Transference of Electric Charge at the Interface between Stabilized Zirconia Ceramics and Brazing Filler Containing Titanium

Takahisa Yamazaki[†] and Akio Suzumura

Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-Okayama, Meguro-ku, Tokyo 152-8852, Japan

Electrochemical methods were used along with brazing stabilized zirconia ceramics in order to investigate the reaction behavior between the ceramics and reactive metal titanium added to the silver-copper eutectic brazing filler. A 10 Hz, 5 V rectangular wave signal was applied to a brazing specimen and a comparative specimen, which consists of stabilized zirconia ceramics in order to compare each output signal. The output signals were observed during the brazing process using a digital storage oscilloscope. When the brazing filler foil began to melt, the waveform of the signal from the brazing specimen became sloped. The gradient of the slope was large at the beginning. As the brazing time proceeded, the gradient of the slope gradually decreased. It was suggested that the electric double-layer was formed at the brazing interface by titanium positive ions and oxygen negative ions, and that the capacitance of the layer was gradually decreased with the growing reaction layer. It was considered that titanium positive ions and oxygen negative ions are combined to form an electrical neutral reaction layer. These experimental results were analyzed from the point of view of transient phenomena in electric circuits. Calculation results agreed with the decreasing capacitance of the electric double-layer.

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I. Introduction

An electrochemical measurement technique was used for monitoring the reaction behavior in bonding ceramics using brazing filler added reactive metal⁽¹⁾. Stabilized zirconia ceramics were selected as a specimen due to their conductivity of oxygen ions. It is expected that the electrical monitoring method will be able to detect the interaction between oxygen ions and the reactive metal. In our previous study, this method was able to detect the growth of the reaction layer and the segregation of the reactive metal under heat-treatment for a pre-brazed specimen.

There are many difficulties in monitoring the brazing behavior under thermal non-equilibrium circumstance with the previous method. When a 10 Hz sinusoidal signal was applied to the specimens, a thermoelectromotive force was generated at the interfaces between the ceramics and carbon electrodes, and about a 17 Hz signal added to the 10 Hz signal was observed. We stopped using the sinusoidal signal for monitoring the brazing behavior. A rectangular signal was used instead for monitoring in this study, because it is easy to observe the change in the waveform. The 10 Hz frequency was selected to avoid ion blocking at the interface with the carbon electrodes and provide enough relaxation time for the transference of ions. It is important to detect the signal related to the transference of oxygen ions at the brazing

interface. The 10 Hz rectangular signal is considered to be proper for monitoring.

The observed waveforms were analyzed using the calculations from the transient phenomena in the electric circuits. They suggested the formation of an electric double-layer at the brazing interface. Models of the brazing interface, which is composed of titanium positive ions and oxygen negative ions, were used to explain the calculation results.

II. Experimental Procedure

1. Preparation of the specimens

A Stabilized zirconia ceramic rod, which was supplied by the Nihon Gaishi Co., Ltd., (NGK) was cut into about 2 mm thick disks. Carbon electrodes were adhered to one side of the disks in order to apply the regulated electric signals. The brazing filler laminated foil consisted of Ag-26.7Cu-4.5Ti (mass%). Titanium flakes are sandwiched between the silver-copper eutectic foils. The brazing filler foil was put between two these disks. They were surrounded with quartz walls to prevent movement in the lateral direction as shown in Fig. 1. A comparative specimen was prepared so as to compare the signal from the brazing specimen. They were stabilized zirconia ceramic disks with a thickness of about 4 mm. Two carbon electrodes were also adhered to both sides of it.

The brazing specimen and the control were set in a reverberatory furnace as shown in Fig. 1. The furnace was in a vacuum chamber evacuated using a turbomolecular pump to 2×10^{-3} Pa or less. The brazing tem-

[†] Special Postdoctoral Researcher, The Institute of Physical and Chemical Research, RIKEN 2-1, Hirosawa, Wako, Saitama 351-0198, Japan.

Fig. 1 Experimental brazing equipment and electric measurement electrodes.

perature was measured on a ceramic backup jig using a Pt-Pt13%Rh thermocouple, and the measured value was between 1080 and 1090 K.

2. Electrical measurement

A 5 V, 10 Hz rectangular wave signal was applied to both the brazing specimen and the control. Trigger signal was output from the control. The output signal from the brazing specimen was compared with that from the comparative specimen using a digital storage oscilloscope at the same time. The measurement circuit is shown in Fig. 2. Standard 100 Ω resistors are used in order to protect these specimens from transient electricity. Potentiometers of 100 Ω are adjusted to 100 Ω on the specimens' side, because it is easy to analyze the transient phenomena in the electric circuit.

Fig. 2 Electric measurement circuit for investigation of transference of electric charges at brazing interface.

III. Results

Typical waveforms of the output signals are shown in Fig. 3. These three figures show the transitions of the signals with brazing time. The first figure shows the waveforms of the comparative specimen signal and the brazing specimen signal at 1080 K where brazing filler foil starts to melt. The channel 1 signal is the output from the comparative specimen, and the channel 2 signal is the output from the brazing specimen. The signal from the brazing specimen is smaller than that from the control. The waveform is composed of two slopes. The first steep slope was observed for about 4 ms, while the second gentle slope followed the first one. On the other hand, the waveform of the signal from the control is composed of only one gentle slope. The following figure shows the waveforms after 60 s. The waveform of the signal from the brazing specimen changed to only one curve 60 s later. The initial value of the signal from the brazing specimen is larger than that from the comparative specimen. The final value is smaller than that from the comparative specimen. The third figure shows the waveform of the signals after 300 s. The initial value of the signal from the brazing specimen is the same as that in the second figure, but the final value is larger than that in the second figure. The waveform approaches the waveform of the comparative specimen.

Fig. 3 Waveforms of signal change with brazing time proceeding; CH1: comparative specimen, CH2: brazing specimen.

IV. Discussion

1. Examination of the waveforms

Calculations from transient phenomena in the electric circuits will explain the changes in the waveforms. In this subsection, the calculations will be carried out for the time constant in the transient phenomena of the two electric equivalent circuits. The transient phenomena can be defined after the determined equivalent circuits. At first, the calculations for the comparative specimen were carried out. The equivalent circuit of the comparative specimen used for the calculations is shown in Fig. 4. The precise equivalent circuit of a stabilized zirconia ceramic as a solid state electrolyte and the interfaces with the carbon electrodes is more complex, but it is difficult to estimate the time constant using the precise equivalent circuit. More studies are needed to determine the precise equivalent circuit of the brazing interface, but it is difficult to carry out impedance analyses under thermal non-equilibrium circumstances like brazing. In this subsection, a simple equivalent circuit composed of simple resistors and simple condensers is used. These elements are arranged and quoted from the literature⁽²⁾⁽³⁾. They are considered to be the total electric resistance and total capacitance of the precise elements in the precise equivalent circuit connection. In the figure, C_g denotes the geometric capacitance of the opposite probe electrodes. In this case, the probe electrodes are the carbon electrodes. R_y denotes the bulk electric resistance of the stabilized zirconia ceramics and the carbon electrodes. C_p denotes the capacitance that consists of the electric double-layer between the electrodes and the stabilized zirconia ceramics and diffusion impedance in the stabilized zirconia ceramics. R_p denotes the resistance that consists of the charge transfer process resistance and electrode contact resistance.

If C_g has a certain effective value, an observed voltage at the start, V_{start} , has to be $0.5V_0$, where V_0 is the input voltage of 5 V. The observed voltage is about 1.2 V. The value is much smaller than $0.5V_0$. A large electric current can pass through R_y and not pass through C_g . It is considered that C_g is negligible when compared with C_p in the equivalent circuit. V_{start} is given by

$$V_{start} = V_0 - \frac{R_y + 100}{R_y + 200} V_0 = 1.200 \quad (1)$$

Fig. 4 Equivalent circuit for comparative specimen, stabilized zirconia ceramics-carbon electrode system.

R_y is determined from eq. (1) as 216.7 Ω . The final value of the observed voltage, V_{end} , is given by

$$V_{end} = V_0 - \frac{R_y + R_p + 100}{R_y + R_p + 200} V_0 = 0.9750 \quad (2)$$

R_p is determined as follows. $R_y + R_p$ is equal to 312.8 Ω , and hence R_p is 96.13 Ω .

The transient voltage depends on time, t , and is given by

$$V = V_{end} + (V_{start} - V_{end}) \exp\left(-\frac{t}{T}\right) \quad (3)$$

T denotes the time constant related to the transient phenomena in the electric circuit, and t denotes the brazing time. By using the data shown in Fig. 3, the time constants at each brazing time were calculated, and the average value is 19.55×10^{-3} s.

The time constant has a relationship with the capacitance, C_p , in the following equation:

$$T = C_p \times \frac{R_p(R_y + 200)}{R_p + R_y + 200} \quad (4)$$

C_p can be determined from eq. (4). C_p is equal to 0.250×10^{-3} F.

Then calculations for the brazing specimen from the transient phenomena analyses were carried out. In the calculations, the data about the waveforms of the brazing specimen are taken at 60 s later and at 300 s later. An equivalent circuit for the brazing specimen is shown in Fig. 5. C'_g denotes the geometric capacitance of the carbon electrodes. R_x denotes the bulk resistance of the brazing specimen and the carbon electrodes. C_{int} denotes the interfacial capacitance that consists of the electric double-layers and diffusion impedance. R_{int} denotes the interfacial resistance among the brazing filler foil, the stabilized zirconia ceramics and the carbon electrodes. W denotes the Warburg impedance related to the diffusion and the reaction of the electric carrier at the brazing interface.

C'_g is negligible for the same reason as the comparative specimen. V_{start} of the brazing specimen at 60 s is given by

$$V_{start} = V_0 - \frac{R_x + 100}{R_x + 200} V_0 = 1.313 \quad (5)$$

R_x is solved from eq. (5) to be 181.0 Ω . It is slightly smaller than R_y , and it is a reasonable value by when compared with R_y . The difference between R_x and R_y is due to the difference in the initial values between the channel 2

Fig. 5 Equivalent circuit for brazing specimen, brazing filler/stabilized zirconia ceramics-carbon electrode system.

signal and the channel 1 signal in Fig. 3. It is important that R_x and R_y have the same values in order to observe them in the same range on the oscilloscope. The final voltage, V_{end} , is given by

$$V_{\text{end}} = V_0 - \frac{R_x + R_{\text{int}} + \text{Re} \dot{Z}_W + 100}{R_x + R_{\text{int}} + \text{Re} \dot{Z}_W + 200} V_0 = 0.6750 \quad (6)$$

$\text{Re} \dot{Z}_W$ in eq. (6) denotes the real part of the Warburg impedance. $R_{\text{int}} + \text{Re} \dot{Z}_W$ is solved as follows. $R_x + R_{\text{int}} + \text{Re} \dot{Z}_W$ is equal to 540.7Ω , and hence $R_{\text{int}} + \text{Re} \dot{Z}_W$ is 359.8Ω . This value is much larger than R_p , and it is predicted that $\text{Re} \dot{Z}_W$ is a large value. Based on the calculation using eq. (3), the average time constant, T_{ave} , is equal to $15.86 \times 10^{-3} \text{ s}$. The time constant, T , for the brazing specimen has a relationship with $C_{\text{int}} + \text{Im} \dot{Z}_W$, where $\text{Im} \dot{Z}_W$ is the imaginary part of the Warburg impedance.

$$T = (C_{\text{int}} + \text{Im} \dot{Z}_W) \frac{(R_{\text{int}} + \text{Re} \dot{Z}_W)(R_x + 200)}{R_x + R_{\text{int}} + \text{Re} \dot{Z}_W + 200} \quad (7)$$

$C_{\text{int}} + \text{Im} \dot{Z}_W$ is calculated from eq. (7) to be $0.0857 \times 10^{-3} \text{ F}$. In the same way, R_x , $R_{\text{int}} + \text{Re} \dot{Z}_W$ and $C_{\text{int}} + \text{Im} \dot{Z}_W$ for the brazing specimen at 300 s are calculated to be 177.6Ω , 203.6Ω and $0.1200 \times 10^{-3} \text{ F}$, respectively. R_x at 300 s is not different from R_x at 60 s, but the value of the Warburg impedance significantly changed.

2. Analysis of Warburg impedance

From the results in the previous subsection, the Warburg impedance changes with the brazing time. The differential value, $\Delta \text{Re} \dot{Z}_W(300\text{s}-60\text{s})$, is equal to -156.2Ω and the differential value, $\Delta \text{Im} \dot{Z}_W(300\text{s}-60\text{s})$, is equal to $0.03426 \times 10^{-3} \text{ F}$. In the previous subsection, the transient phenomena in the electric circuits were considered, but in this subsection, the alternating impedance of the Warburg is discussed. If the alternating impedance is not considered, the value of $\Delta \text{Re} \dot{Z}_W(300\text{s}-60\text{s})$ must be zero. This assumption conflicts with the analyses in the previous subsection. It will also be accepted by the reason why the diffusion and reaction of oxygen ions are influenced by the alternating current frequency in the previous study⁽¹⁾. Figure 6 shows the one-rung ladder circuit. The Warburg impedance denotes the infinite-rung ladder circuit which consists of capacitance, ΔC , and resistance, ΔR ⁽⁴⁾. The one-rung circuit shown in Fig. 6 is used as the Warburg impedance for easy estimation in this subsection. In order to analyze the complex impedance, a 10 Hz rectangular wave signal is transformed to a Fourier

Fig. 6 One-rung ladder electric circuit composed of ΔC and ΔR for simplified Warburg impedance.

series. The rectangular wave is transformed to the summation of the sinusoidal waves that have frequencies which are an odd number of times as large as 10 Hz. The first term of the Fourier series is only used in order to operate the Warburg impedance, because the analyses are not quantitatively treated. The impedance of the circuit shown in Fig. 6 is $(\omega^2 \Delta C^2 \Delta R^2 + 2 + j\omega \Delta C \Delta R) / (\omega^2 \Delta C^2 \Delta R^2 + 4)$, where the letter j denotes an imaginary number, and ω denotes an angular frequency. The real part of $\dot{Z}_W$ is given by

$$\text{Re} \dot{Z}_W = 1 - \frac{2}{\omega^2 \Delta C^2 \Delta R^2 + 4} \quad (8)$$

The imaginary part is given by

$$\text{Im} \dot{Z}_W = \frac{\omega \Delta C \Delta R}{\omega^2 \Delta C^2 \Delta R^2 + 4} \quad (9)$$

So, the following relations exist:

$$\Delta \text{Re} \dot{Z}_W = \frac{2}{\omega^2 \Delta C_{60\text{s}}^2 \Delta R_{60\text{s}}^2 + 4} - \frac{2}{\omega^2 \Delta C_{300\text{s}}^2 \Delta R_{300\text{s}}^2 + 4} < 0 \quad (10)$$

$$\Delta \text{Im} \dot{Z}_W = \frac{\omega \Delta C_{300\text{s}} \Delta R_{300\text{s}}}{\omega^2 \Delta C_{300\text{s}}^2 \Delta R_{300\text{s}}^2 + 4} - \frac{\omega \Delta C_{60\text{s}} \Delta R_{60\text{s}}}{\omega^2 \Delta C_{60\text{s}}^2 \Delta R_{60\text{s}}^2 + 4} > 0 \quad (11)$$

From these relationships, $\Delta C_{60\text{s}} \Delta R_{60\text{s}} > \Delta C_{300\text{s}} \Delta R_{300\text{s}}$ is determined. There is no need to calculate ΔC and ΔR , because ΔC and ΔR are used in the assumption of the one-rung ladder circuit.

The resistance, ΔR will increase with the growing reaction layer, so $\Delta R_{60\text{s}}$ is smaller than $\Delta R_{300\text{s}}$. According to this consideration, $\Delta C_{60\text{s}}$ is larger than $\Delta C_{300\text{s}}$.

3. Reaction models of the brazing interfaces

A model of a primary brazing interface is shown in Fig. 7. Titanium ions start to move to the brazing interface when the brazing filler foil start to melt. Electric double-layers are formed there by titanium positive ions and oxygen negative ions. The capacitance induces electric carriers not to go through the layer. The amplitude of the signal rapidly decreases as shown in Fig. 3 at melting. A model where reaction layers formed as a function of the brazing time is shown in Fig. 8. Titanium positive ions and oxygen negative ions combine to become a neutral

Fig. 7 Model of the transference of electric charges at brazing interface at the beginning of brazing.

Fig. 8 Model of brazing interface where reaction layers are formed. Electrons are not blocked at the brazing interface.

reaction layer. The capacitance of electric double-layer is then smaller than that of the primary brazing interface. For this reason, a rapid decrease in voltage was not observed. A series of these models does not conflict with the results of the calculations in the previous subsection.

V. Conclusions

A 10 Hz, 5 V rectangular wave signal was applied to the brazing specimen so as to monitor the reaction behavior in the brazing stabilized zirconia ceramics using the brazing filler foil added reactive metal. When the brazing filler foil begins to melt, the waveform of the signal from the brazing specimen changes from the rectangular wave to a sloped one. It is considered that an electric double-

layer is formed at the interface between the brazing filler and the ceramics. The monitoring signal was influenced by the capacitance of the double-layer. The gradient of the slope becomes smaller with brazing time. This suggested that the capacitance of the double-layer gradually decreased. It is considered that titanium positive ions and oxygen negative ions combine to form a neutral reaction layer. From the results of these analyses about the Warburg impedance, the model of the brazing interface, where titanium positive ions and oxygen negative ions exist, is consistent with the analyses. For this reason, it is considered that titanium atoms move as positive ions.

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