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Thermal conductivity of Ni-Al powder compacts for reaction synthesis

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Abstract

Thermal conductivity of 3Ni–1Al elemental powder compacts was measured using a laser-flash method as a function of temperature, compact density and heat treatment. Temperature dependence of thermal conductivity of the compacts is similar to that of pure Ni and Al metals. Heat treatment has a significant effect on the thermal conductivity of the compacts as particles are joined together to form Ni solid solution and intermetallic phases on powder surfaces. Fast diffusion on powder surfaces during heat treatment results in the formation of intermetallic phase zones in the interior of the former Ni particles. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Reaction synthesis has recently been studied by many researchers as a novel processing technique for fabrication of high temperature ordered intermetallic alloys from elemental powders [1–3]. This technique has advantages over conventional ingot metallurgy in achieving alloy homogeneity, near net shape, and no contamination from crucibles, resulting in cost and energy savings. The reaction sustains itself with heat generated by forming intermediate phases through interdiffusion processes, and it is, therefore, called self-sustaining high-temperature synthesis (SHS). The heat generation and transfer are key factors controlling the degree of reaction evolution.

In a previous study, it was shown that the initiation of reaction synthesis in 3Ni–1Al mixed powder compacts is strongly affected by initial compact thickness [4]. Full or partial reaction was observed in the specimens having a thickness of 7–6 mm within a few minutes when heated to 620°C; however, such SHS was not observed in a 5 mm thick Ni-Al mixed powder compact even after 1.8 ks at 620°C. Note that all the tests were under a uni-axial compressive stress of about 10 MPa. It is believed that the accumulation and transfer of the heat generated by the formation of intermetallic phases are sensitive to the specimen thickness and can be predicted by modeling.

For the modeling the rate of heat generation can be estimated through the formation rate of intermediate phases in terms of bulk diffusion, whereas the heat transfer is controlled by thermal conductivity [5,6]. Some of physical properties required for understanding and predicting the SHS process have been compiled and listed in the literature, but other information is quite limited [7–13]. Among them available data on the thermal conductivity of intermetallics and those of mixed powder compacts are very limited, which are important for understanding the evolution of reaction synthesis. Although a few equations have been proposed to estimate the thermal conductivity of porous materials, it would be much better if the thermal conductivity can be directly measured from experiments. The thermal conductivity of powder compacts is expected to be affected

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by many factors such as powder size and their distributions, mole fraction of substances, material purity, particle surface condition, particle shape, mixing condition, and deformation of powders during compaction [14]. Moreover, a formation of low-thermal conductivity intermediate phases during reaction synthesis may also affect the thermal conductivity of compacts.

In this study, the effects of heat treatment, test temperature, material density, and formation of intermediate phases on the thermal conductivity of elemental powder compacts with a nominal composition of 75Ni–25Al in mole fraction are investigated using a laser-flash method.

2. Experimental procedures

A powder mixture which contains 75Ni–25Al in mole fraction was prepared from these elemental powders by milling with Al_2O_3 balls. Ni and Al elemental powders used previously [4,15] had an average particle size of approximately 5 and 15 μm, respectively.

In order to investigate the effect of relative density and temperature on the thermal conductivity, two groups of powder compacts were prepared. Disc specimens of 25 mm in diameter and 2 mm in thickness were shaped by applying a uni-axial stress of about 140 or 350 MPa. Loading time of a few minutes was used in order to achieve a preset compact density. The powder samples were then compacted to a density, relative to the bulk Ni_3Al, of 60% at an applied stress of 140 MPa, and 72% at 350 MPa. These values will be referred to as "nominal" relative density for each group of compact samples.

The effect of heat treatment on the thermal conductivity of compact samples with a relative density of 60%, produced by 140 MPa, was studied. In the previous work, powder compacts were heated to a temperature of 620°C, just below the melting point of Al, for several minutes for SHS initiation [4]. In the present study heat treatments were conducted at 400°C in order to avoid SHS for 48 or 1000 h in an evacuated quartz tube.

The microstructure of heat-treated specimen was observed using a scanning electron microscopy (SEM) operated at 20 kV and compositional analysis was conducted by an energy dispersive X-ray spectroscopy (EDS) equipped on the SEM. Thermal conductivities of these specimens were measured by a laser-flash method. Details of the method were described elsewhere [16].

3. Results and discussion

3.1. Thermal conductivity of powder compacts

Fig. 1 compares the temperature dependence of the thermal conductivity of powder compacts with 72 or 60% relative density with that of pure Ni and Al metals obtained from the literature [10]. The thermal conductivity for each group of compact samples is lower than those of the metals, however, their temperature dependences are quite similar. The temperature dependence of the thermal conductivity of the compacts can thus be attributed to those of elemental materials. This similarity suggests that the thermal conductivity at high temperature region can be estimated from the data at ambient temperature.

The effect of relative density on the thermal conductivity of powder compacts without heat treatment is shown as open symbols in Fig. 2. As can be expected, the compact with a higher density has a higher thermal conductivity. In this figure, several curves are calculated based on the equation proposed by Russell [17] to predict the thermal conductivity of pure Ni or Al powder compacts under different assumptions. In one case where voids with the same size are separated by solid walls, referred as the isolated-void model, the thermal conductivity of such compact can be given as,

$$\frac{k_c}{k_s} = \frac{P^{2/3} + \frac{k_s}{k_a}(1-P)}{P^{2/3} - P + \frac{k_s}{k_a}\left(1 - P^{2/3} + P\right)} \tag{1}$$

where k_c is thermal conductivity of a compact, k_s for solid, k_a for air space, and P for porosity fraction. The

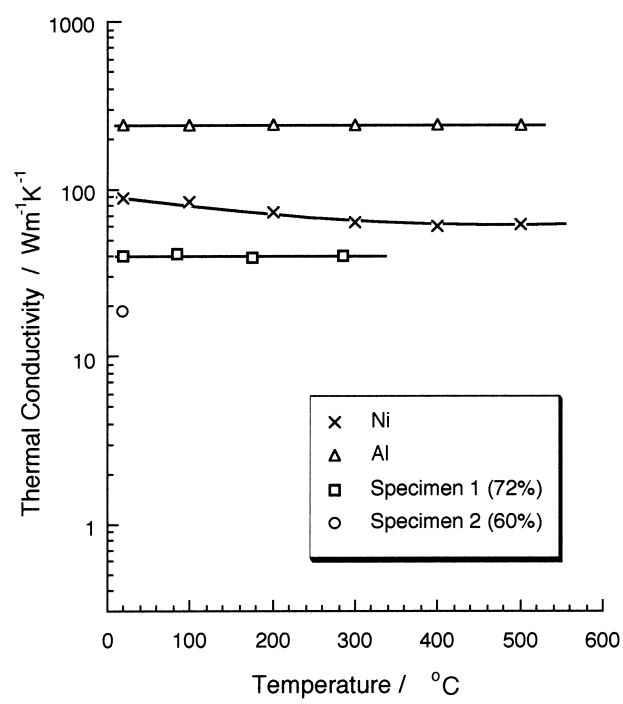

Fig. 1. The temperature dependence of the thermal conductivity of a 3Ni–1Al mixed powder compact (specimen 1) with 72% relative density, Ni and Al elemental bulk specimens from the literature [10]. The room temperature thermal conductivity of a powder compact (specimen 2) with 60% relative density (without heat treatment) is also plotted.

thermal conductivity of air is used for k_a. Both the calculated thermal conductivities of pure Ni and Al powder compacts are shown in Fig. 2 for comparison.

In another case where solid particles of the same size are surrounded by air or vacuum, a reverse of the isolated-void model, referred to as the isolated-particle model, the conductivity is still given in the same type of equation, except that P is replaced with $(1-P)$ and k_s is changed with k_a. In this case, there is no difference in the calculated thermal conductivity of Ni and Al compacts with the relative density lower than 98% as shown in Fig. 2. Note that the assumption of the isolated-particle is not applicable to 3Ni–1Al powder compacts with much higher thermal conductivities measured experimentally.

The values measured experimentally are rather lower than those predicted by the isolated-void model using the thermal conductivity of bulk Ni metal with "nominal" relative densities. In view of the volume fraction and particle sizes used in the present study, it is reasonable to assume that large Al powder particles are surrounded by small Ni powder particles. Al oxides are expected to form on Al powder surfaces, which will serve as a thermal barriers. The 3Ni–1Al powder compacts can be thus considered as Ni network separated by "Al" voids (Al oxide coated Al particles). This configuration of powder compacts will effectively reduce the

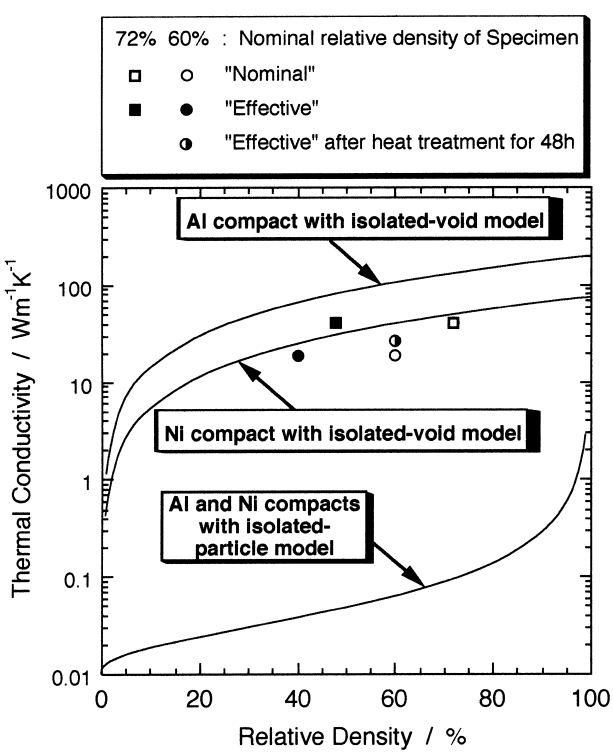

Fig. 2. Effect of relative density on the thermal conductivity of compacts with and without heat treatment. In order to evaluate the Ni powder network as a heat conducting path, "effective" relative densities of both powder mixtures are calculated based on the amount of Ni particles in each compact.

relative density from 60% (normal density) to 40% (effective density), and from 72 to 48%. As indicated in Fig. 2, the solid data points based on the effective density agree well with the theoretical prediction for Ni powder compact. The higher thermal conductivity of the compact sample with a higher relative density than the theoretical value may be achieved by considering that Al_2O_3 layer on Al particles are broken mechanically during pressing.

3.2. Formation of intermediate phases and their effect on thermal conductivity

Before ignition or during combustion reaction, intermediate phases are formed, and these phases may affect the thermal conductivity of powder compacts. To simulate microstructural evolution produced by annealing at 620°C for a few minutes, typical duration prior to ignition, specimens were heat-treated for 48 or 1000 h at 400°C. These heat treatment durations will result in the formation of Al_3Ni and Ni_2Al_3 in Ni–Al diffusion couple [7,9,12]. Fig. 3 shows the back scattering electron-image of the compact by the SEM, which was heat-treated for 1000 h at 400°C, corresponding to heat treatment for about 300 s at 620°C in terms of bulk diffusion rate [7,9,12]. Observed in the figure are only intermetallics such as Ni_2Al_3, NiAl and Ni_3Al, and Ni-solid solution with no residual Al powder particles. Through the analysis by EDS, it is found that darker regions contain a higher amount of Al. It is noteworthy to mention that intermetallics are formed not only between former Ni and Al elemental particles but also between former Ni particles. As shown in Fig. 3, phase contour lines indicating the boundaries of intermediate phases are visible in concentric configurations in the interior of the former Ni particles. In view that no liquid phase formation in the specimen, this configuration can be attributed to a transport of Al across Ni particle boundaries by fast diffusion on free and/or contacting surfaces, followed by slower bulk diffusion into former Ni particles.

Fig. 4 shows the effect of heat treatment duration on the thermal conductivity. The thermal conductivity of the compact specimen without heat treatment is 18.6 W/m/K, and it increases to 26.4 W/m/K after heat treatment for 48 h at 400°C. This increase is considered to be caused by the destruction of the oxide layer on Al particles and the joining of Al–Ni particles by interdiffusion. If all the oxide layers on Al particles are broken, Al particles should contribute to the thermal conduction thoroughly and not "effective" but "nominal" relative density should be taken. The Al particle, which has a higher thermal conductivity than the Ni particle, is expected to raise the thermal conductivity of the compact to the value higher than the theoretical one predicted by the Ni-powder compact curve shown in Fig. 2. The

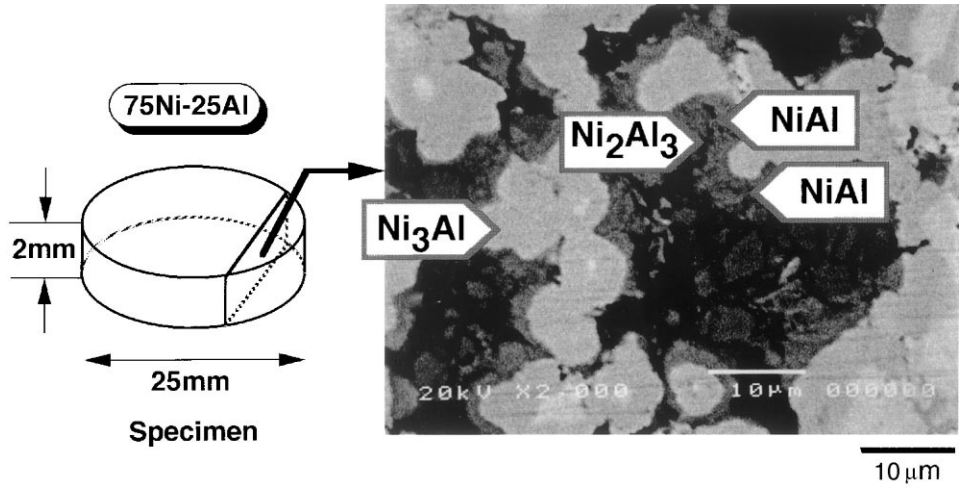

Fig. 3. The back scattering electron-image of compact by SEM, which was heat-treated for 1000 h at 400°C.

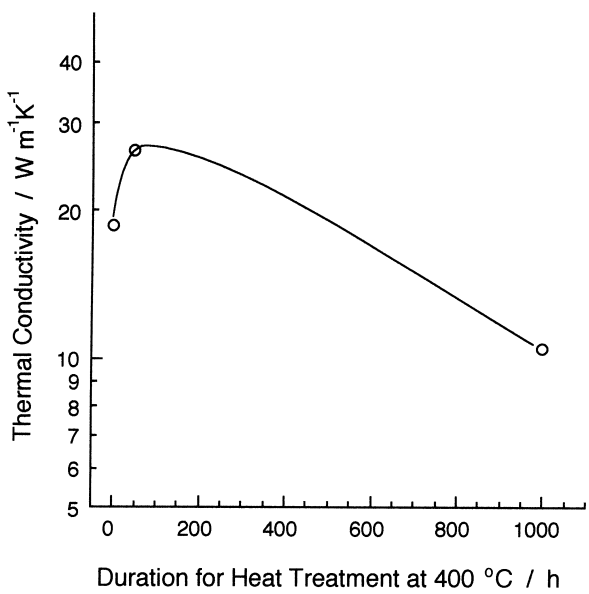

Fig. 4. Effect of heat treatment duration at 400°C on the thermal conductivity of Ni–Al powder mixture compact with a relative green density of 60%.

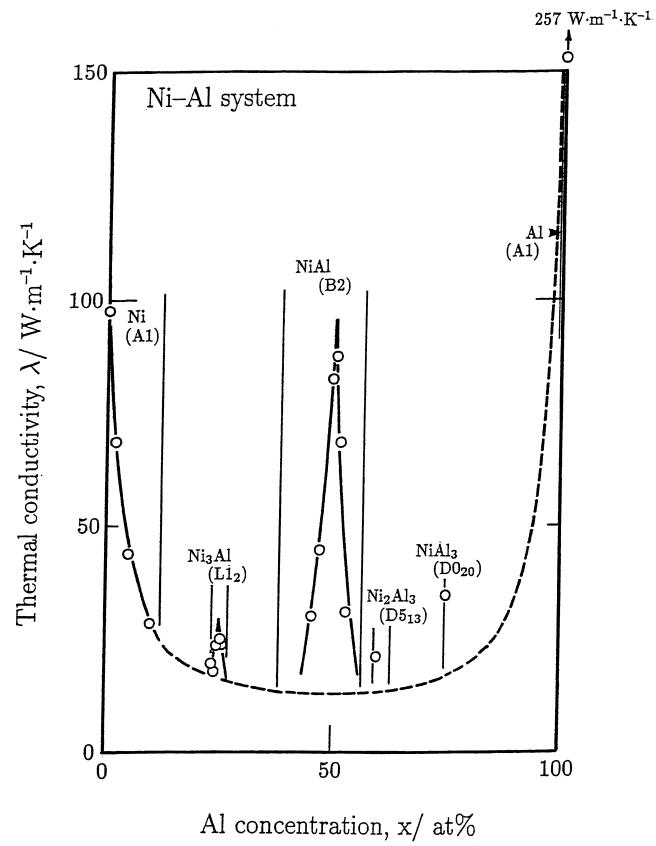

Fig. 5. Thermal conductivities of various phases in the Ni–Al alloy system. The U-shaped line represents the conductivity of disordered

thermal conductivity after heat treatment for 48 h (a half-filled symbol) becomes close to but is still lower than the predicted value from the relative density of 60%, as shown in Fig. 2. This comparison suggests that not all oxide layers on Al and Ni particles are broken at this moment.

Thermal conductivity decreases to 10.5 W/m/K after heat treatment for 1000 h at 400°C, which must be associated with the formation of intermetallics and Ni-solid solution layers on particle surfaces as shown in Fig. 3. Fig. 5 shows that the thermal conductivity of a solid solution alloy is much lower than that of pure elements [16,18]. It is found that thermal conductivities of intermetallic phases are rather higher than interpolated values for disordered states with corresponding compositions; however, they are still lower than those of pure elements that compose the alloys. These intermetallic phases and Ni-solid solution formed between and inside of particles, govern the thermal conductivity of the long-term heat-treated compact. The formation of those phases through the interdiffusion process is also a key nature of the reaction synthesis. This implies that the thermal

conductivity of compact changes during reaction synthesis and the measurement of the thermal conductivity of initial mixed powder compact itself is not enough for precise modeling of the reaction synthesis, unless all the effects of the formation of intermetallic phases during heat treatment or pre-ignition duration are taken into account.

As mentioned above, intermediate phases and Ni-solid solution are formed not only between former Ni and Al particles but also between former Ni particles, because of fast diffusion on free and/or contacting surfaces. Nevertheless, the data on such diffusion processes are quite limited [10]. As the activation energies for diffusion on free and/or contacting surface are generally smaller than that for bulk diffusion, the effect of such diffusion on the thermal conductivity and microstructural evolution during the reaction synthesis becomes dominant over a bulk diffusion at low temperatures. It also suggests that such diffusion processes will play a key role in simulating the reaction synthesis.

4. Conclusions

Thermal conductivity of 3Ni–1Al elemental powder compacts was investigated as a function of temperature, compact density and heat treatment. The following conclusions can be drawn from this work.

1. Thermal conductivity of the compacts is much lower than those of elemental bulk specimens, although temperature dependences are quite similar. Highly densified specimen virtually has higher thermal conductivity.
2. Not only between former Ni and Al elemental particles but also between former Ni particles, various intermetallic phases are formed after long-term heat-treatment. The contour lines are observed in former-Ni particles as a result of the transport of Al into Ni particle boundaries by fast diffusion on a free and/or contacting surface followed by slower bulk diffusion.
3. Thermal conductivity of a specimen after heat treatment for 48 h at 400°C is 40% higher than that without heat treatment. This increment is caused by the contribution of Al particles to the thermal conduction as a result of destruction of surface oxide layers on Al particles and joining of them together.
4. Thermal conductivity after heat treatment for 1000 h at 400°C decreases to 10.5 W/m/K (being about 40% of that after heat treatment for 48 h). This decrease is caused by the formation of layers of low thermal conductivity materials such as intermetallics and Ni-solid solution between and inside of former Ni particles.

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