INFLUENCE OF SINTERING TEMPERATURE ON MICROSTRUCTURE AND HARDNESS OF AlCoCrFeNiTi$_{0.5}$ HIGH ENTROPY ALLOY

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Abstract

High entropy alloy AlCoCrFeNiTi0.5 was produced by a combination of mechanical alloying (MA) and spark plasma sintering (SPS) processes. In our study we have investigated the effect of four different sintering temperatures (ranging from 1150 to 1300 ºC) on microstructures and phase composition of sintered samples by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and Vickers microhardness tests. In all cases, full density has been achieved. The influence of sintering temperature has been determined to be very small for cases when the powder is in solid state during sintering. For highest sintering temperature of 1300 ºC, partial powder melting took place, significantly decreasing obtained hardness.

Keywords: High entropy alloy, powder metallurgy, sintering

1. INTRODUCTION

Powder metallurgy route is an alternative way for production of complex materials with avoiding liquid phase processing thus avoiding segregations and unwanted inhomogeneities [1]. Combination of mechanical alloying of elemental powders followed by spark plasma sintering (SPS) as an efficient way to obtain full density bulk samples has been utilized in many areas, especially in ceramic materials processing, and its use is increasing also for metallic materials and metal-matrix composites [2]. The nature of SPS process allows to retain extremely fine grains of previously mechanically alloyed (extensively cold deformed) powders due to very short sintering times and simultaneous application of pressure and electric current. Samples are heated from the inside by production of Joules heat, as opposed to a normal sintering where heat is applied from outside atmosphere. Thus SPS has been proved to produce metallic and ceramic bulk nano-structures [3, 4]. The properties of processed complex materials significantly depend on the technological parameters of powder mixtures, and on the parameters of pressing and sintering processes, which include temperature, sintering time etc. [5].

High-entropy alloys (HEAs) proposed by Yeh et al. [6] are multicomponent solid solutions consisting of more than five equimolar and/or near equimolar elements. HEA concept is based on stabilization of solid solution phases, instead of mixture of ordered compounds by increased configurational entropy [7]. This yields their very good mechanical properties from inherent ductility of simple solid solutions and extreme solid solution strengthening derived from difference in atomic diameters of used elements. In the last decade, they have been thoroughly studied all around the world revealing very interesting properties like low temperature fracture resistance, wear resistance, extremely slow diffusion kinetic etc. [8-10]. Majority of the alloys is produced by classical metallurgical approach - melting and casting, mostly because of this method simplicity and ability to rapidly produce broad range of compositions [11]. Due to usage of water cooled copper molds for arc melted alloys and therefore very rapid cooling from liquid phase, non-equilibrium phases are sometimes retained to room temperature. Usually significant phase changes are recorded upon annealing of such structures [12, 13]. Consequently phase stability of these materials is also questionable.

In our study we used a combination of mechanical alloying process and SPS as a promising way to attain nano-structured high entropy alloy bulk materials [14]. The influence of sintering temperature has been

determined as the main parameter with most significant impact on final microstructure, on mechanically alloyed high entropy powders. All other adjustable sintering parameters remained consistent.

Elemental composition is a critical factor in the alloy design, which will definitely affect the alloying behaviors and phase transformations [15]. The alloy composition has been chosen based on preliminary research for its good combination of mechanical properties [15, 16]. As such, alloy has a potential to replace commonly used structural materials.

2. EXPERIMENTAL

Elemental powders of Co, Fe, Ni, Ti, Cr with particle sizes of around 45 μm (325 mesh) and purity over 99% were blended to get AlCoCrFeNiTi0.5 (in atomic proportion) composition and then processed by high energy mechanical alloying in planetary ball mill Fritch Pulverisette 6. Powders were milled for 24 hours with 400 RPM milling speed, with 10:1 ball to powder ratio (BPR). 10 mm diameter bearing steel balls were utilized. Approximately 2 wt.% of methanol as a process control agent was used to prevent powder particle coarsening during the processing. Powders were then consolidated by SPS (Thermal Technology LSS model 10-4) using 20 mm graphite mold. Graphite foils were placed between powders and the die walls to avoid powder sticking to mold walls. The temperature of 1150 °C, 1200 °C, 1250 °C and finally 1300 °C with 50 MPa pressure and 10 minutes soaking time were applied under vacuum atmosphere. XRD technique was used to observe the structural changes of powders before and after SPS. Philips X´Pert diffractometer (40 kV) with Co Kα radiation (λ = 0.1790307 nm) was exploited for measurements. The XRD patterns were recorded in the 2θ range of 30-120°. Polished samples were analyzed by ZEISS Ultra Plus SEM at an accelerating voltage of 20 kV and 10 kV followed by energy dispersive microanalysis method (EDS). Hardness measurement was carried out on Vickers microhardness tester with 300 g work load on polished samples. Porosity was measured by image analysis with ImageJ software on polished samples.

3. RESULT AND DISCUSSION

3.1. XRD phase analysis

Figure 1 depicts XRD patterns of powder and bulk materials in different states. In the premixed powder, elemental peaks of used powders were observed only. During the process of mechanical alloying, formation of only one BCC solid solution took place roughly fitting Cr and Fe elements with very wide peaks, pointing out to abnormal grain refinement induced by repeated cold deformation process during MA. This phenomenon is usually a proof that alloying reaction occurred as it has been reported many times in other research [e.g.18].

Previously mentioned BCC solid solution transforms into mixture of different phases after SPS. This suggests metastable nature of the BCC solid solution formed by non-equilibrium processing. Phase composition for different temperatures of SPS is basically the same, only with negligible differences in peak intensity. Therefore we present only pattern for 1200°C. First major phase is disordered FCC solid solution. The second major phase has an ordered B2, NiAl like structure with forbidden superlattice (100) reflections clearly visible in the pattern, suggesting at least partially ordered nature of the phase. Smaller amounts of tetragonal FeCr-like sigma phase are also present. Peaks of second phase with FCC lattice structure are also present that are determined to be TiC or (Ti,Cr)C carbide phase. This is obviously a result of carbon contamination induced by presence of methanol during MA. Supposedly, methanol decomposition during milling causes carbon to dissolve into the lattice of milled powders. After heating to higher temperatures the carbon formed stable ceramic compounds. From present elements, titanium has the highest affinity to carbon. In the FCC lattice of TiC, also other elements like Cr can dissolve, which would explain small peak shifts to higher angles. Phase composition of the investigated powder alloy turned out to be little different than two phase B2/BCC structure in previously reported cast alloy [16]. This phenomenon should be explained by the fact, that titanium is in our case bonded to carbon and, in turn, its concentration in other phases is lower. This could lead to differences

in phase composition. Presence of sigma phase in similar alloy systems has never been reported before. Because of much slower cooling speed after SPS when compared to copper mold casting used before, its appearance could be simply the result of slower cooling from sintering temperature.

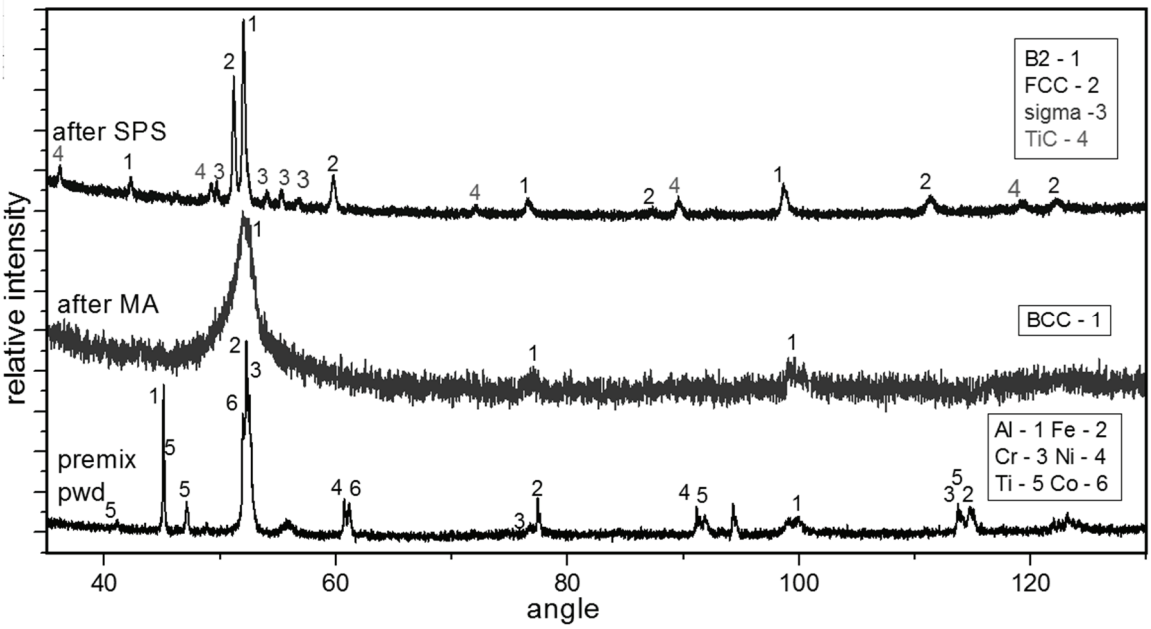

Figure 1 XRD patterns of materials after different processing steps

3.2. Microstructure analysis

Overall chemical composition of our alloys is presented in **Table 1**. No significant differences to desired composition are observed. We can assume that no excessive element evaporation took place during MA or SPS. The only difference is noted for Fe element, which can be associated to slight steel milling media abrasion during very intensive milling.

SEM pictures of microstructures after SPS at different sintering temperatures are illustrated in **Figure 2**. Very small differences in microstructural features in case of sintering temperatures of 1150 °C, 1200 °C and 1250 °C can be seen. No grain coarsening occurred even when the difference in SPS temperature is 100°C.This can be associated to very short sintering times (only 10 min.) and also good thermal stability of the structure. By far the biggest difference is observed when the sintering temperature reaches 1300 °C. At least partial melting of the powders took place and as the consequences much coarser nature of all phases was obvious. In the first three cases most of the grains are well under 1µm in size. This is the result of retention of nanosized grains that were formed by severe plastic deformation of the powders during MA. On the other hand the size of present phases grains did not allow to perform reliable EDS point analysis but, considering our XRD results and other studies on alloys with similar compositions [19], we can assume that structure consists of white Fe-Cr enriched FCC phase, grey Ni-Al enriched phase and very fine black TiC particles and oxides. Unfortunately, strings of oxide particles are present along the original surfaces of the milled powders. Most likely methanol remainders were still present on the powder surfaces during SPS process and due to applied pressure of 50 MPa were trapped between particles, forming aluminum and titanium oxides. The other alternative is that powder surfaces were overly oxidized during short exposure of powders to air. This undesirable effect would have probably increasingly negative influence on mechanical properties, e.g. tensile ductility contributing to crack initiation and propagation by weakening effect of oxides strings. Very good densification was observed for all cases with no apparent visible porosity. Only in case of the highest SPS temperature, few bigger pores are present leading to overall porosity of 1.1%. This is most likely also a consequence of powder melting during sintering.

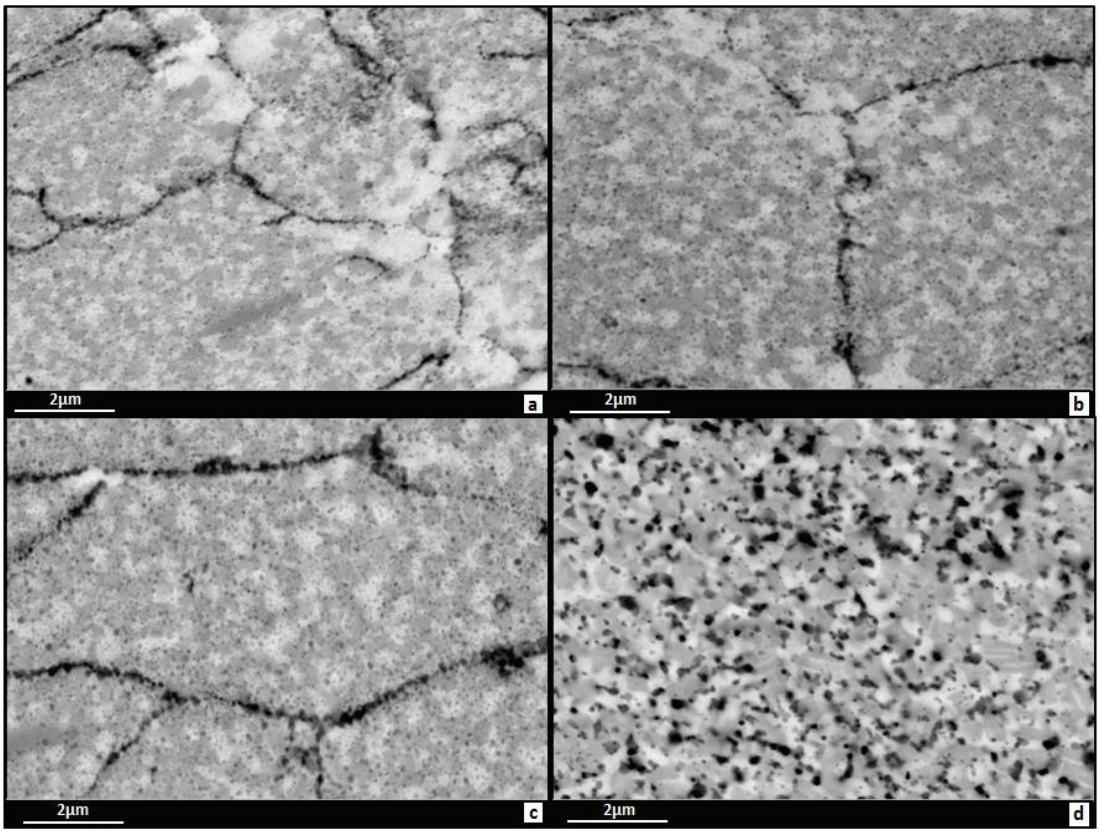

Figure 2 SEM backscattered images of bulk materials microstructures after a) 1150 °C b) 1200°C c) 1250 °C d) 1300 °C

Table 1 Average chemical composition obtained by SEM EDS measurement

Composition (at. %)	Fe	Co	Ni	Cr	Al	Ti
Desired	18.18	18.18	18.18	18.18	18.18	9.1
Obtained	20.39	18.31	17.71	18.41	16.33	8.85

3.3 Microhardness measurement

Results of hardness measurement presented in **Table 2** suggest very high hardness for sintering temperatures of 1150 °C, 1200 °C and 1250 °C and again only negligible differences are measured. High hardness is attributed to strengthening by ultra-fine grains and dispersions of fine carbides. After sintering at 1300 °C, partial melting (observed during SPS) and grain coarsening has been observed, and is most probably responsible for sharp hardness decrease. Negative effect of afore mentioned surfaces contamination of original particles resulted in indentation cracks along this boundaries in some cases denoted by red arrows in **Figure 3**

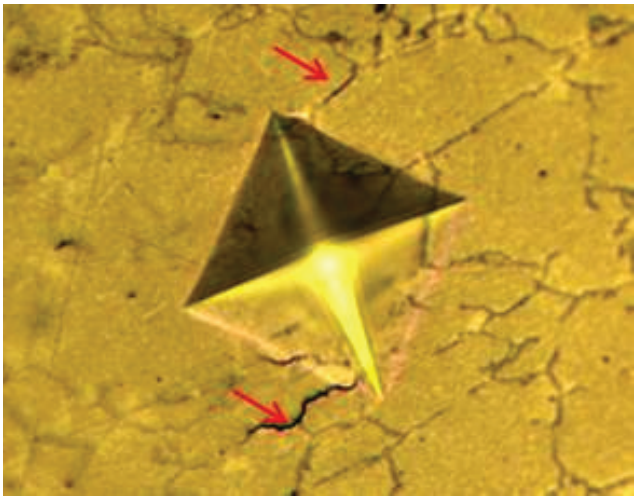

Figure 3 OM image of indentation cracks caused by oxide strings

Table 2 Hardness of the samples after SPS

Sintering temperature (°C)	1150	1200	1250	1300
Porosity (%)	<0.5	<0.5	<0.5	1.1
Hardness HV0.3	803	799	796	526

4. CONCLUSIONS

The influence of sintering temperature on phase composition, microstructure and mechanical behavior of mechanically alloyed powders of $AlCoCrFeNiTi_{0.5}$ high entropy alloy has been evaluated by XRD, SEM and microhardness test methods:

- When spark plasma sintering has been done between 1150 to 1250 ºC low influence of temperature on properties has been observed.
- Negative effect on hardness and porosity is seen when sintering temperature of 1300 ºC is used, caused by partial melting of powder during process.
- By sintering in the range of 1150 to 1250 ºC, fully dense ultra-fine grained structure with considerably high hardness of around 800 HV0.3 is obtained

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