COMBUSTION AND PLASMA SYNTHESIS OF HIGH-TEMPERATURE MATERIALS

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Shock-Induced Chemical Synthesis of Intermetallic Compounds

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ABSTRACT. Shock-synthesis experiments were performed on elemental powder mixtures of Ni-Al and Nb-Al to study the effect of material parameters on solid-state chemical synthesis. Elemental powders of different morphologies were premixed in a proportion of ~65 wt % Ni or Nb and 35 wt % Al. Shock-compression loading experiments were conducted on Ni-Al mixtures at 19–22 GPa pressures, using the Sandia Bear fixtures, and on Nb-Al mixtures at 30–40 GPa pressures, using a 12-capsule Sawaoka recovery fixture. In the case of Ni-Al mixtures, the starting powder morphology plays a significant role in determining the extent of the reaction. The Nb-Al powder mixtures that were shock processed at higher pressures underwent complete reactions.

Key Words: differential-thermal-analyzer characterization, morphological effects, nickel aluminides, niobium aluminides, shock-induced mixing, shock synthesis

Introduction

In the work presented here, explosively generated shock-compression waves were used to synthesize aluminides of Ni and Nb from elemental powder mixtures, and at the same time to induce bonding between the powder particles. This shock-induced chemical synthesis, which involves the simultaneous application of very high pressure and high-strain-rate deformation, is a nonequilibrium processing technique that produces new materials with special microstructures. In 1961, the technological potential of shock processing was first demonstrated by the pioneering work of DeCarli and Jamieson,[1,2] namely the synthesis of diamond from rhombohedral graphite. Since that time, shock-induced chemical synthesis has been successfully

used, not only to induce phase changes, but also to synthesize compounds from elements in ceramic[3–7] as well as metallic systems.[8–14]

The first systematic investigation of shock-induced chemical synthesis in intermetallics was conducted by Horie, et al.,[8–9] Simonsen et al.,[10] Hammetter et al.,[11] and Graham et al.[12] They synthesized aluminides of Ni and Ti, starting with mechanically mixed powders of the respective elemental constituents, using ratios appropriate to form stoichiometric Ni_3Al and Ti_3Al. In the case of the Ni-Al powder mixtures, they observed that the nickel-aluminide products were readily synthesized and controlled by the shock conditions (peak pressure and mean bulk temperature). Large yields of Ni_3Al were produced, and the material had a hardness similar to that of cold-worked Ni_3Al, even though the material had low defect concentration. In contrast, the reaction yield was very limited in the case of the Ti-Al powder mixtures. The work presented here is an extension of the work presented in the above-mentioned studies.[8–12] Instead of concentrating on optimizing the processing parameters, (pressure and temperature), the emphasis of this effort is on determining the influence of material parameters upon the extent of the reaction and the nature of the reaction products.

Experimental Procedure

Shock-compression experiments were conducted on mixtures of Ni and Al powders of different morphologies (shape and size). Table 1 lists the five types of powders used in the study. The powder particle sizes ranged from 1 to 45 μm for Al and from 3 to 45 μm for Ni. The morphology of the powders was either flaky or spherical. Characteristic scanning electron micrographs of the powder mixtures containing flaky and spherical Ni particles and rounded Al powders are shown in Figures 1a and b, respectively.

The premixed Ni-Al powders, prepared by combining the pure elemental powders (65 wt % Ni and 35 wt % Al) under an argon atmosphere and then mixing in a ball mill, were packed into copper capsules at approximately 65% theoretical density. These were then sealed and placed in the Sandia Momma Bear "A" Fixture[15] for shock-compression loading. Composition B was used as a high explosive to generate the shock waves (shock pressure of 19–22 GPa), which were transmitted

Table 1. Characteristics of Mixtures of Ni and Al Powders

Powder lot no. SNL—*	Shot no.	Nickel powder shape	Nickel powder size (μm)	Nickel powder purity (%)	Aluminum powder shape	Aluminum powder size (μm)	Aluminum powder purity (%)	Green density (g/cm³)
0887—1	35G876	spherical	3–7	99.9	round	1	99.9	4.090
0887—2	38G876	spherical	10–20	99.9	spherical	10–20	99.5	4.147
0887—3	39G876	spherical	−40 + 20	99.9	spherical	−44	99.8	4.154
0887—4	6G876	flaky.	~44	99.9	spherical	~44	99.8	4.20
0887—5	41G876	spherical	−45 + 20	99.9	spherical	5–15	99.9	4.164

*SNL; Sandia National Laboratories.

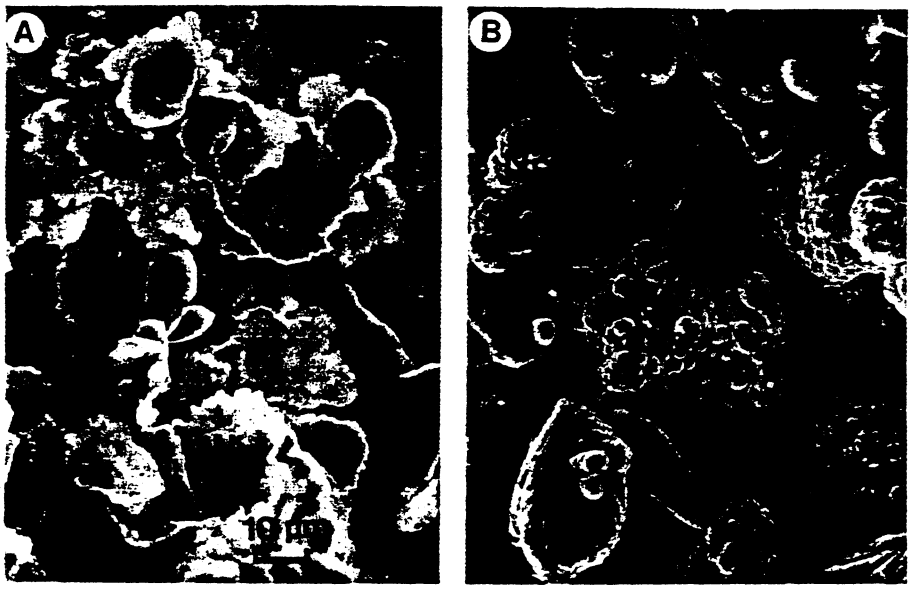

Figure 1. Characteristic scanning electron micrographs of the powder mixtures, containing (A) flaky and spherical Ni particles, and (B) rounded Al particles.

through the driver plate and into the powder. For the Nb-Al system, only one type of powder was used, namely, Nb (irregular, −325 mesh) and Al (irregular, −325 mesh). The powder mixture (65 wt % Nb and 35 wt % Al) was prepared by hand mixing in argon atmosphere and packed into stainless-steel capsules at 65% of theoretical density. The capsules were embedded in a 12-capsule recovery fixture backed by a momentum trap, which was impacted by an explosively driven flyer plate at a velocity of 1700 m/s.[16] The planar/parallel impact of the flyer plate creates high-amplitude shock waves (30–40 GPa shock pressure) that transmit through the powder.

After shock loading, the compacts of both Ni-Al and Nb-Al powder mixtures were recovered from the shock-recovery fixtures and characterized by differential thermal analysis, microscopy, and X-ray diffraction analysis.

Shock Processing of Ni-Al

Ni-Al Compact Characterization by Microstructural Analysis

Optical-microscopy observations revealed that in the case of the fine powder mixture compact (Shot No. 35G876), and the one containing flaky Ni powder (Shot No. 6G876), a complete reaction had occurred. The recovered compact from Shot No. 35G876 was very poorly bonded together and almost fragmented, whereas the compact of Shot No. 6G876 remained well bonded. Figure 2 shows a corner and central cross-section region of the recovered compact of Shot No. 6G876. Compacts from Shot No. 38G876, 39G876, and 41G876 exhibited nearly identical

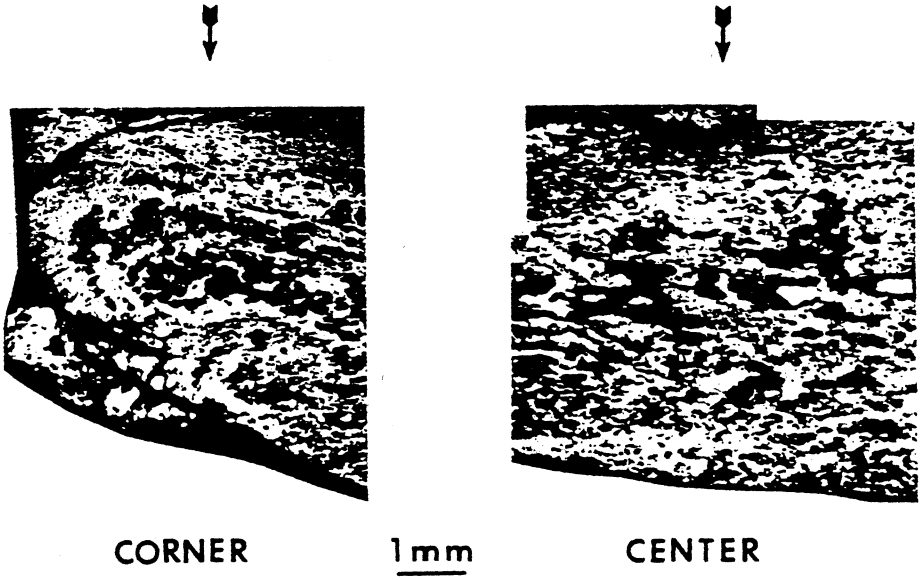

Figure 2. Optical micrograph of the central and corner region along the cross-section of sample No. 6G876 showing fully reacted regions, with spherical voids.

characteristics, but unlike the fine or flaky powder compact, the bulk of the material remained unreacted. The fully reacted regions in these compacts were observed to be isolated along the circumference (or actually in a triangular area located near the corners) as observed in micrographs of cross-sectional planes of the compacts. These, in fact, are regions subjected to the maximum shock-induced mean bulk temperature, as predicted by numerical simulations that were performed using the two-dimensional CSQ code.[15] No unreacted Ni and Al was detected in this triangular region. Figure 3a is an optical micrograph of part of the cross-section of sample No. 39G876 that shows a typical triangular reaction region. The etching contrast generated reveals five dissimilar phase regions (A, B, C, D, and E, as shown in the figure). These regions correspond to the following phases and structures: regions A and B correspond to unreacted Ni and Al powders; region C shows a reacted Ni_xAl_y compound; region D is a reacted, melted, and rapidly resolidified amorphous material; region E is also a reacted, melted, and resolidified compound showing a fine dendritic or microcrystalline structure. A scanning electron micrograph of one interface region is shown in Figure 3b. The bright contrast of the Ni particles and dark contrast of the Al particles is clearly observed in this micrograph. A transition area of approximately 150-μm thickness between totally unreacted material and bulk reaction products appears to contain an Al-rich compound (with dendritic grains) between the Ni particles. The bulk reaction product, on the other hand, is contrast-free and has Ni_3Al stoichiometry.

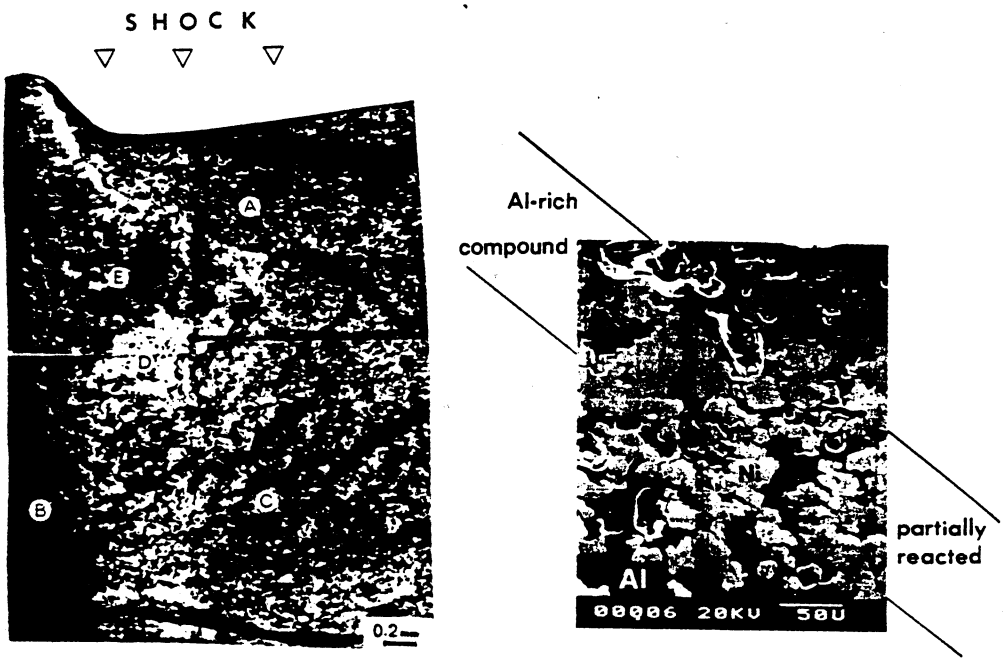

Figure 3. Optical (left) and scanning (right) electron micrograph of a part of the cross-section of sample No. 39G876, showing reacted and unreacted regions.

DTA Characterization of Powders

Samples of the five powder mixtures were run in a DuPont 9900 Differential Thermal Analyzer (DTA) to observe any variation in the powder reactivity before shock-compression processing. The DTA scans of the powders are compiled in Figure 4. Ni and Al powders react together at 640°C (slightly below the melting temperature of Al), resulting in an exothermic self-sustaining reaction.[11] From the DTA scans shown in Figure 4, we observe that the powder-mix No. SNL–0887–4 (325-mesh flaky Ni and spherical Al) shows maximum reactivity, which arises from the efficient mixing of the Ni (flaky) and Al (spherical) powders. The fine-powder mixture, in spite of possessing maximum surface area, shows lower reactivity. This is attributed to improper mixing of the powders, in particular because of the tendency of the very fine powders to agglomerate with like particles.

In order to verify the reaction regions evidenced by the different etching contrasts in the optical micrographs, small samples were taken from different areas of the shocked compacts and analyzed in the DTA. Typical DTA traces are shown in Figure 5: Samples from the fully reacted regions of all the compacts show a smooth trace in the DTA, indicating no subsequent reaction while heating in the DTA, whereas the samples from unreacted regions exhibit two exothermic peaks.

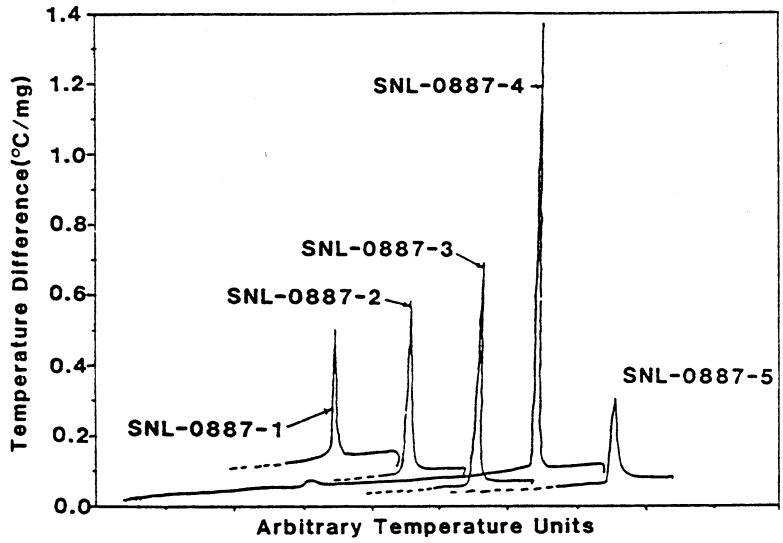

Figure 4. DTA scans showing exotherms of the reaction between different grades of Ni and Al powders.

The first exothermic peak is believed to be a "preignition" phenomenon. This phenomenon was not observed in the unshocked powder mixtures heated in the DTA (Fig. 4) and is characteristic of shock-induced processes. The latter peak is the exotherm corresponding to the complete reaction between Ni and Al. Similar observations were also made by Hammetter et al.,[11] who conducted X-ray diffraction

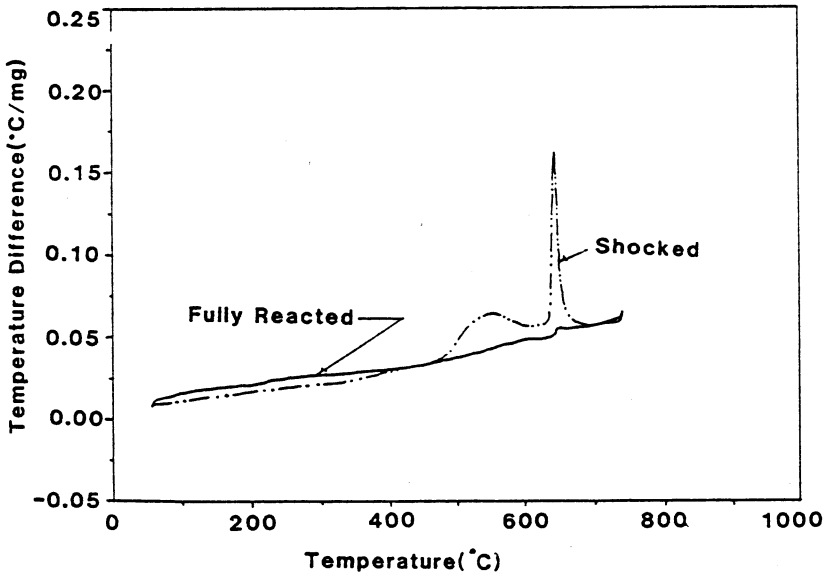

Figure 5. Typical DTA traces from small samples of reacted regions (solid line) and unreacted regions dashed line of a shocked compact.

studies at elevated temperatures and observed the formation of Al-rich compounds in shock-treated samples that had not undergone a reaction.

From DTA analysis performed on shock-processed powders, it was concluded that the bulk of the material in sample Nos. 35G876 and 6G876 had been reacted. Shocked sample Nos. 38G876, 39G876, and 41G876 had undergone a partial reaction only, and the reaction regions were confined to the outer circumference of the disk.

X-ray Diffraction Analysis

In order to identify the compounds and the structure of the bulk products formed during shock-induced chemical synthesis, X-ray diffraction analysis was performed

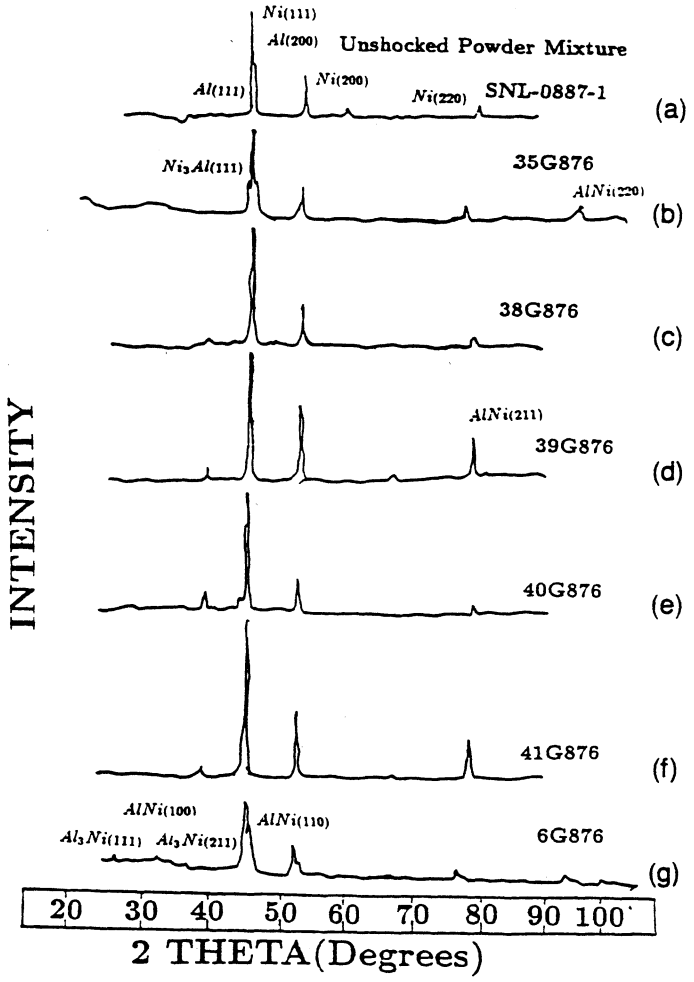

Figure 6. X-ray results showing diffraction peaks obtained from the unshocked powder mixtures and recovered compacts.

on the mechanically blended Ni and Al powder mixtures and the entire cross-sectional surface of the various shock-processsed Ni-Al compacts. The X-ray diffraction results are summarized in Figure 6. Curve (a) shows the Ni and Al diffraction peaks obtained on the blended powder (Mix No. SNL-0887-1). X-ray diffraction scans obtained from the central cross-sectional surfaces of the different compacts are given as: curve (b), Shot No. 35G876; curve (c), Shot No. 38G876; curve (d), Shot No. 39G876; curve (e), Shot No. 40G876; curve (f), Shot No. 41G876; and curve (g), Shot No. 6G876.

It can be seen from these X-ray diffraction results that all of the recovered compacts show at least some degree of reaction, and the reaction products formed range from Al-rich to Ni-rich compounds. It is obvious that in curves (b) and (g), which correspond to sample Nos. 35G876 6G876, the Al(111) peak is missing, implying the complete depletion of Al particles in the reaction process (within the limits of detectability). The X-ray diffraction trace of the 6G876 compact indicates the presence of an AlNi compound along with elemental Ni and some Ni_3Al, whereas the traces for 35G876 show Ni_3Al as the predominant reaction product.

Shock Processing of Nb-Al

Shock processing the Nb-Al powders resulted in small disks 12 mm in diameter by 5-mm thick. Although the disk was almost totally fragmented by the shock pressures produced in the powders upon impact at 1700 m/s, it could be established that most of the powder mixture had undergone reaction. Figure 7a shows a macrophotograph of the cross-section of a recovered Nb-Al powder compact. Most of the section had a microdendritic structure except the upper-left-hand corner, where no reaction took place. The Vickers microhardness measurements are shown in Figure 7a. The reacted region had a higher hardness (800–900 kg/mm^2) than the unreacted region (~100 kg/mm^2). Figure 7b shows the microdendritic structure at a high magnification. The heat generated from the exothermic reaction between Nb and Al was enough to melt the reaction products, which solidified to a microdendritic structure. Shrinkage voids formed during solidification are also seen in Figure 7a.

X-ray diffraction analysis was performed on the unshocked Nb-Al powders, as well as on the cross-section of the recovered shock-processed compacts.

The Nb-Al powder mixture is shown in trace (A), while the shock-synthesized material is shown in trace (B) in Figure 8. Two intermetallic compounds, Al_3Nb and $AlNb_2$, can be identified from the X-ray diffraction analysis of the shocked compacts.

Summary of Results

Shock-compression processing is used to chemically synthesize nickel and niobium aluminides, starting with the constituent elemental powders. In the case of Ni-Al mixtures, the starting powder morphology plays a significant role in determining the extent of reaction. Very fine and flaky powders undergo intimate shock-induced mixing, and thereby, result in complete reactions. The shock-induced reaction prod-

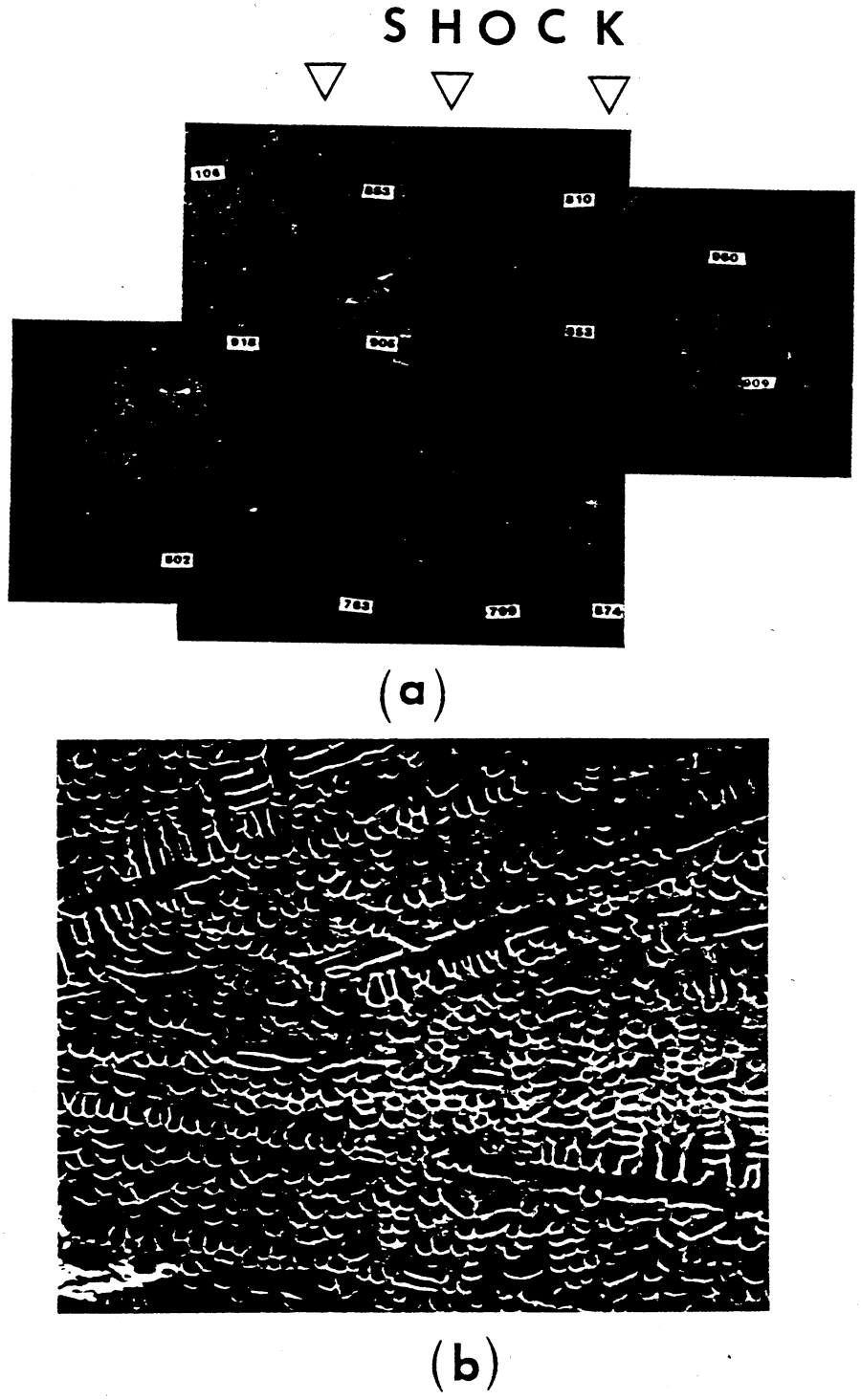

Figure 7. (a) Macrophotograph of a cross-section of the fragmented powder compact containing 65 wt % Nb and 35 wt % Al powders. (b) Optical micrograph showing a dendritic structure at high magnification.

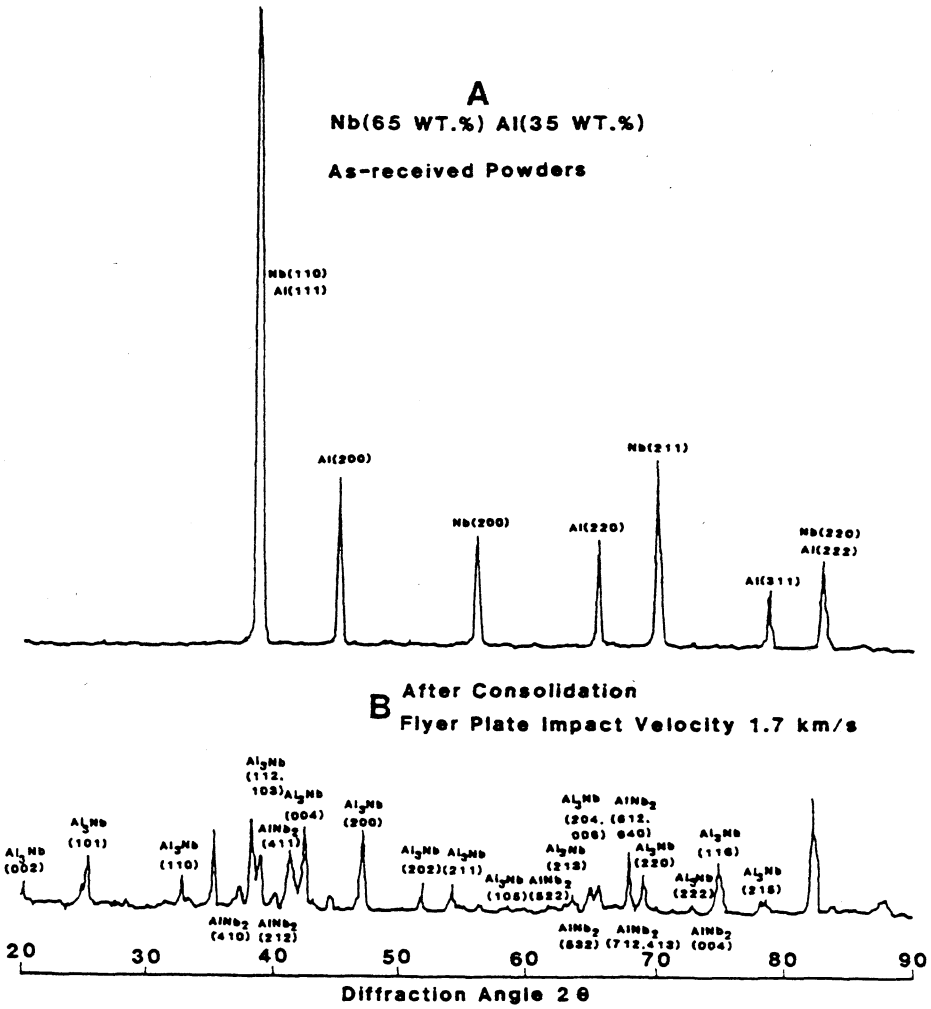

Figure 8. X-ray diffraction results obtained from a Nb-Al powder mixture (A) and the shock-synthesized compact (B).

ucts formed range from an equiatomic NiAl compound with the use of flaky nickel morphology to a Ni_3Al compound with fine powders.

Nb-Al powder mixtures, when shock processed at higher pressures, undergo almost complete reactions to Nb_2Al and $NbAl_3$ compounds with a microhardness of 800–900 kg/mm^2.

Acknowledgments

The Ni-Al work was funded by the Sandia National Laboratories under the Sandia/University Research Program. Support for the Nb-Al work was provided by McDonnell Douglas Research Corporation. The scanning electron microscopy was performed at the University of New Mexico with the help of Mr. George Conrad. We also acknowledge Mr. Edward Binasiewicz of Sandia National Laboratories for his assistance with the DTA work.

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