Preparation of (Ti,Al)N Solid Solution by Mechanical Alloying

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ABSTRACT

(Ti,Al)N is widely used as a hard coating material for high speed cutting tools. The presence of AlN provides to the coating improved mechanical properties and oxidation resistant at elevated temperatures. Various coating approaches are applied in order to obtain thin films of complex nitride phase, with AlN concentration much higher than its solubility limit in TiN. The information about bulk materials based on (Ti,Al)N is missing in literature. The present study is focused on the fabrication of bulk materials based on (Ti,Al)N, using powder metallurgy approach. The main goals of the investigation are preparation of nano size particles of supersaturated TiN-AlN solid solution by high energy ball milling (HEBM) of TiN and AlN powders and their consolidation by Spark Plasma Sintering (SPS) approach, which allows extremely fast heating up to high temperature (1600-2000°C) and possibly to preserve the solid solution during powder consolidation. In the present stage of the investigation the results of (Ti,Al)N preparation by HEBM and thermal stability of the obtained (Ti,Al)N phase are presented and discussed. It was established that HEBM for 100hours allows preparing nano size particles of TiN-AlN solid solution with 20mol% of AlN. This solid solution is stable after annealing at 950°C for 2hours. Systematic XRD analysis allows to estimate the level of the residual stresses in the nano size particles and to detect an initial stage of the solid solution decomposition.

INTRODUCTION

The interest in transition metal nitride has grown rapidly in the last two decades. Their high hardness and good wear resistance made them suitable for coating of cutting tools in order to improve their tribological and high-temperature properties. (Ti,Al)N has been widely used as a hard coating material for such applications (1). The improved performance of cutting tools coated by (Ti,Al)N is attributed to its high hot hardness due to age hardening (2) and excellent oxidation resistance up to 700 °C (3, 4) due to the formation of a protective Al-rich oxide layer at the surface (5).

AlN (hexagonal wurtzite structure) and TiN (cubic B1 NaCl structure) show virtually no solubility under equilibrium conditions at temperatures below about 1500°C (6). Since the solubility of AlN in TiN is very low, metastable (Ti,Al)N solid solution can be produced only under non-equilibrium conditions, where an external source of energy is involved. Non stable thin films of (Ti,Al)N is fabricated using cathodic arc deposition (7-16) and magnetron sputtering (18-24). The thickness of this film is limited and does not exceed 10μm. The attempts to fabricate TiN-AlN composite were reported in [25, 26], however these composites were made from two separated nitrides phases.
In the present study we suggest to apply powder metallurgy approach to fabricate bulk (Ti,Al)N specimens. Non-stable supersaturated (Ti,Al)N nano powder has to be prepared by mechanical alloying (MA) using high energy ball milling (HEBM) (27, 29). Consolidation of ball-milled composite powders has to be conducted using SPS apparatus that allows significantly shortening duration of a high temperature treatment and preventing supersaturated solid solution decomposition.

**EXPERIMENTAL PROCEDURES**

TiN and AlN (80:20 molar ratio) powders have been by ball milling in a high energy planetary ball mill (Retsch PM 100, Germany) using container and balls (10mm diameter) made from chromium hardened steel. The ball to powder (8g) weight ratio was 20:1. Rotational speed was 400 rpm and milling time was varied from 0 to 100 hours. XRD analysis was applied to characterize the milled powder.

The XRD data were collected on Panalytical X’Pert Pro X-ray Diffractometer with Cu $K_{\alpha}$ radiation ($\lambda=0.154$ nm), operating at 40 kV and 40 mA. Data collection was performed by step scanning of the specimen over the $2\theta:20-85^\circ$ angular range in steps of 0.05° with 3s per step. The XRD line profile parameters were then fitted with Rietveld procedure using the PowderCell for Windows (PCW) program. The crystallite size and lattice strain of powder during milling were determined from broadening of XRD peaks by Williamson-Hall (WH) method (30). The WH approach considers the case when domain size effect and lattice deformation are both simultaneously operate and their combined effects give the final line broadening parameter $\beta$, which is the sum of $\beta_{\text{grain size}}$ and $\beta_{\text{lattice strain}}$. The value of $\beta$ may be calculated according to equation

$$\beta \cos \theta = \frac{\lambda}{D} + 4\varepsilon \sin \theta$$

where $D$ is the average domain size, $\varepsilon$ is the elastic strain and $\lambda$ is a wavelength of the X-ray radiation, respectively. From a plot of $\beta \cos \theta$ vs $4\sin \theta$ one can evaluate the contribution of micro-strain and domain size to the XRD line broadening. The intercept of the plot with the ordinate (the values are expressed in radians) represents the reciprocal of the average crystallite size and the slope of the line is $\varepsilon$.

**RESULTS AND DISCUSSIONS**

XRD patterns of the TiN-AlN powder mixtures after various milling durations are presented in Fig. 1. The peaks of starting powders are well defined and reflect their crystalline structure and grain size more than several microns. With increasing of the milling time the peaks of hexagonal AlN become weaker and almost disappear after 100 hours of milling. The peaks of TiN become broader and shift to higher angles. The measured lattice parameter of cubic TiN phase is decreased from 4.24 Å for starting powder to 4.20 Å for powder after 100h milling. These results are in a good agreement with the reported data (7, 9, 17, 19) and confirm that formation of the supersaturated (Ti,Al)N solid solution takes place and Al atoms substitute Ti atoms in their lattice sites (31).
Fig. 1 The diffraction patterns of the powder mixtures after various durations of milling. The crystallite size and the lattice strain vs the time of the milling process are shown on Fig. 2 a,b. The practically linear dependence of the domain size decreasing and the lattice strain increasing vs logarithm of time are observed.
Fig. 2. Average domain size (a) and lattice strain as a function of milling duration.

According to the results presented in Fig. 2 the average particle size of supersaturated (Ti,Al)N solid solution is less than 20 nm. In order to estimate thermal stability of the supersaturated (Ti,Al)N the milled (100h) powder was annealed in Ar in 800-1000°C temperature range for various holding time. The diffraction patterns of the sample after 100h milling and of the same sample after annealing are presented in Fig. 3.
Fig. 3 The diffraction patterns of the sample after annealing at 800°C 2h; 900°C 2h and 1000°C 25h.

The lattice parameters, average crystallite size and lattice strain of these samples are summarized in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter (Å)</th>
<th>Crystallite size (nm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 h milling</td>
<td>4.205</td>
<td>25</td>
<td>0.0094</td>
</tr>
<tr>
<td>100 h milling +800°C 2h</td>
<td>4.211</td>
<td>16</td>
<td>0.0026</td>
</tr>
<tr>
<td>100 h milling +900°C 2h</td>
<td>4.221</td>
<td>17</td>
<td>0.0017</td>
</tr>
<tr>
<td>100 h milling +1000°C 25h</td>
<td>4.227</td>
<td>20</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

According to the presented data, supersaturated (Ti,Al)N solid solution only partly decomposes even after 25 h annealing at 1000°C. Very wide peaks of free AlN (marked by arrow in Fig.3) are hardly observed on the diffraction pattern.

It has to be pointed out that crystalline size only slightly changes during heat treatments, while the lattice strains significantly decreases. This phenomenon may be attributed to the mechanism of the solid solution decomposition. At the early stage the (Ti,Al)N phase undergoes the iso-structural decomposition into two coherent cubic phases as a result of Al diffusion in the metal sub-lattice. We suggest that this decomposition has a spinodal nature. At the latest stages of matrix and transform to hexagonal AlN. Similar mechanism
was observed for Ti$_{1-x}$Al$_x$N thin films with high content of Al (33).

CONCLUSIONS

High energy ball milling of TiN and AlN powders leads to the formation of the supersaturated (Ti,Al)N solid solution. The particle size after 100 h milling was about 20-25 nm. This unstable solid solution only partly decomposes after heat treatment at 1000°C for 25h. The analysis of the XRD data allows suggesting that the decomposition has spinodal nature. Further investigations have to be conducted in order to determine thermal stability of the obtained supersaturated (Ti,Al)N solid solution at higher temperatures and to find out the parameters of the SPS consolidation process.

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