonies" exist as shown in Figs. 5 and 6.

Though (i) makes the process of the transition of individual atoms from the solid into the liquid phase complicate, it should finally be included in formula (1). Therefore, in this case it is better to think by adding condition (ii). In short, we should take the influence of detached grits existing in the molten tin, in other words, "*colonies effect*" into consideration.

Then, formula (1) can be indicated as (2).

$$\frac{dn_t}{dt} = k(n_o - n_t) \quad (2)$$

The compound layer breaks up, and each grit grows by detaching from base metal and enters into molten tin, but some part of them resolves into liquid tin. The number of grits increases rapidly with the progress of time in the early stage, the rate of increasement decreases according to the progress of time. Now, "*colonies effect*" is expected to show the character which prevent the velocity of attacking process. Therefore, it will be rational to presume the existance of the following relationship,

$$\frac{dn_t}{dt} \propto \frac{1}{t^p} \quad p > 0 \quad (3)$$

where  $p$  = colonies effect index. Accordingly, the time dependence of  $k$  in Equation (2) may be modified by introducing the colonies effect of Equation (3);

$$\frac{dn_t}{dt} = K'(n_o - n_t) t^{-p} \quad (4)$$

where  $K'$  = proportional constant which is independent of time, but is a function of temperature. Now, the attacked depth  $l$  is propotional to solution concentration as first approximation.

$$\frac{dl_t}{dt} = K(l_o - l_t) t^{-p} \quad (5)$$

Where  $l_t$  = attacked depth at time  $t$ ,  $l_o$  = saturation attacked depth at the fixed temperature,  $K$  = apparent solution-rate constant for the process at the fixed temperature, independent of time, but it is a function of temperature, exposed solid area and volume of solvent etc..

Thus the attacked-depth/time relationship established for the attack of the solid copper by molten tin, shown in Figs. 3 and 4, were analysed in terms of expression

(5). The above Equation (5) can be integrated to the form :

$$\log \log \frac{l_0}{l_0 - l_t} = (1 - p) \log t + \log \frac{K}{2.3(1-p)} \quad (6)$$

If  $\log \log (l_0/l_0 - l_t)$  is plotted as a function of  $\log t$ , a straight line with a slope of  $(1 - p)$  should be observed. Value of  $l_0$  was obtained by calculation using value  $n_0$  against each temperature acquired from Copper-Tin phase Diagram.<sup>10)</sup> Fig. 7

Rate Equation for The Attack of Cu by Liq. Sn

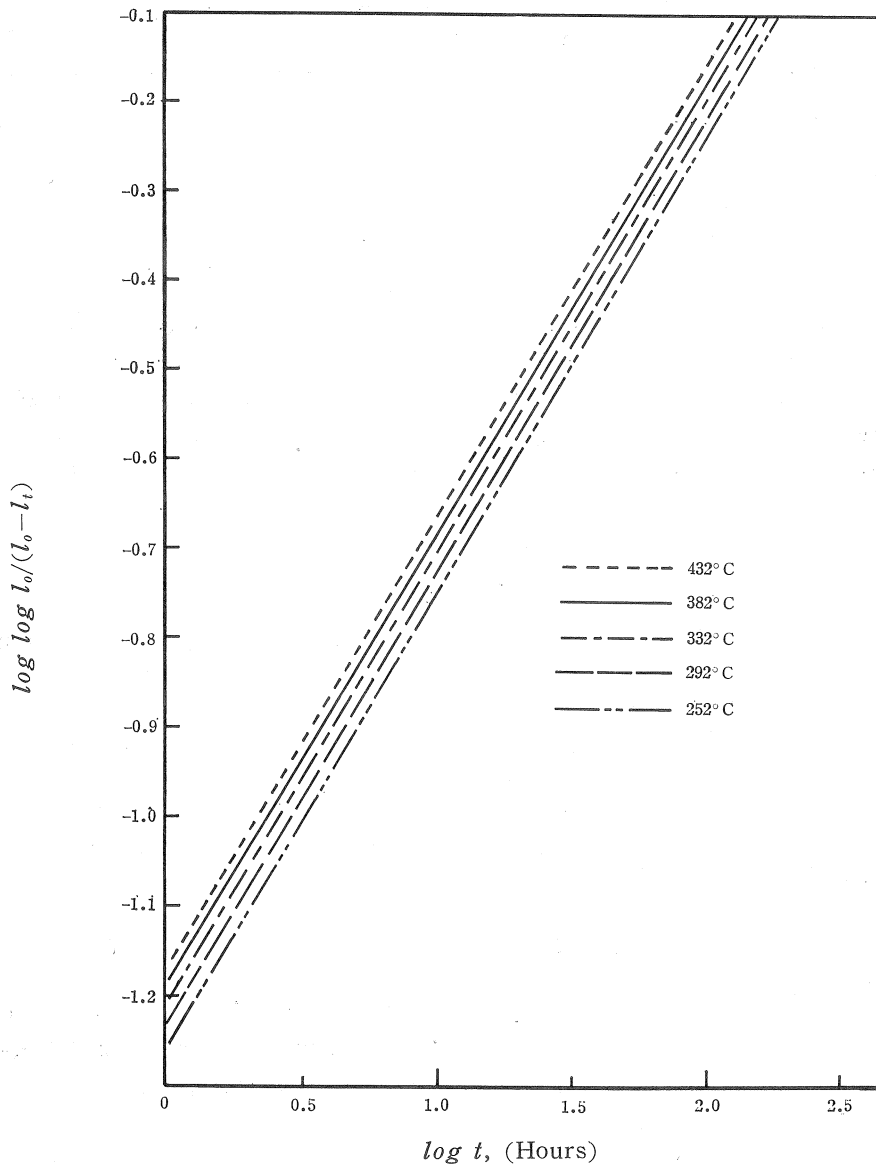


Fig. 7

shows the validity of this formulation, and slope of the line yields a value of 0.5 for  $p$ . Solution-rate constants derived from Fig. 7 in conjunction with expression (5) are presented in Table II, and plots of  $\log K$  against  $1/T$  are shown in Fig. 8, where  $T$  = absolute temperature.

Temperature Dependence of Rate Constant "K"  
for the Attack of Cu by Liq. Sn

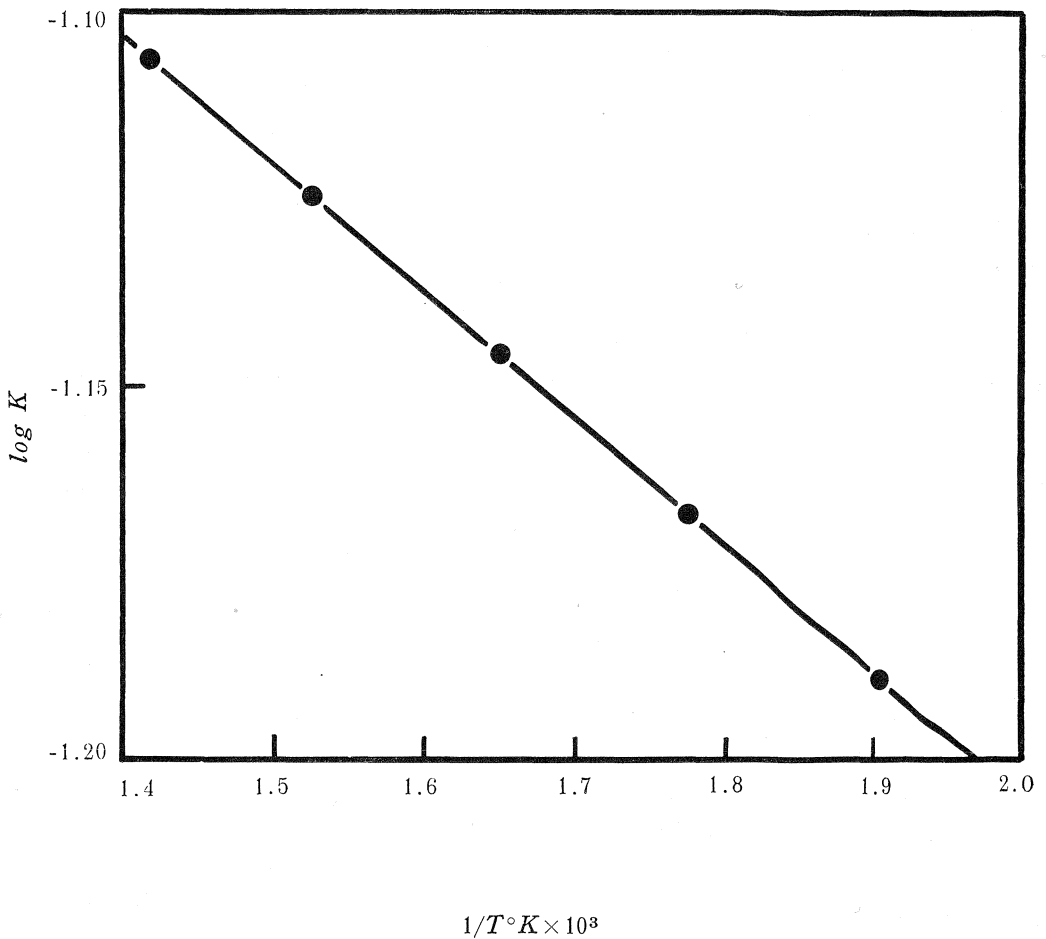


Fig. 8.

(Table II. Apparent solution-rate constants)

For  $2r = 12\text{mm}$  Fig. 1-Type specimens.

Molten tin = 60g

Temperature		$\log \log \frac{K}{2.3(1-p)}$	$p$	$K$
$^{\circ}\text{C}$	$^{\circ}\text{K}$			
432	705	-1.17	0.5	0.068
382	655	-1.19	0.5	0.065
332	605	-1.21	0.5	0.062
292	565	-1.23	0.5	0.059
252	525	-1.25	0.5	0.056

According to Fig. 8, the variation of solution-rate constant with temperature is of the form :

$$K = K_0 e^{-\frac{Q}{RT}} \quad (7)$$

where  $Q$  may be taken as the overall activation energy for the attack process, and  $R$  is the universal gas constant ; value of  $Q$ , calculated from Fig. 8, is  $8.2 \times 10^2$  cal/mol $^{\circ}\text{K}$ .

Attacked-depth/log. time relationship, calculated from the expression (5) and superimposed on the experimental points, are shown in Fig. 9. The temperature dependence of solution-rate constant was relatively small and was not too much different from the experimental error, as shown in Table II and Fig. 8, we had better to say only that the solution-rate constant had a tendency to increase with the increase of temperature. In other words, we should not put overweighted valuation on the significance of Equation (7) and the value  $Q$  derived by calculation from this equation. As Ward and Taylor<sup>2)</sup> pointed out these constants were actually dependent on the flow pattern in the system to a large extent, and the natural convection effects introduced through density changes in the liquid bath accompanying dissolution were unavoidable even in the test under nominally static conditions. In our experiment, this flow pattern of natural convection must be more complicate because of the existance of grit-collonies. Therefore, it is also difficult to acquire the temperature dependence of  $K$  from Table II and to pursue  $K$  how to change by the solid exposed area and solvent volume in the same experiments against the materials ( $2r = 8.5\text{mm}$ ,  $6.9\text{mm}$  and  $6\text{mm}$ ). But the results of experiments against the materials ( $2r = 8.5\text{mm}$ ,  $6.9\text{mm}$  and  $6\text{mm}$ ) were shown by Equation (5), moreover,  $p = 1/2$ . The relationship of  $p = 1/2$  always comes into existance. Namely, "colonies effect" is shown in the form of

$$\frac{dl_t}{dt} \propto \frac{1}{\sqrt{t}}$$

The Attack of Cu by Liq. Sn

(Fig. 1 Type Test-Piece,  $2r = 12\text{mm}$ )

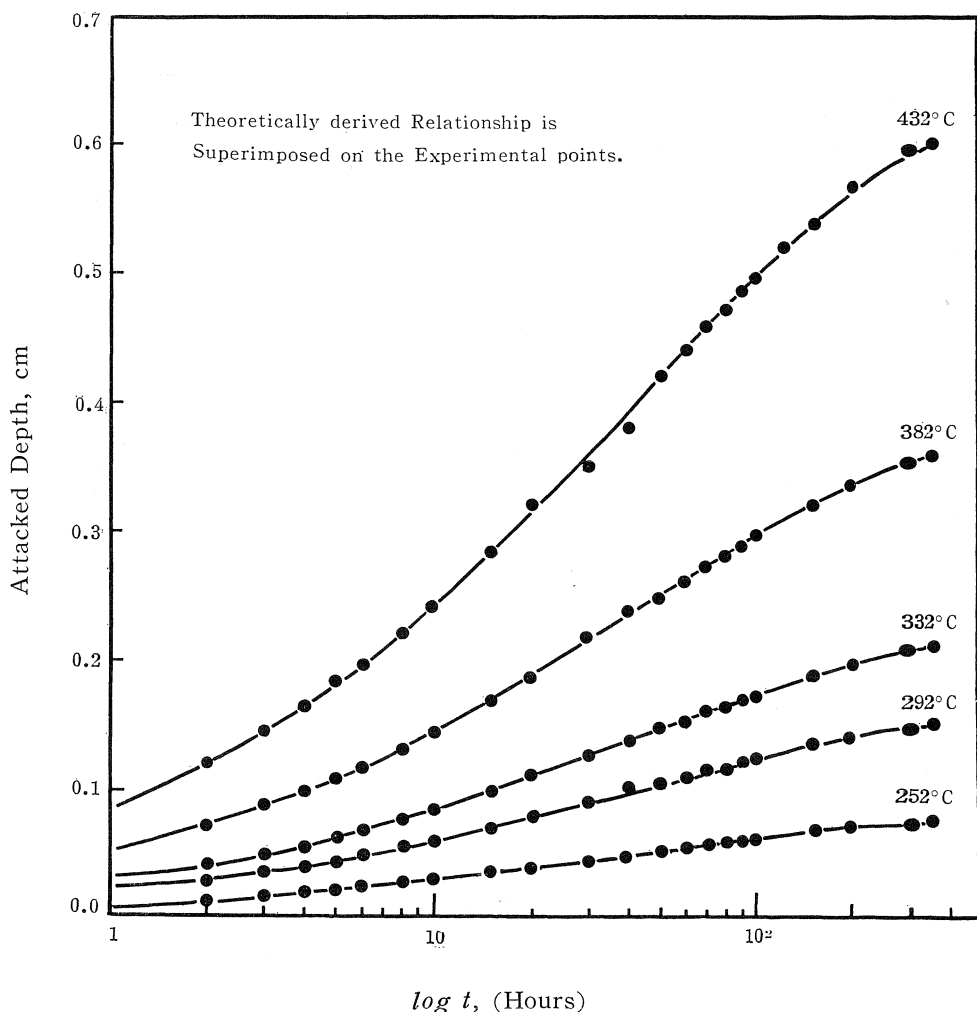


Fig. 9

It is possible to rearrange expression (5) so as to eliminate the parameters  $K$ , and obtain the reduced equation ;

$$\frac{l_t}{l_x} = \{ 1 - e^{[\log(1-x)](t/t_x)^{1-p}} \} / x, \quad p = 1/2 \quad (8)$$

where  $l_t$  = attacked depth at time  $t$ ,  $l_x = x l_o$  = any fraction of the saturation attacked depth  $l_o$  at any given temperature, and  $t_x$  = time required for the attacked depth in solid to reach the value  $l_x$ . Equation (8), in general, comes into existence regardless of exposed area of the materials and the quantity of molten tin, because

of not having  $K$  in the equation. The theoretically derived relationship for  $x=0.9$  is superimposed on the experimental points in Fig. 10 for comparison.

Reduced-attacked-depth/reduced-time relationships  
for the solid-Cu / liquid-Sn system

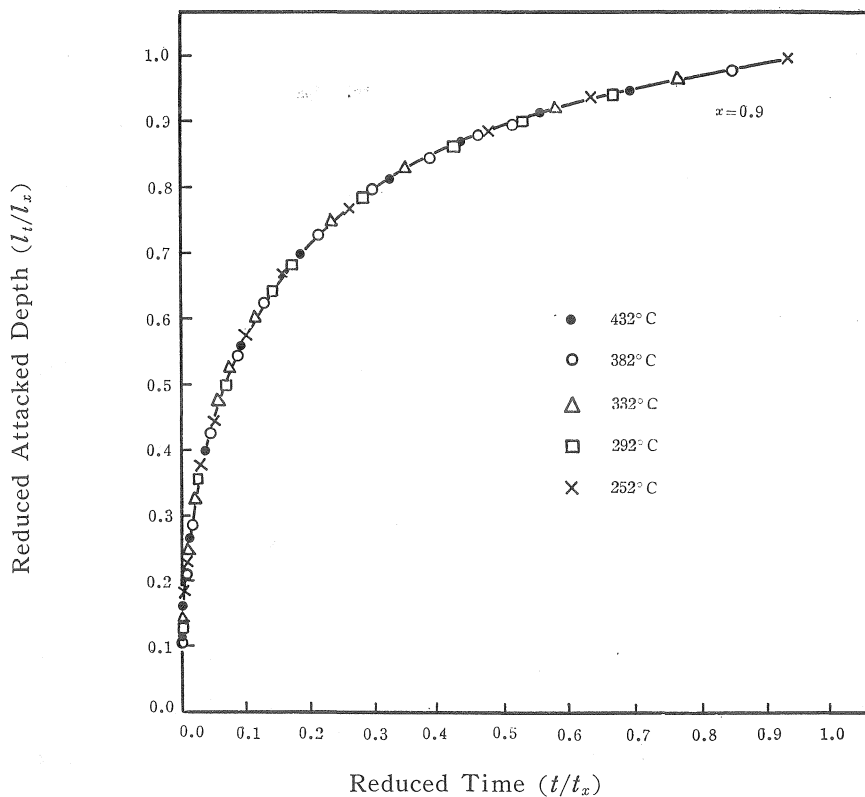


Fig. 10

### CONCLUSIONS

A study has been made of the kinetics of the attack of solid copper by molten tin under nominally static and isothermal conditions at temperatures in the range from 252°C to 432°C. The conclusions obtained were as follows:

(1). Metallographic observations showed that the duplex intermetallic compound layer existed in the solid-liquid interface.

(2). According to X-ray analysis, immediately adjacent to copper was a band of  $\text{Cu}_3\text{Sn}$ , separated from the molten tin by a band of  $\text{Cu}_6\text{Sn}_5$ , and their thickness were nearly constant irrespective of the period or temperature of reaction.

(3). The compound layer broke up and detached from the copper base, and formed "grit colonies". The influence of "colonies effect" on the attack-rate was remarkable.

(4). The attack process conformed exactly to an expression of the form:

$$\frac{dl_t}{dt} = K (l_o - l_t) t^{-p}, \text{ or } l_t = l_o (1 - e^{-\frac{K}{1-p} t^{1-p}})$$

where  $l_t$  = attacked depth at time  $t$ ,  $l_o$  = saturation attacked depth at the fixed temperature,  $K$  = apparent solution-rate constant for the process. Experimental result yields a value of 1/2 for  $p$ .

(5). It was concluded that, in the system studied, the effective rate of attack was controlled by the "colonies effect" besides by the factors reported by Ward and Taylor<sup>(1,2)</sup> for the dissolution of solid copper in liquid lead and bismuth.

(6). The apparent solution-rate constant  $K$ , was rather complex, and it was difficult to make obvious the functional relationship of  $K$  to the temperature, area of solid exposed and volume of molten tin etc..

(7). As a consequence of (4) in conjunction with (6), a general expression of the form:

$$\frac{l_t}{l_x} = \frac{1 - e^{[\log(1-x)]\sqrt{t/t_x}}}{x}$$

was obtained;  $l_x = xl_o$  = attacked depth at any time  $t_x$ ,  $x$  = any fraction  $< 1$ . With this expression, general attacked depth/time relationship would be derived from the limited experimental data.

The author wishes to express his gratitude to Dr. T. Terada and Dr. H. Syoji for their kind advice and helpful suggestions. The author's thanks are also due to Mr. S. Mori, Mr. K. Tokumaru, Mr. A. Fukunaga, Mr. Y. Dōi, Mr. J. Shirao, Mr. K. Takahashi, Mr. Y. Ōno, Mr. T. Kozurido and Mr. K. Kuribayashi for their great assistance. His acknowledgement is also due to Dr. B. Miyoshi and Mr. M. Yoshimura for their interest, and Mr. S. Abe, President of Ōsaka Asahi Metal Co. for his kind offering of virgin ingot tin used in this investigation.

#### REFERENCES

- (1). A. G. Ward and J. W. Taylor : J. Inst. Met. 85, (1956), 145.
- (2). A. G. Ward and J. W. Taylor : J. Inst. Met. 86, (1957), 36.
- (3). J. D. Harrison and C. Wagner : Acta. Met. 7, (1959), 722.
- (4). T. B. Crow : J. Inst. Met. 35, (1926), 55.
- (5). E. J. Daniels : J. Inst. Met. 58, (1936), 199.
- (6). G. L. J. Bailey and H. C. Watkins : J. Inst. Met. 80, (1952), 57.
- (7). E. L. Read : J. Am. Ceramic Soc. 37, (1954), 146.
- (8). R. N. Lyon : "Liquid-Metals Handbook" U. S. Government Printing Office. (1954).
- (9). W. D. Johnes : J. Inst. Met. 58, (1936), 193.
- (10). A. S. M. Metals Handbook, 1948 Edition and 1954 Supplement.