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Co-effect of heat and direct current on growth of intermetallic layers at the interface of Ti–Ni diffusion couples

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ABSTRACT

The growth of the intermetallic layers at the interface of Ti–Ni diffusion couples was investigated under the co-effect of heat and direct current. Isothermal diffusion treatments for Ti–Ni couples were conducted at 500, 600 and 700 °C for 5, 10 and 15 h with and without the passage of DC current of 10 A intensity. It was found that both Ti_2Ni and $TiNi_3$ layer form at the Ti–Ni interface in all couples treated by different process, but TiNi layer forms in the couples annealed above 600 °C without current or at 500 °C with current. The growth of the whole interfacial layer shows a parabolic relationship with time. The apparent activation energy of growth for the whole interfacial layer is 83.76 kJ/mol in the couple treated by heating without a current, and it decreases to 42.11 kJ/mol in the couple treated with a direct current of 10 A during heating. The effect of the current on the growth of different intermetallic layers varies with its direction.

1. Introduction

Titanium and its alloys have been widely applied in areas of aerospace, vessels, metallurgy, etc. for their better properties in specific strength, toughness, and high heat and corrosion resistance. The fabrication of many structure components often needs to connect titanium alloys with other metals, which have to be well tackled for the application of titanium alloys. Brittle intermetallic phases form usually in the joint of titanium alloys and other metals such as steel, and they decrease the plasticity and toughness of the joints.

At present, in order to reduce the harmful phase at the interfaces, additional materials are often employed to form transition layers between two metals to be welded. For the connection of titanium alloys and steels, Al, Ni, Cu and V are often used as transition metals [1–3]. Among them, Ni can improve the corrosion resistance of the joint. It can form an infinite solid solution with Fe and can form three equilibrium intermetallic phases with Ti, which are $TiNi_3$, TiNi and Ti_2Ni. Fig. 1 shows the Ti–Ni equilibrium phase diagram [4].

The efficiency and the quality of bonding joints are related closely to the diffusion behavior of atoms, which are influenced by various physical fields, such as temperature field, stress field, electromagnetic field and electric current field.

Up to now, extensive research efforts have been dedicated to the effect of electric current, electric field or high density electric current pulses on the processing and property of metals, which may produce significant changes in the microstructure and provide a possible way to improve the metal's mechanical performance.

Pei et al. [5] studied the effect of the electric current on the high temperature deformation behavior of TC6 titanium alloy. They found that the high temperature ductility and failure strain of TC6 alloy are significantly improved by the external electric field at 600 °C due to the retarded effect of the electric field on the phase transformation process of β to α. The high temperature strength is also increased due to the promotion effect of the electric field on the precipitates and the phase transformation process at 700, 800 and 900 °C. Wang and Song [6] found that the electropulsing treatment brings a significant increase in total elongation of cold-rolled TA15 sheet. Ross et al. [7] reported that an electric current can dramatically improve the formability of Ti–6Al–4 V alloy. Li et al. [8] found that the average grain size of AZ91D magnesium alloy fabricated through electromagnetic vibration technique decreases first and then increases with the increase of electric current intensity. Ma et al. [9] obtained the fine equiaxed grains of pure Al by applying electric current pulse. Wang et al. [10] found that with the application of direct current, the aging process of Cu–Cr–Zr alloy is accelerated and the electrical conductivity of the alloy is increased.

Some work shows that the application of electric current can affect the sintering process and quality of materials. Liu et al. [11] reported that the composition of sintering products of W–C–CO depends on the magnitude of the current intensity. Li et al. [12] found that an intensive electric current can decrease the sintering

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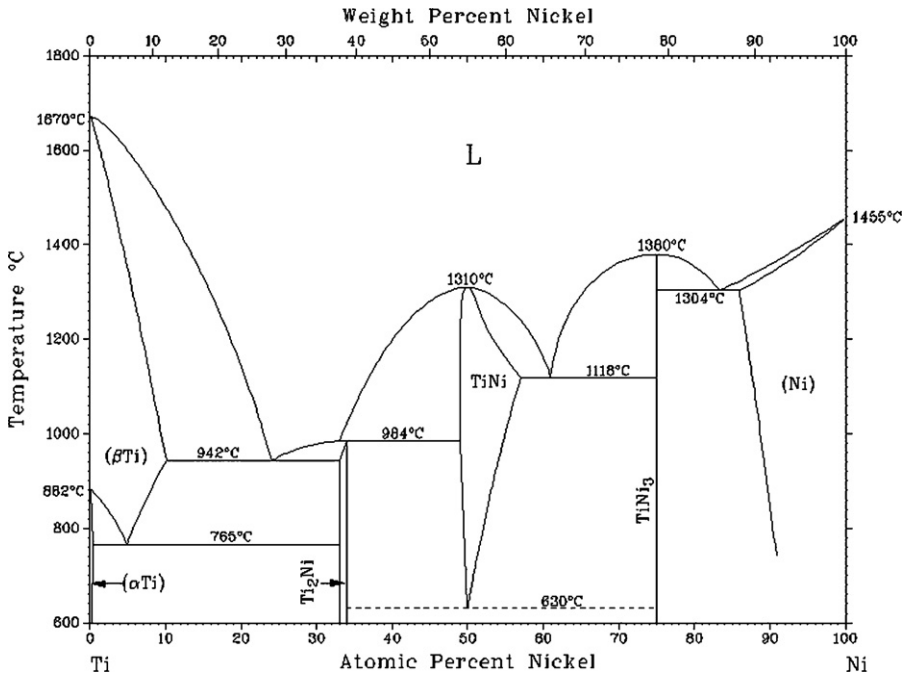

Fig. 1. Ti–Ni phase diagram [4].

temperature and shorten the sintering time of W–4Ni–2Co–1Fe powders and increase the relative density of products. Similarly, Swarnakar, Huang and other scholars' studies confirmed that the electric current can densify the sintering products [13–16]. In addition, many scholars have investigated the effect of electric current on the interfacial reactions and the mechanical properties of different solder joints and diffusion couples [17–21].

Up to now, the mechanism of the effect of electric current is still ambiguous though some scholars have tried to explain the micromechanism by electromigration theory based on the promoting or inhabiting effect of the electric current on the atomic diffusion [22–27].

The application of current supplies an extra driving force for the migration of atoms. The co-effect of the driving forces from the current and the chemical potential on the atom flux can be written as [22]:

$$J_i = -D_i \frac{N_i}{RT}[RT\partial \ln(N_i/\partial x) + \mathrm{FEZ}_i^*/f_i] \quad (1)$$

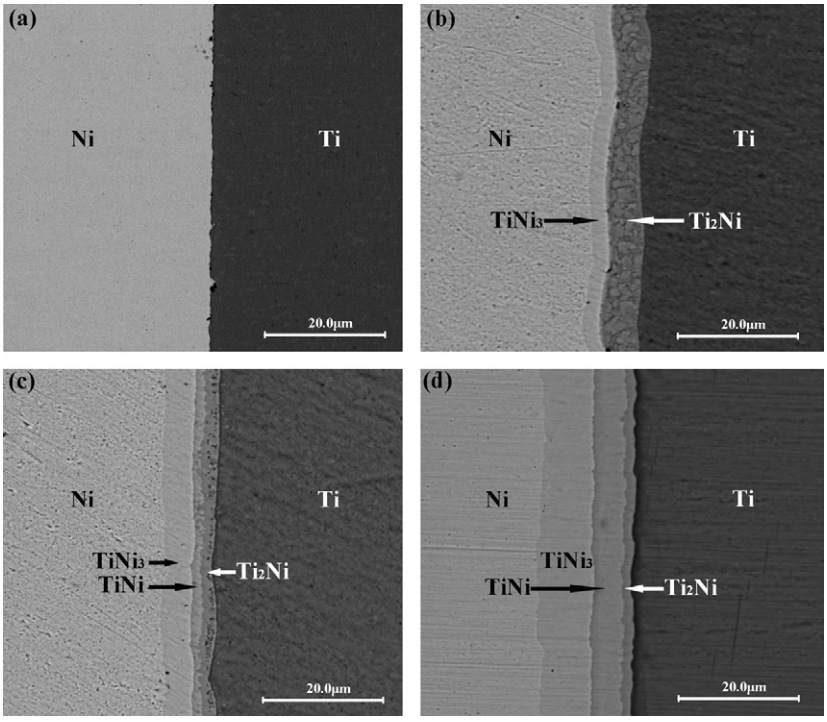

Fig. 2. SEM images of interfaces of Ti–Ni couples annealed at different temperature. (a) As-bonded; (b) 500 °C/10 h; (c) 600 °C/10 h; (d) 700 °C/10 h.

where i represents the diffusion element, J_i the diffusion flux, D_i the diffusion coefficient, N_i the mole fraction, T the temperature, R the universal gas constant, x the layer thickness, Z_i^* and f_i the effective charge and correlation coefficient of atom i respectively, F the Faraday's constant, and E the electric field intensity.

The first term inside the bracket at the right-hand side of Eq. (1), i.e. FEZ_i^*/f_i represents the driving force of chemical potential, while the second term, i.e. represents the effect of electric field.

If the effect of the second term is much weaker compared to that of the first term, no matter in any direction, the current has little effect on the growth of intermetallic phases, as in the case of Sn–Cu system [27]. The diffusion flux resulting from the chemical potential gradient is usually a strong function of temperature. However, the electromigration resulted from the momentum transfer of moving electrons is not significantly affected by temperature. Thus it is reasonable that at a higher temperature the current affects little on Sn–Ag system because that the flux caused by the concentration gradient becomes larger than that caused by the electromigration [25]. However in Au–Al [26] and Al–Ni [27] systems, the current accelerates the growth of intermetallic phases significantly and its direction has no apparent effect. These results deny the effect of electromigration. N. Bertolino [26] has given another explanation that the current can enhance the atom diffusion along crystal defects and so promotes the nucleation of intermetallic phases and accelerates their growth. Asoka-Kumar [28] confirmed that the passage of a current increases the concentration of vacancies in metals through positron annihilation spectroscopy investigation. Javier E. Garay et al. [29] found that the current could enhance the mobility of defects in $TiNi_3$. According to the above results, the enhancement of nucleation rate caused by the defects with high concentration and high mobility may be another reason for the promoting effects of current on the growth of intermetallic phases.

In this paper, the co-effect of heat and direct current on the growth of interfacial layers in Ti–Ni couples was investigated, and the method to control the growth of interfacial layers under the coupled heat and direct current is expected to be developed. We try to seek after the mechanism of the effect of electric current on the phase growth in Ti–Ni couple.

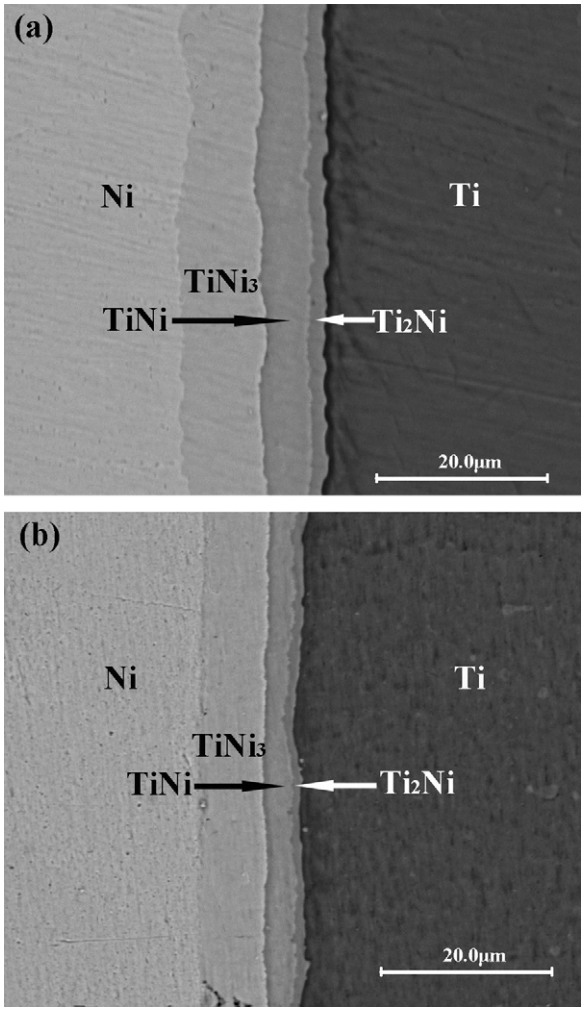

Fig. 3. SEM images of Ti–Ni interfaces in couples annealed at 500 °C for 10 h with 10 A current. (a) Ti end connected to anode; (b) Ni end connected to anode.

2. Experimental details

The materials used for test are pure titanium and nickel wires with a diameter of 1 mm. Upset butt welding was employed to fabricate Ti–Ni couples. In order to avoid harmful effect of oxidation at Ti–Ni interface, the welding was conducted immediately after the end faces of Ti and Ni weirs were polished and cleaned with ethanol.

The diffusion couples were annealed in a temperature range from 500 to 700 °C for various durations from 5 to 15 h, with a temperature control accuracy of ±5 °C, and the couples are air cooled after heating. DC Constant-Current Source was applied to impose a current of 10 A on Ti–Ni couples, and the current direction was interchanged. The morphology of the reaction zone and the thickness of each intermetallic layer were observed and measured using scanning electron microscope (SEM), respectively. The composition of the products in the reaction zone was determined through energy dispersive spectrometer (EDS).

3. Results and discussion

3.1. Intermetallic layers in Ti–Ni couples annealed with/without current

The interfacial morphology of the Ti–Ni couples fabricated by upset butt welding is shown in Fig. 2(a). A straight interface with low porosity is shown in it and it indicates that Ti and Ni specimens are welded successfully. No intermetallics are observed at the Ti–Ni interface. Several intermetallic layers form after annealing at 500, 600 and 700 °C for 10 h, see Fig. 2(b)–(d). According to the examination of EDS, three intermetallic layers at the interface are $TiNi_3$, TiNi and Ti_2Ni in turn from Ni side to Ti side of couples annealed at 600 and 700 °C for 10 h, respectively, as shown in Fig. 2(c) and (d). TiNi layer is not observed at the interface of couple annealed at 500 °C for 10 h without current, as shown in Fig. 2(b). The TiNi layer forms and the whole interfacial layer, $TiNi_3$ and TiNi layers widen with the increase of annealing temperature. However, when the TiNi layer forms at the interface the thickness of Ti_2Ni layer becomes narrow above 600 °C and it changes a little with temperature. From the above results, it is inferred that the TiNi layer grows by consuming the Ti_2Ni and $TiNi_3$ layer. According to the reaction, $0.2TiNi_3 + 0.4Ti_2Ni = TiNi$, the consumption of Ti_2Ni is twice more than that of $TiNi_3$ for forming TiNi phase. Therefore, the apparent thickness of $TiNi_3$ and Ti_2Ni layer is controlled both by their own growth and by their consumption due to TiNi growing. The growth of $TiNi_3$ layer is quick enough to restore the consumed amount of $TiNi_3$ for the formation of TiNi layer, while the lower growth rate of Ti_2Ni is not enough to restore the consumed amount due to reaction, therefore the thickness of $TiNi_3$ and Ti_2Ni increases and decreases, respectively, with temperature.

The morphology of the interfaces in Ti–Ni couples annealed at 500 °C for 10 h with a current of 10 A is shown in Fig. 3, which is similar to that illustrated in Fig. 2(c) and (d). After annealing at 500 °C for 5–15 h with a current of 10 A, three intermetallic layers, i.e. $TiNi_3$, TiNi and Ti_2Ni, appear at the interface. According to the Ti–Ni equilibrium phase diagram (see Fig. 1), the TiNi phase only exists in the temperature range of 630–1310 °C, that is, TiNi layer cannot form at the interface of Ti–Ni couples annealed at 500 °C

without current because of its instability below 630 °C. However, the TiNi layer appears at the interface of couple annealed under the co-effect of heat and current (500 °C/10 A/5–15 h). This means that the current may supply extra energy for the nucleation of TiNi phase and promote its formation below 630 °C. Owing to the fast cooling speed (air cool), there is no enough time for TiNi phase to transform into $TiNi_3$ and Ti_2Ni completely, so the TiNi phase forming at 500 °C can be kept as a metastable phase at room temperature. The whole interfacial layer, including each intermetallic layer, becomes thicker in Ti–Ni couples annealed with current as the heating time prolongs. Comparing the results with and without current, it can be known that the current accelerates the growth of $TiNi_3$ and TiNi layer. But the effect of current on Ti_2Ni growth cannot be identified exactly. The growth of Ti_2Ni cannot restore its consumed amount to form TiNi phase, so that, the Ti_2Ni layer is thinner in the couples treated by heating and current than that in the couples simply treated by heating.

The thickness of each intermetallic layer in the couple whose Ni end connected to anode is thinner than that in the couple whose Ti end connected to anode. This means that the interchange of current direction alters the growth rate of intermetallic layer and that the current flowing from Ni end to Ti end through the couple inhibits the growth of intermetallic layer compared with that flowing from Ti end to Ni end.

3.2. Kinetics and apparent activation energy for growth of intermetallic layers

Fig. 4 shows the time dependence of the thickness of intermetallic layers in couples annealed at 500 °C with 10 A current.

It is well known that at a given temperature the dependence of the thickness of an intermetallic layer on diffusion time can be described by the following empirical formula [30]:

$$\Delta x = k' t^n \tag{2}$$

or(3)$\ln \Delta x = n \ln t + \ln k'$where Δx is the thickness of the intermetallic layer, k' the rate constant, t the diffusion time, and n the kinetic exponent.

The thickness of intermetallic layer (Δx) and the annealing time (t) were measured in this work and their relationship can be expressed as:

$$\Delta x^2 = kt \tag{4}$$

k is independently evaluated by a least-squares method from the corresponding experimental points in Fig. 4.

Fig. 5 presents the temperature dependence of the growth rate constants of the whole interfacial layer, where the linear relationship is gained between the logarithmic values of the rate constant and the reciprocal of absolute temperature. Usually, the growth rate of intermetallic layer is represented by a simple Arrhenius-type of relationship:

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{5}$$

where A is the frequency factor, E the apparent activation energy for the growth of intermetallic layer, R the gas constant and T the absolute temperature. From the temperature dependence of the growth rate constants, the values of the frequency factor (A) and the apparent activation energy (E) for the growth of intermetallic layer with and/or without the current were determined from the intercept (I) and slope (S) of the curves as shown in Fig. 5. The results for the whole interfacial layer are presented in Table 1.

k_0 and k_I represent the growth rate constants of the whole interfacial layer without and with the passage of 10 A current flowing

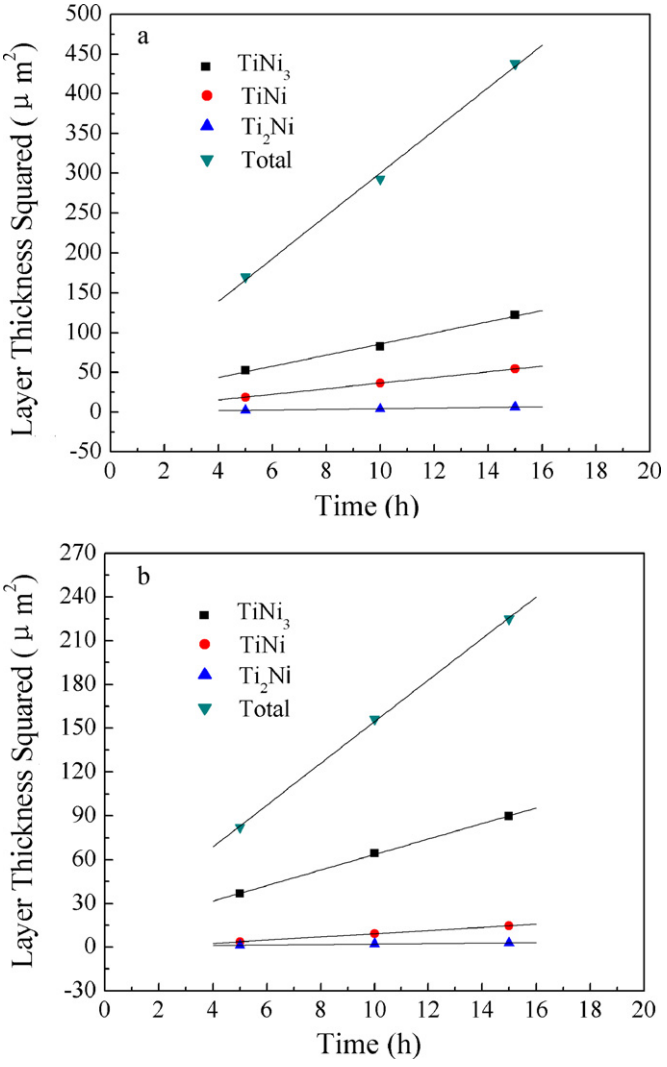

Fig. 4. Time dependence of the thickness of intermetallic layers under 500 °C/10 A. (a) Ti end connected to anode; (b) Ni end connected to anode.

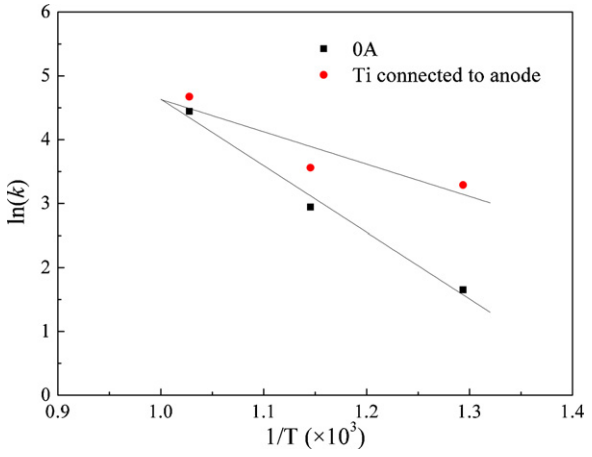

Fig. 5. Temperature dependence of growth rate constant of the whole interfacial layer.

Table 1
The frequency factor (A) and the apparent activation energy (E) for the growth of whole interfacial layer under different conditions.

Condition	I	S	A ($\mu m^2/s$)	E (kJ/mol)
0 A	14.26	1.01×10^4	1.55×10^6	83.76
10 A (Ti end connected to anode)	9.69	5.07×10^3	1.62×10^4	42.11

from Ti to Ni end, respectively, and they could be expressed as:

$$k_0 = 1.55 \times 10^6 \cdot \exp\left(-\frac{83.76 \times 10^3}{RT}\right); \quad (6)$$

$$k_I = 1.62 \times 10^4 \cdot \exp\left(-\frac{42.11 \times 10^3}{RT}\right); \quad (7)$$

From Table 1 it is known that the growth activation energy of the whole interfacial layer decreases greatly by 50% in the couples annealed by heating and the current of 10 A simultaneously compared with those annealed only by heating. The drop of the activation energy is beneficial to the growth of intermetallic layers, so that the intermetallic layer becomes wider in the couple annealed by heating and current together.

According to the results of this work, the effect of current on the growth of intermetallic phases for Ti–Ni couple should be confirmed though its mechanisms are blurry now. For a Ti–Ni couple, the current, flowing in both directions, may increase the concentration [28] and the mobility [29] of defects, which plays a main role in promoting the growth of intermetallic layers. The current's electromigration effect, which varies with the direction of the current, may accordingly slow or accelerate the growth of intermetallic layers, and it plays the secondary role. The current's electromigration effect and the defects act simultaneously, and consequently the current flowing in both directions can promote the growth of intermetallic layers in different degrees. Further investigations are needed to be carried out.

4. Conclusions

In this paper, the co-effect of heat and direct current on growth of $TiNi_3$, TiNi and Ti_2Ni intermetallic layer at the interface of Ti–Ni diffusion couples has been investigated, the following conclusions can be made:

(1) The current accelerates the growth of $TiNi_3$ and TiNi layer; Ti_2Ni layer becomes narrow due to the reactive formation of TiNi layer, and the effect of current on the growth of Ti_2Ni layer needs further investigations.
(2) The growth of whole interfacial layer has a parabolic relationship with time when heating with/without the current. The growth rate constant of the whole interfacial layer satisfies the Arrhenius-type relationship.
(3) The current could decrease the growth activation energy of the whole interfacial layer. With a current of 10 A flowing from Ti to Ni end, the growth activation energy of the whole interfacial layer in Ti–Ni couple is 42.11 kJ/mol, but it increases to 83.76 kJ/mol in the couple treated without the current.
(4) The interchange of the current direction changes the growth rate of intermetallic layers. The current flowing from Ti end to Ni end may promote the growth of intermetallic layer greatly.

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