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Citation	ISIJ International, 37(1), 87-92 <a href="https://doi.org/10.2355/isijinternational.37.87">https://doi.org/10.2355/isijinternational.37.87</a>
Issue Date	1997-01-15
Doc URL	<a href="http://hdl.handle.net/2115/75734">http://hdl.handle.net/2115/75734</a>
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Type	article
File Information	ISIJ Int. 37(1) 87.pdf



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# Grain Refinement of Combustion-synthesized NiAl by Addition of Al<sub>2</sub>O<sub>3</sub> Particles

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(Received on July 15, 1996; accepted in final form on November 12, 1996)

An intermetallic compound of mononickel aluminide (NiAl) is combustion-synthesized from a mixture of nickel and aluminum powders by a pseudo-Hot-Isostatic-Pressing (pseudo-HIPing) method. The effects of the addition of alumina (Al<sub>2</sub>O<sub>3</sub>) particles on the microstructure and mechanical properties of the combustion-synthesized NiAl is investigated. The density and hardness of the NiAl significantly increase with increasing pseudo-HIPing pressure applied during the combustion synthesis. The increase in the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> particles leads to a slight decrease in the density of the NiAl, but it does not affect the hardness. The grain size of NiAl decreases, as the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> particles increases and as the size of the Al<sub>2</sub>O<sub>3</sub> particles decreases.

KEY WORDS: powder metallurgy; reactive sintering; combustion synthesis; intermetallic compound; mononickel aluminide; mechanical property; grain refinement.

## 1. Introduction

An intermetallic compound of mononickel aluminide (NiAl) has the attractive combinations of low density (5.86 Mg/m<sup>3</sup>), high melting temperature (1911 K), high strength, good corrosion and oxidation resistance, high thermal conductivity, low cost, and use of non-strategic elements. Therefore, as Darolia<sup>1)</sup> pointed out, NiAl offers new opportunities for developing low-density and high-strength structural alloys which might be used at temperatures higher than currently possible with conventional titanium- and nickel-base alloys. One of the potential applications of NiAl is as a high-pressure turbine blade material. Low-density NiAl turbine blades can reduce the turbine rotor weight by as much as 40% compared with nickel-base superalloys. The thermal conductivity of NiAl is four to eight times that of nickel-base superalloys. Therefore, the temperature distribution in a NiAl turbine blade is much more uniform, and the life limiting "hot spot" temperature is reduced by as much as 50 K.<sup>1)</sup>

Thus, NiAl is a promising potential high temperature material which may take the place of conventional nickel-base superalloys. However, the most significant disadvantage of NiAl is brittleness at low temperatures. Schulson and Barker<sup>2)</sup> investigated the effects of the grain size of NiAl on its tensile properties at 673 K, and found that the tensile elongation of NiAl dramatically increases when the grain size is small. Their procedure to produce fine grain NiAl includes the following four steps: (1) casting of molten NiAl into

cylindrical ingots (50 mm in diameter), (2) extrusion of the ingots at 1273 K (7 to 1 reduction ratio), (3) extrusion at 823 K (7 to 1 reduction ratio), and (4) heat treatment for recrystallization of the doubly extruded product at temperatures between 973 and 1073 K.

Because the procedure by Schulson and Barker includes many steps, it may be of low-efficiency and high-cost. In this study, we produce fine grain NiAl by a very simple fabrication technique based on powder metallurgy processing; *i.e.* combustion synthesis<sup>3-7)</sup> of NiAl from a mixture of nickel and aluminum powders by using a pseudo-hot-isostatic-pressing method.<sup>8-10)</sup> The purpose of this study is to investigate the effects of the addition of alumina (Al<sub>2</sub>O<sub>3</sub>) particles on the grain size of the combustion-synthesized NiAl.

## 2. Experimental Procedure

Carbonyl nickel powder (99.8% pure, 4 to 7 μm in diameter) and gas-atomized aluminum powder (99.8% pure, 40 to 150 μm in diameter) were mixed in an atomic proportion of 1:1 with the addition of a small amount of ethanol and Al<sub>2</sub>O<sub>3</sub> particles. The maximum amount of the added Al<sub>2</sub>O<sub>3</sub> particles was 5 vol%, and the size of the Al<sub>2</sub>O<sub>3</sub> particles was varied from 0.5 to 130 μm in diameter. The powder mixture was cold-pressed into a cylindrical compact in a metal mold by applying uniaxial pressure of 700 MPa. The diameter and height of the green compact were 19 and 25 mm, respectively.

Type B thermocouple (Pt-30mass%Rh/Pt-6mass%Rh) with a diameter of 0.5 mm was used to measure the

temperature of the compact during the pseudo-Hot-Isostatic-Pressing (pseudo-HIPing). A thermocouple well (3.5 mm in diameter and 12 mm in depth) was drilled from the bottom surface of the compact, and the thermocouple covered with an alumina tube (3 and 2 mm in outer and inner diameters) was inserted into the well.

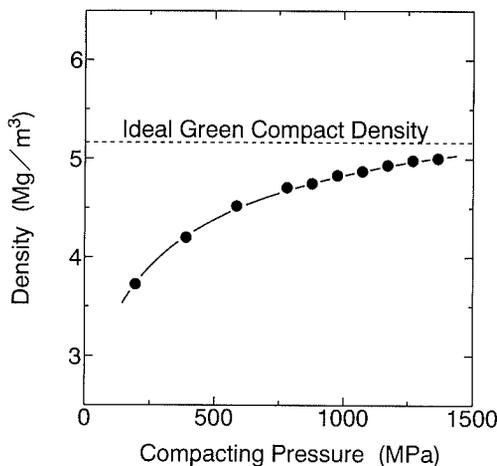
After the side surface of the green compact was coated with alumina cement for insulation, heating wire of an Fe-23mass%Cr-6mass%Al alloy (1.0 mm in diameter) was wound on to it, and then the compact was placed in a pseudo-HIPing vessel (36 mm in inner diameter and 80 mm in depth). The compact was pressed pseudo-isostatically at a pressure of 265 MPa through a pressing medium of Al<sub>2</sub>O<sub>3</sub> powder (500 μm in diameter) and was heated at a rate of 2 K/s by applying electric power to the heating wire. The sample was removed from the pseudo-HIPing vessel after 300 s passed from the onset of the exothermic reaction of the combustion synthesis, which had been monitored through a sudden increase in temperature.

A longitudinal cross section of the combustion-synthesized sample was etched with Marble's reagent to reveal the grain boundary structure. The structure of the sample was photographed, and the average grain size was calculated as the area-equivalent diameter<sup>11)</sup> from the area of the photograph and the number of the grains in it. An electron probe microanalyzer (JXA-8900M, JEOL) was used to determine the nature and distribution of the phases in the synthesized sample. The density and hardness of the sample were measured by using Archimedes' method and a Vickers hardness tester with an applied load of 98 N.

### 3. Results and Discussion

#### 3.1. Green Compact

To investigate the effect of the compacting pressure on the density of the green compact over a wide range of pressure, we used a smaller metal mold (16 mm in inner diameter) compared with that used to make the green compact to be combustion-synthesized. **Figure 1** shows the relationship between the compacting pressure



**Fig. 1.** Effects of the compacting pressure on the density of the green compact.

and the density of the green compact. As the compacting pressure increases, the density gradually increases toward the ideal density of 5.17 Mg/m<sup>3</sup>, which was calculated by using Eq. (1).<sup>12)</sup>

$$\rho_{\text{Mix}} = \frac{\rho_{\text{Al}}\rho_{\text{Ni}}}{(1-f_{\text{Ni}})\rho_{\text{Ni}} + f_{\text{Ni}}\rho_{\text{Al}}} \dots\dots\dots(1)$$

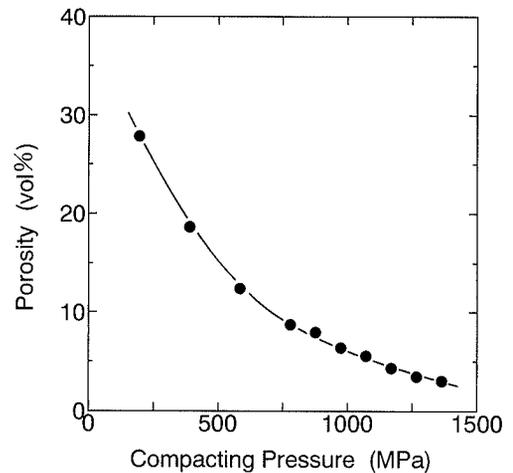
where  $\rho$  and  $f$  are the density and mass fraction of the material indicated by the subscript.

**Figure 2** shows the relationship between the compacting pressure and the volume fraction of the pores remaining in the green compact. This relationship was calculated from Eq. (2) by using the results shown in Fig. 1.

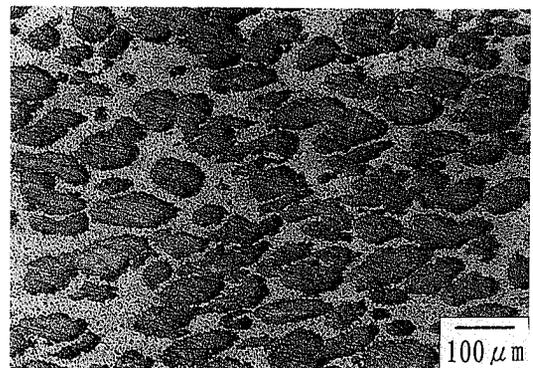
$$p = (\rho_0 - \rho) / \rho_0 \dots\dots\dots(2)$$

where  $p$  is porosity (the volume fraction of the pores), and  $\rho_0$  and  $\rho$  are the ideal and real density of the compact, respectively. The porosity of the green compact is reduced down to approximately 3% by applying the maximum compacting pressure of 1365 MPa.

**Figure 3** shows the microstructure observed on a section perpendicular to the compression axis of the cylindrical green compact pressed at the maximum compacting pressure of 1365 MPa. The deformed particles of aluminum powder are homogeneously dispersed in the matrix phase of nickel. Small pores with a diameter



**Fig. 2.** Relationship between the compacting pressure and the volume fraction of the pores remaining in the green compact.



**Fig. 3.** Microstructure on a section perpendicular to the compression axis of the cylindrical green compact pressed at the maximum pressure of 1365 MPa.

of about 1  $\mu\text{m}$  remaining at the interface between nickel powder particles were observed at a higher magnification.

The results shown in Figs. 1 through 3 indicate that a much higher compacting pressure than 1500 MPa is required to produce a very dense green compact by compaction at room temperature. The pores remaining in the green compact are unfavorable, when the reactive sintering<sup>13-16)</sup> of the compact is performed at temperatures below the lowest melting temperature in the Al-Ni binary system. However, when combustion synthesis is performed, it is possible to produce a dense product from the green compact with relatively high porosity, because the compact is partially or entirely melted by the heat from the exothermic reaction of the synthesis. Lebrat *et al.*<sup>17)</sup> produced dense trinickel aluminide ( $\text{Ni}_3\text{Al}$ ) by combustion synthesis from the green compact containing pores of 20 vol%. But they reported that the microstructure of the product which had been combustion-synthesized from the green compact containing pores of 46 vol% consisted of nickel cores surrounded by an annular region of  $\text{Ni}_3\text{Al}$  phase, the rest of the matrix being the more aluminum-rich NiAl phase. They also reported that an X-ray diffraction pattern measured for the product from the green compact containing pores of 28 vol% indicated the presence of only  $\text{Ni}_3\text{Al}$  and NiAl phases, with no pure nickel phase present. Therefore, too high porosity is unfavorable even for combustion synthesis. From the results shown in Figs. 1 through 3 and those reported by Lebrat *et al.*, we used a compacting pressure of 700 MPa, which corresponds to approximately 10 vol% of porosity. Reducing the compacting pressure makes it possible to enlarge the size of the green compact. A larger size of the green compact is preferable from the view point of heat loss, because the pressing medium consumes some of the heat from the exothermic reaction of the combustion synthesis and it suppresses the self-sustaining reaction.<sup>13)</sup>

### 3.2. Synthesis of NiAl by pseudo-HIPing

Figure 4 shows the change in the temperature of the

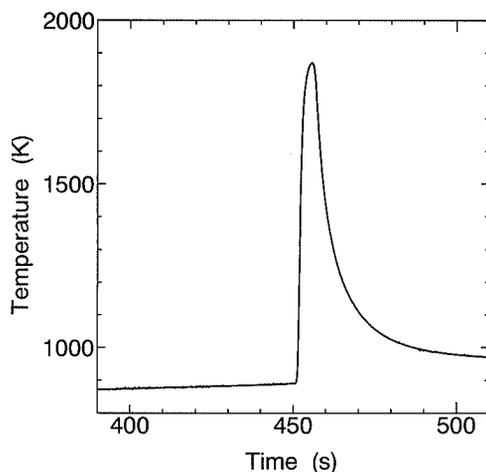


Fig. 4. Change in temperature of the compact during heating under the pseudo-HIPing pressure of 265 MPa, showing a sudden exothermic reaction of the combustion synthesis of NiAl from the mixture of nickel and aluminum powders.

compact during heating under a pseudo-HIPing pressure of 265 MPa. When the temperature of the compact reaches approximately 900 K, which is just below the lowest eutectic temperature in the Al-Ni binary system, the temperature of the compact suddenly goes up to approximately 1900 K in a very short time. This sudden increase in temperature is caused by the exothermic reaction of the synthesis of NiAl from the mixture of nickel and aluminum powders.

Nishimura and Liu<sup>13)</sup> investigated reactive sintering of  $\text{Ni}_3\text{Al}$  under uniaxial compressive stresses ranging from 0 to 120 MPa, and gave a detailed description of the entire reaction process from nickel and aluminum to  $\text{Ni}_3\text{Al}$ ; *i.e.*  $\text{Ni} + 3\text{Al} \rightarrow \text{NiAl}_3$ ,  $\text{NiAl}_3 + \text{Ni} \rightarrow \text{Ni}_2\text{Al}_3$ ,  $\text{Ni}_2\text{Al}_3 + \text{Ni} \rightarrow 3\text{NiAl}$ ,  $\text{Liquid} + \text{Ni} \rightarrow \text{NiAl} + \text{Ni}_3\text{Al}$ , and  $\text{NiAl} + 2\text{Ni} \rightarrow \text{Ni}_3\text{Al}$ . In our study, the final product is not  $\text{Ni}_3\text{Al}$  but NiAl. However, it is likely that some similar reactions occur also in our study, because Inoue and Sukanuma<sup>18)</sup> found that  $\text{Ni}_2\text{Al}_3$  was formed as an intermediate product in the reactive sintering of NiAl. The very sharp increase in temperature shown in Fig. 4 implies that the series of reactions occurred in a very short time. Figure 5, showing a dendritic structure of the synthesized NiAl, indicates that the liquid phase of NiAl existed in a stage of the pseudo-HIPing. Since the maximum temperature of the sample must have exceeded the melting temperature of NiAl of 1911 K,<sup>19)</sup> the temperature shown in Fig. 4 seems to be underestimated.

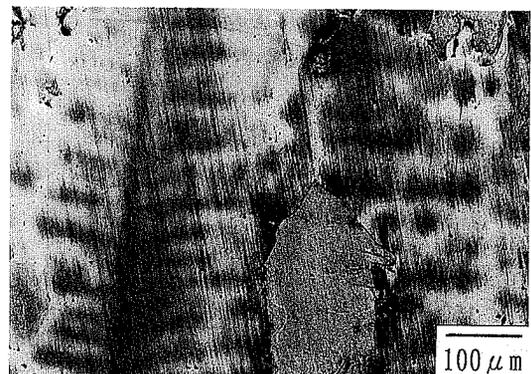


Fig. 5. Dendritic structure of the synthesized NiAl, indicating that the liquid phase of NiAl existed in a stage of the pseudo-HIPing of the compact.

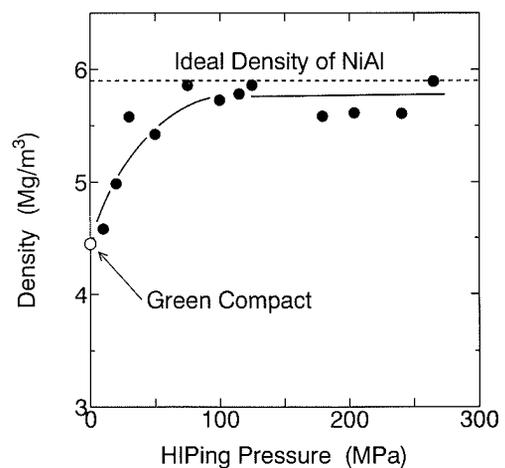


Fig. 6. Effect of the pseudo-HIPing pressure on the density of the synthesized NiAl.

It is considered that the thermocouple and the alumina tube which covered the thermocouple absorbed some of the heat from the exothermic reaction.

**Figure 6** shows the effect of the pseudo-HIPing pressure on the density of the combustion-synthesized NiAl. As the pressure increases, the density goes up close to the ideal density of NiAl. The increase in density is caused by the decrease in the porosity. **Figure 7** shows the effect of the pseudo-HIPing pressure on the Vickers hardness of the combustion-synthesized NiAl. The hardness increases with the pressure. It is suggested from the results shown in Figs. 6 and 7 that because the behavior of the hardness change is very similar to that of the density change, the increase in hardness is considered to be caused by the increase in density.

### 3.3. Addition of Al<sub>2</sub>O<sub>3</sub> Particles

**Figure 8** shows the effect of the volume fraction of Al<sub>2</sub>O<sub>3</sub> particles added to the compact on the density of the synthesized NiAl. The density slightly decreases with increasing volume fraction of Al<sub>2</sub>O<sub>3</sub> particles, due to the fact that the density of Al<sub>2</sub>O<sub>3</sub> is lower than that of NiAl. The change in the ideal density in Fig. 8 was calculated from the density of Al<sub>2</sub>O<sub>3</sub> (3.99 Mg/m<sup>3</sup>) and that of NiAl (5.86 Mg/m<sup>3</sup>).

**Figure 9** shows the effect of the volume fraction of the

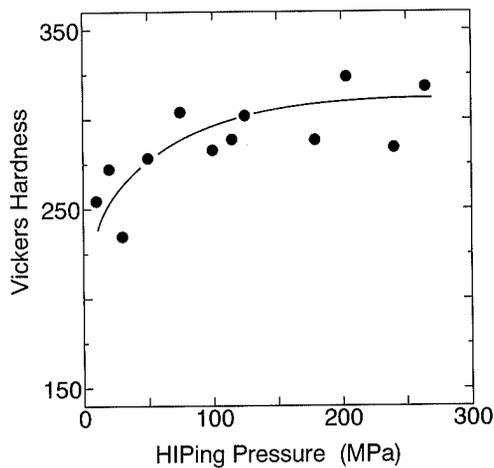


Fig. 7. Effect of the pseudo-HIPing pressure on the Vickers hardness of the synthesized NiAl.

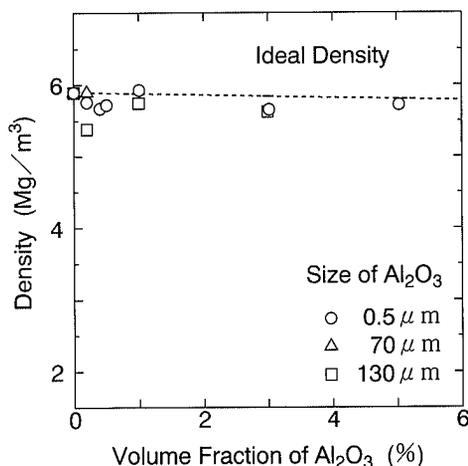


Fig. 8. Effect of the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> powder on the density of the synthesized NiAl.

added Al<sub>2</sub>O<sub>3</sub> particles on the Vickers hardness of the synthesized NiAl. The addition of Al<sub>2</sub>O<sub>3</sub> particles up to 5 vol% does not affect the hardness of NiAl. Any effect of the size of Al<sub>2</sub>O<sub>3</sub> particles on the hardness is not observed.

**Figure 10** shows the microstructures of the synthesized NiAl. When Al<sub>2</sub>O<sub>3</sub> particles are not added, the grain size of NiAl is very large (see Fig. 10(a)). However, when only 0.4 vol% of Al<sub>2</sub>O<sub>3</sub> particles are added to the compact, the grain structure of the synthesized NiAl is significantly refined (see Fig. 10(b)).

**Figure 11** shows the results of an electron probe microanalysis (Fig. 11(a)) and an image of a scanning electron microscope (Fig. 11(b)) of the synthesized NiAl containing 1 vol% of Al<sub>2</sub>O<sub>3</sub> particles with a diameter of 0.5 μm. The results show (1) NiAl is perfectly synthesized without any intermediate products and the elemental

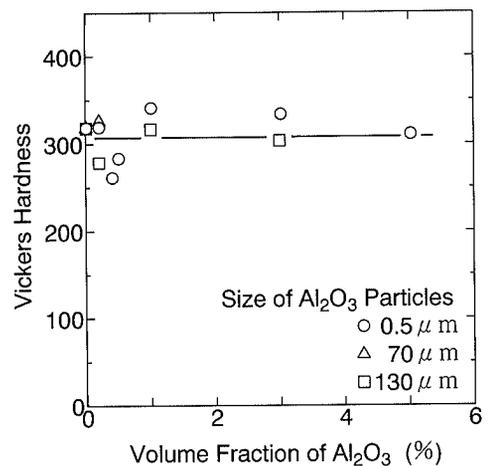


Fig. 9. Effect of the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> powder on the Vickers hardness of the synthesized NiAl.

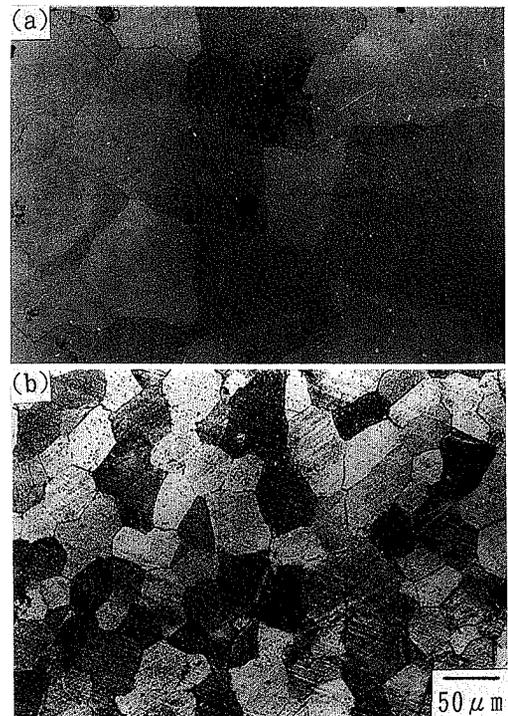


Fig. 10. Microstructure of the synthesized NiAl containing (a) 0 vol% and (b) 0.4 vol% of 0.5 μm Al<sub>2</sub>O<sub>3</sub> particles.

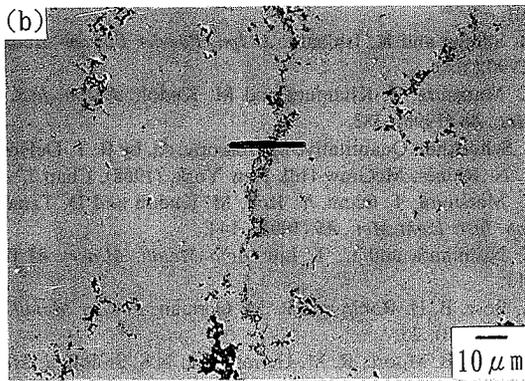
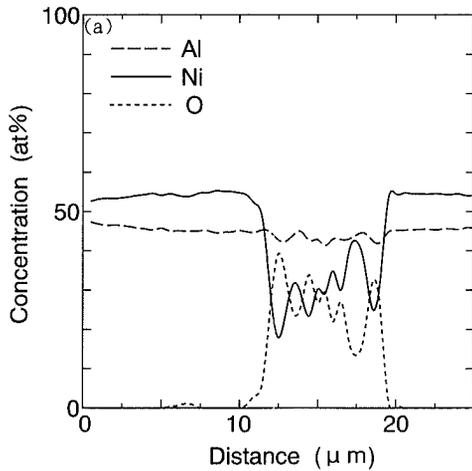


Fig. 11. (a) EPMA analysis across the grain boundary and (b) SEM image of the synthesized NiAl containing 1 vol% of 0.5 μm Al<sub>2</sub>O<sub>3</sub> particles.

metal phases remaining, in spite of the addition of Al<sub>2</sub>O<sub>3</sub> particles, and (2) the added Al<sub>2</sub>O<sub>3</sub> particles are segregated at the grain boundary of NiAl.

Figure 12 shows the effect of the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> particles on the average grain size of the synthesized NiAl. As the volume fraction of Al<sub>2</sub>O<sub>3</sub> particles increases, the average grain size of NiAl decreases. When the size of Al<sub>2</sub>O<sub>3</sub> particles is small, the decrease in the grain size is remarkable. This implies that the number of the particles is also an important parameter.

3.4. Mechanism of Grain Refinement by Al<sub>2</sub>O<sub>3</sub> Addition

When Al<sub>2</sub>O<sub>3</sub> particles are added to the compact of the powder mixture of nickel and aluminum, the grain size of the synthesized NiAl is small. We discuss the mechanism of grain refinement by the addition of Al<sub>2</sub>O<sub>3</sub> particles.

3.4.1. Heat Sink

The temperature of the compact goes up to a very high temperature above the melting temperature of NiAl owing to the exothermic reaction of the synthesis (see Fig. 5). When Al<sub>2</sub>O<sub>3</sub> particles are dispersed in the compact, they will act as a heat sink and absorb the heat from the synthesis reaction. As a result, the degree of the superheating will be reduced, and the cooling rate of the molten NiAl will be increased. Because the increase in the cooling rate leads to an increase in the number of crystals, the increase in the volume fraction of Al<sub>2</sub>O<sub>3</sub>

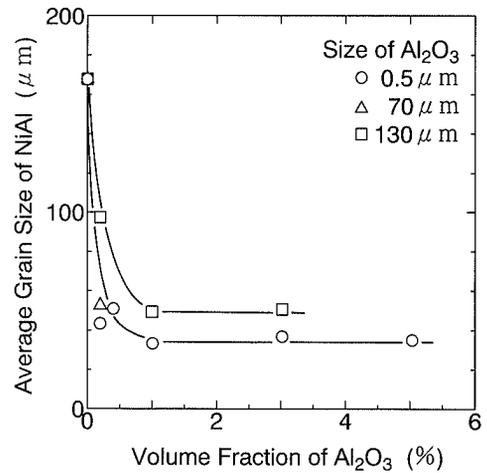


Fig. 12. Effect of the volume fraction of the added Al<sub>2</sub>O<sub>3</sub> particles on the average grain size of the synthesized NiAl.

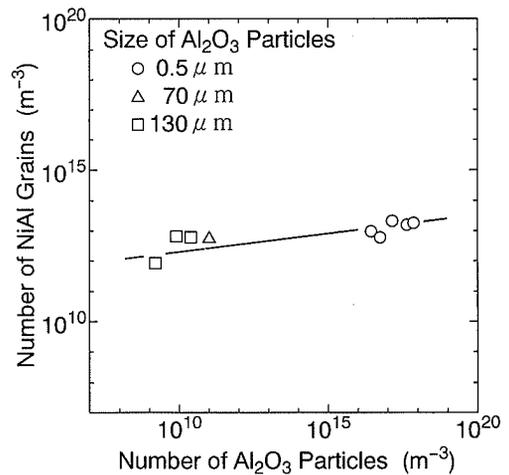


Fig. 13. Effect of the number of the added Al<sub>2</sub>O<sub>3</sub> particles on the number of the crystal grains of the synthesized NiAl.

particles leads to the decrease in the grain size, as shown in Fig. 12.

3.4.2. Nucleation Site

When the size of Al<sub>2</sub>O<sub>3</sub> particles is small, the average grain size of NiAl is small, as shown in Fig. 12. This result indicates that the number of the NiAl grains increases with the number of the Al<sub>2</sub>O<sub>3</sub> particles. It is suggested that the surface of the “cold” Al<sub>2</sub>O<sub>3</sub> particles which are dispersed in the “hot” molten NiAl could become a nucleation site of NiAl crystals.

3.4.3. Retardation of Crystal Growth

Figure 13 shows the relationship between the number of Al<sub>2</sub>O<sub>3</sub> particles and that of NiAl grains. The number of grains was calculated from the average area-equivalent grain diameter<sup>11)</sup> measured on the section of the sample, by assuming that the three dimensional shape of the grain is tetrakaidehedral,<sup>20,21)</sup> and by using Eq. (3).<sup>22,23)</sup>

$$N = \left[ \frac{4}{3} \pi \left( \frac{D_{eq}/0.75}{2} \right)^3 \right]^{-1} \dots\dots\dots(3)$$

where *N* is the number of the grains and *D<sub>eq</sub>* is the average

area-equivalent grain diameter. The number of grains increases with the number of  $\text{Al}_2\text{O}_3$  particles, which implies that the  $\text{Al}_2\text{O}_3$  particles act as the nuclei of the solidification of NiAl, as described in the last paragraph. However, when the amount of the added  $\text{Al}_2\text{O}_3$  particles is small, the number of NiAl grains exceeds the number of  $\text{Al}_2\text{O}_3$  particles. This implies that other nuclei coexist with the added  $\text{Al}_2\text{O}_3$  particles. On the other hand, when the amount of  $\text{Al}_2\text{O}_3$  particles is large, the number of NiAl grains is smaller than that of  $\text{Al}_2\text{O}_3$  particles, which implies that many of the  $\text{Al}_2\text{O}_3$  particles do not act as nuclei. They may move with the solidification front and pile up in the liquid side at the solid/liquid interface. The migration of the solidification front covered with  $\text{Al}_2\text{O}_3$  particles will be retarded, and the nucleation of NiAl will be activated at the site of the  $\text{Al}_2\text{O}_3$  particles which are dispersed in the liquid phase away from the solidification front. This leads to the grain refinement of NiAl.

#### 3.4.4. Retardation of Grain Growth

A great number of  $\text{Al}_2\text{O}_3$  particles are segregated on the grain boundary surface of NiAl, as shown in Fig. 11. They retard the migration of the grain boundary after solidification, and the grain size remains small.

## 4. Conclusions

An intermetallic compound of mononickel aluminide (NiAl) was produced from a mixture of nickel and aluminum powders by using combustion synthesis and a pseudo-Hot-Isostatic-Pressing (pseudo-HIPing) method. The effects of the addition of alumina ( $\text{Al}_2\text{O}_3$ ) particles on the microstructure and mechanical properties of the combustion-synthesized NiAl was investigated. The results are summarized as follows:

(1) The density and hardness of the combustion-synthesized NiAl significantly increase with the pseudo-HIPing pressure. The increase in the volume fraction of the added  $\text{Al}_2\text{O}_3$  particles leads to a slight decrease in density, but it does not affect hardness.

(2) The grain size of NiAl decreases, as the volume fraction of the added  $\text{Al}_2\text{O}_3$  particles increases and as the size of the  $\text{Al}_2\text{O}_3$  particles decreases.

(3) The mechanisms of the grain refinement of NiAl by the addition of  $\text{Al}_2\text{O}_3$  particles are considered to be

(i) the role of a heat sink by the non-exothermic inclusions of  $\text{Al}_2\text{O}_3$ , (ii) the role of the nucleation site of NiAl by the "cold" surface of  $\text{Al}_2\text{O}_3$  particles, (iii) retardation of crystal growth of NiAl by  $\text{Al}_2\text{O}_3$  particles piled up at the solid/liquid interface, and (iv) retardation of grain growth of NiAl by  $\text{Al}_2\text{O}_3$  particles segregated at the grain boundary.

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