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Infiltration and combustion synthesis of an intermetallic compound Ni_3Al

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Abstract

Utilising a combination of infiltration and combustion synthesis, a new method for fabricating a high melting point metallic compound (Ni_3Al) with only a few pores and little change in the shape, at a low temperature and at atmospheric pressure, has been established. The main procedure for this method is the dropping of molten aluminium or Al–Ni alloys (Ni content up to 18 mass%) onto a sintered nickel sample with 34–36 vol.% pores at 1073 K. Immediately after a molten aluminium or an Al–Ni alloy is dropped onto a sintered nickel sample, the molten metal infiltrates into the sintered material accompanied by an exothermic reaction. When a molten Al–Ni alloy (with a nickel content of over 10 mass%) is dropped, a Ni_3Al material is fabricated with only a few pores and little change in the shape. The addition of nickel to the drop delays the onset of the interfacial reaction though the total heat produced is not very different. The delay in the onset of the interfacial reaction allows the infiltration to finish or proceed to some extent before a certain critical point in the interfacial reaction. As a result. a uniform Ni_3Al compound is produced. The experimental data clearly relate to the adiabatic combustion temperatures, which indicates that the heat loss is relatively low. As a result, a high melting point metallic compound can be produced at a low temperature and at atmospheric pressure. © 1997 Elsevier Science S.A.

Keywords: Aluminium; Combustion synthesis; Exothermic reaction; Infiltration; Interfacial reaction; Intermetallic compound; Ni_3Al; Nickel; Wetting

1. Introduction

Intermetallic compounds have been expected to be used as high-temperature and oxidation resistance materials in, for example, turbine blades or the nozzle of a gas burner. In particular, intermetallic compounds based on aluminium have attractive properties such as low density, high strength and good corrosion resistance. In spite of these attractive properties, however, intermetallics have limited application due to their extreme brittleness and the resulting difficulties in shaping.

For the fabrication of an intermetallic compound, various methods have been tried, such as melting and casting, powder metallurgy using alloying powder, and reactive sintering with pure original materials, for example, pure aluminium and nickel powder in the fabrication of Ni_3Al.

In the melting method, a variety of techniques such as vacuum induction melting, argon induction melting, electroslag remelting, vacuum arc remelting, plasma melting and electron beam melting have been used to produce intermetallic ingots. However, high temperature forming of castings is very sensitive to composition [1] and the change in the composition due to contamination by impurities from the crucible and the vapour loss during the melting process, is a great problem.

Powder metallurgy is ideal for the fabrication of complex shaped intermetallic compounds. However, when alloying powder is used, the productivity is not good. On the other hand, when reactive sintering is conducted with pure original materials [2,3] a high density material is not easily manufactured and a subsequent treatment such as HIP is required. Especially in a system where the density of the new product is lower than that of the original materials, the pores increase in size during the process [4]. This is caused by the fact that the liquid produces a network and the existing gas contained in the pores can not escape.

Thus, the production or shaping of intermetallic compounds is difficult. As a result, few intermetallic compounds are put to practical use. Therefore, an easy

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and inexpensive method of fabricating intermetallic compounds with no subsequent shaping would have many practical advantages.

In this study, utilising a combination of the concepts of infiltration and combustion synthesis, a new method of fabricating intermetallic compounds has been devised. The object of this study is to establish a method for fabricating an intermetallic compound with no requirement of subsequent shaping, at a low temperature and at atmospheric pressure.

2. Concept of the new method

The concept of the new method consists of infiltration and combustion synthesis.

When the contact angle between a solid and a liquid is less than 90°, the liquid spontaneously infiltrates into a sintered material, made of the solid. The contact angle between nickel and molten aluminium is much lower than 90°, for example less than 20° at 1073 K (apparent contact angle 20°) [5]. Therefore, molten aluminium infiltrates into the sintered nickel spontaneously. The infiltration speed is proportional to the square root of the cosine of the contact angle [6,7]. The smaller the contact angle, the greater the speed of infiltration. Therefore, unlike infiltration in ceramic/metal systems, in a Ni/Al system no pressure is necessary. As a result, the intermetallic compound can be produced at atmospheric pressure.

When Ni_3Al is formed from pure aluminium and pure nickel, a great amount of heat is released. For example, Ni_3Al is formed at 1073 K, the adiabatic combustion temperature is 1730 K. Therefore, the intermetallic compound can be produced at a low temperature.

Utilising these characteristics, an attempt was made to fabricate Ni_3Al without any deformation or pores at atmospheric pressure and at a low environmental temperature. The main procedure for this method consists of the following two steps:

(1) Nickel is sintered with approximately 35 vol.% pores for molten aluminium to infiltrate, taking into account the density of the final product, Ni_3Al.
(2) Molten aluminium or Al–Ni alloy is dropped onto the sintered nickel.

The considerable merits of this method, compared with ordinary reactive sintering are as follows:

(1) When ordinary reactive sintering is used, the pores are likely to remain because the gas in the pores can not escape. The proposed method, on the other hand, enables the gas to escape because the pores are big enough to be interconnecting and the liquid infiltrates in one direction only.
(2) When ordinary reactive sintering is used in a system where the density of the product is lower than that of the original materials, either the pores in the material become larger or the product itself shrinks. With the new method, however, this problem does not occur, as the aluminium is added after forming.
(3) When ordinary reactive sintering is used, an oxide film inevitably remains on the aluminium particles. However, in the new method, the oxide film on the aluminium surface is removed mechanically during the drop and the oxygen content in the product is reduced.

3. Experimental apparatus and procedure

Nickel samples with 34–36 vol.% pores were sintered using nickel powder with a mean particle diameter of 50 μm. The volume ratio of pores was controlled by the pressure of forming. The dimensions of the sintered nickel were approximately 15 × 10 × 6.5 mm and the purity was 99 mass%. As liquid samples, 99.99 mass% Al and Al–Ni alloys (intended nickel content: 10 and 18 mass%) were used. The chemical composition of pure aluminium and Al–Ni mother alloys is shown in Table 1. Alloys with a different composition from those shown in Table 1 were made by mixing two of the base materials.

The experimental system consists of a sealed chamber, a purification system for the atmospheric gas ($He + 3\%H_2$) in the chamber, a set of vacuum pumps to evacuate the chamber, and a video recording camera with bellows and macro lenses [8,9]. The sealed chamber has four viewing windows and contains a molten aluminium dropping device and a molybdenum cylindrical heater with three concentric reflectors located around the dropping device. The aluminium dropping device is a tube of pure alumina (99.9 mass%) with a 0.5 mm hole in its base.

After a sintered nickel sample had been set in a horizontal position under the dropping device, the chamber was evacuated to 1.3×10^{-5} Pa (approximately 10^{-7} Torr) and then the temperature was raised at a rate of about 30 K min^{-1}. When the temperature reached the experimental temperature (1073 K), the purified $He + 3\%H_2$ atmospheric gas was introduced and the pressure raised to 120 kPa (1.2 atm). After that, an aluminium or Al–Ni pellet was inserted into the

Table 1
Chemical composition of the dropping sample (mass%)

Sample	Ni	Fe	Si	Others
Al	<0.001	0.002	0.004	Al, >99.99; Cu, 0.001; Ca, 0.002
Al–10Ni	9.83	0.003	0.010	
Al–18Ni	19.49	0.011	0.014	

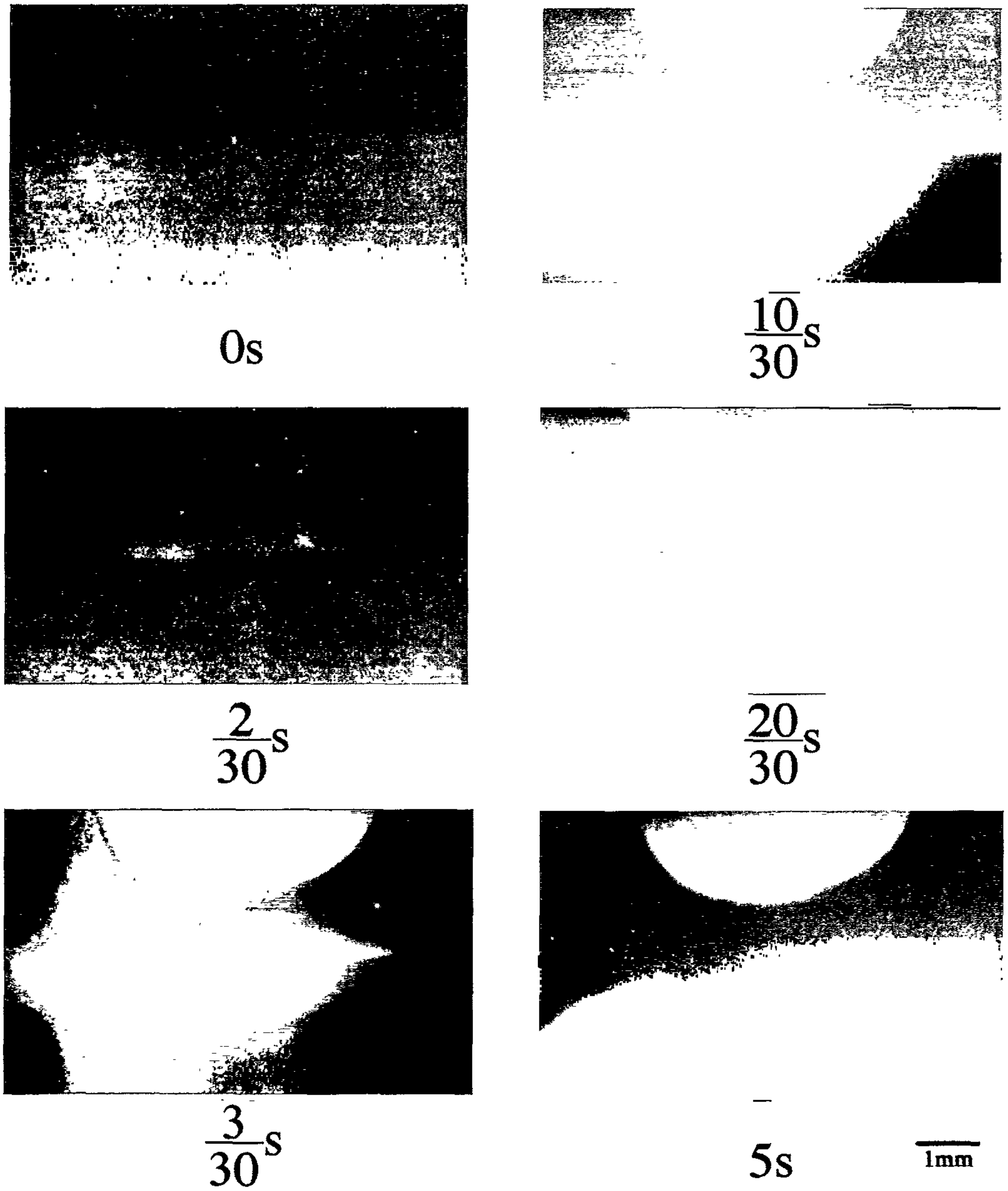

Fig. 1. Photographs showing pure Al dropped onto sintered Ni (50 μm, 1073 K).

dropping device. When the aluminium or Al–Ni pellet had been heated to the experimental temperature, it was, as a liquid, forced through the hole in the base of the tube by a small decrease in the atmospheric pressure in the chamber. At that time the oxide film of the liquid surface was mechanically removed by the action of passing through the hole.

The dropping event was recorded in detail using a video camera to observe the exothermic reaction. Subsequently, the cooked samples were analyzed by EPMA and X-ray microdiffractometry.

4. Experimental results and discussion

4.1. *Appearances of formation of Ni_3Al*

Fig. 1 shows the action of pure aluminium dropped onto the sintered nickel. As shown in this figure, the molten aluminium immediately infiltrates into the sintered material with an exothermic reaction. An emission by exothermic reaction was observed from 3/30 s for about 45 s with a video camera. However, at this

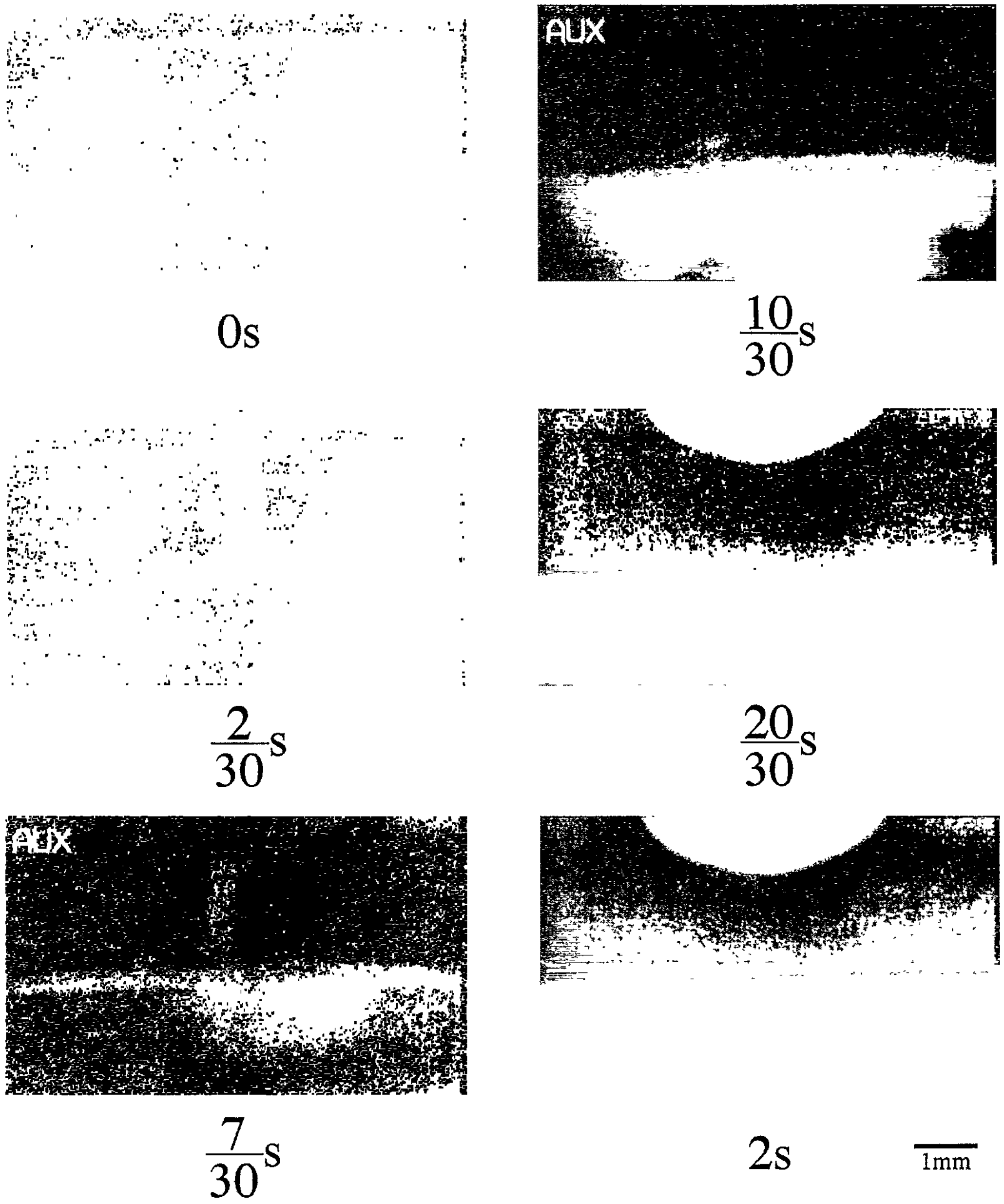

Fig. 2. Photographs showing Al–10mass%Ni dropped onto sintered Ni (50 μm, 1073 K).

time, the original shape of the sintered nickel sample is lost because the heat of the reaction is too great.

On the other hand, when an Al–Ni alloy, in place of aluminium is dropped onto a sintered nickel sample, the sample does not transform, as shown in Fig. 2. This success is apparently caused by the heat control with the inclusion of nickel into aluminium. The sample starts emitting light by an exothermic reaction after a moment and remains bright for about 1 min.

Fig. 3 shows the cross section of the product, etched by 50% nitric acid and 50% glacial acetic acid. Uniform Ni_3Al is obtained throughout the sample, as shown in this figure. The black dots in the product are the remaining pores. Therefore, the product is not perfectly compact. However, considering the simplicity of this method, this is regarded as a good product.

4.2. The relationship between the composition obtained and the adiabatic combustion temperature

In order to investigate the relationship between the composition obtained and the reached temperature, some experiments were conducted. Dropping a Al–Ni alloy, in place of aluminium, onto a sintered nickel sample was very effective in controlling the exothermic reaction, as mentioned before. Reducing the quantity of the dropping liquid is another possible way of controlling the exothermic reaction.

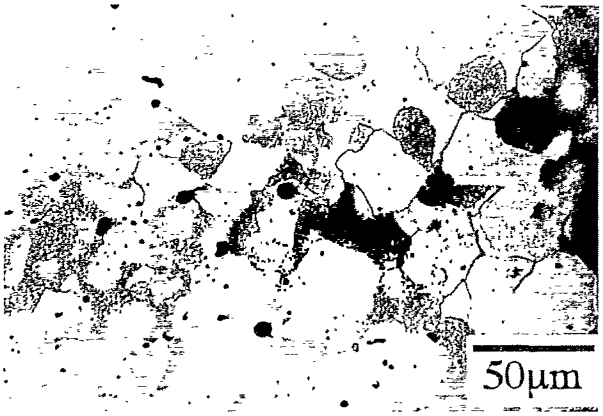

Fig. 3. Cross section of a product.

Fig. 4 shows the composition of the material obtained after dropping, using various levels of nickel content in the molten alloy and various ratios of dropped liquid to volume of pores in the sintered nickel sample. The calculated adiabatic combustion temperatures are also shown in this figure. Here, almost all the thermochemical data are cited from Barin's work [10]. However, because the heat of solution ($\Delta H_{\mathrm{solution}}$) of nickel to aluminium at 1073 K is not known, the data for heat of solution of nickel at 1873 K to aluminium at 1123 K, as reported by W. Oelsen [11] are used, on the assumption that $\Delta H_{\mathrm{solution}}$ does not depend on the temperature.

1668 K is the melting point of Ni_3Al and 1406 K is the melting point of Ni_2Al_3. 1668 K covers a wide range due to the heat of fusion of Ni_3Al. This indicates that the quantity of liquid Ni_3Al increases toward the upper line of 1668 K and the quantity of solid Ni_3Al increases toward the lower line of 1668 K. In Fig. 4, the nickel content of the Al–19.49mass%Ni alloy is regarded as 18 mass% because the nickel solubility in aluminium at 1073 K is 18 mass% [12] and the excess nickel seems to remain in the dropping device.

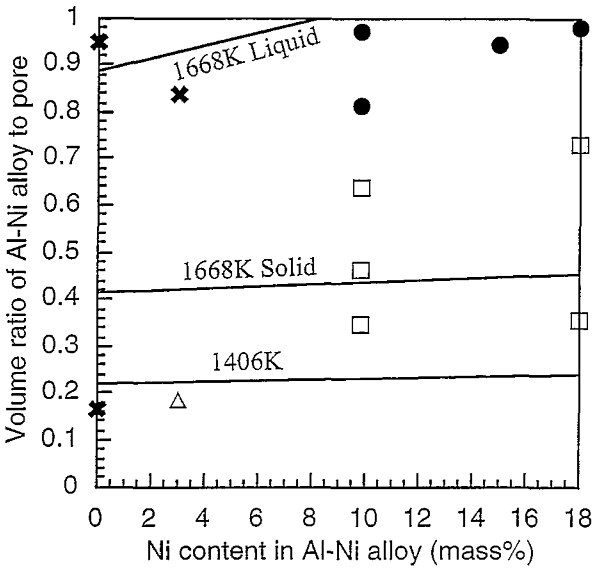

Fig. 4. Relationship between composition of formed material and adiabatic temperature. (×, Deformation; △, (Ni) + Ni_2Al_3; □, (Ni) + NiAl + Ni_2Al_3; ●, Ni_3Al).

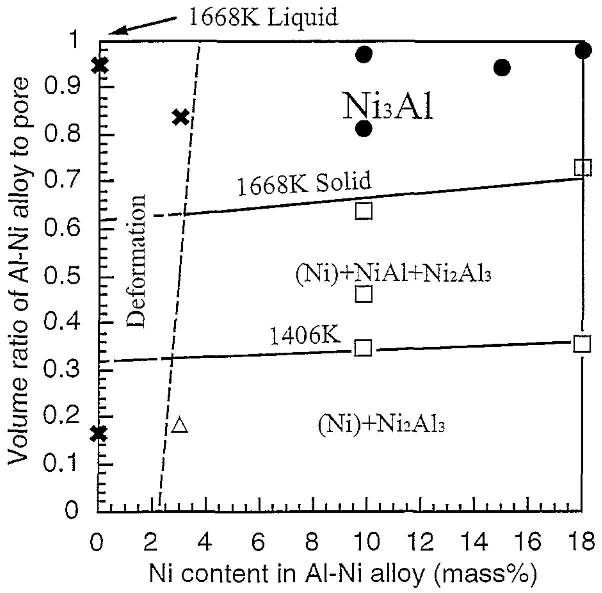

Fig. 5. Temperature attained, assuming 1/3 heat loss.

Because in an actual experiment some heat escapes, the adiabatic temperature can not be reached. Accordingly, taking into account the obtained results of composition, a heat loss of 1/3 is estimated. On this assumption, the temperature reached is calculated as shown in Fig. 5.

The calculated temperature lines clearly divide the results into three sections. When the temperature is higher than 1406 K, the melting point of Ni_2Al_3, NiAl should be formed in the sintered nickel sample because solid Ni_2Al_3 is not formed at the interface [12]. When the temperature is at 1668 K, the liquid phase of Ni_3Al emerges. This phenomenon probably changes the formation speed of Ni_3Al drastically.

The results indicate the reaction is so quick that it is close to an adiabatic combustion. Thus, a high temperature can be obtained to produce a high melting point metallic compound at a low environmental temperature. However, whether the shape changes or not, does not depend on the calculated temperatures: it depends on the relationship between the infiltration speed and the dissolution speed, as discussed in the next section.

4.3. Relationship between infiltration and interfacial reaction

The change in enthalpy when Ni_3Al is formed from pure molten aluminium and solid nickel, is about −

173 kJ mol^{-1} [8] and the change in enthalpy when Ni_3Al is formed from Al–18 mass% Ni and solid nickel is calculated to be about -161 kJ mol^{-1} under the previous assumption. Therefore, when an Al–Ni alloy is dropped, in place of pure aluminium, the heat is reduced. However, the ratio of the reduction in the heat is only about 6.9%. The obtained sample, on the other hand, is drastically different.

When pure aluminium is dropped, the shape changes even when the quantity of aluminium is small, which indicates that the combustion temperature is much higher than 1406 K. The fact that the shape does in practice change when the calculated adiabatic combustion temperature is lower than 1406 K, points to an inadequacy in the method of calculation, that is in the assumption that the temperature is the same throughout the sample. When pure aluminium is dropped, the dissolution of nickel into aluminium occurs very quickly and only the upper part of the sample seems to be heated. At this time, although the average temperature is lower than 1406 K, the temperature of the upper part of the sample must obviously be 1668 K or higher. Calculation shows the temperature of the uppermost part may reach as much as 2800 K.

The extent of the difference is caused by the change in relationship between the infiltrating speed and the interfacial reaction speed such as in the dissolution of nickel into aluminium. Fig. 6 shows the relationship between the onset time of light emission and nickel content of the drop; Fig. 7 shows the relationship between light emission duration and nickel content. It is clear that the addition of nickel delays the starting time of emission but does not have much effect on emission duration. This means that the addition of nickel delays the starting time of interfacial reaction though the total heat does not change very much. When pure aluminium is dropped, the dissolution of nickel into aluminium is probably the first reaction. In contrast, when Al–18mass%Ni is dropped, the first reaction is the formation of intermetallic compounds such as $NiAl_3$ or Ni_2Al_3 because 18 mass% is the solubility level of nickel. Therefore, we can conclude that although the heat in dissolution is small, compared with the total heat as mentioned before, the rate is very quick and affects the condition of the product.

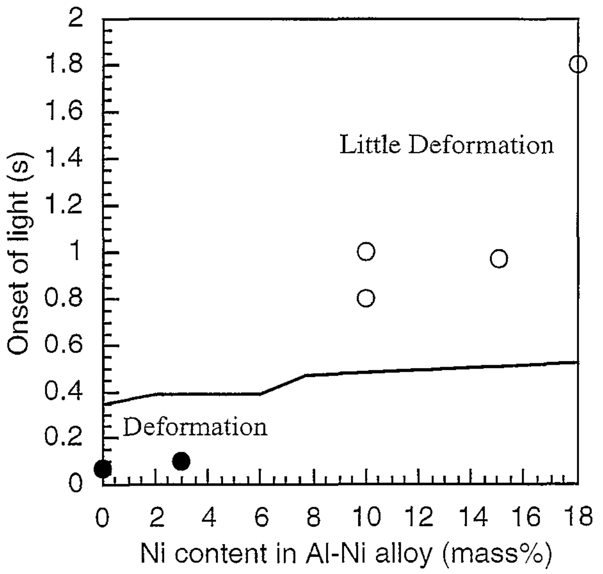

Fig. 6. Relationship between onset of light and Ni content in Al–Ni alloy.

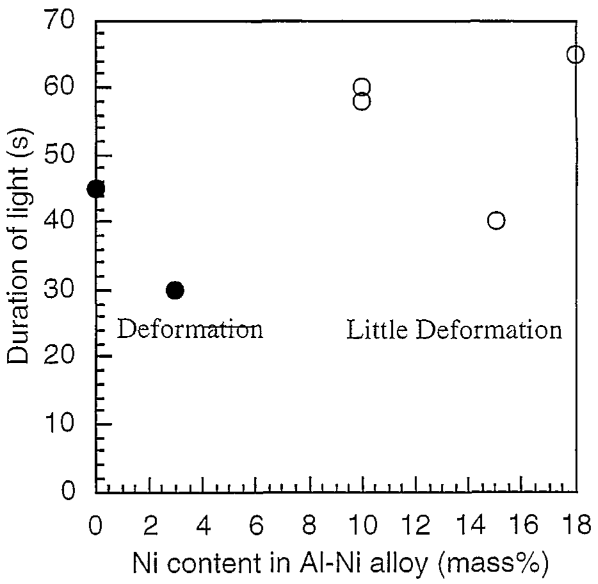

Fig. 7. Relationship between duration of light and Ni content in Al–Ni alloy.

According to Huang's model [6], the change in infiltration length h over time into a sintered material where cylinders with a radius of R are oriented in three dimensions, is expressed as follows:

$$h = \left(\frac{R\gamma_{\mathrm{lv}}\cos\theta}{18\eta}\right)^{1/2} t^{1/2}$$

where γ_{lv} is the surface tension of the liquid, θ is the contact angle between the liquid and the solid, η is the viscosity of the liquid and t is the time.

Using this equation, the time of the completion of infiltration is estimated. At this time, the estimation of the correspondent R is difficult and it is necessary to set up a model. First, all particles are assumed to be 50 µm, which is the average diameter, and the number of the particles per unit volume is determined. Also, it is assumed that the particles are dispersed uniformly throughout the sample and connected to each other without any change in the volume and the gravity centre of each particle, producing cylinders in three dimensions during the sintering process. On these assumptions, the diameter of the cylinders is estimated to be 19 µm.

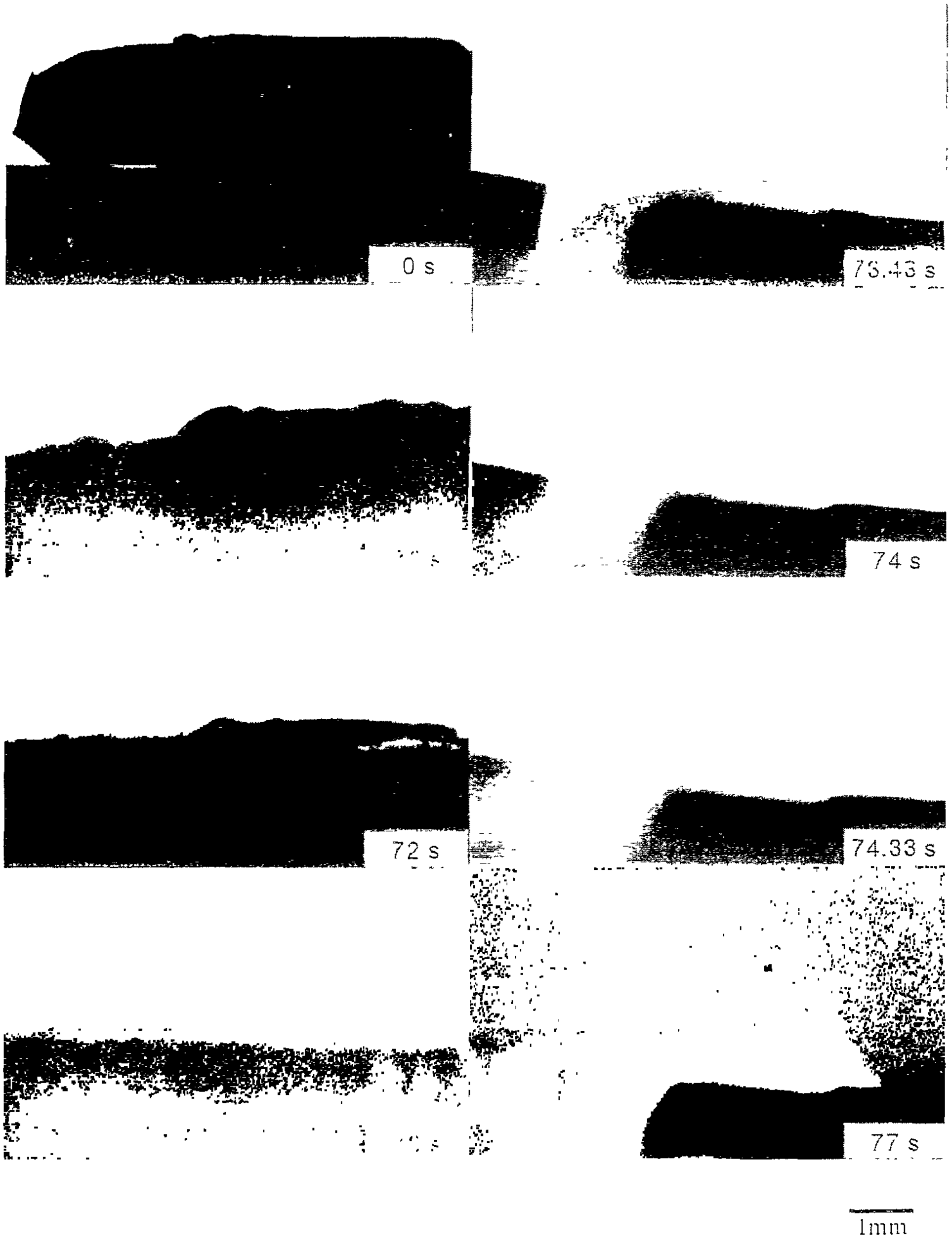

Fig. 8. Photographs showing pure Al placed on sintered Ni (50 μm, 1073 K).

The surface tension of aluminium is 847 mN m^{-1} at 1073 K [13]. Also, because, according to Mori et al. [14], the addition of nickel to aluminium does not have much effect on the surface tension, the surface tension of the Al–Ni alloys is assumed to be equal to that of pure aluminium. The value of 14° was used for the contact angle: Mori et al. reported the contact angle to be between 8° and 20° at 1073 K [5,14]. For the values of viscosity, Jones and Bartlett's data for 1073 K was used [15]. The line shown in Fig. 6 is the calculated result.

As shown in this figure, when the infiltration is completed before the onset of the emission, that is, the onset of the main reaction. the material does not transform. On the other hand, when emission starts before the infiltration finishes, a transformation does take place.

As a reference, when the temperature increases due to the exothermic reaction, the viscosity and the surface tension decrease. For example, when the temperature reaches 1668 K, the viscosity decreases by approximately 48% [16] and the surface tension decreases by approximately 11% [13]. At this time, cos θ increases, by at least 3%. Thus, the infiltration speed at 1668 K is estimated to be approximately 1.8 times as great as the speed at 1073 K.

The infiltration rate is proportional to the square root of dimension of pore [6,7]. In order to reduce the infiltration rate, a similar experiment was conducted using 2.5 μm mean particle sintered nickel. The time of the completion of the infiltration is calculated to be 6.7 s using the previous equation. At this time, pure aluminium or an Al–Ni alloy can not infiltrate into the whole of the nickel. Also, because the area of the interface is larger at this time, the effect of dissolution is also larger. Much brighter emitting light was observed in the upper part of the sample, which indicates the reached temperature was higher. As a result, the sample was deformed or broken.

Another experiment was also conducted where a solid aluminium or Al–Ni alloy was placed on sintered nickel and then heated, as in ordinary reactive sintering. In this method, the liquid was not able to infiltrate into the whole of the nickel. Also, the upper part of the sample was transformed, as shown in Fig. 8. First, the aluminium or Al–Ni alloy melts and starts to react with the sintered nickel at about 913 K [3,17] (close to the melting temperature of Al–Ni eutectic). The heat of the reaction then causes the aluminium to melt and infiltrate the sintered sample. In this method, interfacial reaction occurs before the infiltration. As a result, a uniform Ni_3Al was not able to form. Also, because the starting temperature of the interfacial reaction (913 K) can not be changed in this method, it is difficult to control the heat. This is a defect of this method and ordinary reactive sintering.

In summary, it is concluded that to keep the order ‘infiltration — interfacial reaction’ is a crucial element in the fabrication of a uniform product. The present method enables us to control the interfacial reaction with both the composition of drop and the temperature of the sample.

5. Conclusion

1. Using a combination of the infiltration and combustion synthesis, a new method of fabricating an intermetallic compound has been developed. By dropping Al–Ni alloys onto a sintered nickel sample, a Ni_3Al material, which has only a few pores and little change in the shape, is fabricated at atmospheric pressure and at a low temperature of 1073 K.
2. By adjusting the composition and/or the volume of the dropping metal, the transformation and the composition of the produced material are controlled.
3. The results of the formed composition clearly relate to adiabatic temperatures. The results indicate that the reaction is close to an adiabatic combustion. Consequently, it is possible to produce a high melting point metallic compound at a low environmental temperature (1073 K).
4. In order to produce a uniform Ni_3Al, the rate of interfacial reaction has to be controlled so that the infiltration might occur before the interfacial reaction.

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References

[1] J.H. Schneibel, W.D. Porter and J.A. Horton, Jr., *Metall. Trans.*, *18A* (1987) 2157.
[2] A. Bose, B.H. Rabin and R.M. German, *Powder Metall. Int.*, *20* (3) (1988) 25.
[3] K.A. Philpot, Z.A. Munir and J.B. Holt, *J. Mater. Sci.*, *22* (1987) 159.
[4] A. Hibino and R. Watanabe, *J. Jpn. Inst. Metals*, *55* (1991) 1256.
[5] N. Mori, S. Matsuo, K. Ogi and K. Matusda, *51* (1987) 240.
[6] H. Huang, Y. Lee and H. Nakae, *J. Jpn. Soc. Powder, Powder Metall.*, *41* (1994) 136.
[7] K.A. Semlak and F.N. Rhines, *Trans. Met. Soc. AIME*, *212* (1958) 325.
[8] N. Yoshimi, H. Nakae and H. Fujii, *Mater. Trans. JIM*, *31* (1990) 141.
[9] H. Fujii, H. Nakae and K. Okada, *Acta Metall Mater.*, *41* (1993) 2963.
[10] I. Barin, *Thermochemical Data of Pure Substances*, VCH, Weinheim, 1989.
[11] W. Oelsen, *Kaiser Wilhelm Inst. Eisenforsch*, *19* (1937) 1.
[12] T.B. Massalski et al., *Binary Alloy Phase Diagrams*, Vol. 1, American Society for Metals, USA, 1986, p. 140.
[13] G. Lang, P. Paty, J.C. Joud and P. Desre, *Z. Metallk.*, *68* (1977) 113.
[14] N. Mori, H. Miyahara, M. Koga and K. Ohgi, *J. Jpn. Inst. Metals*, *55* (1991) 444.
[15] W.R.D. Jones and W.L. Bartlett, *J. Inst. Metals*, *81* (1952–1953) 145.
[16] E.A. Brandes and G.B. Brook (eds.), *Smithells Metals Reference Book*, 7th edn., Butterworths, 1992, pp. 14–7.
[17] A. Hibino, *J. Jpn. Inst. Metals*, *56* (1992) 1435.