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Changes in Microstructure and Mechanical Properties during Solid Sintering of Ni-Al Mixed Powder Compact

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Low temperature reactive sintering of Ni-Al mixed powder compact is performed, and the effects of temperature, time and pressure of sintering on the microstructure, density, hardness and ductility of the compact at room temperature are investigated. During sintering, intermetallic phases and pores are formed and grow. The growth of the former increases the hardness of the compact, while the growth of the latter reduces the density. The volume fraction of aluminum phase decreases in accordance with the parabolic law, and the parabolic rate constant is described as

$$k = 3000\exp(-60400R^{-1}T^{-1})$$

where R and T are the gas constant and absolute temperature. The ductility of the compact, evaluated by the critical rolling reduction, dramatically increases by short sintering and then gradually decreases with sintering time. The increase in the ductility is caused by the diffusion junction at the interface between powder particles, while the decrease by the formation of intermetallic compound phases at the interface. Application of pressure to the compact during sintering brings about remarkable increase in the density and hardness of the compact.

Keywords: powder metallurgy, reactive sintering, intermetallic compound, nickel aluminide, mechanical properties, ductility, hot press

I. Introduction

Intermetallic compounds in the Ni-Al system such as Ni_3Al and NiAl are the promising potential high temperature materials which may take the place of conventional nickel-base superalloys. Tri-nickel aluminide Ni_3Al demonstrates extraordinary properties, such as high melting point, positive temperature dependence of strength, good resistance to creep and oxidation, and relatively low density.[1]-[3] On the other hand, mono-nickel aluminide NiAl receives much attention due to its higher melting point, lower density, and better oxidation resistance than Ni_3Al.[4][5] Excellent properties of these nickel aluminides make them attractive for aerospace and structural applications at elevated temperatures. However, the most significant disadvantage of these nickel aluminides is room temperature brittleness, although the brittleness of Ni_3Al is reduced to some degree by microalloying[6] and that of NiAl by grain refinement.[7][8] One possible solution to this problem is utilization of the near-net-shape fabrication technique such as powder metallurgy processing. Reactive sintering[9]-[14] of mixed powder compact is one of the novel and attractive processes. In the present study, changes in the microstructure and mechanical properties of Ni-Al mixed powder compacts during low temperature reactive sintering are investigated.

II. Experimental Procedure

Carbonyl nickel powder(99.8 % pure, 4 to 7 μm in diameter) and gas-atomized aluminum powder

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(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. The powder mixture was cold-pressed into cylindrical green compacts in a metal mold. The maximum compacting pressure was 1400 MPa. The diameter and height of the compact were 16 mm and 12 mm. The compact was sintered in air at a temperature between 698 K and 748 K. Sintering under a high pressure was also performed to reduce the porosity of the compact. The microstructure change of the compact during sintering was investigated. The density, hardness and ductility of the compact were measured at room temperature. The density was evaluated by Archimedes' method, the hardness by a Vickers hardness tester and the ductility by the critical rolling reduction which was defined as the value of rolling reduction at which cracks propagated from the side edge to a quarter width of the rolled compact. The initial thickness of the rolled compact was 6 mm and the reduction per pass was 0.25 mm.

III. Results and Discussion

1. Green Compact

Figure 1 shows the effect of compacting pressure on the density of the green compact. The density gradually increases toward the ideal density of 5.17 Mg/m^3 with increasing compacting pressure. Because the density after pressing to the maximum of 1400 MPa is 5.01 Mg/m^3, the final volume fraction of the pores remaining in the green compact is calculated to be no more than 3 %, according to Eq. (1). [15]

$$p = 1 - \rho_{Mix}(\rho_{Ni} f_{Al} + \rho_{Al} f_{Ni})/(\rho_{Al}\rho_{Ni}) \quad (1)$$

where ρ and f are the density and mass fraction of the material indicated by the subscript.

Figure 2 shows the microstructure on a section perpendicular to the compression axis of the cylindrical green compact. Aluminum powder particles are dispersed homogeneously in the matrix phase of nickel. Very small pores are observed in the matrix phase.

2. Change in the Structure

Figure 3 shows the microstructure of a sintered compact. Intermetallic phases (light gray area) are formed at the interface between aluminum and nickel phases. Small pores (dark spots) are observed at the interface between intermetallic phases and aluminum particles and also inside the intermetallic phases. The formation of these pores is explained to be caused by Kirkendall effect. [16]

Figure 4 shows the results of EPMA analysis

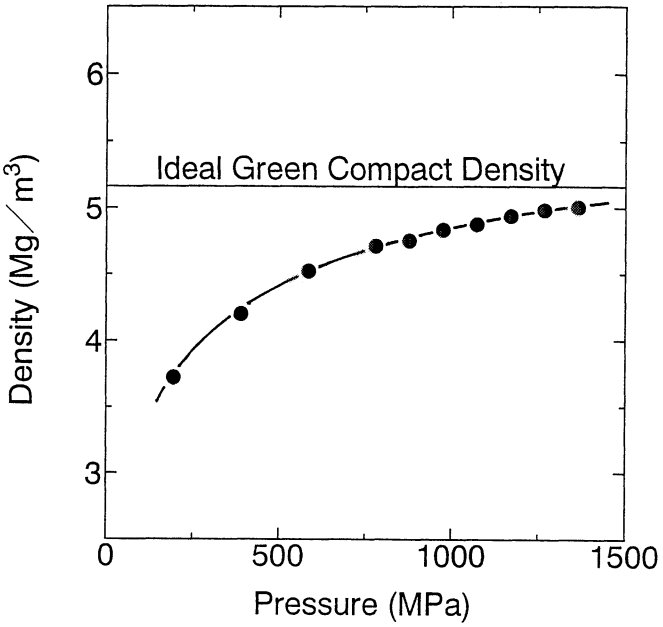

Fig. 1 Effect of compacting pressure on the density of the green compact.

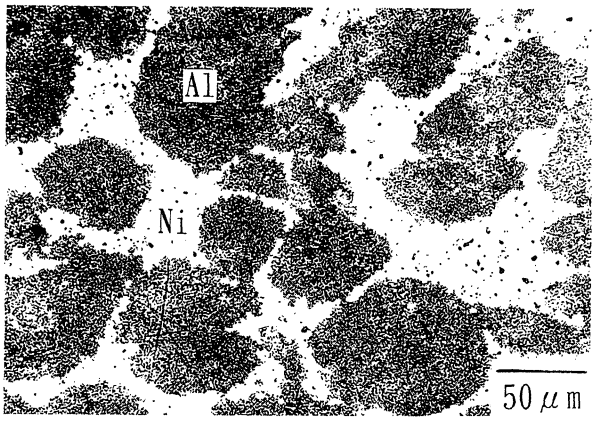

Fig. 2 Microstructure of the green compact.

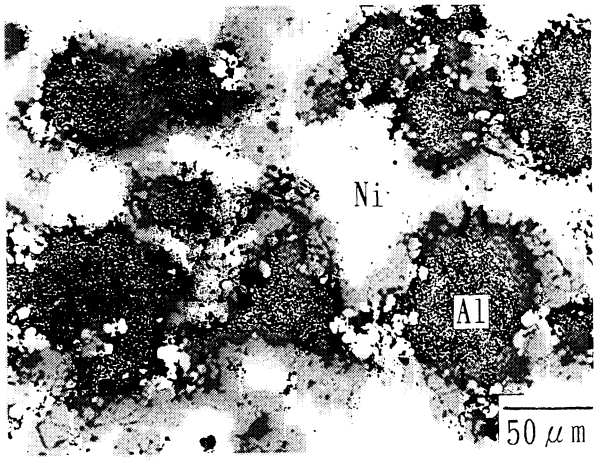

Fig. 3 Microstructure of a compact sintered at 723 K for 40 ks.

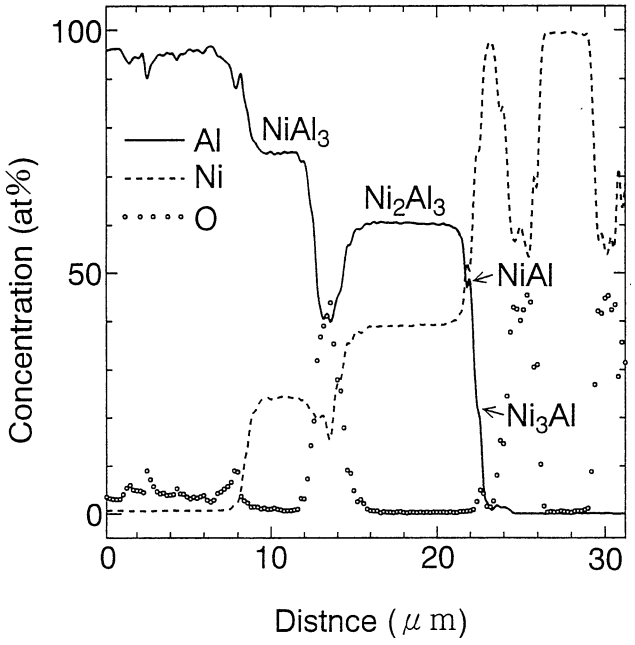

Fig. 4 EPMA line analysis of a compact sintered at 723 K for 160 ks.

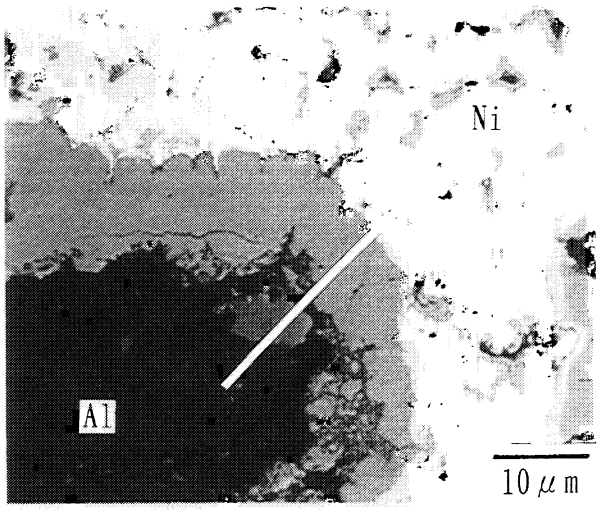

Fig. 5 Microstructure of the sintered compact analyzed by EPMA, shown in Fig. 4.

performed on the cross section of the sample shown in Fig. 5. The white straight line shown in Fig. 5 indicates the trace of probing. The results shown in Figs. 4 and 5 can be summarized as follows: (1) particles of $NiAl_3$ phase are formed in aluminum phase, (2) a thick rim of Ni_2Al_3 phase surrounds the $NiAl_3$-aluminum mixed regions, (3) very thin layers of NiAl and Ni_3Al phases surround the rim of Ni_2Al_3 phase, and (4) relatively thick films of a nickel oxide phase are formed at the interface between nickel powder particles.

Hibino[17] investigated the reaction process of combustion synthesis of Ni_3Al from mixed powder of nickel and aluminum, and reported that only Ni_2Al_3 was detected by EPMA analysis of the intermetallic phase formed at the interface between nickel and aluminum. It is, however, considered to be reasonable that several intermetallic phases are formed between the metallic nickel and aluminum phases, since they are thermodynamically stable, according to a Ni-Al binary equilibrium phase diagram[18].

As the regions of intermetallic phases grow, the volume fractions of nickel and aluminum phases decrease. Figure 6 shows the relationship between the conversion ratio[19] of aluminum phase and the square root of sintering time. The conversion ratio of aluminum phase is defined in Eq. (2).

$$C_W = (f_0 - f_t)/f_0 \qquad (2)$$

where f_0 is the volume fraction of aluminum phase before sintering, and f_t is that at a sintering time, t. It is shown in Fig. 6 that the conversion ratio increases in accordance with the parabolic law described in Eq. (3).

$$C_W = kt^{1/2} \qquad (3)$$

where k is the parabolic rate constant evaluated from the slope of the straight lines in Fig. 6.

Figure 7 shows the relationship between the natural logarithm of the parabolic rate constant and the inverse of sintering temperature, T. This relationship is regressed as Eq. (4).

$$k = 3000\exp(-60400R^{-1}T^{-1}) \qquad (4)$$

where R is the gas constant. The value of the activation energy of 60400 J/mol is much larger

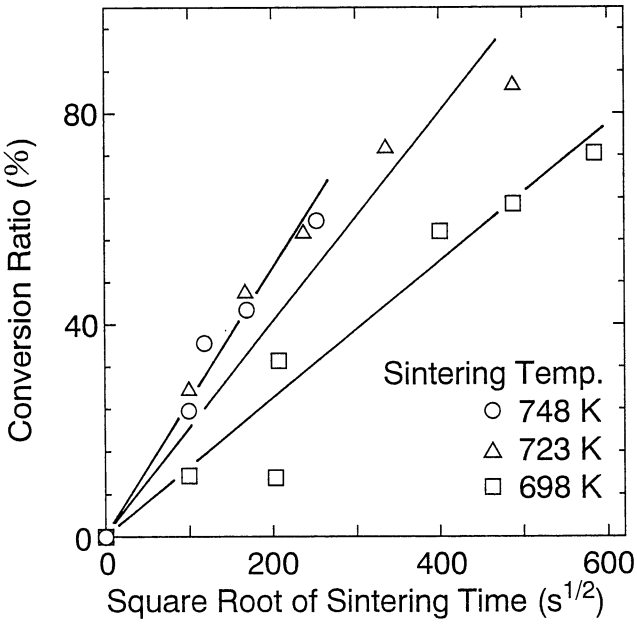

Fig. 6 Relationship between the conversion ratio of aluminum phase and the square root of sintering time.

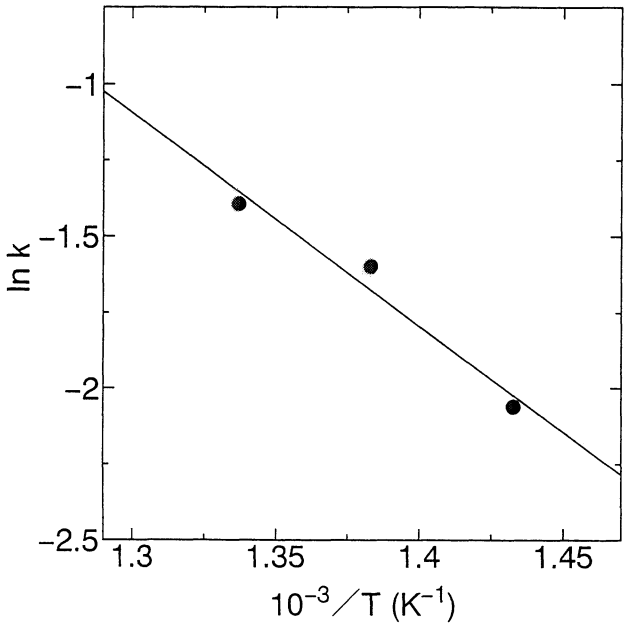

Fig. 7 Relationship between the natural logarithm of the parabolic rate constant of the conversion ratio of aluminum phase and the inverse of sintering temperature.

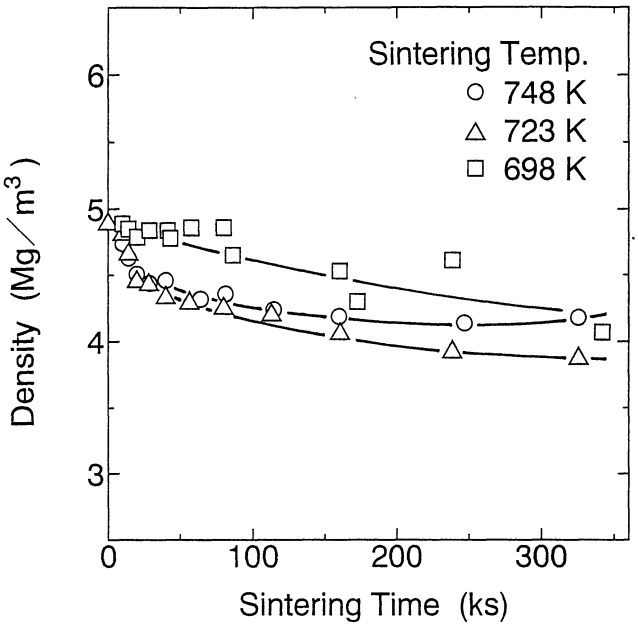

Fig. 8 Change in density of the compact during sintering.

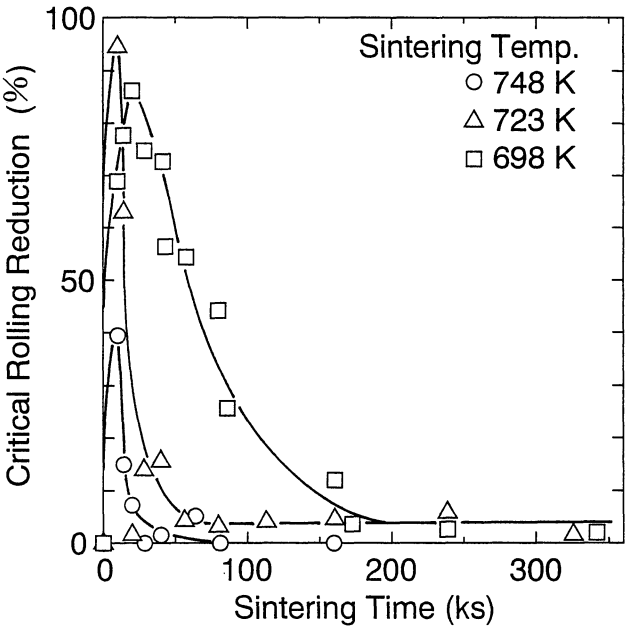

Fig. 9 Change in the critical rolling reduction of the compact during sintering.

than 25700 J/mol which was evaluated by Green and Swindells[20] for the diffusion of nickel and aluminum in NiAl phase, but it is comparatively close to 89000 J/mol which was evaluated by Hibino[19] for the diffusion of aluminum in Ni_2Al_3 phase. Therefore, it may be suggested that the decrease in aluminum phase during sintering is rate-controlled by the diffusion of aluminum in Ni_2Al_3 phase. As a supporting evidence, very thick layer of Ni_2Al_3 phase is formed at the interface between nickel and aluminum (See Figs. 4 and 5.).

3. Change in the Mechanical Properties

Figure 8 shows the change in density of the compact during sintering. The density slowly decreases with time. When sintering temperature is elevated from 698 K to 723 K, the density decreases remarkably. However, when the temperature is elevated to 748 K, decrements in density become less remarkable and the density increases with time after approximately 300 ks. As sintering proceeds, both pores and intermetallic phases grow. The growth of pores leads to the decrease in density of the compact, while that of intermetallic phases leads to the increase, because the density of Ni-Al alloys is higher than the ideal density of the green compacts of the powder mixture.[21] The results in Fig. 8 suggests that the balance of these opposite effects changes depending on temperature.

Figure 9 shows the change in ductility of the compact evaluated by the critical rolling reduction. It is impossible to roll the green compact. However, with increasing sintering time, the critical rolling reduction dramatically increases. The maximum critical rolling reduction reaches 95 %, when sintering temperature is 723 K. The increase in ductility of the compact is considered to be caused by diffusion junction at the interface between powder particles, while the decrease observed for the oversintered compact is explained by the formation of hard in-

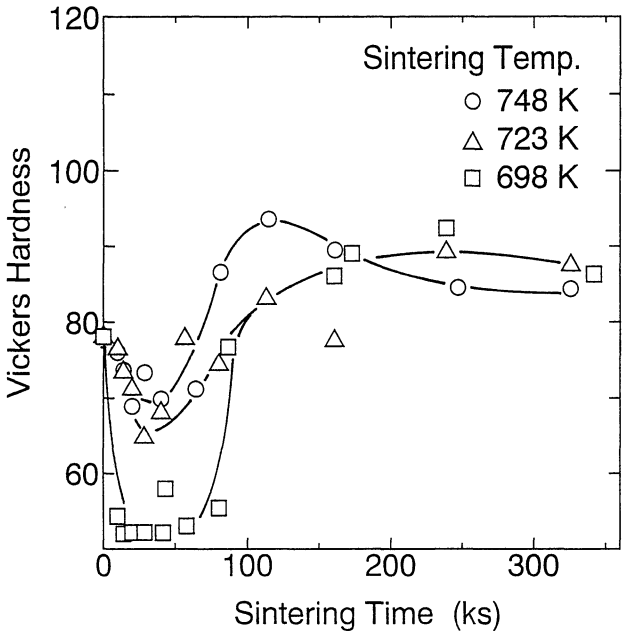

Fig. 10 Change in the Vickers hardness of the compact during sintering.

termetallic compound phases at the interface.

Figure 10 shows the change in the Vickers hardness of the compact during sintering. The hardness decreases in the early stage of sintering, but then it increases with time. The decrease in hardness is caused by the relaxation of strain energy in the green compact which was introduced in green compaction under a very high pressure, while the increase in hardness is due to the dispersion hardening by intermetallic compound phases or to the solid solution hardening by interdiffusion of metallic elements. The increase in hardness, however, stops at about 150 ks. We suspected that the generation and growth of pores during sintering prevented hardening of the compact. Therefore, we planed to sinter the green compact under a high pressure to reduce the porosity in the compact and to increase the hardness.

4. Sintering under Pressure

Green compacts were uni-directionally hot-pressed in a cylindrical mold. Figure 11 shows the microstructures of the sintered compact on a section parallel to the compression axis. When pressure is not applied (Fig. 11(a)), large pores are seen, while when a pressure of 240 MPa is applied during sintering (Fig. 11(b)), aluminum powder particles and the surrounding intermetallic phases are compressed in the pressing direction, and pores are hardly seen.

Figure 12 shows the effect of the sintering pressure on the density of the compact. The den-

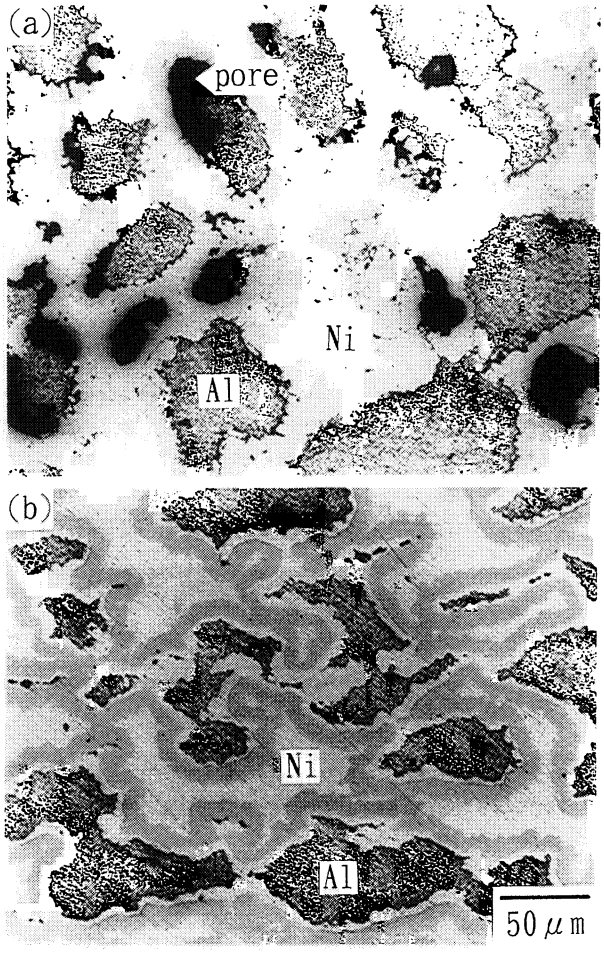

Fig. 11 Effect of the sintering pressure on the microstructure of a compact sintered at 748 K for 43 ks. Sintering pressure: (a) null and (b) 240 MPa.

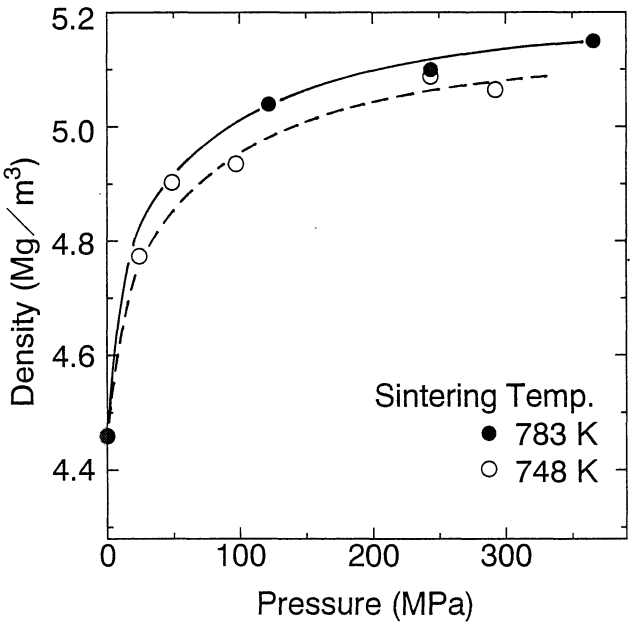

Fig. 12 Effect of the sintering pressure on the density of the compact. Sintering time: 43 ks.

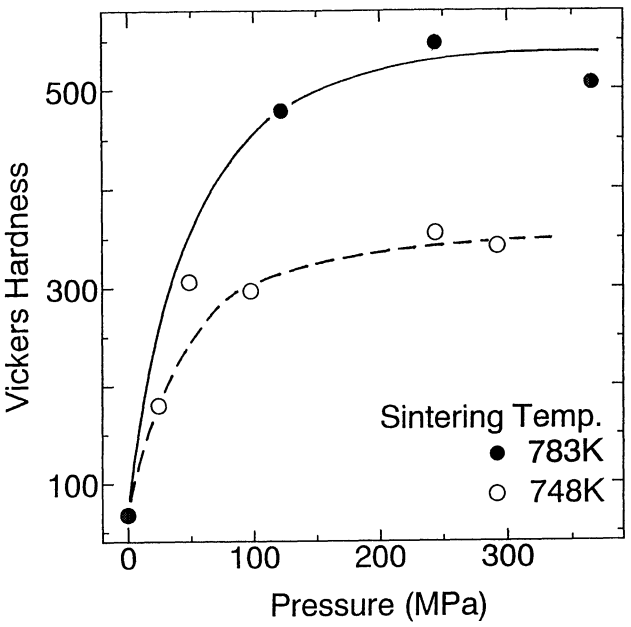

Fig. 13 Effect of the sintering pressure on the hardness of the compact. Sintering time: 43 ks.

sity increases with increasing pressure. The effect is particularly remarkable in the low pressure region.

Figure 13 shows the effect of the sintering pressure on the Vickers hardness of the compact. The hardness reaches 500, when a sintering pressure of approximately 300 MPa is applied during sintering at 783 K.

IV. Conclusions

A powder mixture of nickel and aluminum in the 1:1 atomic proportion was cold-pressed into cylindrical green compacts. The compacts were sintered at lower temperatures than the eutectic temperature in Ni-Al binary system. Changes in the microstructure and the mechanical properties during sintering were investigated. The results are summarized as follows:

(1) During sintering, several types of intermetallic compound phases and pores are formed and grow. The former is formed at the interface between nickel and aluminum phases, while the latter at the interface between the intermetallic phases and aluminum phase and also inside the intermetallic phases. The growth of the former brings about the increase in hardness of the compact, while that of the latter the decrease in density of the compact.

(2) The volume fraction of aluminum phase decreases during sintering in accordance with the parabolic law, and the parabolic rate constant is described as

$$k = 3000\exp(-60400R^{-1}T^{-1}).$$

(3) The ductility of the compact dramatically increases by short-time sintering and then gradually decreases with longer sintering time. The increase in the ductility is caused by diffusion junction at the interface between powder particles, while the decrease by formation of hard intermetallic compound phases at the interface.

The increase in the Vickers hardness of the compact stops at about 80, in spite of the increase in sintering time. Because this was considered to be caused by the presence of pores in the compact, sintering under a high pressure was performed in order to reduce the porosity. It was found that applying a pressure higher than 100 MPa to the compact during sintering brings about a remarkable increase in the density to about 5 Mg/m^3 and hardness to about 500.

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