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PADDING, WELDING AND FREEFORM FABRICATION OF NICKEL ALUMINIDE INTERMETALLIC COMPOUND BY REACTIVE RAPID PROTOTYPING PROCESS

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A novel method for padding, welding and freeform fabrication of intermetallic alloys based on an exothermic synthesis reaction between powder and droplets is proposed, and its feasibility is examined using nickel monoaluminide, NiAl, as a demonstration material. In an experiment for NiAl padding on steel, a small amount of nickel powder was fed onto a steel surface, followed by supplying an aluminum droplet onto the powder. The nickel and aluminum exothermically reacted and produced a NiAl bead on the steel surface, bringing about strong bonding between the NiAl bead and the steel. In an experiment for welding of NiAl, when an aluminum droplet was dropped onto nickel powder fed into a root gap between two NiAl base metals, they exothermically reacted and produced a molten NiAl bead. The heat from the reaction melted the base metals near the interface with the molten NiAl bead. After solidification of the molten NiAl bead and the melted parts of the base metals, welding of the base metals was completed. In an experiment for freeform fabrication of NiAl, when an aluminum droplet was dropped onto a nickel powder bed, the two metals reacted and produced a small NiAl bead. When a next droplet was fallen to a position very close to the NiAl bead, a new NiAl bead was similarly produced and was bonded to the former one. By continuous dropping of aluminum droplets a two-dimensional structure of the NiAl beads was configured. After the two-dimensional structure was finished, nickel powder was added until it wholly covered the structure on the former plane, and then a new structure was similarly configured in the added nickel powder bed. The NiAl beads were bonded to each other in both horizontal and vertical directions. Finally, a three-dimensional structure was finished after repeating the addition of the powder and the supply of the droplet.

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1. Introduction

In the last few decades, many kinds of intermetallic compounds such as aluminides and silicides have been nominated as candidates for the advanced materials that may take the place of conventional superalloys. One of the most promising intermetallic compounds will be nickel monoaluminide, NiAl, which offers many advantages over conventional superalloys, such as higher melting point, lower density, greater specific modulus and higher thermal conductivity. However, it is reported that due to its poor ductility below approximately 800 K, joining of NiAl by a conventional fusion welding process is difficult. Therefore, in order to fully utilize NiAl in structural applications, joining methods appropriate to NiAl will be required.

Gale and Orel studied joining between NiAl blocks by the transient liquid phase (TLP) bonding using a nickel-silicon-boron ternary eutectic alloy foil as the interlayer material. The TLP bonding has an advantage that the composition of the interlayer material changes into that of the base metal by diffusion. On the other hand, it also has a disadvantage that it requires a long processing time at a high temperature, 72 hours at 1338 K, for example. Utilization of heat generation for joining is a major advantage of their method. On the other hand, the most significant disadvantage will be a difficulty of controlling the reaction temperature and hence the temperature of the reaction product of NiAl, owing to the use of the powder mixture where the SHS reaction always starts when a liquid phase appears. The temperature of the reaction product is one of the most important processing parameters in the reactive joining method.

In this study, we propose a new reactive joining method where the temperature of the reaction product can be controlled, and we apply it to padding, welding and freeform fabrication of intermetallic compounds.

2. Method

2.1 Principle

Figure 1 shows a schematic illustration of the present methods for (a) padding, (b) welding and (c) freeform fabrication of intermetallic compounds, using NiAl as a demonstration material. In the case of padding, as shown in Fig. 1(a), aluminum droplets are continuously supplied onto nickel powder fed onto a base metal. When an aluminum droplet reaches the nickel powder, a molten NiAl bead is produced by an exothermic reaction, Ni + Al → NiAl. The molten NiAl bead immediately solidifies and is bonded to the neighboring beads and also to the base metal. A plane made of the beads finally coats...
the base metal. By using the CAD/CAM files through the computer, the positions of the nozzles, their moving speeds and the temperatures and feeding rates of the materials can be controlled.

This method can be applied to welding, as shown in Fig. 1(b). Aluminum droplets are supplied onto nickel powder fed into the root gap between the two base metals. When a molten NiAl bead is produced, the heat from the bead melts the base metals near the interfaces with the molten NiAl bead. After solidification of the molten NiAl bead and the melted parts of the base metals, the bead joins the two base metals together.

Figure 1(c) shows a schematic illustration of freeform fabrication of NiAl. Aluminum droplets are supplied onto a nickel powder bed. When an aluminum droplet reaches the nickel powder bed, the two metals exothermically react and produce a molten NiAl bead, which immediately solidifies into a small bead. When the next droplet falls to a position very close to the former NiAl bead, a new NiAl bead is similarly produced and is bonded to the former one. After a two-dimensional structure is finished, the nickel powder is fed on the structure, and the aluminum droplets are similarly supplied onto the nickel powder to form the next structure. The NiAl beads are bonded to each other in both horizontal and vertical directions. Finally, a three-dimensional structure is finished after repeating the feeding of the powder and droplets.

To examine the feasibility of each process of the padding, welding, and freeform fabrication, simple experiments were performed.

### 2.2 Experimental

Figure 2 shows a schematic illustration of the experimental procedure. All the equipments shown in the figure were placed in a chamber filled with argon of five-nine purity. Aluminum blocks of 99.9% in purity were melted in a graphite vessel. After holding the molten aluminum for 5 min at a temperature between 1173 K and 1473 K, a droplet of the molten aluminum was dropped.

In the padding (Fig. 2(a)), the aluminum droplet was dropped onto the nickel powder of 99.8% in purity and 45 µm in diameter placed on a base metal of 2 mm in thickness. A stainless steel of SUS 316 L, a nickel-base superalloy of Inconel #600 and an intermetallic compound of NiAl were used as the base metal. The initial temperatures of the nickel powder and the base metal were same and were varied from 773 to 1473 K. The weights of the nickel powder and the aluminum droplet were 1.52 g and 0.70 g, respectively, which corresponds to a molar ratio of 1 to 1.

In the welding (Fig. 2(b)), two NiAl plates of 4 mm in thickness were placed apart from each other, making a root gap between them. The NiAl plates were prepared from an ingot made by the reactive casting method. Nickel powder was heaped up in the root gap, and then an aluminum droplet was supplied onto it. The initial temperatures of the nickel powder and the NiAl plates were same and were varied from 1373 to 1473 K. The root gap was varied from 2 to 3 mm. The weights of the nickel powder and the aluminum droplet were same as those for the padding experiment.

In the freeform fabrication (Fig. 2(c)), aluminum droplets of 37 mg and 1173 K were supplied one after another onto a nickel powder bed of 773 K. Aluminum droplets were dropped close to the former ones.

### 3. Results and Discussion

#### 3.1 Maximum temperature of NiAl synthesized

To succeed fully in padding, welding and freeform fabrication of NiAl, strong joint between the NiAl bead and the base metal or between the NiAl beads is necessary, and therefore, it is essential that the contact surfaces of them should be melted by the heat generated from the exothermic reaction of the NiAl synthesis. To melt the surface of the adjacent NiAl bead, the maximum temperature of the NiAl synthesized must exceed at least the melting point of NiAl, 1911 K. The maximum temperature of the NiAl synthesized can be calculated from the heat of formation of NiAl and the initial temperatures of the aluminum droplets and nickel powder. The results of the calculation are shown in Fig. 3. Lines in the figure show the
relationships between the initial temperature of aluminum and the maximum temperature of the NiAl synthesized for several initial temperatures of nickel. The calculated results show that liquid NiAl of approximately 2200 to 2800 K, which are much higher than the melting point of NiAl, can be produced by the reaction between liquid aluminum and solid nickel. Thus, it was predicted that the exothermic reaction between aluminum liquid and nickel powder could generate sufficient heat to melt the surface of the base metal or the adjacent NiAl beads. However, the calculations were carried out under a simplified condition of the adiabatic one. Therefore, the feasibility of the padding, welding and freeform fabrication was investigated by performing simple experiments, and the results are described below.

3.2 Padding
3.2.1 Effect of initial temperature on reactivity

Figure 4 shows (a) the appearance and (b) the cross section of a padded sample produced under a condition that the initial temperature of the aluminum droplet was 1273 K and the initial temperatures of both the nickel powder and the base metal were 773 K. The base metal was SUS 316L stainless steel. In Fig. 4(a), a bead of approximately 10 mm in diameter was formed on the base metal. However, the reaction between aluminum and nickel seems to be uncompleted, because in Fig. 4(b) the structure of the bead is divided into some parts having different contrasts, indicating that the bead consists of some different phases. In Fig. 5, an EPMA analysis performed on the line AB drawn in Fig. 4(b) reveals that the bead consists of $\gamma$-Ni, Ni$_3$Al, Ni$_5$Al$_3$, NiAl, Ni$_2$Al$_3$ and NiAl$_3$ phases, which indicates that the reaction between the aluminum droplet and the nickel powder was not finished completely. Those phases of the solid solution and intermetallic compounds were identified from their chemical compositions based on a nickel-aluminum equilibrium phase diagram.\(^{(14)}\)

The calculation under the adiabatic condition predicted that the temperature of the NiAl synthesized would reach approximately 2400 K. However, the results shown in Figs. 4 and 5 indicate that the temperature of the reaction products did not reach even the melting point of NiAl, 1911 K, which is the highest melting point in nickel-aluminum binary system, because many intermetallic phases including the reactant material existed in the bead. Those intermetallic phases are considered to be the intermediate products that appear in the process of the NiAl synthesis from nickel and aluminum. It was suggested that heat absorption by the base metal prevented the self-propagating exothermic reaction of NiAl synthesis from continuing to the end. Therefore, the initial temperatures were raised by 100 K and a similar experiment was performed.

Figure 6 shows (a) the appearance and (b) the cross section of a padded sample produced under a condition that the initial temperature of the aluminum droplet was 1373 K and both the initial temperatures of the nickel powder and the base metal were 873 K. In Fig. 6(b), the contrast of the structure on
the cross section of the bead seems monotone, which is different from the structure in Fig. 4(b). Figure 7 shows the results of an EPMA analysis performed on the line AB drawn in Fig. 6(b). The concentrations of aluminum and nickel in the bead are both approximately 50 mol%, which indicates that the bead has the stoichiometric composition of NiAl. The interface between the bead and the base metal is 0.2 mm away from the initial position into the base metal, which indicates that the heat generated from the reaction melted the surface of the base metal by this depth. The melting of the surface of the base metal will promote the bonding at the interface.

### 3.2.2 NiAl padding of Inconel and NiAl

Figure 8 shows cross sections of padded samples produced using (a) Inconel #600 and (b) NiAl as the base metal. For the sample shown in Fig. 8(a) the initial temperatures of the aluminum droplet, nickel powder and base metal were all 1273 K, while for the sample shown in Fig. 8(b) the initial temperatures were all 1473 K. The beads of approximately 10 mm in diameter are bonded to the base metals in both figures. Therefore, this padding technique can be applied also to base metals of nickel-base superalloys and NiAl.

### 3.3 Welding

#### 3.3.1 Effect of initial temperature on reactivity

Figure 9 shows a cross section of a welded sample produced under a condition that the initial temperatures of the aluminum droplet, nickel powder and base metals were all 1373 K, and the root gap was 2 mm. The base metals were NiAl. In Fig. 9, the structure of the bead is divided into some parts having different contrasts, indicating that the aluminum droplet and the nickel powder did not react completely. Figure 10 shows a microstructure of the sample shown in Fig. 9 at a higher magnification. The corner of the left base metal was not melted, indicating that the base metals were not welded successfully. The structure of the bead is divided into three parts: (i) the upper part consisting of Al, NiAl$_3$ and Ni$_2$Al$_3$, (ii) the middle part consisting of Ni$_5$Al$_3$ and Ni$_3$Al, and (iii) the lower part consisting of Ni. A thin NiAl layer of 50 µm in thickness is recognized between the upper and the middle parts.
Fig. 9 Photograph of a cross section of a welded sample. The initial temperatures of the Al droplet, Ni powder and base metal were all 1373 K. The root gap was 2 mm.

Fig. 10 SEM image of the sample shown in Fig. 9. The calculation based on the adiabatic condition predicts that the temperature of the NiAl produced from nickel and aluminum of 1373 K in initial temperatures reaches approximately 2700 K, which is much higher than the melting point of NiAl. However, a NiAl bead was not produced in the practical experiment. It was again suggested that the heat absorption by the base metals canceled the exothermic reaction of NiAl synthesis. Therefore, the initial temperatures were raised by 100 K to promote the reaction, and a similar experiment was performed.

Figure 11 shows a cross section of a welded sample produced under a condition that the initial temperatures of the aluminum droplet, nickel powder and base metals were all 1473 K, and a root gap was 2 mm. The reaction seems to have proceeded well compared with the photograph shown in Fig. 9, except for the part in the root gap. To investigate more detailed structure in this part, a SEM image was taken and is shown in Fig. 12. The corners of the base metals are melted in this case. An EPMA analysis for this sample revealed that the bead consisted of NiAl in a large region indicated as (i) in the figure and that the rest part of the bead consisted of Ni$_5$Al$_3$ and Ni$_3$Al in region (ii), and Al, NiAl$_3$ and Ni$_2$Al$_3$ in region (iii). We considered that the reason why even the unreacted phase was remained in the root gap was that the heat generation from the reaction was smaller than the heat absorption by the base metals. Therefore, we increased the root gap from 2 to 3 mm in the next experiment to increase the mass of the reactants.

3.3.2 Effect of root gap on reactivity

Figure 13 shows a cross section of a welded sample under a condition that the initial temperatures of the aluminum droplet, nickel powder and base metals were all 1473 K, while the root gap was 3 mm. The contrast of the bead is uniform, indicating that the aluminum droplet and the nickel powder reacted completely. To investigate more detailed structure of the bead, a microstructure of the sample is shown in Fig. 14 at a higher magnification. The interfaces between the bead and the base metals cannot be recognized very clearly, which means that the two base metals were successfully welded. An EPMA analysis on the line AB drawn in Fig. 14 is shown in Fig. 15. The EPMA analysis reveals that the stoichiometric NiAl bead was produced and the NiAl bead welded the two NiAl base metals.

3.4 Freeform fabrication

Figure 16 shows a product of the freeform fabrication. Many beads were bonded to form a T-bar. Figure 17 shows the joint interface between two NiAl beads. An EPMA analysis for this part revealed that the upper region consisted of nickel-rich NiAl, while the lower region consisted...
of aluminum-rich NiAl. No defects such as porosity exist at the joint interface. These results show that the beads were well bonded together. The study on the process control for the freeform fabrication of nickel aluminides is reported elsewhere.15)

4. Conclusions

New techniques for padding, welding, freeform fabrication of aluminide intermetallics utilizing an SHS reaction between...
droplets and powder were proposed, and their feasibility was investigated by simple experiments using NiAl as a demonstration material. The results are summarized as follows.

1) When an aluminum droplet of 0.70 g in weight and 1373 K in temperature was dropped onto nickel powder of 1.52 g and 873 K on a base metal of SUS 316L stainless steel of 2 mm in thickness, they exothermically reacted and produced a molten NiAl bead. The heat generated from the exothermic reaction of NiAl synthesis melted the surface of the base metal contacting the molten NiAl bead, and after solidification of the molten NiAl bead and the melted part of the base metal the NiAl bead was bonded to the base metal.

2) When an aluminum droplet of 0.70 g and 1473 K was dropped onto nickel powder of 1.52 g and 1473 K in a root gap of 3 mm between two NiAl plates of 4 mm in thickness, they exothermically reacted and produced a molten NiAl bead. The base metals near the interface with the molten NiAl bead were melted and the NiAl bead welded the base metals.

3) When an aluminum droplet of 1173 K was dropped onto a nickel powder bed of 773 K, they exothermically reacted and produced a molten NiAl bead, which solidified into a small bead. When a next aluminum droplet was dropped onto a position very close to the former one, a new bead was similarly produced and was bonded to the former one. After repeating the supply of the droplet and the addition of the powder, a three-dimensional structure was finished.

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