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High entropy multicomponent WMoNbZrV alloy processed by mechanical alloying

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ABSTRACT

The aim of this work was to apply mechanical alloying technique for synthesis of high entropy multicomponent equimolar WMoNbZrV alloy and to investigate the phase composition after milling and after heat treatment, as well as to characterize the observed changes of crystallite size, lattice strain and lattice parameter of solid solution formed. It was found that nanocrystalline bcc solid solution was characterized by crystallite size of 10 nm, lattice strain of 0.58% and lattice parameter of 3.1687 Å. Heating the sample up to 700 °C resulted in decrease of lattice strain down to 0.20%, while the crystallite size remained not changed, testifying good thermal stability of nanocrystalline bcc solid solution obtained.

1. Introduction

According to traditional alloy formation concept, majority of alloys are composed of one main metallic element. In the structure of these alloys solid solutions, or amorphous phase can be formed. Other alloying elements result in modification of microstructure and properties of the alloys. High entropy alloys (HEA) are a new class of alloys different from conventional ones based on one or two elements. HEAs contain at least five principal elements with concentrations between 5 and 35 at% of each one, usually in equiatomic ratio. High configurational entropy of HEAs leads to the formation of simple fcc and/or bcc solid solutions rather than complex intermetallic phases [1–3]. HEAs are manufactured by various techniques, like conventional casting, rapid solidification, chemical and physical vapour deposition or mechanical alloying (MA). The last technique is especially useful for high melting point alloys difficult for processing by casting techniques. MA has been widely recognized as an important non-equilibrium solid state processing route for the synthesis of variety of alloys showing different phase compositions and microstructures [4]. Selected high melting point HEAs are widely studied due to their designation for high-temperature and fusion-facing applications [5,6].

According to our literature review, the alloy studied in this work has not been reported before. Similar composition has been investigated by Senkov et al. [7–8]. For WMoNbVTa alloy prepared by arc melting typical dendritic microstructure has been observed.

The present study is taken up to synthesise WMoNbZrV high melting equimolar high entropy alloy using mechanical alloying, as well as to investigate the phase evolution upon milling and after heat treatment. An additional purpose of this work was to verify whether the changes of crystallite size, lattice strain and lattice parameter of single phase solid solution formed upon mechanical alloying of multicomponent alloy are similar to the ones reported for conventional mechanically alloyed binary alloys [4].

2. Experimental details

Commercial pure elemental powders of W, Mo, Nb, Zr and V (purity at least 99.5%, particle size below 50 μm, Alfa Aesar) were used as the starting materials. An equimolar high entropy alloy with composition WMoNbZrV was synthesized (20 at% of each element). The milling processes were performed in a Fritsch P5 planetary ball mill equipped with hardened steel vials and balls of 10 mm diameter. Maximum milling time was 100 h and the process was performed under protective atmosphere of argon. No process control agent was added to the powders. The ball-to-powder weight ratio was 10:1. In order to confirm the alloy formation during milling, small amount of powder was taken out after selected processing times for structural characterization. The milled samples were studied by X-ray diffraction (XRD), using Rigaku MiniFlex II diffractometer with Cu Kα radiation (λ = 1.5418 Å), for phase formation monitoring and for calculation of the crystallite size and lattice strain in milled powders. For this purpose Williamson-Hall approach was adopted [9]. The lattice parameters determination of bcc phase was done by applying Nelson-Riley

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extrapolation method [10]. To evaluate the thermal structural stability, the product after final milling time (100 h) was continuously heated in the calorimeter (Perkin Elmer DSC 7, heating rate 40 K min^{-1}, argon flow) from room temperature up to 700 °C and next subjected to XRD measurements. Chemical composition of the powders has been verified by X-ray fluorescence spectroscopy (XRF) using DELTA analyzer, Olympus.

3. Results and discussion

The sequence of diffraction patterns obtained for the powder mixture subjected to mechanical alloying for selected times is presented in Fig. 1. At the initial state the diffraction lines corresponding to all the starting elements are visible. It can be noticed that with the increase of milling time reduction in the intensity of diffraction lines and gradual disappearance of some of them can be seen at the diffraction patterns. The diffraction lines of Zr and V disappear after 2 and 5 h of processing, respectively. Next, Nb diffraction lines vanish after 20 h of milling. This suggests that in the milled powders synthesis of the alloy takes place.

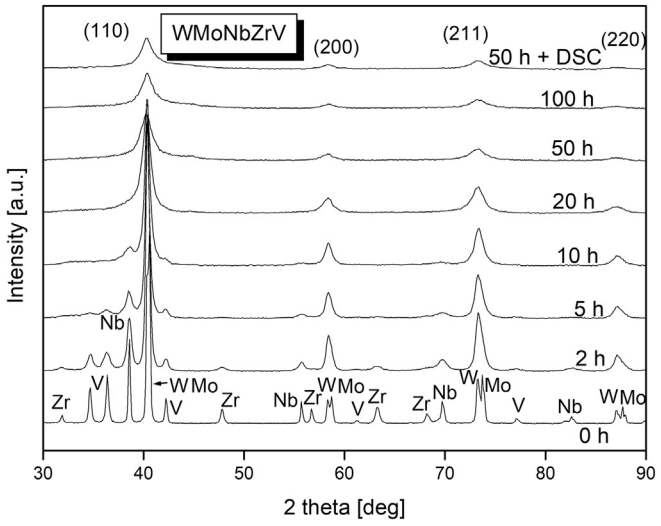

Fig. 1. XRD patterns recorded for WMoNbZrV powders subjected to milling for increasing processing time and after heating in the DSC up to 700 °C.

Milling of the alloy for the time longer than 20 h does not cause major changes in the diffraction pattern and the final product is a single-phase solid solution with the bcc lattice structure. However, further broadening of the diffraction lines related to crystallite size decrease and/or lattice strain increase is registered. The XRD pattern for the sample subjected to milling and next heated in the DSC up to 700 °C is also presented in Fig. 1. The presented pattern is very similar to the one recorded for the sample milled only.

The changes of crystallite size and lattice strain for bcc solid solution as a function of milling time are plotted in Fig. 2. The crystallite size decreases gradually reaching about 11 nm ± 2 nm for the final processing stage. Whereas, lattice strain shows a maximum of 0.58% ± 0.05% for intermediate milling time and decreases with longer processing. Both curves (D and e vs milling time) exhibit a behavior typical for metallic powders subjected to mechanical milling [4]. Additionally, the values of crystallite size and lattice strain of bcc solid solution after heating the sample in the DSC are also marked in Fig. 2. The powder after 50 h of MA was heated in a calorimeter in the temperature range from 50 to 700 °C at constant heating rate of 40 K min^{-1} in order to check the thermal stability of the structure of the obtained alloy. The results of XRD studies indicate that after heating practically there are no qualitative changes in the pattern and the bcc structure is preserved, testifying good thermal stability of the synthesized bcc phase. However, the broadening of registered diffraction lines is smaller in comparison with the powder milled only, suggesting the increase of crystallite size and/or lattice strain decrease.

The Williamson-Hall plots for the samples after 50 h milling and milling followed by DSC measurement are plotted in Fig. 2 (inset). It was found that after heating the crystallite size of bcc solid solution remains nearly the same (about 10 nm) and, simultaneously, lattice strain decreases from 0.35 to 0.20%, comparing to milled powders only (change of the slope of linear fit in Fig. 2, inset).

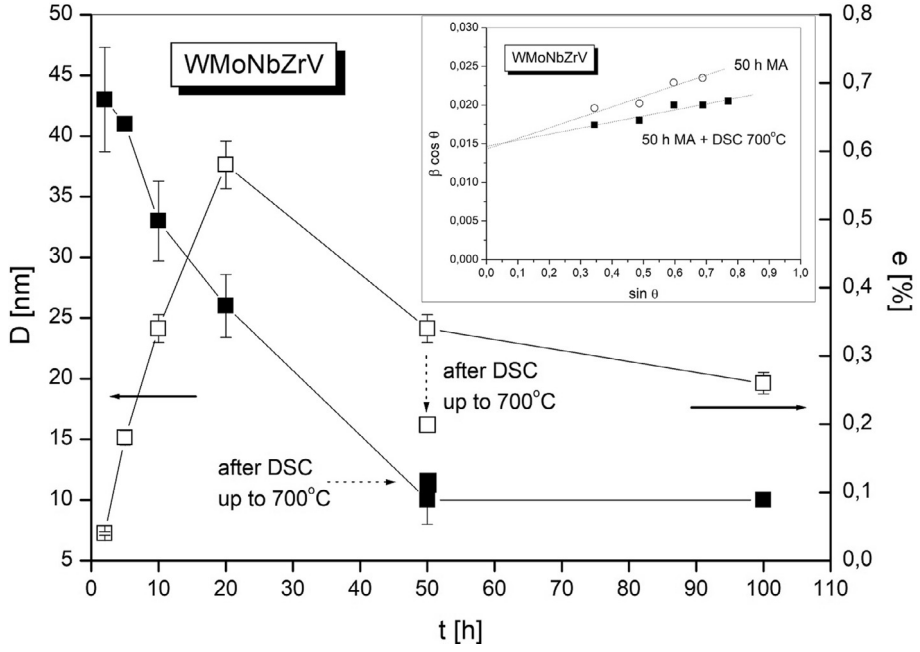

Fig. 2. Crystallite size *D* and lattice strain *e* as a function of milling time and heat treatment; inset: Williamson-Hall plots for the samples subjected to MA for 50 h and MA followed by continuous heating in the DSC up to 700 °C.

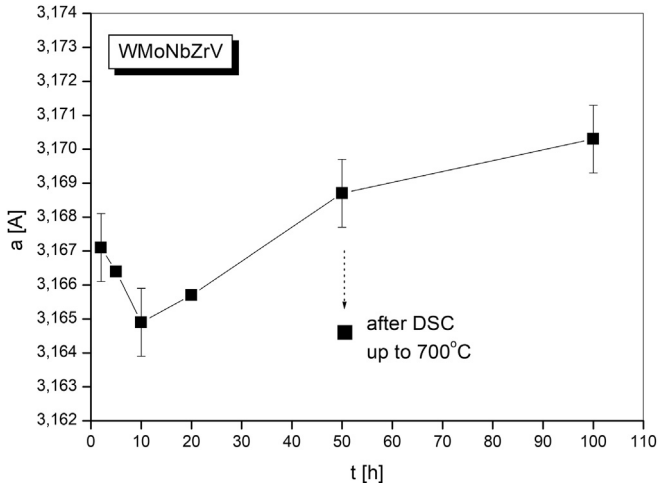

Fig. 3. Changes of bcc phase lattice parameter as a function of milling time and heat treatment.

The powders after final milling time were subjected to chemical composition analysis. Some amount of Fe (2.2 at%) was found as a contamination coming from the milling media (balls and vial).

The changes of bcc phase lattice parameter as a function of processing time are plotted in Fig. 3. At the early milling times, when mainly Zr and V atoms dissolve in the W and Mo matrix, small decrease of lattice parameter is observed. Such behavior can result from the fact, that Zr and V reveal the smallest values of atomic radii, 1.75 and 1.71 Å, respectively, comparing to 1.93 Å for W, 1.90 Å for Mo and 1.98 Å for Nb [11]. However, for longer milling time the slight increase of its value can be noticed, related to further distortion of the lattice. The final value of bcc solid solution lattice parameter after 100 h MA (3.1687 Å ± 0.0005 Å) is located between the smallest one for V (3.0274 Å) and the biggest one for Nb (3.3033 Å).

The value of bcc solid solution lattice parameter after calorimetric measurement (3.1645 Å) was clearly smaller than the one calculated for powders milled only (Fig. 3). These changes of lattice parameter during the heating can indicate that the structure become more relaxed. Simultaneously, single phase bcc structure and nanosize of crystallites are preserved, confirming good thermal stability of this alloy resulting from the slow diffusion due to high entropy of the system.

A question arises why the diffraction lines corresponding to bcc solid solution formed upon milling are located in the vicinity of W/Mo lines. The possible explanation can result from the fact, that W and Mo reveal the highest melting point among the elements forming this alloy and these elements also exhibit very high hardness. Another reason can be related to the values of enthalpy of mixing. Enthalpies of alloys formation for W and Mo with other elements are negative (e.g. −13 kJ/mol for W-Nb, −14 kJ/mol for W-Zr, −9 kJ/mol for Mo-Nb), while for W-Mo this value is zero [12]. It can facilitate earlier and easier dissolution of Nb, Zr and V in W and Mo, as was observed in this work.

4. Conclusions

High melting point high entropy multicomponent WMoNbZrV alloy has been successfully synthesized using mechanical alloying process. The final powder revealed nanocrystalline single phase bcc structure characterized by minimum crystallite size of about 10 nm, maximum lattice strain of 0.58% and lattice parameter 3.1687 Å.

Continuous heating the powders after 50 h of MA in the calorimeter up to 700 °C resulted in lattice strain decrease from 0.35 to 0.20%, while the crystallite size of bcc phase remained unchanged (10 nm). The performed heat treatment also resulted in a slight decreasing of bcc phase lattice parameter. These results confirmed the high thermal stability of the alloy resulting from the slow diffusion of elements due to high entropy of the system.

Acknowledgement

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