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Mechanofused Powders for Thermal Spray

H. Herman, Z.J. Chen, C.C. Huang, and R. Cohen

Mechanofusion is a novel powder processing technique, in which raw powdered materials are fed into the apparatus, and through mechanical-thermal interactions, the powder characteristics are changed, *e.g.*, shape, size, and composition distribution. Mechanofusion has been used in this study to produce intermetallic nickel aluminide compounds and composite powders as feedstock for vacuum plasma spraying. Significant effects of the mechanofusion production route on the powder characteristics and spray deposition features have been observed.

1. Introduction

It has been shown that vacuum plasma sprayed (VPS) aluminides[1,2] have properties that can be superior to such materials formed using competitive methodologies. In particular, VPS nickel aluminides (NiAl and Ni_3Al) display excellent mechanical properties.[3] In addition, composites based on these materials (*e.g.*, with TiB_2) can exhibit even more impressive properties.[4] However, a major issue is the preparation of appropriate feedstock powders for the intermetallics, with and without hardening constituents. The quality of the feedstock powder strongly influences the microstructure and properties of thermal sprayed deposits. Two important powder characteristics for thermal spray processes are powder size and morphology. Powders for thermal spray should ideally be spherical to enhance free flowing so that steady (pulse free) feed rates can be achieved. The particle size should be of a certain distribution so that particles can be melted, but not vaporized, during spraying. Thus, a reasonably narrow particle size distribution is preferred, although the exact particle size and particle size distribution depend on the specific materials and spray conditions and are a subject of controversy.[5-8]

Key Words: feedstock, low pressure plasma spraying (LPPS or VPS), mechanofusion (MF), nickel aluminides, powder morphology, powder processing

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Nickel aluminide has potential for high-temperature structural applications. Preliminary evidence shows that mechanofusion (MF) enables the production of a narrow size distribution of spherical particles. Mechanofusion refers to a process where two or more kinds of particles are dynamically compressed by mechanical energy imposed on the mixed powder. This results in a strong bonding between the core particles (host particles) and the added particles (guest particles).[9]

Composite powders are also of interest. There are several different manufacturing methods for producing composite powders, such as atomization, agglomeration plus sintering, casting plus crushing, chemical cladding, and organic bonding.[10] Each method has distinct attributes and deficiencies. For example,

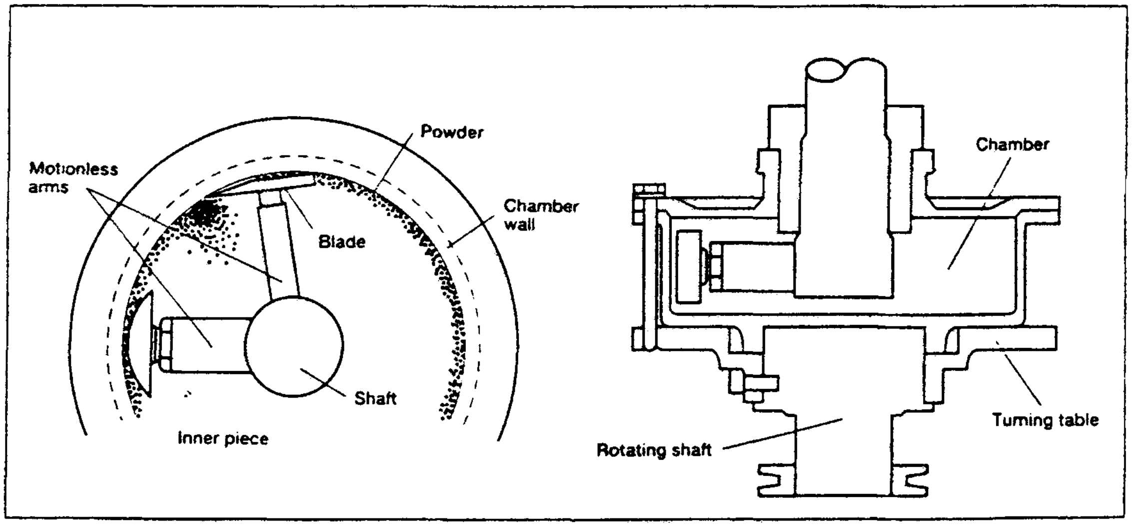


Figure 1 Schematic of the mechanofusion system. Powder is forced against the chamber wall and dynamically compressed through the gap when the chamber rotates (Ref 13).

Table 1 Sample Designation, Powder Properties, and MF Processing Parameters

Sample	Alloy, at.% Ni	Starting size for MF, μm NiAl	Ni	Al	MF parameters Time, min	Speed, rpm
Group I						
NA5021	50	44 to 150	...	...	20	1000
NA5022	50	44 to 150	...	...	20	2000
Group II						
NA4847	48	...	34	19	40	700
NA4811	48	...	82	19	10	1500
Group III						
NA32XX	32	...	1.9	5	...	...
NA3212	32	...	1.9	5	10	2000

Table 2 Spray Parameters

Current, A	600
Voltage, V	63
Argon flow rate, SLPM	50
Hydrogen flow rate, SLPM	8.5
Carrier gas (Ar) rate, SLPM	3
Chamber pressure, mbar	60
Spray distance, cm	30
Powder feed rate, g/min	~40

chemical cladding is commonly used for producing Ni/Al composite powders; however, different phases may separate or segregate, and some clad material may be lost during spraying, so that the deposit has a nonuniform composition and hardness.[10] The MF process offers a relatively easier and less expensive technique for the production of composite powders.[11,12]

2. Experimental Procedure

The equipment used for mechanofusion is shown schematically in Fig. 1. It consists of a rotary shallow cylindrical chamber that contains the powder, a fixed semicylindrical inner piece, and a fixed scraper blade provided in the chamber. The dimensions of the working chamber of the MF equipment used in this study were 15-cm diameter and 2.5 cm high. Throughputs of material for this equipment range from approximately 0.2 to 0.5 kg/hr. Large MF systems can have throughputs up to 60 kg/hr. The radius of the inner piece is smaller than that of the chamber, the gap between the inner piece and the chamber wall being adjustable. Powder is forced against the chamber wall and dynamically compressed through the gap when the chamber rotates. During processing, the powders are intensively mixed and subjected to compression, attrition, and frictional shearing. Therefore, thermal-mechanical energies are generated, resulting in various effects that depend on powder characteristics and process parameters. The particles can be reduced in size and become spherical due to their rolling during the MF process. In composite powders, added particles can be coated-on and adhered-to the core particles, or two different kinds of particles can be agglomerated. Thus, a homogeneous mixed composite powder can be produced with no need for binders. The individual particles are well bonded, and therefore, the different components in the composited particles will not be separated during subsequent processing, such as thermal spray operations. The prime MF parameters are time-of-processing, rotation speed of the chamber, and the gap between the inner piece and the chamber wall.

Table 1 presents sample compositions, particle sizes, and the MF process parameters for the starting powders. The particle sizes given in this paper are median values, except when otherwise specified. The particle sizes were measured using a laser light scattering apparatus (Cilas 715). Three groups of samples were prepared, as detailed below.

In Group I, samples, NA5021 and NA5022, the prealloyed NiAl powder was coarse and exhibited an irregular particle shape with sizes from 44 to 140 μm before the MF treatment. This powder was sprayed in the as-received condition and after MF processing. For samples NA4847 and NA4811 in Group II, the objective was to synthesize the NiAl intermetallic compound from elemental nickel and aluminum powders through the MF and VPS[14] processing routes. Different MF processing parameters and particle size ratios were formed for spraying. Group III materials were samples formed from Ni/Al composite powders produced by the MF process. Micrometer-sized particles were used for the MF feedstock. Both Group II and Group III samples were blended for 15 min at a speed of 270 rpm for the initial MF treatment. They were then processed with the parameters given in Table 1.

Vacuum plasma spraying was performed on a Plasma Technik VPS unit using a PT-F4V plasma gun with internal powder injection, under conditions given in Table 2. X-ray diffractometry with CuKα radiation was used to identify phases. Optical metallography and SEM analysis were also carried out, and energy dispersive spectroscopy (EDS) enabled analysis of elemental distributions. A Hall flowmeter was used to measure flowability of powders.

3. Results and Discussion

Unambiguous effects of the MF process on the powder morphology were found, as shown in Fig. 2(a) and (b). The as-received powder for Group I samples could not be sprayed using previously used intermetallic spraying parameters, because the large irregular-shaped particles (over 100 μm, as shown in Fig. 2a), caused clogging of the gun nozzle. Spherical particles (Fig. 2b), were obtained after 20 min of MF processing of this powder. The size reduction and shape spheroidization effects may be explained as follows. The raw prealloyed NiAl is brittle and coarse, thus forces created by the MF process cause particle fracture and particle size reduction. As the process continues, the fractured particles having irregular shapes become rounded and particle surface fusion occurs yielding spherical particles. These processes are illustrated in Fig. 3.

Based on Hall flowmeter measurements, the flow rate of the as-received powder was 2.7 g/sec. After the MF process, the flow rates of NA5021 and NA5022 powders were 3.5 and 3.4 g/sec, respectively, indicating a 30% increase in flow rate due to the MF process.

Significant effects of the MF-processed powder on deposition thickness were also observed. Samples NA5021 and NA5022 were MF processed with different parameters, *i.e.*, rotation speeds of 1000 and 2000 rpm, respectively. The resulting particle sizes were 84 μm for NA5021 and 72 μm for NA5022. When those powders were sprayed with the identical VPS parameters, the coating thickness achieved for NA5022 was about 70% greater than that for NA5021, *i.e.*, 0.53 mm as compared to

Figure 2 **(a)** Prealloyed NiAl powder. Before mechanofusion, particles were irregular and large, precluding VPS processing (SEM micrograph).

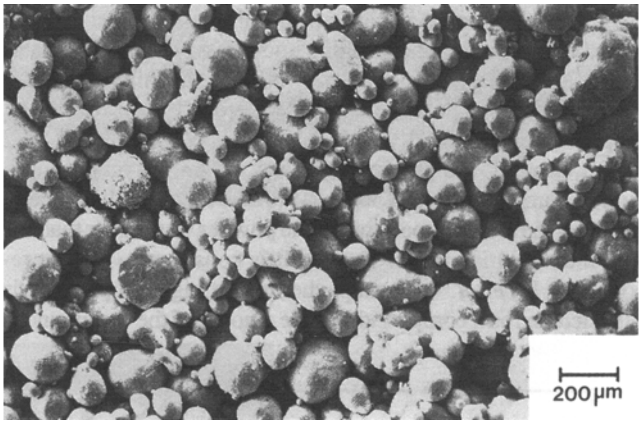


Figure 2 **(b)** Prealloyed NiAl powder. After 20 min of mechanofusion, the particles became spherical and displayed a finer particle size (SEM micrograph).

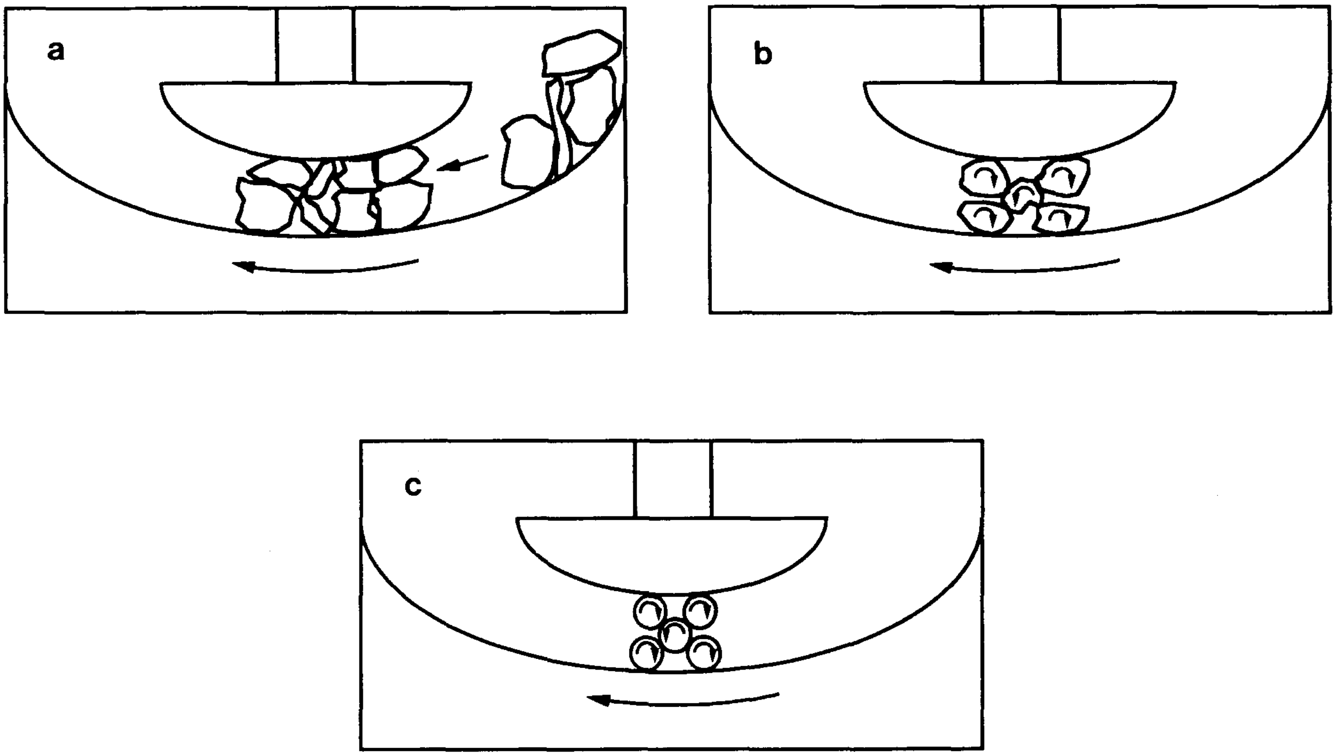


Figure 3 Representation of mechanofusion showing **(a)** reduction in particle size, **(b, c)** particle morphological change occurring during mechanofusion.

0.31 mm. Because the mass of a particle is proportional to the cube of its diameter, the difference between 84 and 72 μm in particle size results in about a 60% mass difference. The mass of the particle will influence the heat and kinetic energy transfer between particle and flame. The heat and kinetic energy obtained from the flame are related to particle temperature and velocity, which are two of the most critical factors directly connected to coating quality. The smaller sized particles will yield proper melting and will achieve higher velocities on impact on the target. The larger particles will tend to fall out of the flame or rebound off the target. The resulting thickness difference indicates that the spray deposition efficiency, which is an important index for thermal spray quality, may be improved significantly by proper MF processing.

For Group II samples, NA4847 and NA4811, no nickel aluminide compounds were observed to form by the MF process, although the local temperature of the powder was higher than the aluminum melting point. The result is consistent with that reported by Ito *et al.*[12] Perhaps the time at high temperature is sufficient to form compounds, or the amount of the compound is too small to be detected. When the MF-processed powders were sprayed by VPS, a series of nickel aluminide intermetallic phases were produced. Single-phase NiAl was obtained after annealing at 1000 °C, as determined by X-ray diffractometry (Fig. 4).

No obvious MF effect was observed for sample NA4847 powder. Because elemental Ni + Al powders were MF processed at a low rotation speed (700 rpm), thermal-mechanical energies generated by MF were insufficient to produce a significant change of powder characteristics. The particle morphologies of the NA4847 powder were essentially the same as those of the original nickel and aluminum powder. Based on SEM micrographs of the powder cross section for sample NA4847, the particles were not observed to be agglomerated. The particles were still separated, as shown in Fig. 5. However, the micrograph of the powder cross section for sample NA4811 indicates that some aluminum particles were coated onto the nickel particles (Fig. 6). This result may be attributed to the rotation

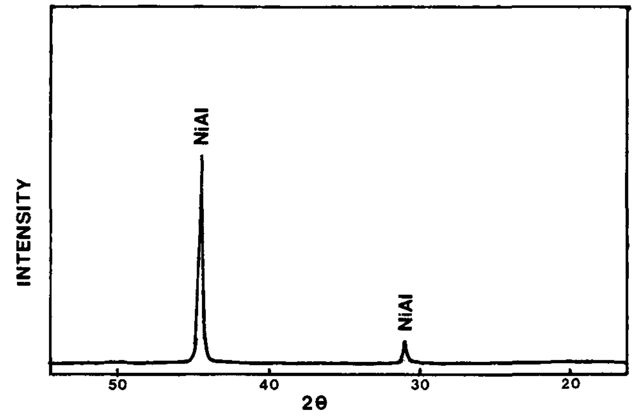


Figure 4 X-ray diffraction pattern of the NA4847 deposit. The single-phase intermetallic compound NiAl was obtained with VPS followed by 1100 °C for 4 hr.

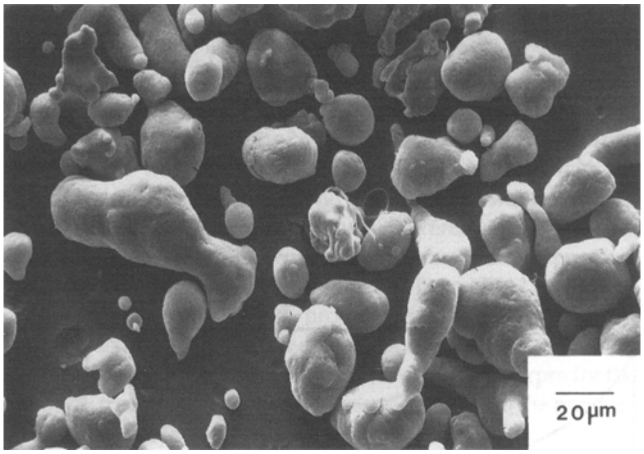


Figure 5 Scanning electron micrograph of NA4847 powder. The particles remain separated from each other.

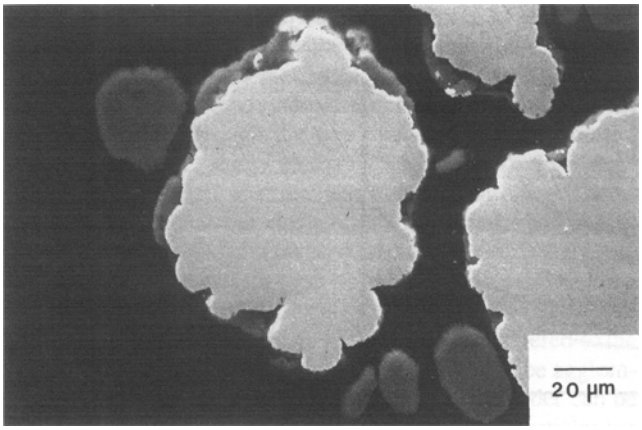


Figure 6 Scanning electron micrograph of the cross section of NA4811 powder. Some aluminum particles (dark) are coated onto the nickel particles (bright).

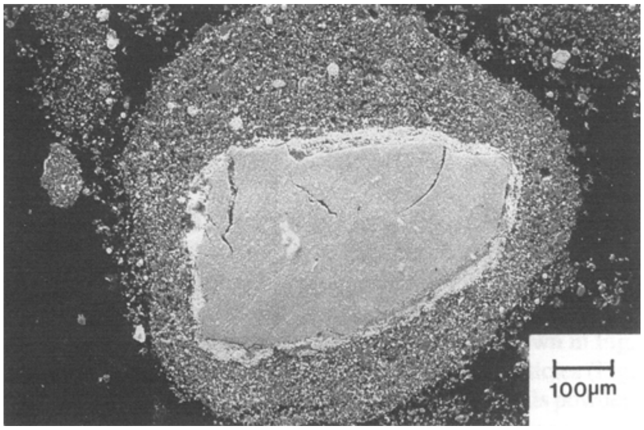
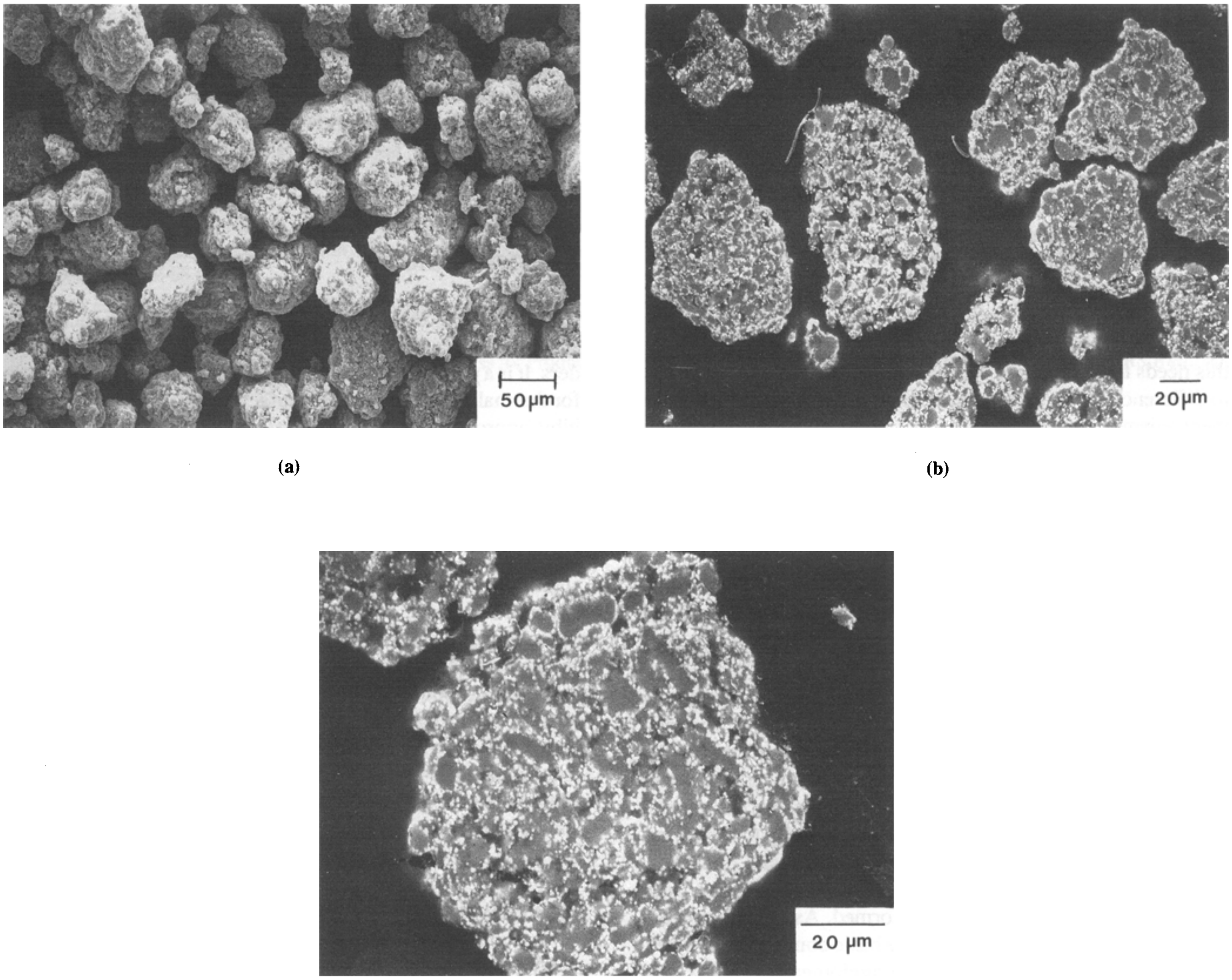


Figure 7 Scanning electron micrograph of cross section of NA32XX powder. Fused aluminum particles (center area) are agglomerated with nickel particles.



(a) (b) (c)

Figure 8 (**a**) Scanning electron micrograph of NA3212 powder after mechanofusion. (**b**) Cross section of NA3212 powder indicating that nickel and aluminum particles are well mixed, forming strongly bonded composite powders (SEM micrograph). (**c**) Using EDS analysis, the dark particles are aluminum, and white particles are nickel.

speed of the MF process (1500 rpm) and the large particle size ratio of the nickel to aluminum. According to a report by Yokoyama *et al.*,[9] the forces exerted on the powders increase with increasing rotation speed. Therefore, MF delivers sufficient energy to fuse the particles, and the small aluminum particles can be coated onto the large nickel particle surfaces. However, as can be seen in Fig. 6, there are some aluminum particles still separated from the nickel particles. This effect is currently being examined.

According to experimental investigations on mechanical processing of powder, as reported by Boldyrev,[15] if two solids are sliding with respect to one another, the energy of friction is transformed mainly into heat at the points of contact. The local temperature is approximated by:

$$\Delta T = (\gamma WV/4aJ)\,[1/(k_1 + k_2)] \qquad [1]$$

where γ is the coefficient of friction, W is the normal contact load, V is the speed of sliding, a is the radius of the contact area, J is the mechanical equivalent of heat, and k_1 and k_2 are the thermal conductivities of the two sliding solids. The local temperature pulse was as high as 800 to 1000 °C.[15] During the MF process, the nickel and the aluminum particles roll and slid with respect to one another. Thus, the above equation may be applied. To achieve a higher local temperature and surface fusion of the powder, higher MF processing speeds (*i.e.*, increasing V values) and smaller particle sizes (*i.e.*, decreasing a values) are needed.

Sample NA32XX was the first test of the MF processing of the Ni/Al composite powder by utilizing micrometer-sized particles. Figure 7 shows a particle of fused aluminum-agglomerated nickel. This indicates that during the MF process the local temperature of the particles was higher than the aluminum melting point. This phenomenon confirms the result reported by Boldyrev.[15] Sample NA3212 is a powder produced after optimizing the MF process parameters (Fig. 8a). The cross section of NA3212 powders indicates that the nickel and the aluminum particles are well mixed (Fig. 8b through c). Based on EDS analysis, the dark particles in Fig. 8(c) are aluminum, and the white particles are nickel.

The forming of composite powders by the MF treatment is complex and poorly understood. A composite-forming process by the MF technique has been proposed by Tanno.[11] However, this needs to be modified for the Ni/Al materials of interest due to differences in materials and particle sizes. We believe that the mechanism of forming the NA3212 composite powder is as follows. First, the chamber is rotated at a low speed of 270 rpm. The inner piece and the scraper in the MF system violently stir and blend the starting powders to form a uniform mixture of particles. When the chamber rotation is increased to a higher speed, such as 2000 rpm, according to Eq 1, the temperature of the particles increase by the heat energy generated through friction and impaction between particles or between the inner piece and the particles. Thus, particles, especially the aluminum particles, would be expected to plastically deform.

During high-speed rotation, the curved inner piece and the chamber wall exert impaction, compression, and shearing forces, etc., on the powders. Interactions also occur between the nickel and aluminum particles. Therefore, the nickel particles are either embedded mechanically into the softened aluminum particles, or adhere physically and metallurgically to the aluminum particles. Up to this point, "basic composite particles," which are the individual aluminum particles combining with nickel particles on the surface, are formed. As the MF process continues, reactions occur among the basic composite particles. Many basic composite particles are agglomerated, fused, and consolidated. Finally, as shown in Fig. 8(b), a homogeneous distribution of composite powder is obtained, which is suitable for thermal spraying.

The composite particle sizes are increased from several micrometers to about 40 μm. This size increasing effect by the MF process on Group III samples is opposite to the size reduction effect on Group I samples. This results in the production of particle sizes suitable for thermal spraying. Moreover, because nickel and aluminum particles are mechanically bonded, this assures that the composite powders do not segregate during material handling, and the nickel and aluminum components are less likely to dissociate during thermal spraying. Therefore, the composition of the deposit will be closer to that of the feedstock powder. However, the phase analysis of the VPS deposit indicates that the aluminum composition in the deposit is about 7 at.% less than in the starting powder. This may arise from the low melting point and high thermal conductivity of aluminum, which vaporized in the high-temperature plasma flame during spraying.

The EDS analysis of the powder also shows no contamination induced by the MF process. However, the micrographs of the NA3212 powder and the deposit show some porosity. By adjusting the MF process, the pores in the powder can be eliminated.[11] For some cases, such as certain wear coatings or abradable coatings, the porosity in the deposit can be beneficial.[6,16] These processed powder characteristics indicate that the MF technique is a competitive means for producing metal matrix composite powders designed for specific uses. Indeed, MF has been successfully applied to fabricate polymer/metals, polymer/ceramics, etc., composite powders.[9]

4. Conclusions

The mechanofusion process can perform size reduction and shape spheroidization for brittle and irregularly shaped powders. It is a promising technique for producing feedstock powder for thermal spray. Powders manufactured by the MF process exhibit improved flow characteristics over the original powders, because a spherical morphology is created. Significant effects of the mechanofusion-treated powder on deposition thickness have been observed. For micrometer-sized Ni + Al powders, through the MF process, the nickel particles are either embedded mechanically or adhered physically and metallurgically into the aluminum particles, forming a basic composite particle. Many of those composite particles are then agglomerated, fused, and consolidated by mechanofusion. Therefore, a strong mechanically bonded Ni/Al composite powder with a uniform phase distribution is produced by mechanofusion. No intermetallic compound was detected after the mechanofusion process. Intermetallics were obtained by vacuum plasma spraying. No contamination was observed to be induced by mechanofusion. Both composite powders and deposits of sample NA3212 contained porosity.

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References

1. H. Herman and S. Sampath, Plasma Spray Forming of Free-Standing Shapes, *Proc. 2nd Plasma Tech. Symp.*, vol 3, Lucerne, Switzerland, S. Blum-Sandmeier, H. Eschnauer, P. Huber, and A.R. Nicoll, Ed., Hafliger Druck AG, Wettingen, 63-73, Jun (1991).
2. A.I. Taub, S.C. Huang, and K.M. Chang, High Temperature Ordered Intermetallic Alloys, *Mater. Res. Soc. Symp. Proc.*, *39*, 221-228 (1985).
3. S. Sampath, B. Gudmundsson, R. Tiwari, and H. Herman, Plasma Spray Consolidation of Ni-Al Intermetallics, *Proc. 3rd Nat. Thermal Spray Conf.*, T.F. Bernecki, Ed., ASM International, Materials Park, 357-361 (1991).
4. R. Tiwari, H. Herman, S. Sampath, and B. Gudmundsson, *Mater. Sci. Eng.*, in press.
5. J.D. Peterson, Effect of Fine Grain, Narrow Band Powders Upon Plasma Coating Characteristics, *Am. Cer. Soc. Bull.*, *47*, 1166-1170 (1968).
6. I.A. Fisher, Variables Influencing the Characteristics of Plasma-Sprayed Coatings, *Int. Mater. Rev.*, *17*, 117-129 (1972).

7. C. Brunet and S. Dallaire, The Importance of Particle Size Distribution on the Plasma Spraying of TiC, *Surf. Coat. Technol., 31*, 1-10 (1987).
8. M. Vardelle, A. Vardelle, A. Denoirjean, and P. Fauchais, Influence of Morphology and Size Distribution on Plasma Sprayed Zirconia Coatings, Part 1: Study of Powder-Plasma Interactions, 12th Int. Thermal Spray Conf., London, Paper 49, The Welding Institute, Cambridge (1989).
9. T. Yokoyama, K. Urayama, M. Naito, M. Kato, and Toyokazu Yokoyama, The Angmill Mechanofusion System and Its Applications, KONA, (5), 59-68 (1987).
10. E.J. Kubel, Jr., Powders Dictate Thermal-Spray-Coating Properties, *Adv. Mater. Proc., 12*, 24-32 (1990).
11. K. Tanno, Current Status of the Mechanofusion Process for Producing Composite Particles, KONA, (8), 74-82 (1990).
12. H. Ito, M. Umakoshi, R. Nakamura, T. Yokoyama, K. Urayama, and M. Kato, Characterization of Ni-Al Composite Powders Prepared by the Mechanofusion Process and Their Sprayed Coatings, *Proc. 4th Nat. Thermal Spray Conf.*, T.F. Bernecki, Ed., ASM International, Materials Park, to be published.
13. L. Hixon and J.V. Cleef, Improved Powder Processing Creates Better Materials, *R & D Mag.*, Apr, 60-63 (1988).
14. H. Herman, Plasma-Sprayed Coatings, *Sci. Am., 256*, Sep, 112-117 (1988).
15. V. Boldyrev, Experimental Methods in the Mechanochemistry of Inorganic Solids, *Treatise on Materials Science and Technology*, vol 19B, H. Herman, Ed., Academic Press, New York and London, 185-221 (1983).
16. H. Herman, Plasma Spray Deposition Processes, *MRS Bull., XIII* (12), Dec, 60-67 (1988).