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RESEARCH REPORT

Combustion synthesis of Al–Ni alloys by a pseudo-HIP process

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Several Al–Ni alloys containing 20 to 80 at% nickel are produced from a mixture of aluminum and nickel powders by a combustion synthesis method using a pseudo-HIP (Hot Isostatic Pressing) process. All the powder mixtures exothermically react and produce intermetallic compounds. The change in the exothermic temperature resulting from the composition of the powder mixture seems to be similar to the change in the melting temperature of the alloy. When the nickel content of the powder mixture is below 30 at% or above 70 at%, the multiphase structure including the elemental phase is formed. When an intermetallic compound phase has a relatively wide concentration range, the monophase structure of the compound is formed. The Vickers hardness of the synthesized alloy which include the elemental phase is 100 to 200 at room temperature. The hardness of Ni_2Al_3 is above 700. The hardness of NiAl changes with the nickel content; it decreases from 400 to 300 as the nickel content increases from 46 to 50 at%, but it increases to 400 as the nickel content increases from 50 to 56 at%.

Keywords: powder metallurgy, reactive sintering, combustion synthesis, intermetallic compound, mechanical property, Al–Ni system

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1. Introduction

In general, the intermetallic compounds based on aluminum have the attractive characteristics of low density, high strength, good corrosion and oxidation resistance, nonstrategic elements and relatively low cost, according to Sims et al.[1]. In fact, intermetallic compounds in the Al–Ni system such as Ni_3Al[2)~4)] and NiAl[5)~7)] are highly promising for applications as structural materials at high temperatures[8),9)]. However, most of the high-strength materials usually have low workability. One possible solution to this problem is the utilization of the near-net-shape fabrication technique such as powder metallurgy processing. Reactive sintering[10)~13)], combustion synthesis[14)~18)], and reactive infiltration[19)] are the novel and attractive processes. Inoue and Suganuma[20)] investigated the reactive sintering behavior of NiAl during hot pressing of the mixture of nickel and aluminum powders, and they reported that for Ni–43.5 at%Al and Ni–47 at%Al alloys, the reactive sintering of NiAl consists of the same three stages that were found by Nishimura and Liu[10)]; i.e. initial, self-propagating and conversion stages. On the other hand, Inoue and Suganuma also reported that for Ni–50 at%Al and Ni–52.5 at%Al alloys, the heat evolution caused by the second and third stages do not appear because of the heat absorption by the fusion of the excessive aluminum, and therefore it is difficult to obtain very dense products.

In this study, we synthesize several Al–Ni alloys containing 20 to 80 at% nickel from the mixture of aluminum and nickel powders by using a pseudo-HIP (Hot Isostatic Pressing) process[21),22)], and investigate the effects of the nickel content of the mixture on the behavior of the exothermic reaction of the synthesis and the mechanical properties of the alloys.

2. Experimental Procedure

Gas-atomized aluminum powder (99.8% pure, 40 to 150 μm in diameter) and carbonyl nickel powder (99.8% pure, 4 to 7 μm in diameter) were mixed with the addition of a small amount of ethanol. The powder mixture was cold-pressed into a cylindrical green compact in a metal mold using a compaction pressure of 650 MPa. The diameter and height of the compact were 19 mm and 25 mm, respectively (See **Fig. 1**).

Type B thermocouple (Pt–30 mass%Rh/Pt–6 mass% Rh) with a diameter of 0.5 mm was used to measure the temperature of the compact during the hot isostatic pressing (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

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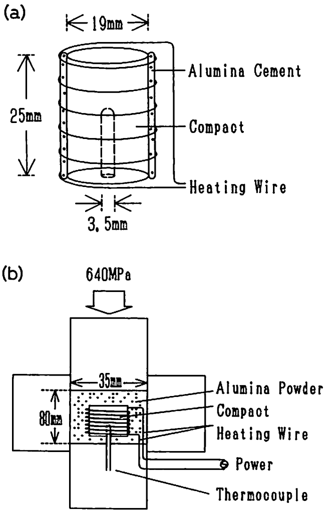

Fig. 1 Schematic illustrations of (a) the sample and (b) the HIPing vessel.

tube (3 mm 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–23 mass%Cr–6 mass%Al alloy (1.0 mm in diameter) was wound on to it, and then the compact was placed in a HIPing vessel. The compact was pressed pseudo-isostatically by a pressing medium of alumina powder (0.5 mm in diameter) and was heated at a rate of 1 K/s by applying electric power to the heating wire. The HIPing pressure was 340 MPa. The sample was removed from the HIPing vessel after 300 s passed from the onset of the exothermic reaction, which was monitored through the rapid increase in temperature.

The samples were metallographically examined by using optical and electron microscopes. An electron probe microanalyzer (JXA–8900M, JEOL), which was calibrated using pure nickel and aluminum, was used to determine the nature and distribution of the phases in the synthesized sample. The density and hardness of the hot-isostatically pressed (HIPed) compact 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

Fig. 2 shows the effect of the compacting pressure on the density of the green compact containing nickel of 20 at%. The density increases remarkably as the compacting pressure increases to approximately 300 MPa, but for higher pressure, the increase in the density becomes modest.

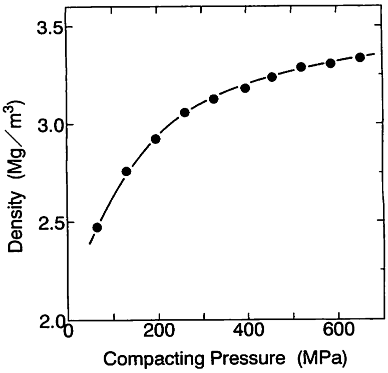

Fig. 2 The effect of the compacting pressure on the density of the green compact containing 20 at% of nickel.

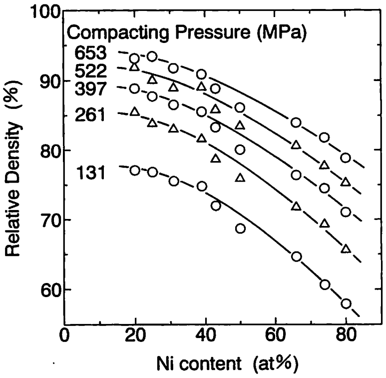

Fig. 3 The effect of the nickel content of the powder mixture on the relative density of the green compact.

Fig. 3 shows the effect of the nickel content of the powder mixture on the relative density of the green compact, which is defined as the ratio of the real density to the ideal. The ideal density of the mixture of aluminum and nickel powders can be calculated from Eq. (1)[23].

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

where ρ and f are the density and mass fraction of the material indicated by the subscript. When the nickel content is low, the relative density reaches approximately 95% for a pressure of 653 MPa. However, the relative density decreases as the nickel content increases. The results shown in Fig. 3 are considered to be related to the higher hardness and smaller size of nickel powder compared with aluminum powder.

Fig. 4 shows the microstructure on a section perpendicular to the compression axis of the cylindrical green compact containing nickel of 50 at%. The deformed particles of alu-

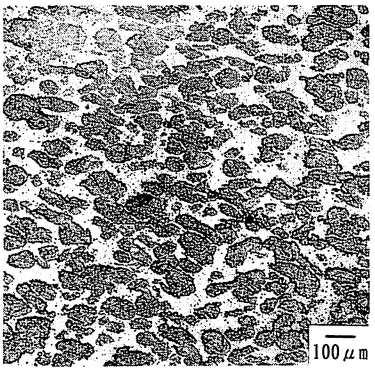

Fig. 4 The microstructure of a green compact containing 50 at% of nickel, showing the homogeneous distribution of aluminum particles (gray) in the matrix of nickel (white). Compacting pressure: 653 MPa.

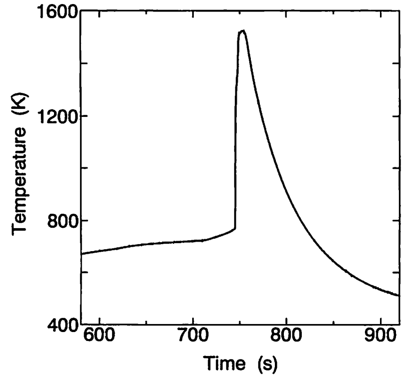

Fig. 5 The change in the temperature of the compact during heating under a pseudo-isostatic pressure of 340 MPa. Nickel content: 56 at%.

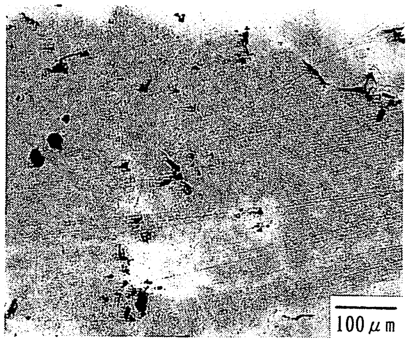

Fig. 6 The dendritic structure of the combustion-synthesized sample, showing that the compact was melted by the exothermic reaction. Nickel content: 56 at%. Etchant: Marble's reagent.

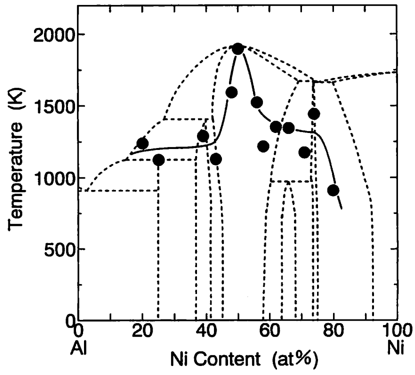

Fig. 7 The effect of the nickel content of the compact on the maximum temperature observed during the combustion synthesis. An Al–Ni equilibrium phase diagram[26] is superimposed.

minum powder are homogeneously dispersed in the matrix of nickel.

3.2 Combustion Synthesis

Fig. 5 shows the change in the temperature of a compact during HIPing. The nickel content of the compact is 56 at%. When the compact was heated slowly to approximately 750 K, the temperature suddenly and rapidly increased to above 1500 K. At the same instant, the heating wire wound on to the compact having fused and power supply having been cut, the temperature decreased in a short time after the finishing of heat generation.

This increase in temperature indicates that the stable intermetallic compounds, of which standard formation free energies are given in a reference[20], are produced by combustion synthesis[24),25] from the elemental aluminum and nickel powders.

Fig. 6 shows the dendritic structure of the HIPed compact. The dendritic structure indicates that the sample was melted during HIPing by the heat of the exothermic reaction shown in Fig. 5, and then solidified. However, the maximum temperature of approximately 1500 K shown in Fig. 5 is lower than the melting temperature of the Al–56 at%Ni alloy by approximately 300 K. It is suggested that the thermocouple and the alumina tube which covered the thermocouple absorbed some of the heat from the exothermic reaction, and therefore the temperature shown in Fig. 5 is underestimated.

Fig. 7 shows the effect of the nickel content of the compact on the maximum temperature observed during the combustion synthesis. The true maximum temperature is considered to be higher than the measured one because of the sensitivity of the thermocouple and the heat absorption described above. However, the relationship between the maximum temperature and the nickel content can be

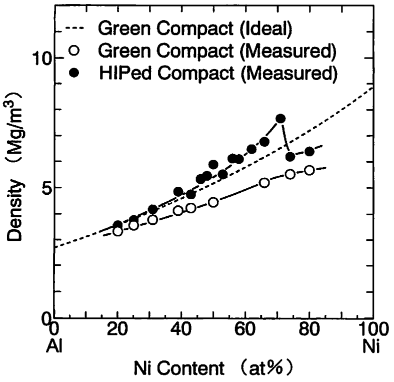

Fig. 8 The effect of the nickel content on the density of the compact.

qualitatively discussed. The temperature is highest when the nickel content is 50 at%. As shown in Fig. 7, the change in the maximum temperature seems to be similar to the change in the melting temperature, although there are some exceptions.

The maximum temperature of the combustion synthesis is considered to be related to the latent heat of fusion of the synthesized compounds. Nishimura and Liu[10] described that many reactions occur when Ni_3Al is produced from the mixture of aluminum and nickel powders, i.e. $3Al + Ni \rightarrow NiAl_3$, $NiAl_3 + Ni \rightarrow Ni_2Al_3$, $Liquid + Ni \rightarrow NiAl + Ni_3Al$, and $NiAl + 2Ni \rightarrow Ni_3Al$. It is likely that the similar reactions occur during the present HIPing, although the nickel content used in this study is of many kinds. The heat which is released from the initial reactions is consumed to elevate the temperature of the reaction products and the remainders and to produce the liquid of materials with low melting temperatures such as aluminum and $NiAl_3$. The liquid spreads over and wets the surface of the reactive materials, and it reacts with them very violently at those reaction interface with an extremely large area. The heat which is released from the final reaction is consumed to fuse the final products. Thus, the change in the maximum temperature appears to be similar to the change in the melting temperature.

3.3 Properties of the Synthesized Material

Fig. 8 shows the effect of the nickel content on the density of the compact. The ideal density of the green compact, which is calculated from Eq. (1), increases monotonously from the density of pure aluminum to that of pure nickel. The measured density of the green compact also increases with the nickel content, but the value is always lower than the ideal, and the difference between them increases with the nickel content. This is explained from the higher hardness and smaller size of nickel powder compared with alumi-

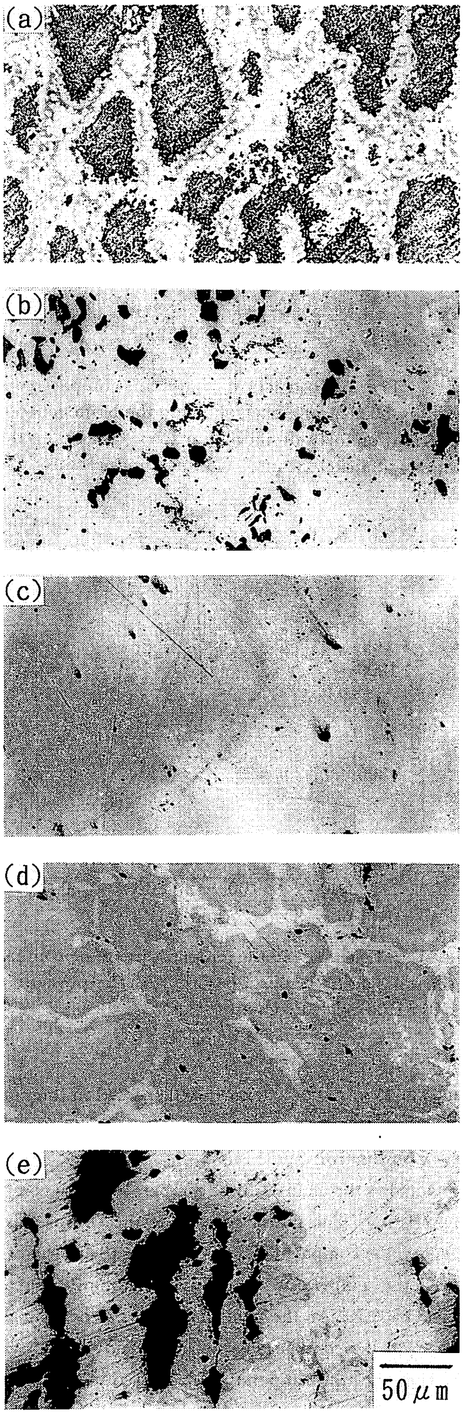

Fig. 9 The microstructures of the HIPed compacts. Nickel content: (a) 31 at%, (b) 39 at%, (c) 53 at%, (d) 66 at% and (e) 74 at%.

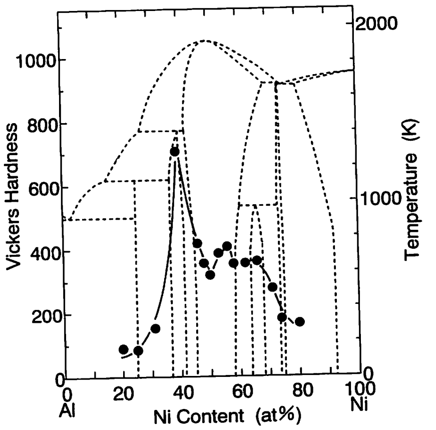

Fig. 10 The effect of the nickel content on the hardness of the HIPed compact. An Al–Ni equilibrium phase diagram[26] is superimposed.

num powder, as described in Section 3.1. The density of the HIPed compact is higher than that of the green compact, except for the compacts with a nickel content above 74 at%.

Fig. 9 shows the microstructures of the HIPed compacts. The monophase structures of Ni_2Al_3 and NiAl are formed from the compacts containing nickel of 39 at% (Fig. 9(b)) and 53 at% (Fig. 9(c)), respectively. However, from other compacts, multiphase structures are formed; aluminum, $NiAl_3$ and Ni_2Al_3 phases for 31 at% (Fig. 9(a)), NiAl and Ni_3Al phases for 66 at% (Fig. 9(d)), and NiAl, Ni_3Al and nickel phases for 74 at% (Fig. 9(e)). It is likely that the monophase structure of the intermetallic compound is formed when the compound has a relatively wide concentration range (See Fig. 7.). The concentration range of Ni_5Al_3 is as wide as that of Ni_2Al_3, but the multiphase structure is formed when the nickel content is 66 at%. It is considered that the peritectoid reaction $NiAl + Ni_3Al \rightarrow Ni_5Al_3$ does not occur because of the rapid cooling rate as shown in Fig. 5. The reason why the elemental phase remains for the nickel contents of 31 at% and 74 at% may be explained from the insufficiency of the contacting area between the two metals due to the large ratio of the content of one metal to the other. The multiphase structures are considered to change toward the stable structures which are predicted from the phase diagram, if the compacts are solid-sintered[13] after the combustion synthesis. When the nickel content is 74 at%, large pores are formed. The formation of the pores leads to the low density of the HIPed compact, as shown in Fig. 8.

Fig. 10 shows the effect of the nickel content on the hardness of the HIPed compact. The compacts which include a metal phase show relatively low hardness (100 to 200), but those composed of intermetallic compounds phases are very hard (300 to 700).

The compacts containing nickel of 46 to 56 at% are composed of the monophase of NiAl, as described above. However, the hardness of NiAl changes depending on the nickel content; it decreases from 400 to 300 as the nickel content increases from 46 to 50 at%, but it increases to 400 as the nickel content increases from 50 to 56 at%. Similar results to these were reported by Westbrook[27], Nagpal and Baker[28], and Tan et al.[29]. According to Bradley and Taylor[30], NiAl has different types of lattice defects between both sides of the stoichiometric composition, i.e. the vacancies at the nickel sites for the aluminum-rich side and the substitutional nickel atoms at the aluminum sites for the nickel-rich side. Tan et al. explained the change in the hardness of NiAl from the change in the lattice parameter[29].

The compact containing nickel of 39 at% is also composed of the monophase of Ni_2Al_3. This compact shows the highest hardness of 700, but at the same time it is so brittle that it fractures when the testing samples are prepared from the HIPed compact.

4. Conclusions

We combustion-synthesized several Al–Ni alloys containing 20 to 80 at% nickel from the mixture of aluminum and nickel powders by using a pseudo-HIP (Hot Isostatic Pressing) process to investigate the effects of the nickel content on the behavior of the exothermic reaction of the synthesis and the mechanical properties of the synthesized alloys, and obtained the following conclusions.

(1) All the powder mixtures exothermically react and produce intermetallic compounds. The change in the exothermic temperature resulting from the composition of the powder mixture seems to be similar to the change in the melting temperature of the alloy.

(2) When the nickel content of the powder mixture is below 30 at% or above 70 at%, the multiphase structure including the elemental phase is formed. When an intermetallic compound has a relatively wide concentration range, the monophase structure of the compound is formed.

(3) The Vickers hardness of the synthesized alloy which include the elemental phase is 100 to 200 at room temperature. The hardness of Ni_2Al_3 is above 700. The hardness of NiAl changes with the nickel content; it decreases from 400 to 300 as the nickel content increases from 46 to 50 at%, but it increases to 400 as the nickel content increases from 50 to 56 at%.

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