Spark Plasma Sintering of Ti$_{1-x}$Al$_x$N Nano-Powders Synthesized by High-Energy Ball Milling

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Abstract

The present study focused on the fabrication of bulk materials from Ti$_{1-x}$Al$_x$N nanopowders using a spark plasma sintering (SPS) apparatus. Super-saturated Ti$_{1-x}$Al$_x$N solid solutions were synthesized by high-energy ball milling (HEBM) of pure nitrides. The complete dissolution of AlN in TiN was achieved after 100 h of milling. The milled powders were characterized by X-ray diffraction and energy-filtered transmission electron microscopy spectra imaging. Thermal stability of the supersaturated Ti$_{1-x}$Al$_x$N solid solution was investigated theoretically using density functional theory (DFT) analysis and experimentally by means of differential scanning calorimetry (DSC), Brunauer-Emmett-Teller (BET) and x-ray diffraction. The results indicated that spinodal decomposition of Ti$_{1-x}$Al$_x$N starts at 800°C, while at temperature higher than 1300°C regular decomposition (nucleation and growth) is occur.

Ti$_{1-x}$Al$_x$N powder with 20 mol-% of AlN was consolidated by high pressure spark plasma sintering (HPSPS) at 1300°C with heating rate of 50°C min$^{-1}$ under uniaxial pressure of 400MPa. Fully dense nanostructured HPSPS-processed specimens display hardness of 2000HV, Young modulus of 420GPa, bending strength of 600MPa and fracture toughness 6.9 MPa·m$^{0.5}$. 

Introduction

In the past decades Ti$_{1-x}$Al$_x$N ceramics attracted large interest because of their high hardness, wear and oxidation resistance at elevated temperatures. These properties result in a significantly improved performance in dry machining [1-4]. However, recent investigations have predominantly dealt with thin or thick films [1-7]. Only few researchers have been reported fabrication of bulk dense samples of titanium aluminum nitrides. The supersaturated Ti$_{1-x}$Al$_x$N solid solution powder was synthesized from AlN, Ti and ammonium carbonate by HEBM for various milling durations[8]. It was established that powder milled with steel grinding media had average particle size below 50nm (after 52h milling) and consists of a remarkable fracture of Fe. This powder was successfully consolidated by Hot Pressing (HP) at 1473K and by Spark Plasma Sintering (SPS) at 1573K. Relatively high hardness (1800-1900HV) of the sintered samples was attributed to the presence of Fe particles that enhanced the sintering process. Borodianska et al.[9] have reported the results of synthesis of Ti$_{1-x}$Al$_x$N powders with 10 and 40 wt.% of AlN from of TiH$_2$ and Al mixtures by HEBM under nitrogen atmosphere. The powders were consolidated by SPS at 1873K and displayed micro-hardness of 17.5GPa and fracture toughness of 7.25MPa·m$^{0.5}$. Authors have attributed the elevated properties of the SPS-processed samples to a precipitation of nonstable cubic AlN particles during consolidation. Nevertheless, the presence of cubic AlN at 1873K is questionable and may be ascribed only by a spinodal decomposition of Ti$_{1-x}$Al$_x$N phase. However, this decomposition, at least in thin films, takes place in the 400-800°C temperature range.
range [10] and at higher temperatures the coherent with TiN precipitates have to disappear. Moreover, the coherent precipitates cannot be detected by SEM and X-ray analysis. Recently, Kim et al. [11] have fabricated of TiN-AlN composites from nano-size powder mixture (1/1 molar ratio) of pure nitrides by the pulsed current activated sintering (PCAS). The consolidated composites were almost fully dense and displayed hardness of 18.4 GPa and fracture toughness of 3.3 Mpa·m^{0.5}. In the mentioned above contributions pressure assisted consolidation was performed under relatively low external pressure (<100 MPa). The extremely high pressure (10 GPa) was applied by Mashhadi et al. [12] for underwater shock compaction of $Ti_{1-x}Al_xN$ powders obtained by HEBM of AlN and Ti. The nanostructured (12 nm crystallite size) AlN–TiN composites displayed only 98% density and low hardness value (8.4 GPa).

The results of a systematic investigation of the synthesis, thermal stability and consolidation of nano-sized $Ti_{1-x}Al_xN$ powders did not appear in the literature.

In the present study, the synthesis of $Ti_{1-x}Al_xN$ nano-powders by HEBM, their thermal decomposition and SPS consolidation were investigated.

**Experimental Procedure**

TiN and AlN grade C micron size powders supplied by Starck H.C. served as starting materials. The powder mixtures with 20 and 50% AlN (throughout the text, concentration is given in mole percent) were treated in a planetary ball mill (Retsch PM 100) using chromium hardened steel and sintered alumina container and balls (10 mm diameter). The ball to powder weight ratio was 20:1, the rotational speed was 400 and 600 rpm and the milling time was varied from 0 to 100 hours.

The phase compositions of the mechanically alloyed and heat treated powders and the sintered samples were determined by X-ray diffraction (XRD) using a Panalytical X'Pert Pro X-ray Diffractometer with CuK$_\alpha$ radiation ($\lambda=0.154$ nm), operating at 40 kV and 40 mA. Data collection was performed by step scanning over the $2\theta:20–85^\circ$ angular range in 0.05° steps, with 3 sec per step. The XRD line profile parameters were treated according to the Rietveld procedure using PowderCell for Windows (PCW) software. The crystallite sizes and lattice strains of the milled particles were determined from a broadening of XRD peaks by the Williamson-Hall (WH) method [13].

Transmission electron microscopy (TEM) investigations of the milled powders were carried out using a JEOL JEM-2100F TEM operating at 200 kV. Samples for TEM characterization were prepared by depositing a drop of an ethanol suspension of the milled $Ti_{1-x}Al_xN$ powder onto a copper grid coated with ultrathin carbon film (Cu, 400 mesh, Ted Pella catalog #01824). Energy dispersive X-ray spectrometry (EDS) analysis was performed using a JED-2300T Energy Dispersive X-ray spectrometer. The probe size during analysis was set to 1 nm to provide high sensitivity analysis at the nm scale. Energy-filtered TEM (EFTEM) spectrum imaging using a Gatan imaging filter (GIF Quantum) was employed for chemical mapping. Sample thickness was measured from a zero-loss image using a 10 eV energy slit width. EFTEM images were obtained by selecting only non-elastically scattered electrons corresponding to inner shell losses of the elemental edge of interest. Three-window background subtraction was used to image the distribution of the Ti–L edge (456 eV), the Al–K edge (1650 eV), the N–K edge (401 eV) and the O–K edge (532 eV). Spatial drift between images was corrected manually using Gatan Digital Micrograph software.

Ab initio calculations, based on Density Functional Theory (DFT) has been used to construct the ternary Ti-Al-N phase diagram and analyze the decomposition of the supersaturated $Ti_{1-x}Al_xN$ solid solution.
The surface areas (particle size) were measured by the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2020 (Micromeritics, Norcross, GA) instrument. Ten-point adsorption isotherms of nitrogen were collected in the P/P0 relative pressure range (P0 = saturation pressure) of 0.05 - 0.30 at -196°C. Prior to the analysis procedure, each sample was vacuum-degassed at 150°C for 4 hours.

Differential scanning calorimetry (DSC) was conducted under argon using a Netzsch high temperature STA 449 F3 (Netzsch, Selb, Germany). Temperature calibration was performed by melting Sn, Ag, and Au standards in alumina crucibles. Sensitivity calibration was performed using single crystal Al2O3 as a heat capacity standard. The DSC measurements were carried out by continuous heating at 20 °C /min with 5 min isothermal holds at 50°C and 1350°C in the heating direction. A typical sample mass of 30 mg was used. After the completion of the first run a second run was performed under identical conditions, without lifting the furnace or disturbing the sample, in order to serve as a material baseline.

The annealing process of the milled powders was performed under Ar atmosphere at 800 and 1000°C for 12h.

The morphologies and microstructures of the fractured sintered specimens were revealed by scanning electron microscopy (SEM; JSM-6510LV, JEOL).

The Ti$_{1-x}$Al$_x$N powder with 20 % AlN and HEBM milled pure TiN powder were consolidated by high pressure spark plasma sintering (HPSPS). A precise description of the tooling setup was presented previously [14]. Sintering was conducted under pressure of 400MPa at 1300°C with heating rate 50 deg. min$^{-1}$ and holding time 30min.

The density of the sintered specimens was determined by the Archimedes method. Bending strength was determined by a three-point bending test (1.5 mm×2mm×10 mm bars) using an LRX Plus apparatus (Lloyd Instruments, Fareham Hants, UK). Five specimens for each sample were tested. The elastic modulus was determined by the “pulse echo” method [15]. Hardness measurements were conducted under a 2 kgf load using a Buehler Micromet 2010 apparatus (Lake Bluff, IL). The lengths of the cracks that appeared at the corners of Vickers indentations were used for evaluating fracture toughness ($Kc$). Empirical equations for fracture toughness estimation depend on the nature of the crack [16]. Two types of cracks systems (Palmqvist and “half penny”) are commonly considered. To identify the nature of the cracks system, a polishing procedure was performed after indentation. Examination of optical micrograph of the sample confirmed the presence of a Palmqvist type crack system (Fig.1, a and b).

![Fig 1. Vickers hardness indentations for TiN-20%AlN sintered under pressure of 63 MPa (a). An optical image of the imprint after additional polishing (b).](image-url)
$K_c$ values were thus calculated according to the equation for the Palmqvist type crack system [16]:

$$K_c = 0.0264(HV \cdot a)(E / HV)^{0.4}(l^{-0.5})$$

where $HV$ is the Vickers hardness, $E$ is the Young modulus, $a$ is the half length of the Vickers indentation diagonal line, and $l$ is the length of the crack from the tip of the indentation.

RESULTS AND DISCUSSIONS

Synthesis Ti$_{1-x}$Al$_x$N Solid Solution Powder

XRD patterns of TiN-20%AlN powder mixtures after various milling durations are presented in Fig.2. For the as-mixed powder (0h), all the expected sharp peaks of TiN and AlN exist.

Fig. 2. The diffraction patterns of the powder mixtures (TiN-20%AlN) after various milling durations.

With increasing milling time the TiN peaks become broader and shift to higher angles, while the intensities of the AlN reflections gradually decrease and completely disappear after 100 hours of milling. The broadening of the peaks is attributed to the reduction of crystallite size and the presence of lattice strain. The shift of TiN peaks to a higher angle indicated reduction of the lattice parameter from 4.24 for pure TiN to 4.14 Å for milled powder after 100 h of milling. The change of the lattice parameters and the absence of AlN peaks reflect the formation of Ti$_{1-x}$Al$_x$N solid solution.

TEM analysis was also carried out to confirm the formation of Ti$_{1-x}$Al$_x$N solid solution. The Al, Ti, N and O elemental maps (Fig. 3 a-d) and a combination of these individual maps (colored map, Fig. 3 e) indicate the homogeneous distribution of Ti, Al, N over the particles.
Fig. 3. EFTEM elemental maps for Ti (a), Al (b), N (c) O (d). The EFTEM colour map (e) is a combination of the individual Ti, Al, N and O maps (Ti-red, Al-yellow, N-green, O-blue).

Fig 4. Regions selected for EDS compositional analysis.

Table 1. The local composition (%) of TiN-20 % AlN milled powder.

<table>
<thead>
<tr>
<th>Region</th>
<th>Ti</th>
<th>Al</th>
<th>Ti/Al molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>23.78</td>
<td>6.66</td>
<td>0.28</td>
</tr>
<tr>
<td>B</td>
<td>19.30</td>
<td>5.79</td>
<td>0.30</td>
</tr>
<tr>
<td>C</td>
<td>17.60</td>
<td>4.05</td>
<td>0.23</td>
</tr>
</tbody>
</table>
The local composition of the selected regions (see Table 1) is close to the starting powder composition. Thus, it can be concluded that prolonged HEBM led to the formation of \( Ti_{1-x}Al_xN \) supersaturated solid solutions with compositions close to those of the starting materials. This solution unstable and tends to decompose into stable c-TiN (NaCl structure) and w-AlN (wurtzite structure). The basic understanding this decomposition is important for choosing appropriate sintering conditions.

**Thermal Stability of the Supersaturated Ti\(_{1-x}\)Al\(_x\)N Solid Solution Using Ab Initio Calculations**

A regular solution approach was applied to analyze thermodynamic stability of the \( Ti_{1-x}Al_xN \) solid solution. According to this approach the molar Gibbs free energy of mixing for \( Ti_{1-x}Al_xN \) per atom in the regular solid solutions approximation is expressed by

\[
\Delta G = x(1-x)L + RT[(x \ln(x) + (1-x) \ln(1-x)]
\]

where \( T \) is the temperature, \( R \) is the universal gas constant and \( L \) is the interaction parameter in the \( Ti_{1-x}Al_xN \) solid solution. This parameter per site on Ti sublattice can be estimated as follow

\[
\Delta E_f = x(1-x)L
\]

where \( \Delta E_f \) is the mixing energy. The mixing energy can be calculated in a conventional way \cite{17}

\[
\Delta E_f = E_{Ti,Al,N} - \left( xE_{Ti,N} + (1-x)E_{Al,N} \right)
\]

Ab initio calculations, based on Density Functional Theory (DFT) has been used to estimate \( E_{Ti,Al,N} \), \( E_{Ti,N} \) and \( E_{Al,N} \). The calculations were carried out in the framework of Density Functional Theory (DFT), using the full-potential method with Augmented Plane Waves + local orbitals (APW+ lo) formalism, as implemented in the WIEN 2k code \cite{18-21}. A k-points grid of \( 10 \times 10 \times 10 \) was used for \( Ti - Al - N \) and \( 15 \times 15 \times 15 \) for TiN and AlN. \( R_{MT} \) radii were chosen equal to 2.0 Bohr for all atoms. With this input data, the accuracy of the self-consistent total energy calculations was \( \sim 10^{-4} \) Ry. The expanded \( 2 \times 2 \times 2 \) supercell for Ti-Al-N system in B1 structure was used to model the dilute substitutional solid solution in \( Ti_{1-x}Al_xN \). The supercell consists of 16 (8 metal and 8 nonmetal) atoms. For all considered structures the optimization of the volume of the supercell was carried out to obtain the equilibrium lattice parameters and the total energies corresponding to the equilibrium of the lattice. The equilibrium total energies were obtained by a least-square fit of the calculated total energy versus volume data to the Murnaghan equation of state \cite{23}. The results of volume optimization for cubic TiN are displayed in Fig.5.
The corresponding values of lattice parameters and total energies are collected in Table 2.

**Table 2.** Calculated lattice parameters and total energies for various structures. The energies after the slash correspond to the energies per formula unit.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>Energy, Ry</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN (NaCl)</td>
<td>4.2639</td>
<td>4.2639</td>
<td>4.2639</td>
<td>-1817.3924</td>
</tr>
<tr>
<td>AlN (NaCl)</td>
<td>4.2400</td>
<td>4.2400</td>
<td>4.2400</td>
<td>-595.3273</td>
</tr>
<tr>
<td>Ti$_7$N$_8$Al</td>
<td>8.4980</td>
<td>8.4980</td>
<td>8.4980</td>
<td>-13317.0129/</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1664.6266</td>
</tr>
</tbody>
</table>

With the energies calculated for extended Ti-Al-N supercell, we obtain per formula unit $\Delta E_f = 7.8 \cdot 10^{-3}$ Ry. This value data allows constructing the quasi-binary TiN-AlN phase diagram (Fig.6).
From this phase diagram we can conclude that depending on the composition and temperature of the supersaturated phase, its decomposition takes place either through spinodal decomposition or through nucleation and growth. The morphology of the solid solution that is obtained after these decompositions may be the reason of the increased hardening of the obtained material.

**Experimental Study of Thermal Stability of Supersaturated \( Ti_{1-x}Al_xN \) Solid Solution**

Thermal stability of \( Ti_{1-x}Al_xN \) solid solutions, obtained from the TiN-50%AlN powder mixture, was investigated by DSC apparatus. The strong exothermic peaks (1-3) were detected in the DSC curve (Fig. 7 a). To make clear the origin of these peaks, the powders were annealed in the 800-1350°C temperatures range for 12 hours and then analyzed by DSC. According to DSC curves b and c, the peaks 1 and 2 disappear after annealing at 800 and 1000°C, respectively. The as milled and annealed powders were characterized by XRD and BET. XRD patterns did not show any change after heat treatments up to 1100°C (Fig.8), while the surface area significantly increases after annealing at 800°C (Table3). We suggest that annealing at 800°C leads to spinodal decomposition of the supersaturated \( Ti_{1-x}Al_xN \) solid solution, accompanied by the precipitation of coherent AlN particles. After annealing at 900°C surface area decreases and only slightly changes after heat treatment at 1100°C. The surface area decreasing in the 900-1100°C temperature range is attributed to the particles growth.
Fig. 7. DSC signal of Ti0.5Al0.5N powders. a) as-milled powder, b) milled and annealed at 800°C powder, c) milled and annealed at 1000°C powder.

Fig. 8. The diffraction patterns of the milled and annealed at various temperatures TiAlN powders.
Table 3. The BET analysis results of Ti$_{0.5}$Al$_{0.5}$N powders for various annealing temperatures.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>5.4</td>
</tr>
<tr>
<td>800</td>
<td>21.8</td>
</tr>
<tr>
<td>900</td>
<td>9.0</td>
</tr>
<tr>
<td>1100</td>
<td>6.6</td>
</tr>
<tr>
<td>1300</td>
<td>12.8</td>
</tr>
</tbody>
</table>

The increasing surface area after annealing at 1300°C we attribute to the formation of newly separated AlN particles with wurtzite structure (w-AlN). The analysis of the XRD patterns supports this behavior: the peaks related to the solid solution shift toward lower angles and weak w-AlN peaks appear. According to the results presented above, it was concluded, that spinodal decomposition of supersaturated Ti$_{1-x}$Al$_x$N solid solution takes place at 800°C and nucleation and grain growth occurs at 1300°C.

Consolidation of Ti$_{1-x}$Al$_x$N and Pure TiN Powders by High Pressure Spark Plasma Sintering.

Examination of the XRD patterns of HPSPS-processed TiN and TiN-20 % AlN samples (Fig. 9)

![XRD patterns](image)

Fig. 9. XRD patterns of: a milled TiN powder, b sintered TiN specimen, c milled TiN-20 % AlN powders and d a sintered TiN-20 % AlN specimen.

revealed that the broadening of titanium nitride peaks observed after milling was reduced significantly, apparently as a result of the stress release and grain growth that take place during sintering. The shift of the Ti$_{1-x}$Al$_x$N reflection peaks towards lower angles indicated that the lattice parameter had increased from 4.14 (milled powder) to 4.24Å (sintered composite). The latter value is close to that of pure TiN. Thus, thermal decomposition of the starting Ti$_{1-x}$Al$_x$N supersaturated solid solution occurred during sintering at 1300°C. However, only a weak and broadened peak of w-AlN appeared. One possible reason for this is the extremely small crystallite size of precipitated AlN. The same results were obtained by Rafaja et al. [23], where it was suggested that high amount of AlN was located at the partially coherent interfaces between w-AlN and c-Ti$_{1-x}$Al$_x$N. The partial coherence of w-AlN and c-TiN at their interfaces leads to an overlap of the strong diffraction lines from w-AlN with the diffraction lines from c-TiN.
HPSPS-processed TiN specimen displayed sub-micron structure, while the specimen from the super-saturated solution presented nano-structure.

![SEM images of the fracture surface of sintered samples: a pure TiN and b TiN-20 %AlN.](image)

Evidently, finely dispersed AlN precipitates acted to inhibit grain growth during sintering. Similar results were obtained by Kim et al. [11].

The hardness, Young modulus, bending strength and fracture toughness of the sintered TiN–20 % AlN sample were significantly higher than were those properties of pure TiN sintered under the same conditions (Table 4).

**Table 4. Properties of sintered pure TiN and TiN-AlN specimens.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Relative Density, %</th>
<th>Microhardness, HV, ±40</th>
<th>Young modulus, GPa, ±5</th>
<th>Bending strength, MPa, ±70</th>
<th>( K_C ), MPa·m(^{0.5} ), ±0.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiN</td>
<td>100</td>
<td>1700</td>
<td>385</td>
<td>330</td>
<td>5.3</td>
</tr>
<tr>
<td>TiN-20 % AlN</td>
<td>100</td>
<td>2000</td>
<td>420</td>
<td>600</td>
<td>6.9</td>
</tr>
</tbody>
</table>

The combination of the mechanical properties of the nanostructured dense Ti\(_{1-x}\)Al\(_x\)N ceramic with 20 % AlN allows for the use of this material in a wide range of applications under extreme conditions.

**Conclusions**

Nanocrystalline powder Ti\(_{1-x}\)Al\(_x\)N has been synthesized from TiN and AlN powders by HEBM. The formation of supersaturated solid solutions was confirmed by XRD and TEM analyses. After 100h of milling all AlN was dissolved into TiN leading to the formation of Ti\(_{1-x}\)Al\(_x\)N solid solution with NaCl structure. After 100h of milling the crystallite size and the lattice strain are about 13nm and 0.63%, respectively. The thermal stability of the Ti\(_{1-x}\)Al\(_x\)N supersaturated solid solution and mechanism of its decomposition were analyzed using ab initio calculations based on Density Functional Theory (DFT), differential scanning calorimetry (DSC), Brunauer-Emmited-
Teller (BET) and XRD. The results of the analysis indicated that at 800°C spinodal decomposition of Ti$_x$Al$_{1-x}$N takes place, while at temperature higher than 1300°C regular decomposition (nucleation and growth) is occurred. The HEBM TiN and TiN-20%AlN powders were successfully consolidated to the fully dense composite by HPSPS at 1300°C under 400MPa pressure. The sintered TiN-20%AlN composite performed high mechanical properties (the Vickers hardness of 2000HV, the Young modulus 420GPa, the bending strength of 600MPa and the fracture toughness of 6.9 MPa·m$^{0.5}$) as compared with pure TiN (the Vickers hardness of 1700HV, the Young modulus 385GPa, the bending strength of 330MPa and the fracture toughness of 5.3 MPa·m$^{0.5}$) obtained under the same conditions.

Acknowledgements

The authors would like to acknowledge Dr. V. Ezersky and Dr. D. Mogilyanski for assistance in TEM and XRD analyses.

References