

Supporting Information for

Chemical Syntheses of Nanocrystalline Nickel Aluminides

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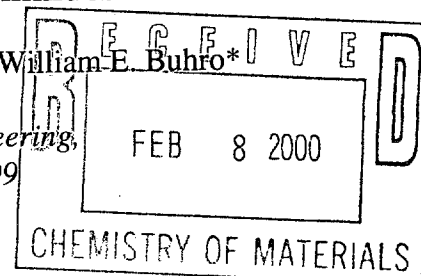


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X-ray Diffraction (XRD) Procedures. XRD patterns were obtained using a Rigaku vertical powder diffractometer with Cu K α ($\lambda=1.541845$ angstroms) radiation and Materials Data Incorporated (MDI) automation and software. The XRD powder samples (1.5×2 cm smear mounts) were prepared in a N $_2$ -filled glovebox and coated with a thin film of polyvinyltoluene (PVT) to minimize air exposure. The PVT film was applied by dripping a toluene solution of PVT onto the prepared XRD slide and evaporating to dryness. The phases were identified using JCPDS cards 20-19 (NiAl), 9-97 (Ni $_3$ Al), and 25-1135 (AlN), etc. For each sample the MDI software was used to correct the baseline, subtract the K α_2 peak, and calculate the coherence lengths for each peak in the collected range (5 or 15 to 100 $^\circ 2\theta$). The mean of the coherence lengths calculated for each peak was used as the mean coherence length of the sample, and the standard deviation in the coherence lengths for the different peaks was used as a measure of the error in the mean coherence length. The long-range-order parameter S was determined using the intensities of the superlattice ($\{100\}$ and $\{110\}$ for NiAl and Ni $_3$ Al respectively) and fundamental ($\{200\}$ and $\{220\}$) reflections in the powder patterns, using the equation⁴⁸

$$\frac{S}{S_0} = \left(\frac{I^s/I_0^s}{I^f/I_0^f} \right)^{1/2}$$

where I^s and I^f are the experimentally measured intensities of the superlattice and fundamental reflections, and I_0^s and I_0^f are the intensities reported in the corresponding JCPDS card for the fully ordered intermetallic (note $S_0 = 1$).

Electron-Microprobe Analyses. The concentrations of Ni, Al, and Cl were obtained by wavelength-dispersive analysis using a JEOL 733 electron microprobe equipped with Advanced Microbeam Inc. automation. Ni, Al, and NaCl standards, and polished samples were

characterized using an accelerating potential of 15 KV on 1-10 μm spots and 100 μm area scans.

X-ray matrix corrections were based on a modified Armstrong CITZAF routine.⁴⁹

Transmission Electron Microscopy (TEM) was performed on a JEOL 2000 FX instrument operating at 200 KeV. Samples were generally prepared by suspending 10 – 50 mg of powder in 10 – 50 mL of dry pyridine by sonication for 15 – 420 min in an ultrasonic cleaning bath. Powders that were loosely agglomerated suspended rapidly, while heavily aggregated powders required sonication for extended periods. While continuing to sonicate the suspension a few drops were removed by syringe and placed on a holey-carbon-coated Cu TEM grid in air. The grid was immediately placed into a tightly capped vial with 2-5 drops of the pyridine suspension, taken directly to the TEM and loaded into the TEM antechamber while still wet with pyridine. A variation on this method was used for the cosuspended Ni, Al, and AlN powders; just before removing the suspending solvent in vacuo a few drops of the suspension were removed and a TEM grid prepared as described above. TEM samples were in a few cases prepared by placing a holey-carbon-coated Cu grid into a powder and retrieving it; this method selected for the finest particles.

Scanning Electron Microscopy (SEM) was performed on a Hitachi S-4500 field-emission instrument. Powder specimens were prepared by dusting powder onto carbon tape on Al stubs immediately before loading specimens into the SEM, to minimize air exposure. In one instance the stub was prepared in a glovebox, taken to the SEM facility in a sealed container, and loaded into the SEM antechamber using an inflatable glovebag to prevent air-exposure. After performing SEM the specimen was air exposed for one minute, and then reinserted into the SEM and reanalyzed. Higher resolution micrographs were obtained and less oxygen was detected by

EDS before air exposure. SEM analyses were conducted on unpolished, polished, etched, or fracture surfaces of consolidated specimens.

Energy Dispersive Spectroscopy (EDS) with light-element detection was performed in conjunction with TEM and SEM using Noran Instruments Voyager II X-ray Quantitative Microanalysis Systems with Digital Imaging.

Solid-State NMR. As-precipitated powders (0.2 g) produced according to eqs 1 and 2 from 1,3,5-trimethylbenzene were loaded into 5 mm NMR tubes and sealed in vacuo. The powders were analyzed by static (not MAS) solid-state ^1H , ^7Li , and ^{27}Al FT-NMR using a magnetic fields of 1.25 Tesla (53 MHz ^1H) and 8.4 Tesla (137 MHz ^7Li , and 92 MHz ^{27}Al) to characterize the species present in the incompletely reacted material. T_2 s were separately obtained from FIDs and echo-decay envelopes (2-pulse echo sequence). T_1 s were measured using the saturation-wait-inspect method. Saturation was accomplished by a train of $10\pi/2$ pulses, spaced by 5 ms for ^1H and ^7Li , and by 200 μs for ^{27}Al . Frequency spectra were taken from the fourier transform of the FIDs. ^1H , ^7Li , and ^{27}Al spectra were referenced to H_2O , LiBr (aq), and AlCl_3 (aq) respectively.

Vickers microhardnesses were measured on polished surfaces using a LECO M-400-H1 hardness testing machine with 500 and/or 1000 g loads applied for 15 seconds. Each hardness reported is the mean of ≥ 10 hardness measurements distributed over the entire surface of each pellet. Asymmetrical indentations were ignored. The pellets pressed from presynthesized nickel aluminide powder were successively polished with 320, 600, 1000, and 2000 grit paper with flowing water, followed by lapping with 1.0 μm and 0.3 μm Al_2O_3 paste. The pellets produced by reactive sintering of nano-Al, nano-Ni, and nano-AlN were successively polished with 600, 1000, 1500, and 2000 grit paper wet with hexane.

Consolidation of Pellets. Pellets 13 mm in diameter and 2 to 12 mm in thickness were pressed from powders prepared by eqs 1 – 4, or from admixtures of nano-Ni and nano-Al, with and without nano-AlN, using a uniaxial hot press inside an Ar-filled glove box. The press employed TZM (molybdenum-based alloy) plungers and die with a disposable graphite sleeve (0.75 inch o.d., 0.5 inch i.d.) for lubrication and ease of pellet removal. The powders from eqs 1 – 4 (1.6 to 6.8 g) were consolidated under an applied pressure of 350 MPa at 700 to 1200 °C for 2 to 4 h. One Ni₃Al pellet pressed at 900 °C was subsequently sintered in the press at 1300 °C for 2 h. The pellets produced from admixtures of nano-Ni and nano-Al, with or without nano-AlN, were heated from room temperature to 1000 or 1200 °C over a 0.5 to 1 h period under a load of 140 MPa. When temperatures of 1000 – 1200 °C were attained the powder was pressed at 350 MPa for 0.75 to 3 h. During several pressings the graphite sleeve broke, and fragmented or barreled pellets were produced.

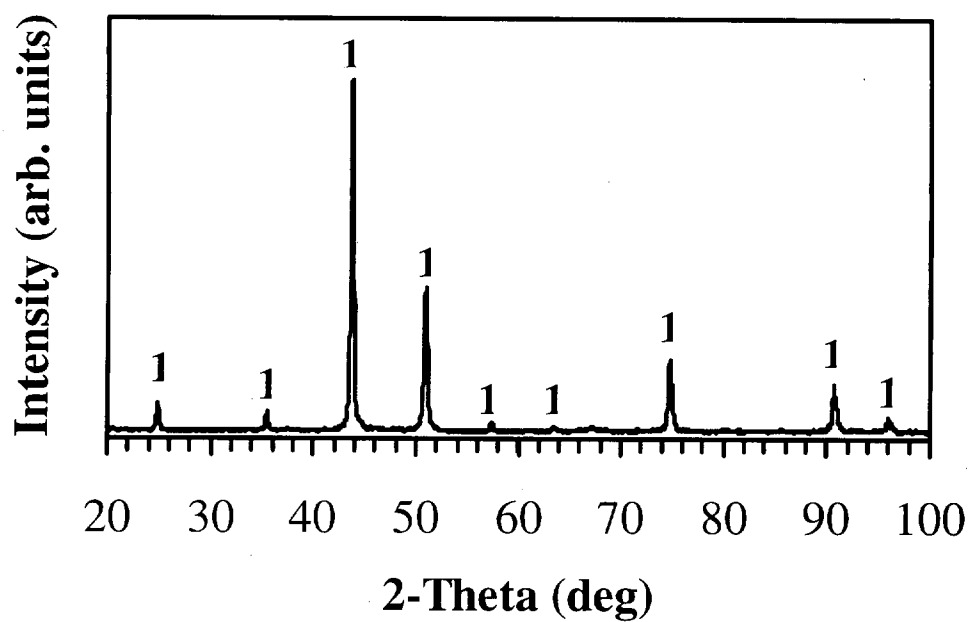


Figure S1. XRD pattern of the product from eq 4 annealed at 750 °C *in vacuo*; **1**, Ni₃Al (40-nm coherence length).

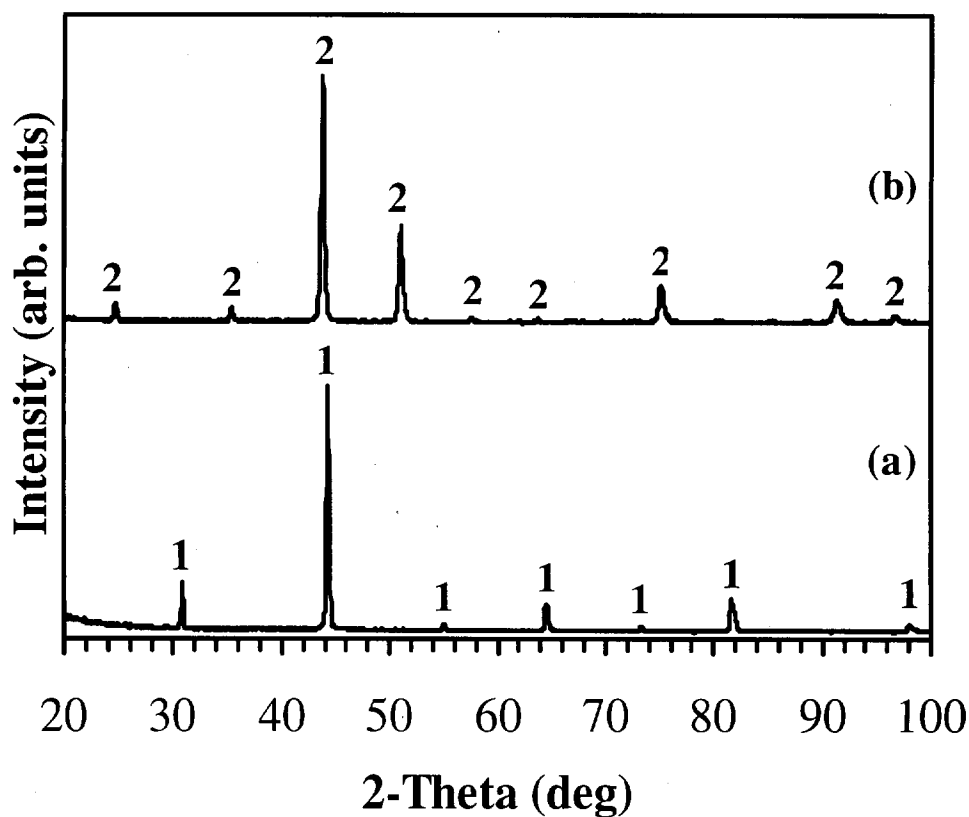


Figure S2. XRD patterns of nickel aluminides produced in synthetic procedures by eqs 1 and 2 and annealed at 650 °C *in vacuo*. Numeral labels identify the reflections of specific component phases; (a) NiAl from eq 1, **1** (54-nm coherence length); (b) Ni₃Al from eq 2, **2** (32-nm coherence length).

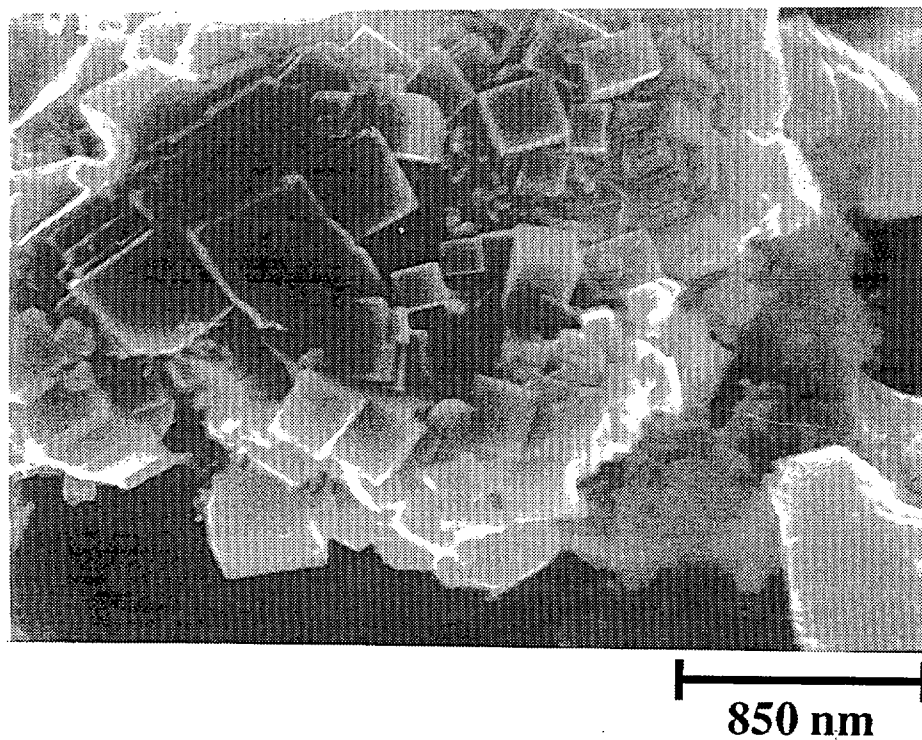


Figure S3. SEM image of Ni_3Al produced by eq 2 and annealed at 650°C *in vacuo*; this microstructure was observed in isolated regions (see text).

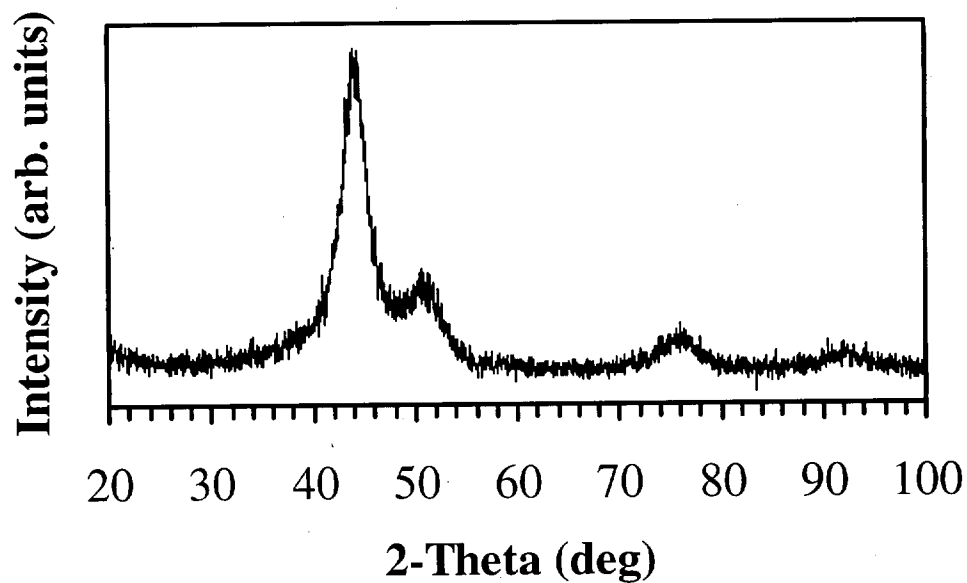


Figure S4. XRD pattern of nano-Ni (coherence length < 5 nm). Each (broad) reflection indexed to fcc Ni.

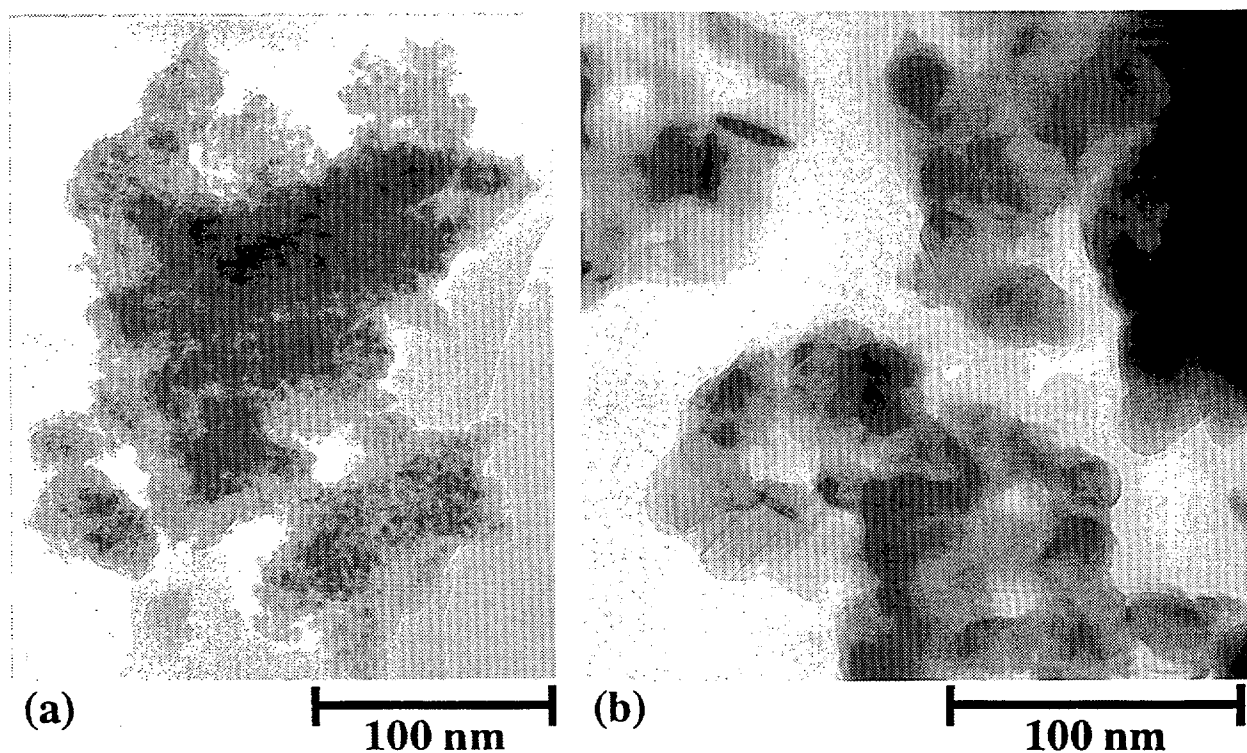


Figure S5. TEM images of nano-Ni. (a) Most aggregates comprised < 2 nm particles, but (b) a minority fraction of 20 – 40 nm particles was also present.

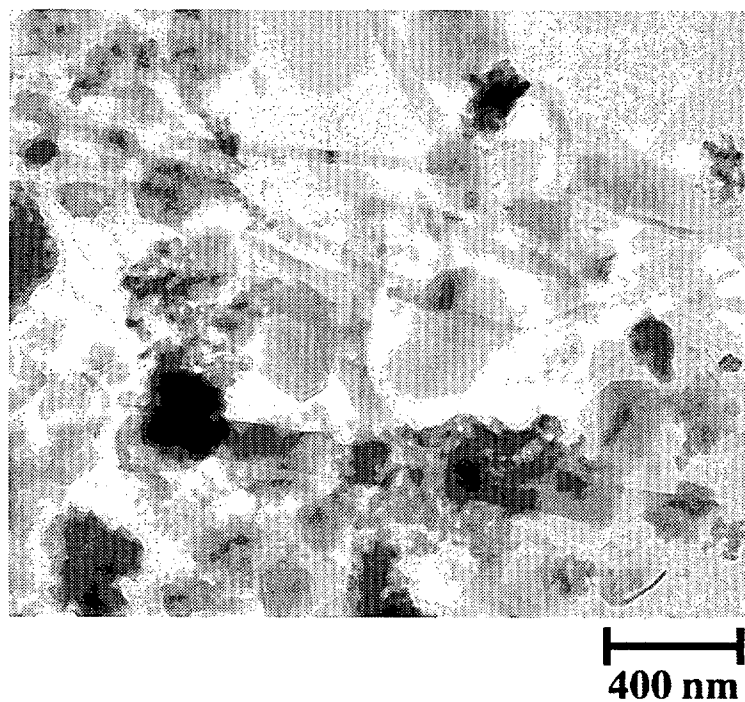


Figure S6. TEM image of a powder admixture consisting of separately synthesized nano-Al (27 wt %), nano-Ni (57 wt %), and nano-AlN (16 wt %) prepared by co-suspension in pyridine. The larger equiaxed particles are nano-Al, the smaller equiaxed particles are nano-Ni, and the whiskers are nano-AlN.

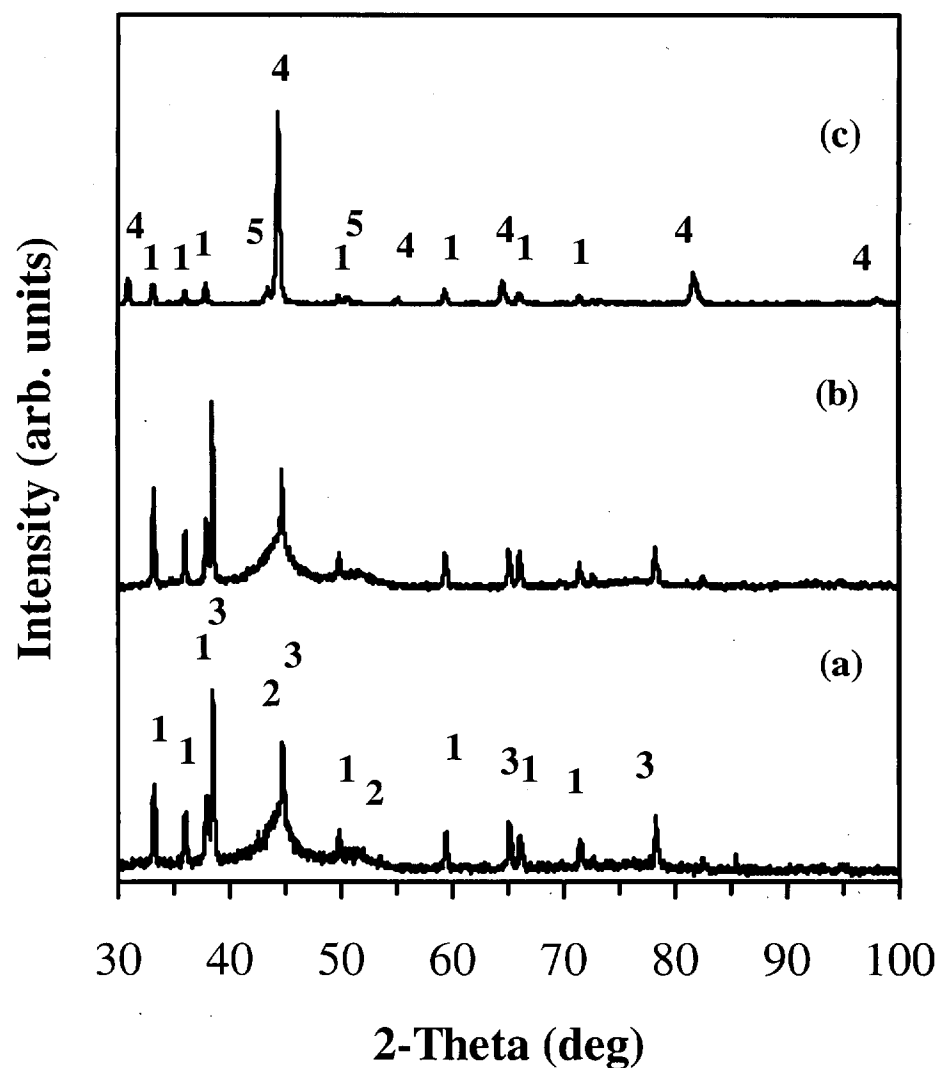


Figure S7. XRD patterns of a powder admixture and a pellet pressed from it. Numeral labels identify the reflections of specific component phases. (a) The powder admixture; **1**, nano-AlN (55-nm coherence length); **2**, nano-Ni (< 5-nm coherence length); and **3**, nano-Al (55-nm coherence length). (b) The pellet after pressing at 150 °C. (c) The pellet after annealing at 400 °C (see text); **1**, nano-AlN (55-nm coherence length); **4**, nano-NiAl (32-nm coherence length); **5**, Ni₃Al (28-nm coherence length).

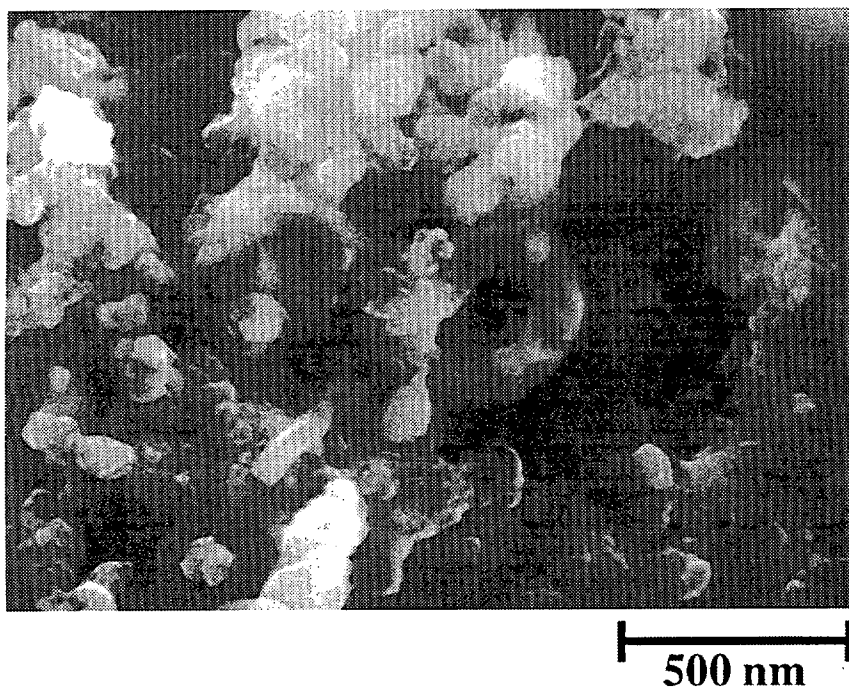


Figure S8. High-magnification SEM image revealing nanometer-scale features on a fracture surface of a pellet fragment obtained by annealing a nano-Al, nano-Ni, nano-AlN powder admixture at 400 °C *in vacuo*.

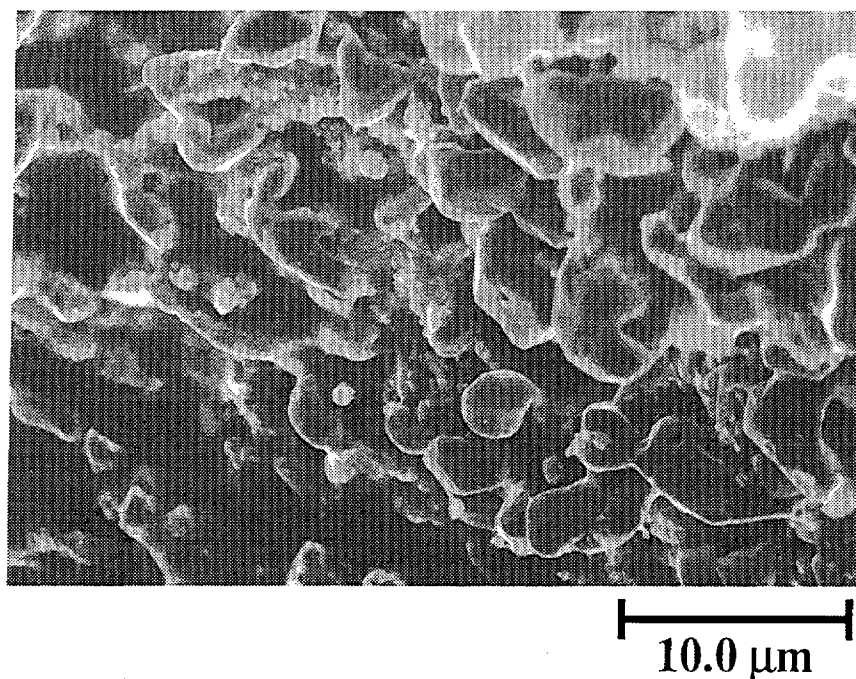


Figure S9. SEM image of the fracture-surface cross section of a Ni₃Al (93 wt %)/AlN (7 wt %) pellet showing a region containing large, faceted, crystalline grains.

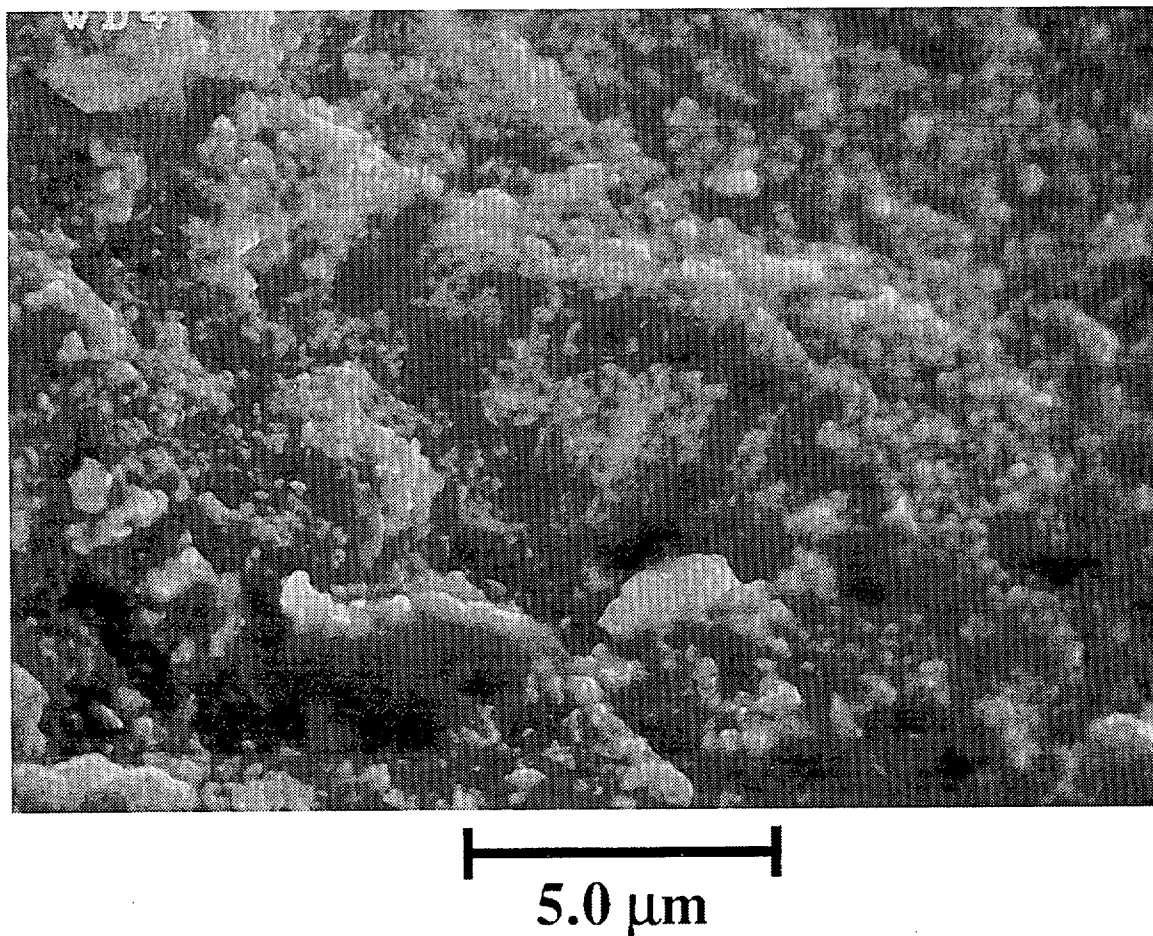


Figure S10. SEM image of an etched NiAl pellet hot pressed at 1200 °C from eq-3 powder, revealing nanometer-sized features (crystalline grains).