THERMAL STABILITY OF SUPERSATURATED (Ti, Al)N SOLID SOLUTION
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ABSTRACT
Titanium aluminum nitride displays high hardness and oxidation resistance at elevated temperatures and is successfully used for coating of various tools for mechanical treatments. The information about TiAlN bulk materials is limited. In the present study thermal stability of the supersaturated $Ti_{1-x}Al_xN$ solid solution powder, prepared by high-energy ball milling (HEBM) for bulk materials fabrication by powder metallurgy approach, was investigated. The results of differential scanning calorimetry (DSC), Brunauer-Emmitted-Teller (BET), x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) analyses were presented and discussed.

INTRODUCTION
Titanium aluminum nitride was developed in the late 1980's as a promising alternative to TiN coatings for cutting and forming tools (1-3). A metastable $Ti_{1-x}Al_xN$ material displays superior oxidation resistance compared to TiN, better cutting behavior enabling the use of higher cutting speeds and very promising physical properties, such as high strength, conductivity and resistance to thermal shock (1-2, 4-8). Due to these properties titanium aluminum nitride may be used for a wide range of high-temperature applications. Bulk materials based on supersaturated (Ti,Al)N solid solution are also very attractive for a wide range of applications. TiAN bulk materials may be fabricated by powder metallurgy approach that involves preparation of the supersaturated TiAlN powder of various compositions by HEBM and its consolidation by one of the sintering processes (9-14).

Thin $Ti_{1-x}Al_xN$ films crystallize in the cubic NaCl structure if AlN mole fractions are in the range of $0 < x \leq 0.66$ (1, 15-20). At higher AlN contents, a mixed (NaCl+ZnS-wurtzite) structure is formed, or films display completely the ZnS structure (18, 19). Due to an extremely limited AlN solubility in TiN (1, 18, 21-24) the mentioned above phases are metastable and spinodal...
decomposition of the supersaturated $Ti_{1-x}Al_xN$ solid solution takes place during heat treatments. Fundamental understanding of the metastable $Ti_{1-x}Al_xN$ solution decomposition is very important for developing strategies of fabrication of bulk materials with improved mechanical properties (25).

In the present study the thermal decomposition of $Ti_{1-x}Al_xN$ powder consists of 50mol % of AlN, prepared by HEBM was investigated.

**EXPERIMENTAL PROCEDURE**

$Ti_{1-x}Al_xN$ powder with 50 mole% of AlN has been ball milled in a high-energy planetary ball mill (Retsch PM 100, Germany) for 100 hours with rotational speed 500 rpm under air and nitrogen atmospheres. The vial and balls were made from chromium-hardened steel and from sintered aluminum oxide. The balls diameter was 10mm.

The milled powders were characterized using DSC, BET, XPS and XRD analysis.

The DSC was conducted using NETZSCH STA449 F3 Jupiter thermal analyzer with a TG-DSC sample carrier system using Pt crucibles. The milled powder was placed in Pt crucibles in the DSC and the heat flow trace was recorded in nitrogen flow of 5 mL/min. The sample was heated from room temperature (RT) to 1300°C of 20°C/min. The baseline was determined by repeating run without disturbing the sample.

The annealing process of the milled powders was performed under Ar atmosphere at 200, 400, 800, 1000, 1100 and 1200 °C for 12h. To monitor a possible thermal decomposition process, the samples were investigated by DSC, XRD and BET after each annealing step.

The XRD data were collected on Panalytical X'Pert Pro X-ray Diffractometer with $CuK_{α}$ radiation ($\lambda = 0.154nm$), operating at 40 kV and 40 mA. Data collection was performed by step scanning of the specimen over the $2θ : 20° - 85°$ angular range in steps of 0.05° with 3s per step.

The surface areas were measured by the BET method using a micromeritics (Micromeritics, Norcross, GA) ASAP2020 instrument.

XPS data were obtained using an X-ray photoelectron spectrometer ESCALAB 250 ultrahigh vacuum (1×10⁻⁹ bar) apparatus with an AlKα X-ray source and a monochromator. Powder samples of the TiAlN were pressed into an indium-foil. The AVANTAGE software was used for data acquisition and analysis. The elemental composition of the surfaces was determined. The atomic concentrations were calculated using elemental sensitivity factors without applying any standardization procedure. The spectral components of Al, Ti, N and O signals were found by fitting
a sum of single component lines to the experimental data by means of nonlinear least-squares curve-fitting. The single-component lines were assumed to have the shape of the sum of Cauchy and Gaussian curves, and deconvolution was performed. To correct for charging effects, all spectra were calibrated relative to a carbon 1s peak positioned at 284.6eV.

RESULTS AND DISCUSSION

The DSC curves of Ti$_{1-x}$Al$_x$N milled and annealed powders are shown in Fig. 1. There are three exothermic peaks labeled with numbers by 1 to 3 in the DSC scan of the milled powder indicating exothermic reactions occurred during heating from RT up to 1300 °C.

![DSC signal of TiAlN powders as-milled and after annealing at various temperatures.](image)

Fig.1. DSC signal of TiAlN powders as-milled and after annealing at various temperatures.

In order to clarify the origin of these peaks, annealing experiments at 800, 1000 and 1100 °C were conducted. The results of the BET analysis of the annealed samples are presented in Table 1.

Table 1. The results of the BET analysis for various temperature of annealing.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>room</td>
<td>5.39</td>
</tr>
<tr>
<td>800</td>
<td>21.75</td>
</tr>
<tr>
<td>900</td>
<td>8.99</td>
</tr>
<tr>
<td>1100</td>
<td>6.62</td>
</tr>
<tr>
<td>1300</td>
<td>12.77</td>
</tr>
</tbody>
</table>
We assume that surface area increasing after annealing at 800°C is attributed to solid solution decomposition, while the decreasing surface area for heat treatment at higher temperatures reflects the particle size growth. The surface area of the powder heat treated at 1300°C may be attributed to the transformation of cubic AlN to the stable wurtzite crystal structure. These results are in a good agreement with the results of DSC study, where the presence of the exothermal peaks were detected (labeled 2, 3 in Fig. 1).

Fig. 2 shows the XRD patterns for the milled and annealed powders at 200, 400, 800, 1000, 1100°C and the powder after DSC analyses.

**Fig. 2.** The diffraction patterns of as-milled TiAlN powder and powders after annealing at various temperatures.

The diffraction pattern of the milled powder consists of Al₂O₃ peaks and spread-out peak that corresponds to Ti₁₋ₓAlₓN solid solution indicating that extremely small crystalline size was achieved during HEBM milling. The origin of Al₂O₃ is a contamination from milling tools and the position and intensity of its peaks do not change with annealing.

The XRD patterns of the annealed samples up to 800°C are very similar and indicate that no phase transformation takes place in this temperature range. The same results were obtained by DSC
analysis. We can see the shape change in the Ti$_{1-x}$Al$_x$N peak shape, which corresponds to the second DSC peak and to the increasing of BET surface area at this temperature.

The diffracted peaks of TiN and AlN appear in the XRD pattern of the milled samples after annealing at 1000°C. The peaks of TiN and AlN phases appear in the XRD pattern after annealing at 1000°C, at this temperature the third DSC peak is appeared.

The chemical bonding structure of the powder samples after various steps of the annealing process has been investigated by XPS. In order to avoid the effect of powder oxidation during milling the TiAlN powder was milling under nitrogen atmosphere using steel milling tools.

The Ti2p region displays three distinct peaks labeled Ti1, Ti2 and Ti3 (Fig.3).

**Fig. 3.** XPS spectra high-resolution window for Ti2p transitions.

The binding energy (BE) of Ti2 (455.88-456.63eV) and Ti3 (457.01-458.49eV) peaks are attributed to TiO$_2$N$_y$ compound and TiO$_2$ respectively (26-28) while the first one could be attributed to TiN as well as to the Ti$_{1-x}$Al$_x$N ternary compound (26, 29-31). Before milling, Ti1 at 455.21eV corresponds to TiN. After milling, it shifts towards lower binding energy (454.91eV) assigned to Ti$_{1-x}$Al$_x$N (32). After annealing at 800°C this peak shifts towards higher energy and may be attributed to decomposition of Ti$_{1-x}$Al$_x$N solid solution. This again proves our suggestion about decomposition of Ti$_{1-x}$Al$_x$N solid solution at 800°C.
The trend of the peak shifts and peak shapes shows that intensity of TiO$_x$N$_y$ increases in the milled and heated powder, while the intensity of TiO$_2$ decreases. This can be explained by the fact that the non-milled powder was much more oxidized with respect to the milled and annealed powders.

Al$_2$p regions for non-milled, milled and annealed powders are presented in Fig.4. The deconvolution of Al$_2$p band of the non-milled powder gives rise to two peaks (see Fig.4 a). The peak at 75.29eV can be attributed to the presence of Al$_2$O$_3$ (34) (66.54at%), while the neighboring peak at 74.29eV corresponds to AlN phase (32,33) (33.46at%). This confirms our suggestion that the non-milled powder was strongly oxidized. After milling, the Al$_2$p peak (Fig.4) shifts to lower energy (73.74eV), which can be corresponded to Al in the phase Ti$_{1-x}$Al$_x$N (32). This is supported by XRD results and by the corresponding Ti$_2$p peak. In the annealed samples, the Al signal has been divided into two peaks that are associated with Ti$_{1-x}$Al$_x$N and AlN phases, respectively. This fact confirms once again that decomposition of the Ti$_{1-x}$Al$_x$N solid solution starts at about 800°C.

**Fig. 4.** XPS peak fitting of Al$_2$p region for a) non-milled powder, b) milled powder, c) annealed powder (4h), d) annealed powder (10h), e) annealed powder (24h)

The identification and the quantitative characteristics of the components of Ti$_2$p and Al$_2$p are summarized in Table 2.
Table 2. The quantitative characteristics of the components of Ti2p and Al2p for Ti$_{1-x}$Al$_x$N powders.

<table>
<thead>
<tr>
<th></th>
<th>TiN at%</th>
<th>TiAlN at%</th>
<th>TiN+ TiAlN at%</th>
<th>TiO$_x$N$_y$ at%</th>
<th>TiO$_2$ at%</th>
<th>AlN at%</th>
<th>Al$_2$O$_3$ at%</th>
<th>TiAlN at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-milled</td>
<td>20.41</td>
<td>-</td>
<td>38.01</td>
<td>41.59</td>
<td>33.46</td>
<td>66.54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Milled</td>
<td>12.8</td>
<td>56.43</td>
<td>30.77</td>
<td>-</td>
<td>23.67</td>
<td>-</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>annealed (800C,4h)</td>
<td>26.54</td>
<td>55</td>
<td>18.43</td>
<td>23.67</td>
<td>-</td>
<td>76.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>annealed (800C,10h)</td>
<td>31.53</td>
<td>39.66</td>
<td>28.81</td>
<td>29.26</td>
<td>-</td>
<td>70.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>annealed (800C,24h)</td>
<td>31.49</td>
<td>46.74</td>
<td>21.77</td>
<td>25.03</td>
<td>-</td>
<td>74.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In addition, the surface atomic composition of the powder samples was calculated. The results of these calculations are summarized in Table 3 and show that the amount of Al at the surface increased after heat treatment.

Table 3. Contribution in percentage for the Ti2p, Al2p, N1s.

<table>
<thead>
<tr>
<th></th>
<th>Ti2p at%</th>
<th>Al2p at%</th>
<th>N1s at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milled</td>
<td>18.47</td>
<td>43.95</td>
<td>37.59</td>
</tr>
<tr>
<td>annealed (800C,4h)</td>
<td>14.91</td>
<td>53.19</td>
<td>31.9</td>
</tr>
<tr>
<td>annealed (800C,10h)</td>
<td>15.53</td>
<td>53.14</td>
<td>31.34</td>
</tr>
<tr>
<td>annealed (800C,24h)</td>
<td>14.84</td>
<td>51.15</td>
<td>34.01</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Thermal stability of supersaturated TiAlN solid solution powder obtained by HEBM has been investigated by DSC, BET, XRD and XPS analysis. It was established that the decomposition starts at the temperature close to 800°C and probably has the spinodal nature.
A complete decomposition of the supersaturated TiAlN solid solution in two stable phases occurs at about 1300°C.

REFERENCES


