Interfacial reaction of infrared brazed NiAl/Al/NiAl and Ni₃Al/Al/Ni₃Al joints

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Received 1 December 2000; accepted 24 January 2001

Abstract

The early-stage microstructural evolution of NiAl/Al/NiAl and Ni₃Al/Al/Ni₃Al in temperature ranges between 800 and 1200°C for 2–290 s was studied by infrared brazing. Al₃Ni phase is firstly formed in both Al-rich melt and the interface between nickel aluminide base material and Al-rich melt for specimens brazing at 800°C. The solid-state interdiffusion between Al₃Ni and base material results in the formation of the interfacial Al₃Ni₂ phase, and further growth of Al₃Ni₂ phase at 800°C is impeded by the Al₃Ni interlayer due to its stoichiometry. For specimens brazing at 1000°C, the reaction changes from hypereutectic into peritectic reaction. The Al-rich melt dissolves more Ni atoms with the increment of brazing temperature to 1000°C. The Al₃Ni₂ phase is now initially formed in both the Al-rich melt and joint interface. The growth of Al₃Ni₂ interlayer at 1000°C is much faster than that at 800°C. Transport of Al atoms in forming Al₃Ni₂ phase at 1000°C is greatly increased due to the contact between Al₃Ni₂ and liquid Al-rich melt. The Al₃Ni shown in the joint is formed upon cooling cycle of the infrared brazing. The microstructural evolution in Ni₃Al/Al/Ni₃Al joint is similar to that in NiAl/Al/NiAl except for the formation of NiAl phase between Al₃Ni₂ and Ni₃Al. It can also be attributed to the solid-state interdiffusion between Ni₃Al and Al₃Ni₂ interlayer. However, the intermediate phase Ni₅Al₃, which is stable below 700°C, is not found in the experiment. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Intermetallics, miscellaneous; D. Microstructure

1. Introduction

With ever increasing demand of materials with better performance in both creep strength and oxidation resistance, great attention has been focused in developing nickel aluminides, including NiAl and Ni₃Al. Meanwhile, many interfacial reactions with various Al–Ni intermediate phases, such as Al/Ni [1–8], Al/Ni₃Al [9–11], Al/NiAl [12] and Ni₃Al/NiAl [13], have been extensively studied. Most researches were focused on temperatures below the melting point of pure aluminum, 660°C. Therefore, solid-state diffusion dominated the reaction kinetics in the joint. Some experiments were performed at temperatures between 660 and 800°C, so the liquid diffusion of aluminum played an important role in the process [8,9]. In addition to the change of microstructure

in the joint, a much faster reaction rate was expected if liquid diffusion was involved in the experiment.

Infrared brazing makes use of infrared energy generated by heating a tungsten filament in a quartz tube as the heating source, providing rapid heating and cooling up to 3000°C/min; therefore, infrared brazing is highly suitable in studying the mechanism of early-stage reaction kinetics in the joint [14–16]. With the aid of accurate thermal cycle control, the transient microstructural evolution of the brazed joint can easily be unveiled by this technique. According to the Al–Ni binary alloy phase diagram, two peritectic reactions can be found at 854 and 1133°C [17]. The brazing of NiAl/Al/NiAl and Ni₃Al/Al/Ni₃Al at 800, 1000 and 1200°C may result in different reaction kinetics. The purpose of this study is infrared brazing two nickel aluminides, NiAl/Al/NiAl and Ni₃Al/Al/Ni₃Al, in the temperature range between 800 and 1200°C. With the aid of a fast infrared heating rate, the early-stage of reaction paths in brazing nickel aluminides will be studied.

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2. Experimental procedures

Two-nickel aluminides, Ni–50.0 at.% Al and Ni–24.0 at.% Al–500 ppm B, were used as base material. Master alloys were prepared by melting pure metal pellets in an induction furnace with Ar protected atmosphere, followed by 1200°C×50 h homogenization treatments. The homogenized NiAl and Ni₃Al ingots were subsequently cut into approximate 10×8×3 mm specimens. All joined surfaces were polished by SiC paper up to grit 600 before infrared brazing. Pure aluminum foils (99.997 wt.%) with 100 μm in thickness and approximately the same size as the base metal were used as filler metal. The aluminum foil was sandwiched between the above two base metals. Both the base metal and aluminum foil were alternatively cleaned by an ultrasonic machine in acetone and ethyl alcohol solution prior to brazing.

There were two types of brazed joints, NiAl/Al/NiAl and Ni₃Al/Al/Ni₃Al, performed in the study. To enhance the absorptivity of brazing specimens to the infrared rays, all specimens were clamped between two graphite plates, and a thermocouple was in contact with the brazing specimen. An ULVAC SINKO-RIKO RHL-P610C infrared furnace with the heating rate of 3000°C/min and Ar atmosphere was used throughout the experiment. Table 1 summaries all process variables used in the study. There is a time delay between the actual specimen temperature and programmer temperature. Based on the data of temperature recorder, there are two time periods including heating and holding time shown in the table. The brazing time specified in the following paragraphs is the actual specimen holding time in the experiment.

The brazed specimens were cut by a low speed diamond saw. Their cross-section were first ground by SiC papers, and subsequently polished by 0.3 μm alumina powder. The polished cross section of the brazed specimens was examined using a Philips XL30 scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS). Quantitative chemical analysis was performed using a JEOL JXA-8600SX

electron probe microanalyzer (EPMA) equipped with a wavelength dispersive spectrometer (WDS).

3. Results and discussion

3.1. Microstructural evolution of the infrared brazed NiAl/Al/NiAl

Fig. 1(a)–(c) shows backscattered electron images (BEIs) of NiAl/Al/NiAl specimens brazed at 800°C×2 s, 1000°C×16 s, and 1200°C×2 s, respectively. Two EPMA line scan profiles indicating Ni (upper line scan) and Al (lower line scan) are also included in the figure. Based on the EPMA quantitative chemical analysis, four phases can be identified in the joint. They are Al-rich, Al₃Ni, Al₃Ni₂ and NiAl as displayed in Fig. 1. It can be noted that the microstructure of the brazed joint changes prominently as the brazing temperature increasing from 800 to 1000°C. A similar microstructure is observed as the brazing temperature increases from 1000 to 1200°C. To explain the microstructural evolution of the joint for different brazing temperatures, an Al–Ni binary alloy phase diagram is included in Fig. 2.

A few Al₃Ni islands are observed in Al-rich matrix as illustrated in Fig. 1(a), and it can be explained by the Al–Al₃Ni hypereutectic reaction at 800°C. Al₃Ni phase is initially formed in both the Al-rich melt and the interface between NiAl and Al-rich melt. According to the Al–Ni binary alloy phase diagram, the liquid melt is not in contact with Al₃Ni₂ phase, so there is no Al₃Ni₂ phase at the beginning of the reaction [17,18]. However, the solid state interdiffusion between Al₃Ni and NiAl interface results in the formation of Al₃Ni₂ phase, and there is no Al₃Ni₂ phase around Al₃Ni islands in the Al-rich melt. Consequently, different formation mechanism can be expected in forming Al₃Ni₂ and Al₃Ni phase. The formation of Al₃Ni₂ phase at the interface must be followed by the formation of Al₃Ni phase. There is no contact between the Al₃Ni₂ phase and Al-rich melt as displayed in Fig. 1(a). With increasing brazing time from 2 to 20 s at 800°C, Al₃Ni islands in the Al-rich melt, Al₃Ni and Al₃Ni₂ phases at the interface grow steadily, as shown in Figs. 1(a) and 3(a). However, both Al-rich melt and Al₃Ni islands are consumed if further extending the brazing time to 290 s at 800°C [Fig. 3(b)]. The continuous growth of the Al₃Ni₂ phase at the interface between Al₃Ni and NiAl is observed in the experiment. It indicates that the Al₃Ni₂ phase is more stable than Al₃Ni phase in the NiAl/Al/NiAl brazing.

As the brazing temperature increases from 800 to 1000°C, the reaction changes from hypereutectic into peritectic reaction as demonstrated in Fig. 2. In such a case, the Al-rich melt dissolves more Ni atoms as increasing brazing temperature to 1000°C. Contrary to the previous case, the Al₃Ni₂ phase is firstly formed in both the

Table 1
Process variables used in infrared brazing two-nickel aluminides

	NiAl/Al/NiAl (heating + holding)	Ni ₃ Al/Al/Ni ₃ Al (heating + holding)
800°C	25 + 2 s 25 + 20 s 25 + 290 s	25 + 2 s 25 + 20 s 25 + 110 s
1000°C	30 + 6 s 30 + 16 s 30 + 46 s 30 + 96 s	30 + 2 s 30 + 16 s 30 + 96 s
1200°C	49 + 2 s	–

(a)

(b)

(c)

Fig. 1. Backscattered electron images (BEIs) and EPMA line-scanning profiles of the NiAl/Al/NiAl specimens: (a) 800°C×2 s, (b) 1000°C×16 s, (c) 1200°C×2 s (a, b, c and d represent Al-rich, Al₃Ni₂, Al₃Ni₂, and NiAl phases, respectively).

Al-rich melt and joint interface. Moreover, the growth of Al₃Ni₂ at the bonding interface is much more prominent than that of Al₃Ni₂ in Al-rich melt as shown in

Fig. 1(b). The transport of Ni atoms are impeded by the thick Al₃Ni₂ phase at interface, so the growth rate of Al₃Ni₂ phase at the interface is much faster than that at Al-melt. It is also observed that the growth of interfacial Al₃Ni₂ at 1000°C is much faster than that at 800°C, as compared between Fig. 1(b) and Fig. 3(a). As discussed earlier, the formation of Al₃Ni₂ phase at 800°C is caused by solid-state interdiffusion of reacting elements, Al and Ni. It is expected that the transport of Al atoms in forming Al₃Ni₂ phase at 1000°C is expedited by the contact between Al₃Ni₂ and liquid Al-rich melt.

The Al₃Ni phase shown in Fig. 1(b) is formed upon the cooling cycle of infrared brazing. When the melt cools down to peritectic reaction at 854°C, the peritectic reaction will be proceeded as below.

This can explain that some Al₃Ni₂ islands are enclosed by Al₃Ni phase as shown in Fig. 1(b). Since the formation of Al₃Ni solely depends upon cooling cycle of brazing, the size of Al₃Ni remains nearly the same as the brazing time increases from 6 s to 46 s, as illustrated in Fig. 4 (a) and (b). Consequently, the formation of Al₃Ni phase during the cooling cycle can be supported by both the microstructural observation and the Al–Ni binary phase diagram. Based on Fig. 4(c), it is noted that the formation of Al₃Ni₂ phase consumes almost all Al-rich melt in the joint at 1000°C for 96 s.

As the brazing temperature further increases to 1200°C, the microstructure of the joint is continuously changed. Based upon Al–Ni binary phase diagram, NiAl should be the first phase formed in the melt at 1200°C. However, the Al-rich melt contains insufficient Ni atoms to form NiAl. Because the Ni concentration in the melt is lower than 50 at.%, there is no possibility to form NiAl in the melt. This is consistent with the microstructural observation in the brazed joint as displayed in Fig. 1(c). There is no NiAl phase observed in the joint. However, the Ni atoms dissolved in Al-rich melt at 1200°C are much more prominent than those at 1000°C. Upon the subsequent cooling cycle, more Al₃Ni₂ and Al₃Ni phases in the joint are expected. In such a case, less Al-rich phase is obtained in the final microstructure as displayed in Fig. 1(c). The Al-rich melt experiences two peritectic reactions during the cooling cycle, and some Al₃Ni₂ are enclosed by Al₃Ni phase. Similarly, both Al₃Ni₂ and Al₃Ni phases forms upon cooling cycle, so it is expected that the volume fraction of these phases is independent of brazing time. This is able to explain why the interfacial thickness of Al₃Ni₂ brazed at 1200°C for 2 s is not thicker than that brazed at 1000°C for 16 s as compared between Fig. 1(b) and (c). The interfacial Al₃Ni₂ phase will grow at 1000°C, but it is not formed yet at 1200°C.

Fig. 2. Al–Ni binary alloy phase diagram [17].

3.2. Microstructural evolution of infrared brazed Ni₃Al/Al/Ni₃Al

Fig. 5 shows the cross-section of an Ni₃Al/Al/Ni₃Al joint after brazing at 800°C with various time periods. It is noted that part of the Al₃Ni phase is fractured, and it could be caused by grinding process before metallographic observation. The microstructure of Ni₃Al/Al/Ni₃Al brazed at 800°C is similar to that of NiAl/Al/NiAl brazed joint except coarser Al₃Ni and Al₃Ni₂ phases in the joint. Since Ni₃Al base material contains more Ni than NiAl base material, the melt can easily dissolve more Ni atoms from Ni₃Al during infrared brazing. The Al₃Ni phase is firstly formed in both melt and interface during brazing, and the Al₃Ni₂ phase can also be observed at the interface between Ni₃Al and Al₃Ni phase. Similarly, the Al₃Ni₂ phase is formed by solid-state interdiffusion between Al₃Ni and Ni₃Al substrate. With the increment of brazing time, the interfacial Al₃Ni₂ phase grows constantly; the volume fraction of Al-rich melt is decreasing after brazing as illustrated in Fig. 5. The consumption of Al atoms in the melt results in growth of Al₃Ni₂ phase at the interface. As discussed earlier, the Al₃Ni₂ phase is more stable than Al₃Ni in Ni₃Al/Al/Ni₃Al joint according to the experiment.

Fig. 6 shows the microstructure of the infrared brazed joint at 1000°C for 2, 16 and 96 s, respectively. As the brazing temperature increases to 1000°C, Al₃Ni₂ is the first phase precipitated from the Al-rich melts. Meanwhile, the Al₃Ni₂ phase is also formed at the bonding interface, and grows continuously with the brazing time

increasing. The Al₃Ni phase is formed upon cooling cycle of brazing. Therefore, the volume fraction of Al₃Ni phase in the joint is not depended upon brazing time only. The consumption of Al in the melt is caused by formation of Al₃Ni₂ phase. The Al-rich melt is almost completely depleted for the specimen brazed at 96 s, and no Al₃Ni phase in the joint after brazing as shown in Fig. 6(c). The intermediate phase NiAl, with a composition between Al₃Ni₂ and Ni₃Al, is not observed until the brazing time increases to 96 s at 1000°C as shown in Fig. 6(c). As discussed earlier, the formation of NiAl can be attributed to the solid-state interdiffusion between Al₃Ni₂ and Ni₃Al interlayer. It is expected that more incubation time is necessary due to the slow solid-state interdiffusion of the reacting elements. This is consistent with the result of other researches performed at lower temperatures [3,9,11,12]. However, the intermediate phase Ni₅Al₃, which is stable below 700°C, is not found in the experiment.

3.3. The growth of Al₃Ni₂ interlayer during the infrared brazing

Based upon previous discussions, the reaction mechanism in both Al₃Ni and Al₃Ni₂ phases is different as the brazing temperature changes from 800 to 1000°C. The Al₃Ni phase is developed upon cooling cycle at 1000°C infrared brazing, and it is formed during 800°C brazing. According to the experiment, the Al₃Ni phase is less stable than Al₃Ni₂ phase in both NiAl/Al/NiAl and Ni₃Al/Al/Ni₃Al joints. The microstructure of the

(a)

(a)

(b)

(b)

Fig. 3. Interfaces of NiAl/Al/NiAl brazed at 800°C for (a) 20 s, (b) 290 s (a, b, c and d represent Al-rich, Al_3Ni , Al_3Ni_2 , and NiAl phases, respectively).

brazed joint is primarily dominated by Al_3Ni_2 phase for longer infrared brazing time, e.g. 96 or 290 s. Moreover, the formation mechanism of the Al_3Ni_2 interlayer may be different between 800 and 1000°C infrared brazing. The solid-state interdiffusion of Al and Ni atoms between Al_3Ni and substrate (NiAl or Ni_3Al) dominates the formation of Al_3Ni_2 phase at 800°C. Since the diameter of Al atom is smaller than that of Ni, it is reasonable that the diffusion of Al atoms is faster than that of Ni atoms. The formation of Al_3Ni_2 interlayer is then rate controlled by the diffusion Al atoms. According to the binary phase diagram shown in Fig. 2, Al_3Ni is a stoichiometric compound, and it can only dissolve very limited range of Al concentration. The flux of Al atoms from the Al-rich melt into the Al_3Ni_2 phase is, therefore, greatly impeded by the formation of Al_3Ni interlayer. Since the formation of a Al_3Ni interlayer can greatly deteriorate the transport of Al atoms, the growth of

(c)

Fig. 4. Interfaces of NiAl/Al/NiAl brazed at 1000°C for (a) 6 s, (b) 46 s, (c) 96 s (a, b, c and d represent Al-rich, Al_3Ni , Al_3Ni_2 , and NiAl phases, respectively).

interfacial Al_3Ni_2 phase at 800°C is much slower than that at 1000°C as compared between Fig. 1(b) and 2(a).

On the other hand, the mass transport of Al atoms in Al-rich melt into the Al_3Ni_2 phase at 1000°C is not

(a)

(a)

(b)

(b)

(c)

(c)

Fig. 5. Interfaces of $\text{Ni}_3\text{Al}/\text{Al}/\text{Ni}_3\text{Al}$ brazed at 800°C for (a) 2 s, (b) 20 s, (c) 110 s (a, b, c, d and e represent Al-rich, Al_3Ni , Al_3Ni_2 , NiAl and Ni_3Al phases, respectively).

limited by the Al_3Ni interlayer. The Al_3Ni_2 phase is a non-stoichiometric compound, and it can dissolve some range of Al concentration. Therefore, it is expected that the growth of Al_3Ni_2 phase at 1000°C is much faster than that at 800°C brazing. Fig. 7 shows the average of

Fig. 6. Interfaces of $\text{Ni}_3\text{Al}/\text{Al}/\text{Ni}_3\text{Al}$ brazed at 1000°C for (a) 2 s, (b) 16 s, (c) 96 s (a, b, c, d and e represent Al-rich, Al_3Ni , Al_3Ni_2 , NiAl and Ni_3Al phases, respectively).

interfacial thickness of Al_3Ni_2 phase for various brazing conditions. It demonstrates that the growth rate of the Al_3Ni_2 at 1000°C is about one order of magnitude larger than that at 800°C , and this is consistent with the previous discussion.

Fig. 7. The average thickness of Al_3Ni_2 interlayer for various infrared brazing process variables.

4. Conclusion

For specimens brazing at 800°C , the Al_3Ni phase is firstly formed in both the Al-rich melt and the interface between nickel aluminide base material and Al-rich melt. The solid state interdiffusion between Al_3Ni and base material results in the formation of the interfacial Al_3Ni_2 phase, and the growth of Al_3Ni_2 phase at 800°C is greatly impeded by the Al_3Ni interlayer due to its stoichiometry.

For specimens brazing at 1000°C , the reaction changes from hypereutectic into peritectic reaction. The Al-rich melt dissolves more Ni atoms with the increment of brazing temperature to 1000°C . The Al_3Ni_2 phase is now initially formed in both the aluminum melt and joint interface. The growth of Al_3Ni_2 interlayer at 1000°C is much faster than that at 800°C . Transport of Al atoms in forming Al_3Ni_2 phase at 1000°C is greatly increased due to the contact between Al_3Ni_2 and liquid Al-rich melt. There is no Al_3Ni interlayer to limit the growth of Al_3Ni_2 phase. The Al_3Ni phase shown in the joint is formed upon cooling cycle of the infrared brazing. The thickness of Al_3Ni_2 at 1000°C is about one order of magnitude larger than that at 800°C .

The microstructural evolution in $\text{Ni}_3\text{Al}/\text{Al}/\text{Ni}_3\text{Al}$ joint is similar to that in $\text{NiAl}/\text{Al}/\text{NiAl}$ except the formation of a NiAl interlayer between Al_3Ni_2 and Ni_3Al . It can be attributed to the solid-state interdiffusion between Ni_3Al and Al_3Ni_2 interlayer. However, the intermediate phase Ni_5Al_3 , which is stable below 700°C , is not found in the experiment.

Acknowledgements

The authors gratefully acknowledge the financial support of this research by the National Science Council (NSC), Republic of China under NSC Grants 88-2216-E149-002 and 88-2216-E002-026.

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