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Solid-State Reaction Bonding of Alumina to Cu-4Ti Alloy†

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Abstract

The solid-state reaction bonding of alumina ceramics to Cu-4Ti alloy was studied. The bonding was carried out in a vacuum (7×10^{-3}Pa) by changing bonding temperture. The bonding strength of alumina/Cu-4Ti alloy joints is bigger than the bonding strength of alumina/Cu joints.

During the solid-state reaction bonding of alumina ceramics to Cu-4Ti alloy, Ti has been condensed at Al_2O_3/Cu-4Ti alloy interface. By assuming the formation of Ti-Al bi-alloy by the reduction of Al_2O_3 by Ti, it is shown that Ti-Al complex oxide can be produced at the bonding interface from thermodynamic calculation.

KEY WORDS : (Solid-State Reaction Bonding) (Alumina Ceramics) (Cu-4Ti Alloy) (Interface) (Metal-Ceramics Reaction) (Thermodynamic Calculation)

1. Introduction

In spite of the fact that bonding of alumina ceramics with Cu using Cu_2O-Cu eutectics has been developed and applied successfully in the production of substrate for microelectronic power element, new possibilities of joining alumina ceramics with Cu are still being sought. It is so first of all because bonding of Cu to alumina through eutectics requires a very precise processe with a controlled protective atmosphere, which is expensive due to high temperature and protective atmosphere. Works on joining Cu with alumina ceramics using such auxiliary metals as Mn[1)] and Ti[2)], which were done recently, are very helpful in the formation of an interface.

It is well known that Ti acts a remarkable role on the bonding of ceramics with metals. Almost all of works on the effect of Ti addition for bonding of ceramics with metals were done on liquid phase bonding, i. e. Ti addition to a filler metal on brazing. Basing on the X-ray diffraction analysis, it was reported that the interface between Al_2O_3 and $Cu_{50}Ti_{50}$ is composed of bi-oxides (Al, Ti) $_2O_3$ and TiO_x[2)]. Also, some works have been reported on the solid state reaction of alumina ceramics with Ti. The interface between the sapphire mono-crystal and Ti was subjected to detailed analysis after having been heated at temperature ranging from 923K to 1273K for 940 hours, and it was found that the interface is composed of two phases, i. e. Ti_3Al and, presumably, (Ti, Al) $_2O_3$[3)]. By an AES methods, it was reported that the presence of reduced layer of Al formed after annealing in a vacuum (4×10^{-5}Pa) at a temperature of 804K for up to 6 hours[4)]. Samples for annealing were prepared so that a 185 nm thick layer of 99.98% pure polycrystalline Ti was applied on a sapphire substrate by electron beam method. They did not exclude a possibility of the presence of Ti_3Al intercrystalline compound. By sintering of Ti powders with Al_2O_3 powders at a ratio of 1:1 for 30min at 1223K and 1773K, Ti-Al alloys were found to exist besides metallic Ti and Al_2O_3[5)]. When a vacuum bonding of alumina ceramics with steel through a Ti layer for 4 and 9 hours at temperature range from 1173K to 1473K was carried out, presence of Ti_3Al or Ti_2Al and TiAl was recognized[6)], but they did not confirm the presence of TiO in obtained joints.

As can seen from this brief review, the results are far from being uniform, and there is no explanation of cause of the formation of specific interface between Ti and Al_2O_3. The purpose of this study is to examine the possibility of obtaining Al_2O_3 to Cu joints with a small content of Ti, and to check the structure of interface formed during the process.

In this paper, the effect of Ti addition on solid state bonding of alumina ceramics with Cu-4Ti alloy is studied. Bonding was evaluated by measuring the tensile strength. Bonding parts were examined by using an optical microscope, SEM and EDX analyzer.

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As an additional work, thermodynamic calculation is performed assuming the alloying of Ti with Al from decomposition of Al_2O_3. To confirm the assumption mentioned above, mixed powders of Ti and Al_2O_3 were heat treated in a vacuum (2×10^{-3}Pa), and the obtained powders were analyzed by X-ray diffraction method.

2. Experimental procedure

As ceramics, two types of sintered alumina of purity 99.6wt% and 96wt% were used. As metals, industrial grade pure copper and Cu-4Ti alloy (containing 4wt% Ti) were used. **Figure 1** shows the size and shape of specimens and an assembly of specimens for solid state reaction bonding. The bonding surfaces of specimens were polished with #1500 emery paper, and degreased in acetone with an ultrasonic bath. Then the specimens were assembled as a metal disk was sandwiched between two alumina disks as shown in Fig. 1. The assembly was set in a vacuum furnace as shown in **Fig. 2**. Then the assembly was heated in a vacuum (7×10^{-3}Pa) to a required temperature at the heating rate of 50K/min. When the temperature reached a required temperature, an external pressure of 50MPa was applied. After keeping at the temperature for 20min the assembly was cooled at the cooling rate of 10K/min. For evaluating the bondability, tensile strength of the bonded joints was measured. Cross section of obtained joints was inspected by optical microscope and SEM and analyzed by EDX.

To examine the reaction between Ti and Al_2O_3, Mixed powers of Ti and Al_2O_3 were heated in a vacuum (2×10^{-3}Pa) at an elevated temperature, and the resulted powders were examined by X-ray diffraction method.

3. Results and discussion

3.1 Solid state reaction bonding

Figure 3 shows the effect of the bonding temperature on the bonding strength of Al_2O_3/Cu-4Ti alloy joints compared with Al_2O_3/Cu joints bonded under a constant external pressure of 50MPa for 20min in a vacuum. As shown in Fig. 3, the bonding strength increased with the increase of bonding temperature, and the bonding strength was saturated above 1073K. The saturated value of the bonding strength is about 40MPa for Al_2O_3/Cu-4Ti alloy joints and about 20MPa for Al_2O_3/Cu joints.

The difference of bonding strength between Al_2O_3/Cu-4Ti alloy joints and Al_2O_3/Cu joints is supported by an observation of fractured surface. **Figure 4** shows the appearance of fractured surface of Al_2O_3/Cu-4Ti alloy joints compared with Al_2O_3/Cu joints. As can be seen in

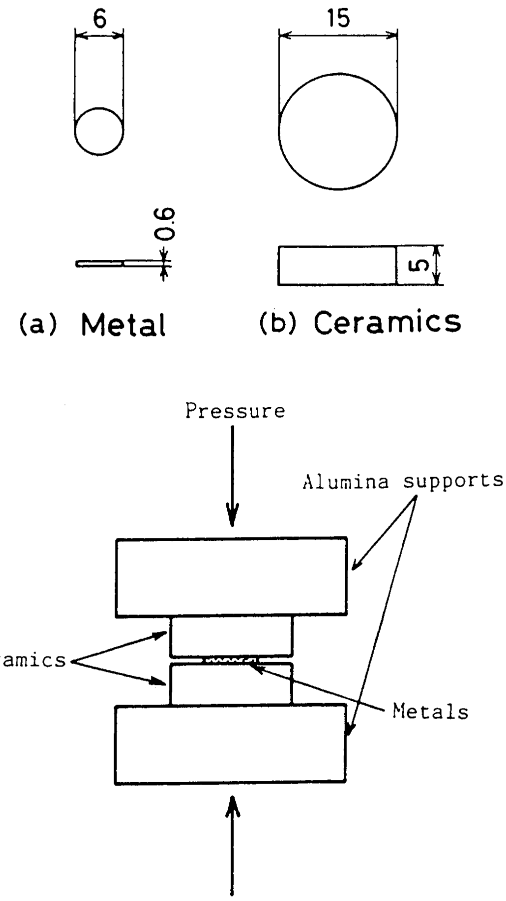

Fig. 1 Size and shape of specimens and schematic drawing of assembly for solid state reaction bonding.

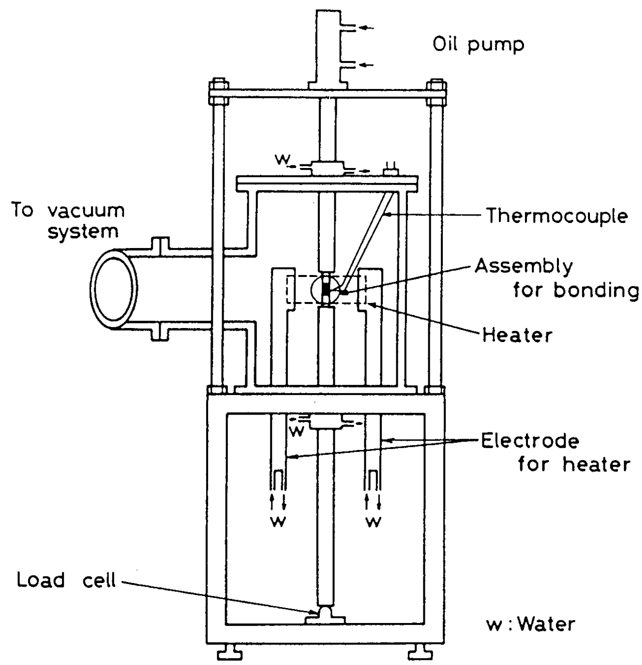

Fig. 2 Schematic drawing of bonding apparatus

Fig. 4, Al_2O_3/Cu joints fractured in Al_2O_3 itself at bonding temperature of 1123K and Al_2O_3/Cu-4Ti alloy joints fractured in Al_2O_3 itself at bonding temperature of above 1073K. On the Cu side fractured surface of Al_2O_3/Cu joints bonded at 1123K, very thin lumps are attached, though fracture of Al_2O_3/Cu-4Ti joints occurred deeply in Al_2O_3 itself. From these results, it is obvious that by using Cu-4Ti alloy, the bonding strength of Al_2O_3/Cu joints can be improved by an addition of small amount of Ti to Cu on solid state bonding.

Figure 5 shows cross sections of Al_2O_3/Cu joint and Al_2O_3/Cu-4Ti joint bonded at 1173K for 20min under external pressure of 50MPa in a vacuum. From these photographs, it is recognized that the interfaces are very smooth for both Al_2O_3/Cu joint and Al_2O_3/Cu-4Ti joint. SEM photographs with EDX line analysis results are shown in **Fig. 6** and **Fig. 7** for cross sections of Al_2O_3/Cu joint and Al_2O_3/Cu-4Ti joint, respectively. It is recognized that Ti has been concentrated at the bonding interface in Cu-4Ti alloy as shown in Fig. 7, though profiles of Cu and

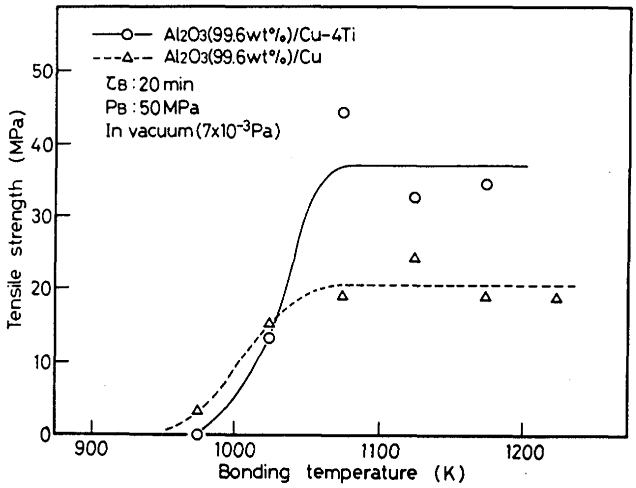

Fig. 3 Effect of bonding temperature on bonding strength of Al_2O_3/Cu-4Ti alloy joints compared with Al_2O_3/Cu joints.

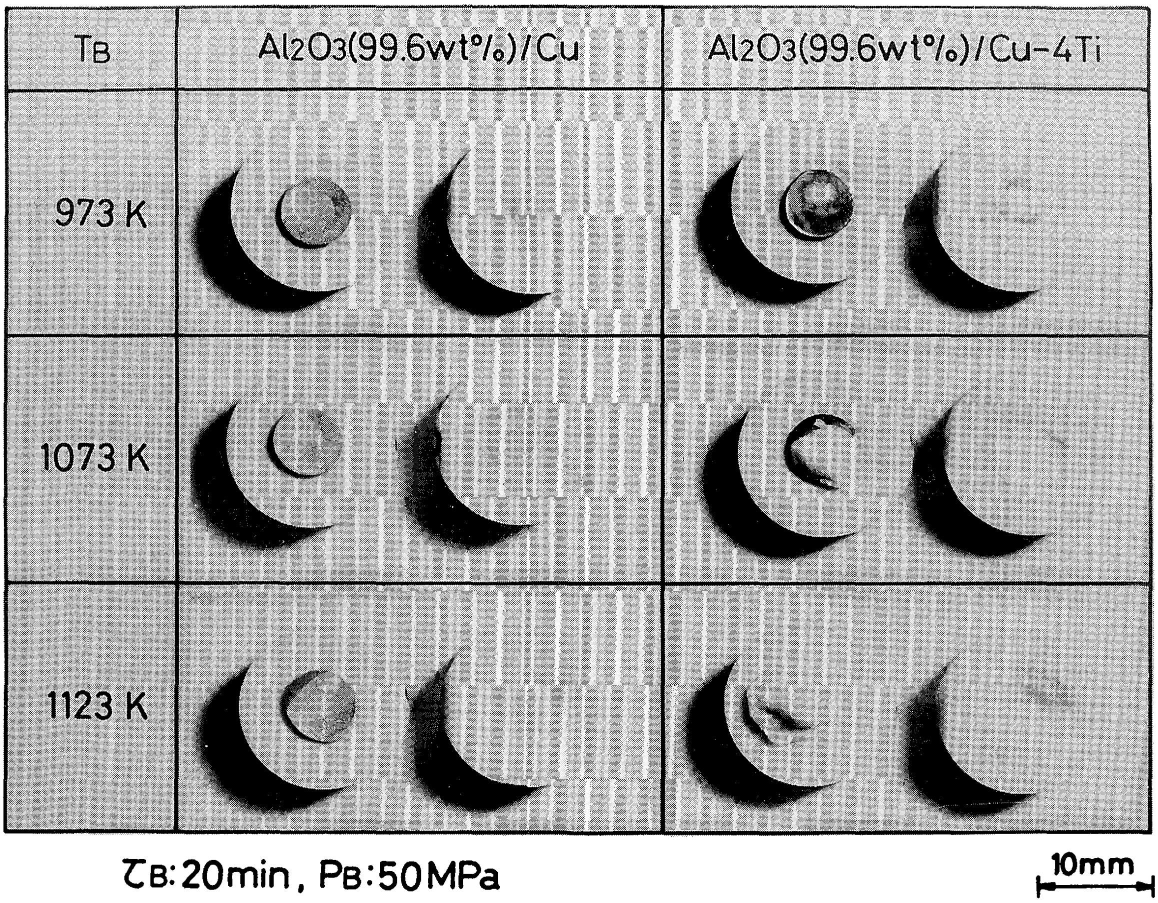

Fig. 4 Appearance of fractured surfaces of Al_2O_3/Cu-4Ti alloy joints compared with Al_2O_3/Cu joints with change of bonding temperature

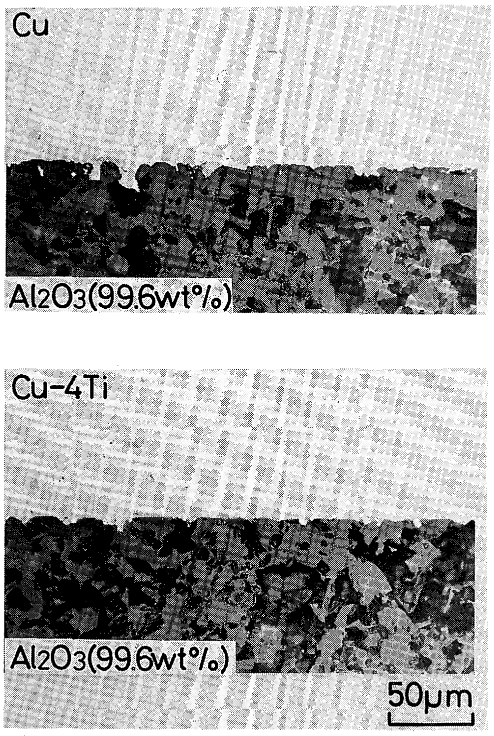

Fig. 5 Microphotographs of bonding interface for Al_2O_3/Cu-4Ti alloy joint compared with Al_2O_3/Cu joint bonded at 1173K for 20min under external pressure of 50MPa in vacuum.

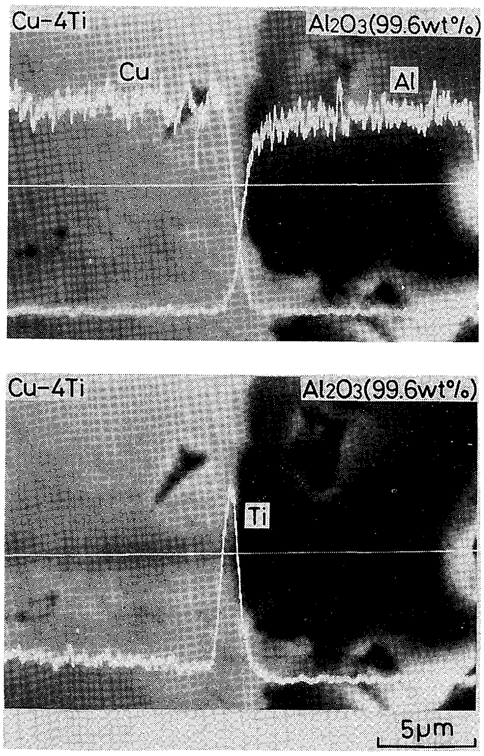

Fig. 7 SEM photographs and EDX line analysis results for solid state reaction bonded Al_2O_3/Cu-4Ti alloy joint bonded at 1173K for 20min under external pressure of 50MPa in vacuum.

Al are almost same in both Fig. 6 and Fig. 7. From these results, it is obvious that when Ti was added in Cu, Ti has been collected at the interface during solid state bonding similar to the brazing of ceramics, but it is difficult to see the change of the bonding interface from Figs. 5-7. Therefore, an accelerated test was performed to make clear the change at the bonding interface. **Figure 8** shows SEM photographs with EDX line analysis results for Al_2O_3/Cu-4Ti joint bonded at 1273K for 60min under a pressure of 50MPa in a vacuum. In Fig. 8, condensation of Ti at the bonding interface part of Al_2O_3/Cu-4Ti joint can be recognized clearly.

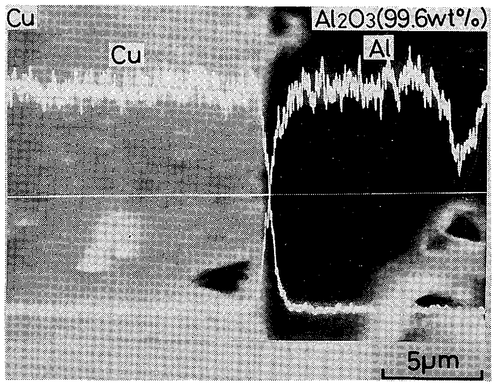

Fig. 6 SEM photographs and EDX line analysis results for solid state reaction bonded Al_2O_3/Cu joint bonded at 1173K for 20min under external pressure of 50MPa in vacuum.

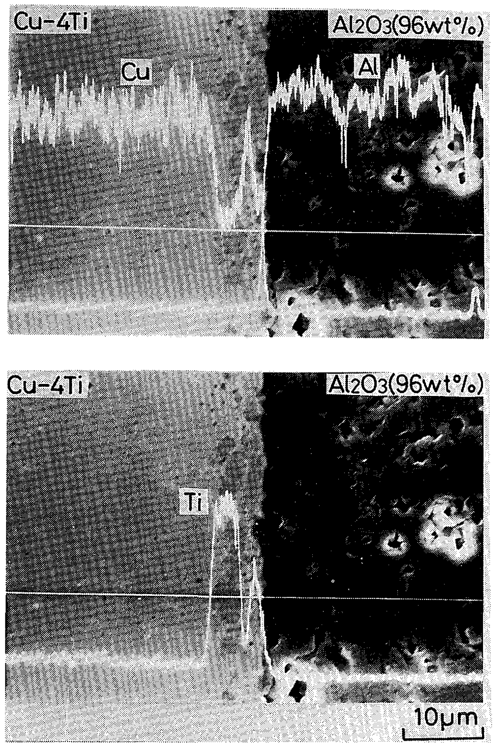

Fig. 8 SEM photographs and EDX line analysis results for solid state reaction bonded Al_2O_3/Cu-4Ti alloy joint bonded at 1273K for 60min in vacuum.

3.2 Thermodynamic calculation

As mentioned above, Ti was concentrated at the interface of Al_2O_3/Cu-4Ti alloy joint during solid state reaction bonding. Therefore, it must be useful to consider a reaction between Ti and Al_2O_3 on bonding of Cu-4Ti and Al_2O_3.

On brazing of alumina ceramics using a filler metal containing Ti, the formation of Ti-Al bi-oxide is considered[2]. But, on the reaction,

$$Ti+\frac{2}{3}Al_2O_3 \rightarrow TiO_2+\frac{4}{3}Al \quad G=+41\text{kcal (at 1273K)} \tag{1}$$

the direct reaction between Ti and Al_2O_3 could not occur since the Gibb's free energy is positive[7].
However, the formation of an Al-Ti alloy must be proceeded by a reduction of Al_2O_3 to a metallic form, and it will be reduced the Gibb's free energy. Therefore, a thermodynamic calculation was done by assuming the formation of an Al-Ti alloy by reduction of Al_2O_3 to a metallic form.

On the reaction,

$$A+B \rightarrow C+D \tag{2}$$

the condition to proceed the reaction (2) is,

$$1nK_T=\frac{\Delta Q_T}{RT}>0 \tag{3}$$

and ΔQ_T is,

$$\Delta Q_T=\sum \nu' i G' i_T-\sum \nu i G i_T \tag{4}$$

where,

- K_T : equilibrium of reaction
- ΔQ_T : change of Gibb's free energy during reaction at temperature T
- Gi_T : Gibb's free molar energy of component "i" at temperature T
- " ′ " : index which denotes the products of reaction

From a general equation it is well known that,

$$Gi_T=Hi_T-TSi_T \tag{5}$$

where,

- Hi_T : molar enthalpies of component "i" at temperature T
- Si_T : entropies of component "i" at temperature T

Hi_T and Si_T take the form as functions of molar heat capacity Cpi_T,

$$Hi_T=Hi_{T_0}+\int_{T_0}^{T_P} Cpi_{1T}dT+\Delta H_{T_P}+\int_{T_P}^{T}\frac{Cpi_{2T}}{T}dT \tag{6}$$

$$Si_T=Si_{T_0}+\int_{T_0}^{T_P}\frac{Cpi_{1T}dT}{T}dT+\frac{\Delta H_{T_P}}{T_P}+\int_{T_P}^{T}\frac{Cpi_{2T}}{T}dT \tag{7}$$

where,

- ΔH_{T_P} : phase transition heat at temperature T
- 1 : denotes phase 1
- 2 : denotes phase 2

The molar heat Cpi_T of component "i" at temperature T is expressed with the polynomial,

$$Cpi_T=Ai+BiT+CiT^2+DiT^{-2} \tag{8}$$

The stable equilibria Ki_T calculated from data in **Table 1** is specified in **Table 2**.

When joining Ti or its alloys with Al_2O_3, the reduction reaction should take place according to equation,

$$Al_2O_3+3Ti \rightarrow 2Al+3TiO \tag{9}$$

The stable equilibria log Ki_T of this reaction is, however, negative and they amount to,

$$\log K_{1223}=-3.438 \text{ or } \ln K_{1223}=-7.92<0 \tag{10}$$

which indicates that this reaction should not take place.

If, however, one assumes real conditions under which the process of bonding is accompanied by the formation of Al-Ti bi-alloy (and this, in turn, is usually accompanied by a drop of Gibb's free erergy) , then the equilibrium of reaction can be shifted. By assuming the formation of Al-Ti bi-alloy, next equation should be obtained,

$$21n f_{Al}+21nx-31n f_{Ti}-31n(1-x)=1nK_T \tag{11}$$

where,

$$1nf_{Al}=\frac{4Q_{max}}{RT}x^2 \tag{12}$$

$$1nf_{Ti}=\frac{4Q_{max}}{RT}(1-x)^2 \tag{13}$$

- x : molar fraction of Al in the mixture of Al with Ti
- Q_{max} : heat change of system by mixing

The culculated value of x in equation (13) for $Q_{max}(=H/2)=-4350$cal/mol and T=1323K is 0.26. Thus, at a temperature of 1223K, the system presented by a chemical reaction of equation (9) remains in the state of equilibrium when the formed Al-Ti bi-alloy is composed of 26at%Al and 74at%Ti. This approximately corresponds to the simultaneous occurrence of two reactions,

$$Al_2O_3+3Ti \rightarrow 2Al+3TiO$$
$$2Al+6TiO \rightarrow 2Ti_3Al \qquad (14)$$

or to a total reaction,

$$Al_2O_3+9Ti \rightarrow 2Ti_3Al+3TiO \qquad (15)$$

As shown in above calculations, it is shown that the reduction of Al_2O_3 by Ti could occur by assuming the Gibb's free energy drop by formation of Al-Ti bi-alloy.

To confirm the reaction between Ti and Al_2O_3, Al_2O_3-50wt%Ti mixed powders were heated at 1323K for 60min in a vacuum (2×10^{-3}Pa) . A X-ray diffraction pattern of the resulted powders is shown in **Fig. 9**. In this figure, Ti_2Al is recognized as a Ti-Al bi-alloy. The produced Ti-Al bi-alloy on a real reaction is different from the calculated one, but it is obvious that the formation of Ti-Al bi-alloy affects the bonding of Cu-4Ti alloy with alumina ceramics.

Table 1 Thermodynamic data for calculation. Data marked with *1 are from reference (8) and marked with *2 are from reference (9).

Component	$H(T_0)$ cal/mol	$S(T_0)$ cal/mol·K	T_p K	$\Delta H(T_p)$ cal/mol	For phase "1" A_1	$B_1\times10^{-3}$	$D_1\times10^5$	For phase "2" A_2	$B_2\times10^{-3}$	$D_2\times10^5$
Al *1,*2	0	6.769	932	2570	4.94	2.96		7.4		
Al_2O_3 *1	-400400	12.175	2303		25.71	3.96				
Ti *2	0	7.334	1155	950	2.25	2.52		7.5		
TiO_2 *2	-123900	8.31	1264	820	10.57	3.6	-1.86	11.85	3.0	
Ti_2O_3 *2	-362900	18.83	473	215	7.31	53.52		34.68	1.3	-10.2
Ti_3O_5 *2	-586700	30.92	450	2240	35.47	29.5		41.6	8.0	
TiO_2 *2	-225500	12.01	2128		17.97	0.28	-4.35			

Table 2 Logarithmic coefficients of equilibrium log K_{iT} calculated from data shown in Table 1.

Component	Temperature (K) 298.15	1000	1323
Al	1.480	2.229	2.679
Al_2O_3	296.202	93.250	73.170
Ti	1.600	2.319	2.661
TiO	92.650	30.154	24.119
Ti_2O_3	270.164	86.784	68.906
Ti_3O_5	436.879	140.749	111.711
TiO_2	167.943	55.871	45.859

From these results, the interfaces formed between Cu-4Ti alloy and Al_2O_3 in the course of solid state reaction bonding can be presented diagrammatically, as shown in **Fig. 10**.

4. Conclusion

The following conclusions can be drawn from the experimental results and from thermodynamic calculation.

(1) By addition of Ti to Cu, the bonding strength with alumina ceramics is improved. The bonding strength of Al_2O_3/Cu-4Ti alloy joints is two times bigger than that of Al_2O_3/Cu joints.

(2) Ti added in Cu is condensed at the interface of Al_2O_3/Cu-4Ti alloy joints during solid state reaction bonding.

(3) From thermodynamic calculation, assuming Gibb's free energy drop by the formation of Ti-Al bi-alloy at the interface, it is shown that the reduction of Al_2O_3 by Ti could occur.

(4) The assumption mentioned in (3) is supported by a re-

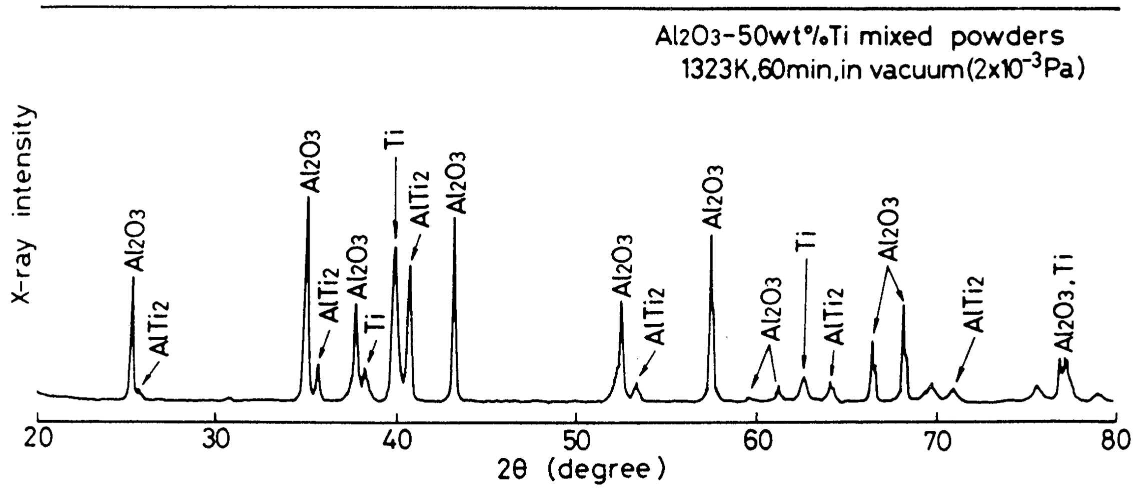

Fig. 9 X-ray diffraction pattern of Al_2O_3-50wt%Ti powders heated at 1323K for 60min in vacuum.

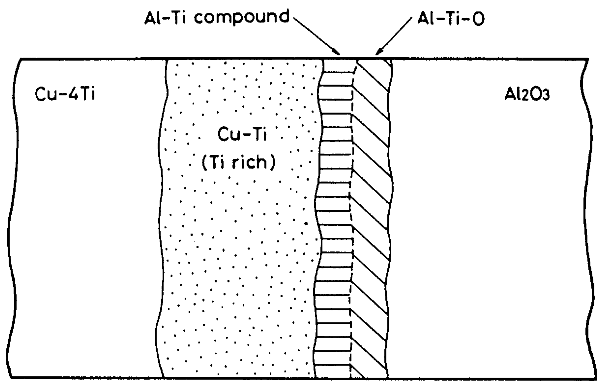

Fig. 10 Schematic drawing of interface part of Al_2O_3/Cu-4Ti alloy joint considered from experimental results and results of thermodynamic calculation.

sults of a X-ray diffraction analysis of heat treated Al_2O_3-50wt%Ti mixed powders. Production of Ti_2Al was recognized as a Ti-Al bi-alloy.

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