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Abstract
By using aluminium nanopowder prepared by wire electrical explosion, pure monophase NiAl compound with fine crystallites ($<10\ \mu$m) and good densification (98% of the theoretical green density) was successfully fabricated by means of self-propagating high-temperature synthesis (SHS) under a high pressure of 50 MPa. Investigation shows that, due to the physical and chemical characteristics of the nanoparticles, the SHS reaction mode and mechanism are distinct from those when using conventional coarse-grained reactants. The SHS reaction process depends on the thermal conditions related to pressure and can occur at a dramatically low temperature of 308 °C, which cannot be expected in conventional SHS reaction. With increasing pressure, the SHS explosive ignition temperature (T_{ig}) of forming NiAl decreases due to thermal and kinetic effects.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Intermetallic compounds such as NiAl and Ni_3Al are emerging as the next generation of high-temperature, oxidation-resistant materials. The fabrication processes can be classified into several categories such as casting, rapid solidification, mechanical alloying, and powder processing. Numerous works on the fabrication of various aluminides have been carried out in the last decade [1–3]. Casting is one possible route, but it has several problems, especially for composites. Powder metallurgy is one of the major processes; however, without pressure, most aluminides are hard to sinter to full density because of the stable surface oxide film, i.e. Al_2O_3. They can be sintered by hot pressing or by hot isostatic pressing (HIP) [4]. On the other hand, foundry processes have much more flexibility than powder metallurgical processes. The production costs are, however, still high, because the casting temperatures of most the aluminides are higher than 1400 °C and because the casting must be done in vacuum [5].

For NiAl, several studies have shown the benefit of using a self-sustained reaction (so-called self-propagation high-temperature synthesis (SHS)) [6–9]. This technique is concerned with the ignition of a composite powder mixture in air or inert atmosphere, producing a chemical reaction, with sufficient heat release (exothermic reaction) that it becomes self-sustaining. Nickel aluminides, primarily the phase NiAl, have been prepared by combustion and in the thermal explosion mode [10–13]. Processing parameters such as pressure [14], particle size, and interfacial quality [15] are reported to exert a great influence on the combustion processes. However, it is difficult to get a homogeneous NiAl compound by the techniques mentioned above.

In all the above studies, conventional coarse-grained powders whose grain sizes are micrometres were used, but using nanometre-sized particles to synthesize intermetallic NiAl has not been reported. Nanopowder prepared by wire electrical explosion (WEE) exhibits distinctive characteristics, especially its high stored energy and high chemical activity [16]. Therefore, the reaction mode and process of using nanoparticles will certainly differ from those when using conventional coarse-grained powders.

The present report is aimed at developing an *in situ* process of fabrication using nanomaterials by the SHS method. The process will offer several benefits in the fabrication of intermetallic materials with good densification and fine crystallites.

2. Experiment

Aluminium nanoparticles prepared by WEE with an average particle size of 40 nm (99.9% purity) and conventional nickel powder (99.9% purity) with an average particle size of 44 μm were used. The powders were dry mixed for 2 h in the molar ratio of 1:1 using a hermetic tubulate-type mixer charged with Ar. Then the resulting blends were cold pressed into compacts with diameter 15 mm and height 6 mm. The thermal explosion press (TEP) technique was used in this study. A schematic illustration of the experimental device is shown in figure 1. Two graphite packing blocks were used as heaters to heat the sample. A 1.0 mm diameter hole, which is normal to the sample axis, was drilled from the lateral face of the cylinder graphite mould to accommodate a W/10% Rh thermocouple to follow the temperature of the sample via a computer-controlled system.

In order to investigate the effect of cold pressure on the SHS process and the nature of the final product, compacts with green densities of 60, 68, 76, 84, 90% were cold pressed under pressures of 20, 40, 70, 100, 120 MPa. With the heating rate of 150 K min^{-1}, the samples were ignited under pressure of not more than 2.5 MPa.

In order to investigate the effect of hot pressure on the SHS process and the densification of the product, samples of 70% green density were ignited at a constant heating rate of 150 K min^{-1} in air under the hot pressure of 10–50 MPa. The nature of the phase products was examined by x-ray diffraction (XRD), and their morphology and composition were determined by a scanning electron microscope (SEM) attached to an energy dispersive x-ray analysis (EDX) system.

3. Results and discussion

3.1. The effect of the cold pressure

In the preparation of aluminides, either the combustion or the thermal explosion mode can be used. In the thermal explosion mode, parameters such as heating rate, pressure, particle size, and green density of the pellet have all been found to influence the SHS reaction.
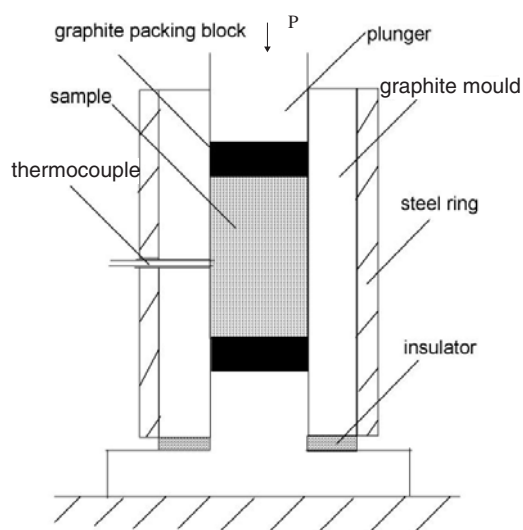
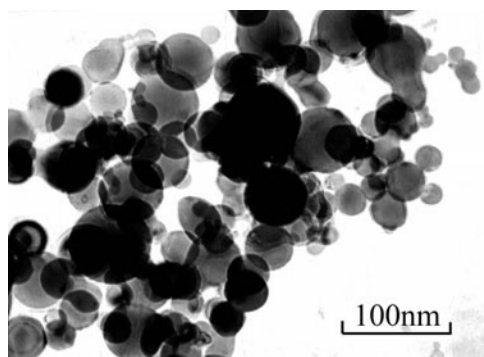**Figure 1.** A schematic illustration of the SHS reaction process.

Figure 2. A TEM image of Al nanoparticles prepared by WEE.

In the present study, the distinctive features of the explosive SHS reaction process and mechanism strongly depend on the green density of the compacts determined by the cold pressure. The effect of cold pressure on T_{ig} could be reflected by the fact that T_{ig} decreases with increasing green density. With pressure increasing from 20 to 120 MPa, the green density of the compacts increases from 60 to 90% and, correspondingly, T_{ig} decreases from 400 to 320 °C, as shown in figure 3.

Under certain pressures, the SHS process and mechanism of using nanoparticles are quite different from those of the conventional SHS reaction. Nanoparticles prepared by WEE are characterized by high stored energy and chemical activity. The result of our previous study on thermal characteristic of Al nanopowder shows that the stored energy was released from 285 °C and most of it was released around 400 °C, where the nanoparticles behave more actively. The released stored energy (7.84 kJ mol^{-1}) of the as-exploded Al compact can even exceed its fusion enthalpy (6.92 kJ mol^{-1}), and is about 65% of the fusion enthalpy (10.68 kJ mol^{-1} [17]) of conventional bulk polycrystalline Al. Figure 2 is a TEM image of Al nanoparticles prepared by WEE.
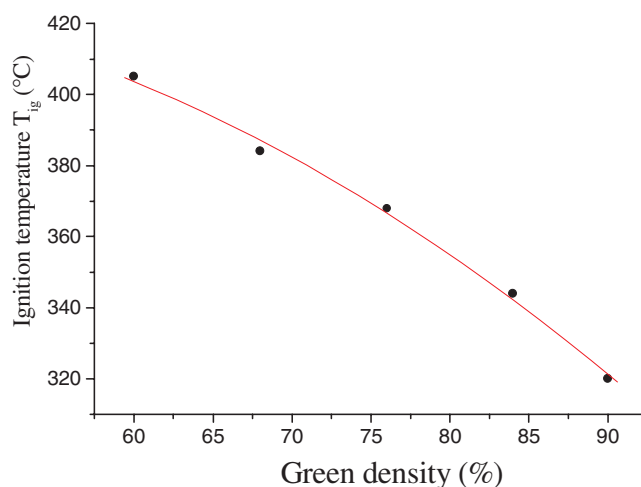
Figure 3. The effect of the green density (determined by cold pressure) on T_{ig}.

Increasing sample density affects the process of inflammation in a complicated way resulting—on one hand, in increasing the overall reaction surface per unit volume and, on the other hand, in decreasing the amount of oxidizer located in pores and retarding its supply from the bulk because of the poorer gas permeability of denser samples.

Besides the cold pressure, green density is related to the particle size. When the conventional thermal explosion technique was used to synthesize NiAl [18], it was observed that an increase in particle size could result in a decrease of T_{ig}. However, on decreasing the particle size to nanometre scale, the opposite result of a significantly low T_{ig} of 320 °C, which is at least 340 °C lower than that for the conventional SHS reaction, was observed in our study. This is due to the characteristics of Al nanoparticles.

In comparison with the grain of conventional size, Al nanoparticles are characterized by small size and large volume of surface area. Therefore, high pressure induces good densification with small pores and more contacts, which can further accelerate the diffusion process of the surface atoms of the reactant particles. Moreover, due to the tight contact of the reactant particles, the stored energy (mainly interfacial energy) of the Al nanoparticles can also be utilized effectively to enhance the diffusion process and the chemical activity of the surface atoms. Therefore, the solid–solid contact reaction can be facilitated effectively, resulting in low T_{ig}. One can easily see that a high level of compaction will provide a high number of contacts between the grains of the reactants. The greater the number of contacts, the greater the amount of exothermic heat released, and the exothermic heat can—inversely—further accelerate the self-sustained process, so the thermal explosion begins earlier than for a warmer compacted sample.

Estimations indicate that the oxidation factor is dominant at larger relative densities, which leads to a significant increase in the ignition delay time [19]. The original oxide film was found to affect the kinetics of the oxidation and, correspondingly, the ignition process substantially. Thereby, less oxidation of nanoparticles—which had been passivated in inert gas Ar for a long time before being mixed—facilitates SHS reaction and thus favours decrease of T_{ig}.

In addition, green density can also have an important effect on heat transfer through the porous structure of a compact. At a constant heating rate, the effects of conduction and convection increase with increasing green density, resulting in a high efficiency of heat
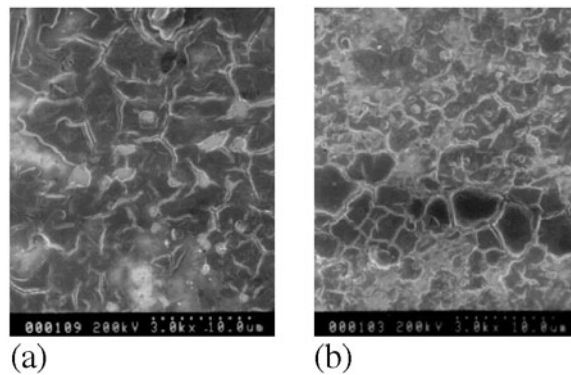
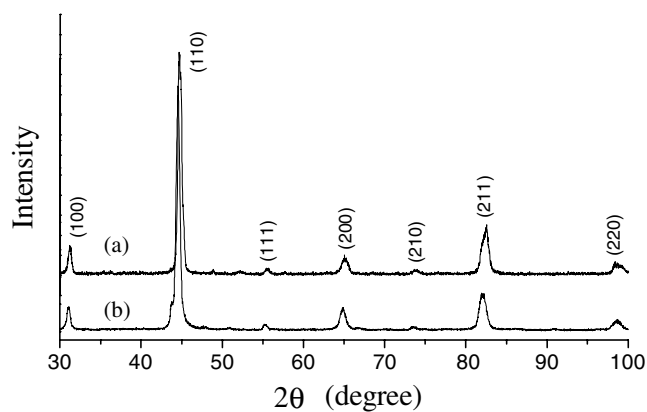**Figure 4.** A SEM image of homogeneous NiAl.

Figure 5. XRD patterns of the SHS products.

transport. In reality, heat transfer in a porous compact can occur by combined mechanisms of conduction, convection, and radiation [14]. Their cumulative effects should be taken into account in the analysis to reflect the effect of porosity. Moreover, the effect of porosity p on the density of the compact must also be considered. The effect of porosity on density can be simply expressed as $\rho = \rho_s(1 - p)$, where ρ_s is the solid density at zero porosity. While the pore sizes are small, decreasing porosity enhances the local conduction process and hence gives rise to an enhanced thermal conductivity and combustion velocity; the grain contact areas will be higher and the diffusion of elements will then be facilitated. Moreover, the propagation rate will also be increased by a reduction in grain size. In general, because of the small grain size, the SHS process is facilitated by increasing the effective heat transfer, and thus T_{ig} tends to move to a lower temperature. Under a low pressure of 2.5 MPa, a sample of 90% green density was ignited at 320 °C and a homogeneous NiAl compound with fine grains ($<10\ \mu$m) and a 95% theoretical density was obtained, as shown in figure 4(a). The corresponding XRD result for the product is shown in figure 5(a).

However, the full influence of nanoparticles on the combustion synthesis reaction is not, as yet, fully understood. More intensive studies should be carried out in order to explore the SHS mechanism when nanomaterials are used.
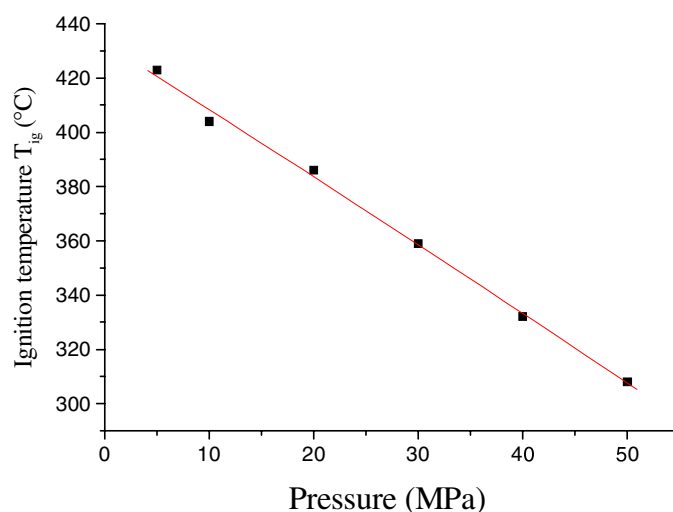
Figure 6. The effect of the TEP pressure on T_{ig}.

3.2. Effect of the TEP pressure

Externally applied pressure has a significant effect not only on the density of the SHS product after fabrication, but also on the ignition of the Ni + Al green body. This is due to the increase in the effective thermal conductivity of the green body as external pressure is applied. This, in turn, increases the rate at which energy is redistributed within the sample and makes the reactions occur homogeneously, thus resulting in a lower T_{ig}.

In this work, samples of 70% green density were ignited under pressures from 5 to 50 MPa; the corresponding T_{ig} varied from 423 to 308 °C (as shown in figure 6) and, correspondingly, products with densities of 77–98% were obtained.

Additionally, higher pressure favours reduction in the electric current passing through the samples, enhancing the ohmic heat and causing the as-compacted samples to warm up; accordingly, a lower T_{ig} can also be expected.

In the reported study [20], it was observed that when as little as 11 MPa was applied to the system of Ti + C/Ni + Al, neither combustion nor the explosive SHS method would ignite the sample. As a result, a mixture of Ti + 2B was used as an igniter in order to ignite the sample. Without applied pressure, the reaction was carried to completion. When external pressure of 22 MPa or more was applied, the reaction was initiated, but was extinguished shortly thereafter. This was due to the increase in the effective thermal conductivity of the green body as pressure was applied, which reduced the local thermal energy accumulation by enhancing the heat conduction from the reaction zone. Instead of achieving a propagating wave, extensive heat losses caused the reaction to cease. The only means by which the Ti + C/Ni + Al sample was ignited under pressure was by combining the use of a Ti + 2B igniter mixture with an initial preheating of the entire system. And it was also found that minimum preheating temperatures of 623 [20] and 773 K [21] were required to allow ignition for the systems of Ti + C/Ni + Al and Ni + Al respectively. In the latter case, the product was initially in the liquid state. However, in our study, neither preheating nor an igniter mixture was needed to complete the stable SHS reaction, and no extinguishing occurred. Without preheating, the SHS reaction can be ignited at such a low temperature as 308 °C where the reactants are still in the solid state, i.e., the SHS reaction was not initiated in the liquid state but in a solid–solid state. It is impossible for

conventional SHS reactions to occur at such a low temperature. This outcome is due to the characteristics of Al nanoparticles mentioned in section 3.1.

The key to densification of the SHS product lies in the use of an externally applied pressure while the SHS reaction is occurring. This is due to the densification of the liquid that is formed from the powder sample that initially contains evacuated pores.

As might be expected, an increase in density was observed as the applied pressure was increased. A product with a higher density of 98% and fine grains (<10 μm) was obtained under the pressure of 50 MPa, as shown in figure 4(b), and the corresponding XRD result for pure NiAl is shown in figure 5(b).

4. Conclusions

(1) With increasing green density resulting from enhanced cold pressure, a significantly low T_{ig} of 320 °C, which is half of the lowest eutectic temperature of the Ni–Al binary system, was obtained. Such a low T_{ig} cannot be observed in conventional SHS reactions, whose initiation temperature is over 640 °C. This phenomenon is mainly related to the characteristics of Al nanoparticles, especially to their particle size, high stored energy, and high chemical activity.

(2) With increasing TEP pressure, T_{ig} decreases dramatically to a low temperature of 308 °C. This also is mainly attributable to the distinctive thermal and chemical characteristics of Al nanoparticles, as well as to the cumulative effects of thermal conductivity and heat redistribution.

(3) Pure NiAl compound with fine grains (<10 μm) and nearly full density of 98% can be obtained under high pressure.

(4) The present study helps to develop a new field of application for nanomaterials. Many kinds of material with fine quality, such as intermetallics, nitrides, ceramics, functionally gradient materials, could be made available by using nanomaterials via the SHS technique.

Acknowledgments

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