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In situ Thermal Observation of Explosive Compound-Formation Reaction during Mechanical Alloying

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The formation of Al-Ni compounds by ball milling of elemental powders has been investigated by means of *in situ* thermal analysis, x-ray diffraction, and scanning electron microscopy. The results show that AlNi forms in an explosive, exothermic reaction, driven by the large heat of compound formation. The mechanism discovered is suggested to explain the mechanical alloying of other systems.

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The technique of high-energy ball milling[1] has been extensively used to synthesize powders with interdispersed phases (for ductile materials) and to reduce the grain size of brittle materials. More recently, it has been discovered that this method can be used for mechanical alloying of elemental powder mixtures on an atomic scale to form metastable (e.g., amorphous) or stable alloys.[2-4] In some cases, ball milling (BM) of intermetallic compounds was shown to lead to their transformation to an amorphous state.[5] Many publications have appeared in recent years which describe the phases resulting from mechanical alloying and their properties, but little is known about the mechanisms governing their formation. A major difficulty is the fact that their is no straightforward method of *in situ* monitoring of the BM process. Schwarz, Petrich, and Saw[6] presented arguments which suggest that melting during collisions is an unlikely event. Later, Eckert *et al.*[7] used the same considerations to show that the milling intensity significantly affects the sample temperature and therefore also the resulting phases. A commonly accepted picture is a combination of deformation, leading to a reduction of the lamellar thickness, and layer diffusion.[8] Although explosive, exothermic compound-formation reactions have been observed in thin films[9] and in bulk,[10,11] no such processes have been reported for mechanical alloying.

We present in this Letter results of milling mixtures of elemental Al and Ni powders. The Al-Ni system was selected because of the variety of intermetallic compounds in its phase diagram and the important high-temperature applications of some of them.[12] *In situ* thermal analysis during milling, as well as scanning electron microscopy (SEM) and x-ray diffraction, was used to characterize the process and its products. Thermal analysis shows that a complete reaction of several grams of powder occurs explosively within 1 sec. For some compositions, a planar, gradual solid-state diffusion mechanism is not likely and melting is suggested to occur.

Samples were prepared in a Spex 8000 laboratory ball mill. Ni and Al powders of nominal purity of 99.9% and 99.8% and average particle size of 150 and 45 μm, respectively, were mixed at the compositions Al_xNi_{1-x} ($x=0.25$, 0.5, 0.75). The powder mixture plus three 12.5-mm-diam and eight 6.25-mm-diam stainless-steel balls, at a ball-to-sample weight ratio of approximately 6:1, were sealed in a stainless-steel vial in an argon atmosphere. A fan was used to keep the vial near room temperature during milling. The sample temperature was monitored with a Chromel-Alumel thermocouple inserted into a hole in the vial side or bottom, drilled to a distance of 1 mm from the inner wall of the vial. A thermal compound was used to insure adequate thermal contact, and the thermocouple wire was 0.13 mm in diameter and mounted carefully so as to avoid its rapid fracture during the fast motion of the vial. X-ray diffraction (XRD) was performed in step-scanning mode using Cu $K\alpha$ radiation from a rotating-anode source, and a Hitachi S 520 SEM with KEVEX 800 x-ray fluorescence analysis was used for sample characterization.

A goal of this study was the characterization of the early stages of the Al-Ni reaction and its comparison to thermal diffusion reactions. For an extended reaction time (10–20 h), the compounds Al_3Ni (orthorhombic), AlNi (CsCl-type), and disordered Ni_3Al (face-centered cubic), the latter being metastable, were obtained from powders of the same average compositions with apparent consumption of the entire elemental phase. For $Al_{75}Ni_{25}$, a trace of Al_3Ni was visible after 4 h of milling. For $Al_{50}Ni_{50}$, reaction of a substantial fraction of the powder to form NiAl was observed after 180 min and longer. For Ni_3Al, Bragg-peak overlap with the elemental phases prevented the use of XRD to observe trace amounts of the compound phase. However, no other compound was observed prior to its formation. The NiAl formation process appeared to be abrupt in some runs, and there seemed to be no stage at which it was present in trace amounts only.

To study the formation of the NiAl compound in more detail, a thermocouple was attached to the vial during the milling process and its voltage monitored as a function of time. It showed slow warming of the vial and approach to within 1 °C of the steady-state temperature of 35 °C after approximately 10 min. Runs up to 120 min

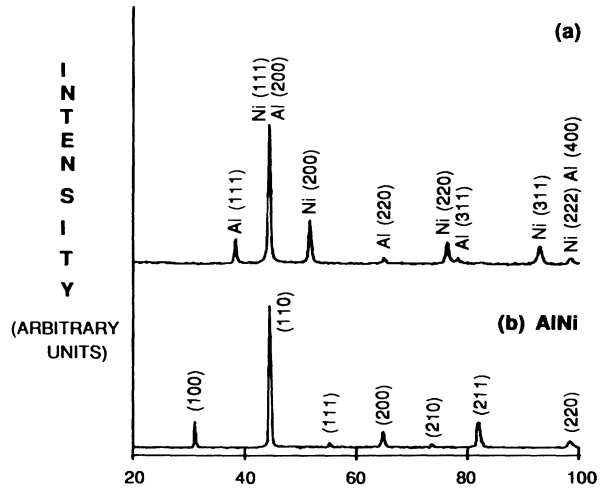

FIG. 1. X-ray diffraction pattern of $\mathrm{Al_{50}Ni_{50}}$ elemental powder mixture (a) ball milled for 120 min and (b) milled for 35 more seconds after interruption. (a) shows a mixture of the elements with no intermetallic compound present; (b) a complete transformation into AlNi.

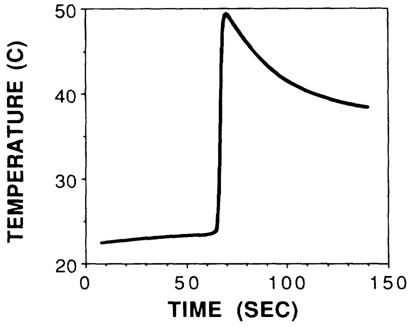

FIG. 2. A temperature trace of the bottom of the vial during resumed milling of 5 g of $\mathrm{Ni_{50}Al_{50}}$ following 120 min of premilling and subsequent interruption.

resulted in a constant temperature after steady state was reached, and the resulting powder was a composite elemental mixture, as verified by x-ray diffraction [Fig. 1(a)]. SEM micrographs show lamellar elemental domains, each approximately 1 μm thick, similar to results obtained by Schwarz, Petrich, and Saw[6] after milling Ni-Ti for 3 h. When the milling process was stopped after 100–120 min, and the vial left sealed under a blowing fan for 30 min or more, then resumption of milling led to an exothermic reaction 30–60 sec later. This was evidenced by the fact that the vial temperature increased by 27 °C within approximately 1 sec (see Fig. 2). The thermocouple mounted on the side of the vial showed an increase of 20 °C within 7 sec. After the spike, the temperature decreased to its previous value with a time constant of tens of minutes. This *in situ* monitoring of the reaction allowed us to stop the process less than a second after the reaction had occurred, so as to minimize the effect of milling on the reaction product. In contrast to the case of uninterrupted milling, x-ray-diffraction results show only the presence of NiAl, with no visible amount of the elemental phases [Fig. 1(b)]. Visual inspection showed that the resulting material consisted of 0.5–5-mm-large aggregates of powder particles. SEM micrographs (Fig. 3) show aggregates with flat interfaces between the particles. The large particles contain cavities whose dimensions are 10–50 μm, some of which appear to be spherical.

The observation that, for two different compositions, AlNi and $\mathrm{Al_3Ni}$, the first phase to form has the same composition as the elemental powder mixture indicates that for at least one of the compositions the reaction does not occur by gradual solid-state layer diffusion. In a layer diffusion mechanism, the initial reaction occurs in a thin interfacial region and the composition of the initially formed phase depends on thermodynamic and kinetic considerations, but not on the overall composition. $\mathrm{Al_3Ni}$ is the first phase to form upon thermal annealing in both $\mathrm{Al_{50}Ni_{50}}$ composites prepared by ball milling[13] and thin-film Al-Ni couples.[14] In the presently reported case of $\mathrm{Al_{50}Ni_{50}}$, we believe the observed temperature spike to be responsible for establishing thermodynamic equilibrium throughout the sample. Since we do not observe any phase in the ball-milled $\mathrm{Al_{25}Ni_{75}}$ sample prior to $\mathrm{AlNi_3}$ formation, a similar process could account for its formation. However, a characterization method com-

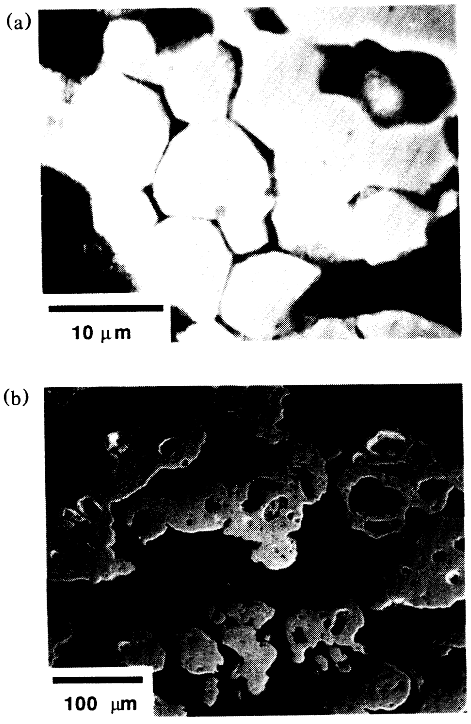

FIG. 3. Scanning electron micrographs of AlNi powder milled 1 sec past the exothermic peak.

plementary to XRD should be used to avoid peak overlap.

When $Ni_{50}Al_{50}$ powder is milled continuously for time in excess of 120 min, gradual NiAl formation can be observed. Because thermal diffusion is known to produce $NiAl_3$ as a first phase,[13,14] we conclude that the observed gradual reaction is the result of explosions in individual grains leading to thermal equilibration. The contrast with the case of interrupted milling can be explained as follows: During continuous milling, each particle, after reaching a critical lamellar thickness appropriate for the steady-state conditions, undergoes a reaction when ignited by a collision. In contrast, particles do not reach the critical condition when milled for less than 120 min, and therefore do not react upon impact. However, interruption and subsequent cooling (and possibly oxidation) result in lower ductility, and therefore resumed milling leads to energy concentration in smaller volumes, resulting in higher local temperature upon impact. At this point, all particles can be ignited, so that each particle reacts following the first impact. In the absence of such an effect, a lower ambient temperature would be expected to imply less favorable conditions for ignition,[15] in contrast to the observed behavior.

The thermal data can be used to further elucidate the BM process. Given the different time scales for heating and for subsequent cooling, the reaction can be considered adiabatic. Because the temperature profile becomes uniform across the vial walls within seconds, the measured temperature is representative of that of the vial. The top and bottom of the vial show a faster and higher temperature increase than the sides because most collisions occur on them. The measured values can be weighted by the corresponding wall volumes to yield an average of $22 \pm 1\,^{\circ}\mathrm{C}$. Using the Dulong-Petit value of 25 J/mol K as the high-temperature limit of the heat capacity of a solid, and given the relative number of moles in the vial and sample, we can estimate the heat released from the sample as 49 kJ/mol, as compared to the reported values of the heat of formation of AlNi [59 kJ/mol (Ref. 16)]. Considering the crudeness of the measurement, the agreement is satisfactory. We believe this to be the first direct measurement of the heat of alloy formation by ball milling.

The experimental results clearly show explosive mixing of Al and Ni. Such a reaction can result in the formation of AlNi in the solid state, or as a liquid, which then solidifies upon heat loss to the vial. The following arguments suggest a picture in which the explosive reaction is accompanied by melting of the solid powder. A simple estimate shows that under adiabatic conditions, i.e., when heat dissipation is considerably slower than its generation, the heat of formation of NiAl is sufficient to bring solid NiAl from room temperature to 100 °C above its melting point. This estimate is based on the Dulong-Petit values of the heat capacity for the solid and the liquid metal, and a value of $1.2R$ (Ref. 17) (R = gas constant) for the entropy of fusion, neglecting the contribution of differences in chemical order between solid and liquid. Although this estimate is crude, a significant fraction of the compound is still expected to melt if it forms in an adiabatic reaction. Because collisions leading to possible melting and subsequent solidification would not occur simultaneously in all grains, the macroscopically observed thermal signal would not be affected by such a melting process. Further support for the hypothesis of melting is given by Fig. 3(a): The planar interfaces between the aggregated particles observed after reaction suggest that the particles were compressed in the liquid state, with possible surface contaminants preventing their coalescence.

The large volume fraction of voids observed in the reaction products [Fig. 3(b)], can be explained as being caused by (1) the 14% density increase[18] upon NiAl formation from the elemental constituents, and possibly (2) impurity gases leaving the matrix during the temperature spike.[10] The spacing between voids indicates a diffusion length of approximately 50 μm for the migration of free volume (if the alloy is in the liquid state) or vacancies (in the solid state) during the reaction. At this point we cannot rule out void formation by vacancy migration in a high-temperature solid.

We suggest explosive reactions as a possible mechanism for the alloying of elements with large heats of formation. When such reactions do not occur in all grains within a short time they cannot be detected by thermal analysis. A self-sustained reaction can also occur in the initial stages of a layer diffusion process, until the alloy layer is sufficiently thick to cause a slowdown in the reaction rate and its termination. For the latter picture, the molten layer could then cool by heat loss to the unreacted phases. The proposed mechanism is particularly likely in mechanical alloying of brittle elements,[19] because the impact energy can be localized in small volumes.

In summary, *in situ* thermal analysis shows an exothermic, explosive formation of AlNi during ball milling of the elemental powders. The heat of compound formation is estimated from this measurement. It is suggested that this process leads to the formation of a liquid alloy, followed by cooling and solidification. The results suggest reaction mechanisms in some alloys observed to form by ball milling.

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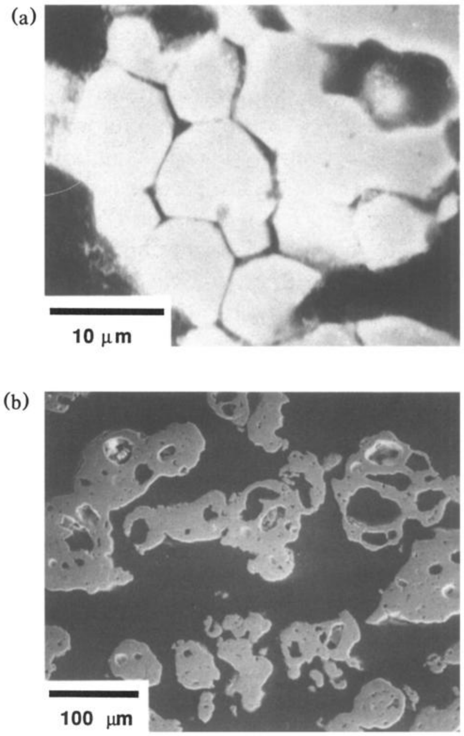

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