EFFECT OF MILLING AGENT (METHANOL) ON PHASE COMPOSITION AND STRUCTURE OF AlCoCrFeNiTi0.5 HIGH ENTROPY ALLOY POWDERS

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Resume

In the last decade, high-entropy alloys (multi-principal element alloys) were developed as a new family of materials with high application potential. The effects of anti-agglomeration milling agent on the phase composition, structure, and size of non-equieutomic AlCoCrFeNiTi0.5 mechanically milled powders were investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) with an energy dispersive spectroscopy (EDS) detector were utilized for microstructural analyses. During mechanical alloying (MA), a supersaturated Cr-based solid solution with BCC structure with significantly reduced grain size was formed after 10 hours of milling. During the annealing of milled powders, this solid solution decomposed into a mixture of four different phases. It was found that the use of milling agent had an extensive influence on the milled powders’ properties. Significant differences in phase composition, microstructure, and powder particle size were observed, with more favourable results in the case of milling in the presence of the milling agent.

Article info

Article history:
Received 09 March 2016
Accepted 06 April 2016
Online 12 June 2016

Keywords:
High entropy alloys;
Mechanical alloying;
Annealing

Available online: http://fstroj.uniza.sk/journal-mu/PDF/2016/03-2016.pdf

Article info

ISSN 1335-0803 (print version)
ISSN 1338-6174 (online version)

1. Introduction

High-entropy alloys (HEAs), proposed by Yeh et al. [1], are multicomponent alloys with simple solid solution phases. They consist of more than four elements in equimolar or near-equimolar ratio, in contrast to traditional alloys, which are based on only one element with a structure composed of a mixture of solid solution and ordered intermediate phases. The stability of any phase in the structure can be calculated by the equation (1):

\[ \Delta G = \Delta H - T \Delta S \]  

(1)

where \( \Delta G \) is the Gibbs free energy, \( T \) is temperature, \( \Delta H \) is the mixing or formation enthalpy, and finally \( \Delta S \) refers to entropy.

The more negative the Gibbs free energy becomes, the more stable the particular phase is. A means of stabilizing solid solution phase is by increasing the entropy (sometimes referred to as the level of disorder). If we consider only the configurational entropy of the solid solution consisting of different elements, it can be calculated by the equation (2):

\[ \Delta S_{conf} \cong -R \sum_{i=1}^{n} c_i \ln c_i \]  

(2)

where \( R \) refers to the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)). From this expression, we can assume that the entropy will be higher when an increasing amount of constituent elements have equiatomic concentrations [2]. When the entropy is high enough, it suppresses the formation of ordered...
phases, and a stable high-entropy state (simple solid solution) is achieved. These alloys should benefit from solid solution strengthening of many elements with different atomic radii present in the lattice, causing severe lattice strain, while retaining reasonable ductility due to inherent BCC and FCC solid solution plasticity [3]. Consequently, many interesting properties arise from this unique structure, such as a good combination of strength and ductility [4], outstanding low-temperature ductility and fracture resistance [5], high-temperature creep resistance and strength [6, 7], high hot wear resistance [8], good electrochemical properties [9], and so on.

Mechanical alloying (MA) is a solid-state powder-processing technique involving repeated cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill [10]. In combination with the proper densification method, it is a simple yet efficient method for preparation of many advanced materials including high-entropy alloys [11, 12, 13]. In the MA process, for efficient milling of metal powders, the use of milling agent is needed to prevent excessive cold welding, which results in coarsening of powder particles, sticking of the powders to the milling vessel and balls, and decreased milling yield [14]. In general, surface-active liquid like ethanol or stearic acid is used. The most significant disadvantage of the introduction of organic milling agents is without doubt the resulting contamination of the powders by elements contained in the milling agent, most notably C, O, and sometimes N. These usually form very stable ceramic compounds and decrease the final mechanical properties of the materials [10]; they can also influence the overall phase composition and alloying behaviour [15]. Another concept could be to use this phenomenon for the production of in situ reinforced metal-ceramic composites [16].

Although HEA powders have been produced by MA in the past, a systematic research on the effect of milling agent use on the phase composition, size, morphology, and structure of powders has not yet been reported.

2. Experimental setup

AlCoCrFeNiTi0.5 (in atomic proportions) HEA powders were prepared by MA of the elemental powders. Elemental powders of Fe, Ni, Cr, Al, Co, and Ti with commercial purity and mean particle size of 45 μm (325 mesh) were put into a steel milling bowl with 15-mm diameter balls and sealed with argon gas. A ball-to-powder ratio of 10:1 was used. The sealed bowl was then moved to a high-energy planetary ball milling machine (Pulverisette 6). Powders were milled at a speed of 400 rounds per minute. The milling process was carried out either in the presence of methanol as a milling medium or without it. After milling, both powders were subjected to annealing in a tube furnace with high purity argon gas for 1 h at 1050 oC with subsequent furnace cooling. The microstructures of the produced materials were evaluated using a Carl Zeiss scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS) detector. The X-ray diffraction (XRD) technique was used to observe the structural changes of powders during milling and annealing. A Philips X’Pert diffractometer (40 kV) with Co Kα radiation (λ = 1.790307 Å) was used for measurements. The XRD patterns were recorded in the 2θ range of 30-120° and analysed with X’Pert High Score Plus software. Rietweld method using has been utilized for crystallite size determination. Hardness measurement was carried out on Vickers microhardness meter Leco LM 247AT with load of 25g.

3. Results and discussion

In Fig. 1a,b, the powder XRD patterns are presented. It can be clearly seen that after mechanical milling, one supersaturated BCC solid solution with a lattice parameter of 2.87 Å
was formed in both cases, regardless of the use of the milling agent (methanol). Extensive peak broadening is a sign of grain refinement induced by drastic cold deformation during the milling process. There is a considerable difference in the calculated crystallite size, which was 50.1 Å for powder milled with methanol and 69.1 Å without this agent. This phenomenon indicates the beneficial effect of the use of milling agent. The phase composition after annealing is however completely different (Fig. 2a, b). Powders milled with methanol are composed of ordered B2 NiAl like phase (visible superlattice (100) peak), face-centred cubic (FCC) phase, a minor tetragonal sigma phase, and titanium carbide phases. The presence of tetragonal sigma phase has been reported in HEA systems in the past [17] and is most likely attributed to slow cooling after the annealing temperature. Titanium carbide is the result of the titanium reaction with methanol during annealing. Methanol is an organic compound consisting of carbon and oxygen. During milling, it disintegrated and dissolved into the powder particles’ lattices. Titanium has a high affinity for carbon and therefore formed titanium carbide upon heating. This process is sometimes referred to as mechanically activated synthesis [18]. Compared to this, the powder milled without methanol consists of only two major phases, namely ordered B2 and sigma phase with traces of FCC peaks. The slight shift in the peak of the B2 phase seen in Fig. 3 suggests a small difference in the phase lattice parameter and therefore a different chemical composition from the previous case. This is most probably the result of the presence of titanium in the B2 lattice, unlike in the case of powder milled with methanol, where titanium was trapped in titanium carbide. Both of these ordered phases, especially the sigma phase, are considered extremely brittle, and therefore bulk materials prepared from this powder would also most probably be brittle.

![Figure 1: XRD patterns of powders after mechanical alloying for 10h with 400RPM milling speed of: a) powder with use of milling agent b) powder without use of milling agent. (full colour version available online)](image-url)
Fig. 2. XRD patterns of powders after mechanical alloying and annealing of: a) powder with use of milling agent b) powder without use of milling agent. (full colour version available online)

Fig. 3. XRD patterns of powders after mechanical alloying and annealing close up: a) powder with use of milling agent b) powder without use of milling agent. (full colour version available online)
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Fig. 4. SEM images of microstructure in backscattered mode after mechanical alloying of a) powder with use of milling agent b) powder without use of milling agent.

Fig. 5. SEM images of microstructure in backscattered mode after mechanical alloying and annealing of: a) powder with use of milling agent b) powder without use of milling agent.

Table 1
Elemental composition of the microstructural features of annealed powders milled with milling agent.

<table>
<thead>
<tr>
<th>Element (at. %)</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey phase (B2+TiC)</td>
<td>23.5</td>
<td>12.4</td>
<td>11.7</td>
<td>14.01</td>
<td>17.1</td>
<td>21.0</td>
</tr>
<tr>
<td>White phase (FCC+sigma)</td>
<td>4.95</td>
<td>1.79</td>
<td>25.6</td>
<td>33.4</td>
<td>20.6</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Table 2
Elemental composition of the microstructural features of annealed powders milled without milling agent.

<table>
<thead>
<tr>
<th>Element (at. %)</th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey phase (B2)</td>
<td>27.67</td>
<td>14.31</td>
<td>5.42</td>
<td>10.25</td>
<td>20.32</td>
<td>22.00</td>
</tr>
<tr>
<td>White phase (sigma)</td>
<td>6.23</td>
<td>2.28</td>
<td>39.10</td>
<td>33.10</td>
<td>13.00</td>
<td>15.90</td>
</tr>
</tbody>
</table>
Comparing the SEM images in Fig. 4, a coarser particle size is evident for the powder milled without methanol, in which structural inhomogeneities were present in the form of layers seen in the close up view in Fig. 4b. These layers with different shades of grey in BSE mode (different chemical compositions) are the remains of the original deformed powder particles. These were not sufficiently fractured during mechanical milling. On the other hand, the powders milled in the presence of methanol show almost perfect chemical homogeneity. Therefore, it can be concluded that methanol, a surface-active agent, is adsorbed on the particle surfaces and promotes powder fracturing and subsequently the quality of the mechano-chemical alloying process. The differences in structures are even more visible in the case of annealed powders (Fig. 5). For powders milled in the presence of methanol, an extremely fine microstructure is obtained. Bearing in mind the results of the XRD phase analysis and EDS point chemical analysis (Table 1 and 2), we can assume that white phase is FCC Cr-Fe enriched phase or a mixture of FCC and sigma phases. Grey phase appears to be an Al- and Ni-enriched ordered B2 phase with fine dispersion of titanium carbide present as black dots. These particles are probably the key cause of the very fine grain size of the whole structure, as they trap grain boundaries during heating, thus preventing grain growth. Unfortunately the size of most grains was well under the resolution limit of EDS point analysis, and therefore it was impossible to measure every phase separately. However, powders milled without the presence of methanol have comparably coarser grains of white Cr-Fe-enriched sigma phase and grey Al-Ni-based B2 phase.

The size of few powder particles was sufficient to perform microhardness test presented in Table 3. Both powders showed very high hardness levels, namely 789HV for powders after milling with methanol and 753HV for powders without methanol. Due to small difference in average hardness values, we can assume that milling agent has only negligible effect on hardness after milling. Relatively high hardness is most probably result of extensive work hardening during milling process. However after annealing process, the difference in hardness becomes more apparent, attributing to differences in phase composition. Annealed powders milled with methanol exhibit hardness of 881HV in contrast to 630HV for powders milled without it. This is most probably due to simultaneous contribution of finer grain structure, and dispersion strengthening of extremely hard carbide phases. Another phenomenon occurred, when softer powders milled without methanol were surprisingly seemingly more prone to cracking during indentations. This could be the consequence of inherently more brittle structure composed of B2 and sigma ordered phases as suggested before.

<table>
<thead>
<tr>
<th>Milling agent</th>
<th>Milled hardness</th>
<th>Annealed hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>789</td>
<td>881</td>
</tr>
<tr>
<td>None</td>
<td>753</td>
<td>630</td>
</tr>
</tbody>
</table>

Based on the previous results it can be summarized that the effect of the milling agent on mechanically milled powders is questionable. It improves the process of alloying during milling and also reduces the powder particle size and crystallite size. It also promotes the formation of the extremely fine stable titanium carbide dispersions preventing the grain coarsening during high temperature annealing thus increasing hardness of the structure. On the other hand dispersion of titanium carbide could decrease fracture toughness of bulk alloy produced from the powders. Therefore its application to the alloying process should be considered, depending on desired properties of the resulting powder compacts.
4. Conclusions

High entropy alloy powders were successfully synthesized by mechanical milling with and without the addition of methanol as milling agent. Significant influence of milling agent on phase composition, powder particles size and milling performance has been observed, namely:

- the milling agent promotes mechanical alloying process during milling and prevents powder agglomeration, therefore decreasing particle size and slightly crystallite size as well;
- by introduction of methanol to process, dispersion of fine titanium carbide is formed upon heating, significantly changing hardness and phase composition of the alloy powders;
- titanium carbide dispersion inhibits grain coarsening of the structure during annealing, its effect on fracture resistance needs further investigation.

Acknowledgements

The research was co-funded by the Ministry of Education, Youth and Sports within the „National Sustainability Programme I“ (NETME CENTRE PLUS - LO1202).

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