PREPARATION AND CHARACTERIZATION OF CoCrNi-Mo METAL MATRIX COMPOSITE BY POWDER METALLURGY

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Abstract

A metal matrix composite - consisting of a matrix of medium entropy alloy CoCrNi and Mo as reinforcement - is reported on the present study. The composite was produced by mechanical alloying (MA) in combination with spark plasma sintering (SPS). The investigation of the microstructural features, chemical composition and basic mechanical properties of the bulk material were subject to study, by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS) and Vickers microhardness testing. A full-density composite has been achieved with the selected sintering conditions, showing an average hardness of 514 HV0.3. Its' microstructure exhibited four different phases, possessing a matrix consisting of FCC solid solution reinforced by BCC particles surrounded by a μ-phase in the interface of the matrix/reinforcement and dispersed HCP precipitates.

Keywords: Metal matrix composite, mechanical alloying, medium entropy alloy, spark plasma sintering

1. INTRODUCTION

High and Medium entropy alloys (HEAs and MEAs, respectively) are an emerging class of metals which contain multiple elements, typically in (near) equiatomic ratio. They are currently receiving extensive attentions from materials science community due to their ability to form superior properties thanks to the four core effects [1] attributed to HEAs - such as superior ductility, good thermal stability, wear resistance and high-strength [2-5].

HEAs and MEAs can possess - but not only - simple crystal structures as solid solutions, such as fcc, and the random distribution of multiple elements have the potential to form stacking faults (SF), rendering low stacking fault energy (SFE) [6]. The CoCrNi composition is a single-fcc MEA which has exhibited outstanding mechanical properties, showing a remarkable combination of fracture resistance and strength [5], due to its superior ductility - which comes from to the formation of a single-fcc solid solution. Its superior mechanical behaviour is mainly governed by the ability to form stress induced (nano-)twins which increase the ability of the material to accommodate plastic strain [5, 7-10].

In regard to engineering applications, however, single-fcc MEAs are not the most appropriate material, since their yield strength is relatively low. For engineering purposes, there is a high demand to attain excellent combination of high strength and good ductility mutually. In order to strengthen the single-fcc MEAs, there are several techniques which have been developed, such as grain refinement and precipitation hardening. Although, further efforts should be subject to approach to improve the strength of single-fcc MEAs even more, since the improvement in strength with the mentioned techniques are not enough [11].

The creation of a metal-matrix composite (MMC) consisting of a matrix of CoCrNi and reinforcements as Mo-particles is a promising route, since the addition of Mo-particles have been verified in several systems and it shows strength improvement [11-13] as well as the MMC creation using CoCrNi-matrix on powder metallurgy route has been proven to be efficient [7, 14]. Therefore, on this paper, the MMC CoCrNi-Mo produced by powder metallurgy was subject to study and the investigation of its microstructural features, chemical composition and basic mechanical properties were carried out.

2. MATERIALS AND METHODS

The composite formed by CoCrNi MEA matrix containing Mo particles was subject to study. The preparation of the composite's matrix was achieved by placing powders of Co, Cr and Ni - with commercial purity of 99.95 % - in a hardened steel milling bowl filled with high purity nitrogen atmosphere (6.0), together with hardened bearing steel balls (100Cr6) of 15 mm diameter, in a 10:1 ball-to-powder weight ratio (BPR). The sealed bowl was introduced into a planetary ball mill (Fritsch Pulverisette 6). The milling was conducted for a total of 30 h in a speed of 300 rpm, in a set time schedule of 60 min milling and 30 min idle, for 30 cycles. After the milling, toluene was added and wet milling has been performed for extra 30 min for complete removal of the powders from the surfaces. For the preparation of the reinforcement, Mo powders, of 99.95 % of commercial purity, were submitted to mechanical milling for 5 h and 30 min idle, for 5 cycles - utilizing the same scheme as for the matrix. After completion, further wet milling has been done for extra 20 min. For the preparation of the composite, the mechanically alloyed matrix's and reinforcements' powders were mixed - in a ratio of 1:1 (matrix:reinforcement) - for 30 min in a hardened steel milling bowl filled with high purity nitrogen atmosphere (6.0), together with hardened bearing steel balls of 10 mm diameter in a 1:1 BPR, using 300 rpm speed.

The milled powders were consolidated by Spark Plasma Sintering (SPS) in Sumitomo Coal Mining, Dr. Sinter SPS machine in Central European Institute of Technology (CEITEC Brno), in vacuum atmosphere, using a 30 mm graphite die. A sintering temperature of 1050 °C with constant 30 MPa pressure was reached for the densification. The densification route was: 100 ºC/min from 0 up to 600 °C; 5 min dwell time at 600 °C (to remove any organic compounds potentially present); 100 ºC/min from 600 °C up to 1050 °C; 10 min dwell time at 1050 °C. The samples were, then, slowly cooled down in vacuum. The resulting bulk specimen was approximately 6 mm high cylinder with 30 mm diameter.

The samples were analysed by SEM (Zeiss Ultra Plus) utilizing energy-dispersive X-ray spectroscopy (EDS). The constituent phases were analysed based on the acquired XRD spectra, obtained using the diffractometer Philips X'Pert, operated under the voltage of 40 kV with current of 30 mA. A continuous scanning was performed with 2θ between 10° and 100° using a speed of 0.02 °/min and step size of 0.0167°. The radiation used was Cu-Kα with λ = 0.154056 nm. CALPHAD calculations were performed using ThermoCalc software, through the TTNI7 Ni-alloys Database v7.4 in order to predict the phase transformations during SPS.

Nanoindentation hardness was performed in order to measure the average hardness of each phase. 15 indentations were performed, with a Berkovich diamond indenter, using CSM Instruments NHT2 nanoindentation tester, by Oliver & Pharr method, on acquisition rate of 10 Hz, maximum load of 100 mN, in a loading and unloading rates of 200 mN /min, dwell time of 10 s.

Additionally, Vickers hardness measurements were carried out using loads of 300 g (composite) and 100 g (matrix), as well as dwell time of 10 s on the polished samples (15 measurements) using LM 247AT microhardness tester.

3. RESULTS AND DISCUSSION

The XRD pattern analysis of the composite CoCrNi-Mo SPSed bulk is presented in **Figure 1**. The major matrix is a FCC Ni-base solid solution phase was formed during SPS, possessing a calculated volume fraction of 48.7 % and lattice parameter of 0.3598 nm. The second phase is BCC Mo solid solution - further confirmed by EDS analysis - corresponding to the desired reinforcement, with a calculated volume fraction of 24.4 % and lattice parameter of 0.3141 nm. The third phase is μ-phase, corresponding to Co_7Mo_6-like Rhombohedral intermetallic phase, with corresponding volume fraction of 21.3 % and lattice parameter of a = 0.4757 nm and c = 2.561 nm. At last, the fourth phase corresponds to a Co_3Mo-like HCP precipitates' phase, comprising 5.6 vol.% and lattice parameter of a = 0.4933 nm and c = 0.4534 nm.

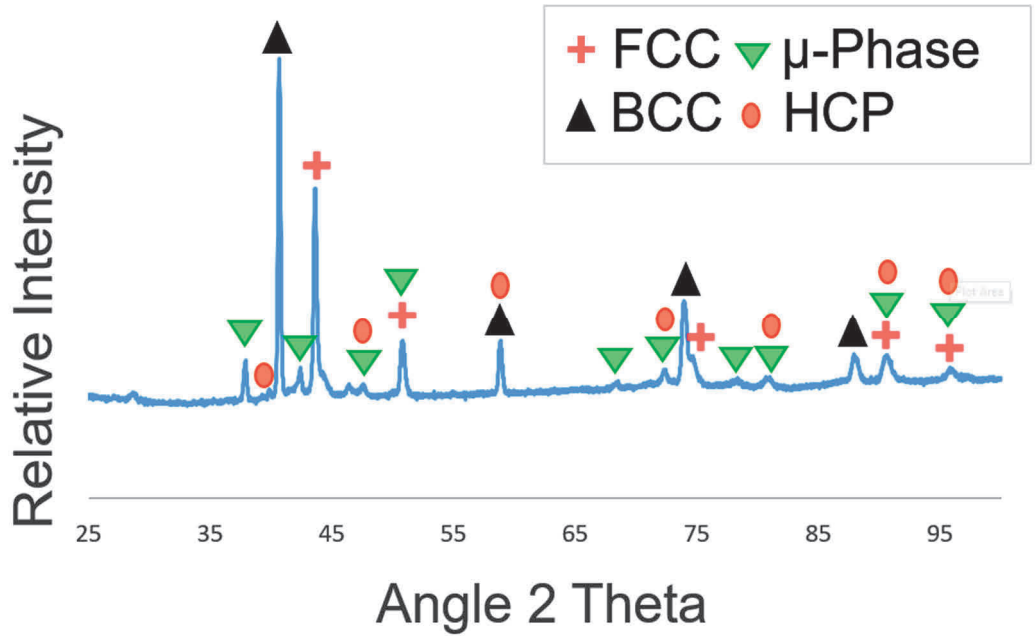

Figure 1 XRD Pattern of the CoCrNi-Mo SPSed bulk material

In **Table 1**, it is possible to observe the corresponding chemical composition of each phase detected by XRD, on which the FCC matrix consists of a solid solution of Ni, Co and Cr in almost the same proportions and small traces of Mo. The BCC phase is pure Mo. The intermetallic μ-Phase, though, could consist of 37% of Mo and the Co atoms could be replaced in the unit cell for atoms of Cr or Ni, forming a rhombohedral microstructure. The analysis of the HCP phase was not possible due to the considerable small particle size correspondent to the phase, which was below the detection threshold of the EDS measurement.

Table 1 EDS point analysis of each phase on CoCrNi-Mo SPSed bulk (at.%)

Element	Co	Cr	Ni	Mo
FCC	32	29	37	3
BCC	0	0	0	100
μ-Phase	17	26	20	37

In **Figure 2**, the SEM micrographs of the composite bulk after SPS are shown. The FCC Ni-base solid solution, the BCC Mo-microstructure and the μ-phase are denoted by yellow arrows in **Figure 2a**. As it can be observed in **Figure 2b** in more detail, the μ-phase is surrounding the interface of the boundaries between the FCC and BCC microstructures, as a result of the reaction between Mo and Co (Ni or Cr substitutionally). The small HCP precipitates are represented in **Figure 2c** and are visible in **Figure 2d** as well. Annealing twins have been observed on the FCC matrix in **Figure 2d** due to the SPS procedure, as typically expected for CoCrNi [6, 7, 9, 10], on specific boundaries with low energy which favours their appearance instead of normal grain boundaries - as in typical FCC materials.

Figure 3 represents the phase diagram of CoCrNi varying the amount of Mo. It is possible to conclude that the μ-phase is a result of the reaction among the elements of the matrix (Co, Cr, Ni) and Mo, while the remaining Mo in the microstructure (BCC phase in **Figure 2b**) did not react with the other elements due to the short SPS procedure time. Due to the concentration gradient of the elements within the microstructure, the HCP phase appears as resulting reaction during slow cooling from SPS at 600 °C, forming small precipitates mainly on the boundaries between the matrix and the μ-phase, as it is evidenced in **Figure 2c**.

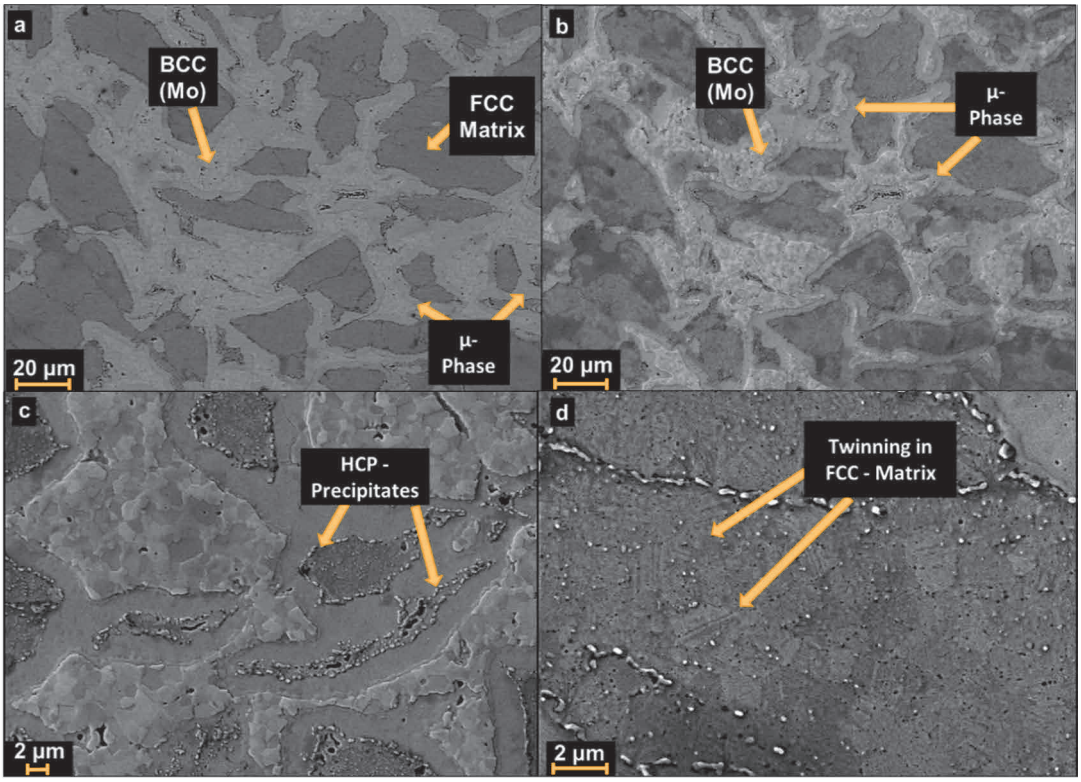

Figure 2 Micrographs of CoCrNi-Mo SPSed bulk: a) Electron backscattered detector - FCC, BCC and μ-phase identified by the arrow; b) Secondary electrons - BCC and μ-phase marked; c) Secondary electrons - HCP precipitates are indicated; d) Secondary electrons - twins on the FCC matrix.

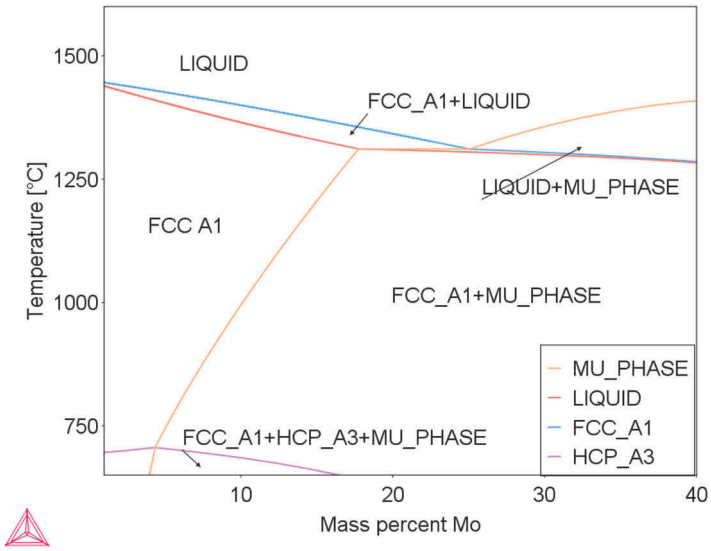

Figure 3 CALPHAD calculation of CoCrNi-Mo using TTNI7 v7.4 database from ThermoCalc software

Using nanoindentation hardness, it was possible to verify the average hardness level of each phase separately - except for the small HCP precipitates, due to its very limited area, below the detection threshold of the nanoindentation's measurement. By means of Vickers microhardness, it was possible to obtain the average value of hardness of the composite as a whole, since the indentation area is considerably larger. The average hardness values are presented in **Table 2**.

Table 2 Nanoindentation hardness of CoCrNi-Mo performed on each phase and average microhardness.

Nanoindentation hardness	**HIT** (MPa)	**EIT** (GPa)
Matrix CoCrNi	6373.1 ± 135	239 ± 3
Reinforcement Mo	6535 ± 50	293 ± 4
μ-phase (Interface)	11911 ± 442	1126 ± 42
Microhardness		
CoCrNi-Mo Composite	531 ± 14 [HV0.3]	
Matrix CoCrNi	323 ± 11 [HV0.1]	

The average hardness of the SPSed material is 531 ± 14 HV0.3 and the matrix possesses hardness of 323 ± 11 HV0.1. The reinforcements' hardness was not possible to be measured due to its too small area. According to the nanoindentation measurements, the hardness of the matrix CoCrNi is about 6373.1 ± 135 MPa with calculated elastic modulus of 239 ± 3 GPa. On the other hand, the BCC Mo-reinforcement possesses (6535 ± 50) MPa of hardness, comprising an elastic modulus of 293 ± 4 GPa. The μ-phase, though, comprises a much higher hardness level, possessing 11911 ± 442 MPa and elastic modulus of (1126 ± 42 GPa. The μ-phase can be expected to improve the strength of the alloys due to its extremely high hardness [15] and possesses intrinsic brittleness [16].

4. CONCLUSION

In this paper, a metal matrix composite consisting of CoCrNi-Mo was prepared by powder metallurgy. The major conclusions of the work are drawn as follows:

- Metal Matrix Composites may be prepared by the combination of mechanical alloying and spark plasma sintering.
- It was possible to create a full-density composite bulk with the selected SPS parameters.
- The reinforcement reacted with the matrix, forming phases on the interfaces' boundaries.
- With the addition of Mo, the hardness of the material increases 66 % as compared to the pure CoCrNi prepared by PM (originally 309HV0.3) due to the formation of a multiple phase microstructure consisting of FCC, BCC, μ-phase and small HCP precipitates in comparison with a single FCC phase for pure CoCrNi.

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