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CoCrFeNiTi High Entropy Alloy Prepared via Mechanical Alloying and Spark Plasma Sintering

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Mechanical alloying and subsequent compaction with spark plasma sintering was chosen for the fabrication of investigated CoCrFeNiTi alloy method. The alloy was characterized in terms of chemical and phase composition with X-ray fluorescence spectroscopy and X-ray diffraction spectrometry, respectively. The microstructure was examined using light microscopy and scanning electron microscopy equipped with an energy dispersion spectrometer. The alloy showed an ultra-fine grained uniform microstructure composed mainly of an FCC solid solution with a volume fraction of HCP Laves phases. Regarding mechanical properties, the prepared specimen reached an ultimate compressive strength of 1340 MPa with the hardness of 757 HV 30. The wear rate of the sample reached $1.19 \cdot 10^{-4}$ $mm^3 \cdot N^{-1} \cdot m^{-1}$ showing traces of adhesive-abrasion wear mechanism.

Keywords: High entropy alloys, Mechanical alloying, Spark plasma sintering, Mechanical properties

1 Introduction

High entropy alloys (HEA) are a fast-developing group of modern materials first defined in 2004 [15]. Since then, they have been gaining continuously more attraction throughout the years due to the intensive research on these types of materials. HEAs are typical for their composition usually consisting of 5 or more elements, each in the range of 5-35 at. % [14]. Multi-element composition results in an increase in mixing entropy, which stabilizes solid solutions in the structure of these materials leading to attractive mechanical properties [9]. The high number of elements is challenging in terms of composition design because it increases dramatically the variability among these systems. The most well-known system is CoCrFeNi as it is one of the first-ever described [1]. A standard fabrication method for HEA is casting, although it results in inhomogeneous microstructure thus the alloys need to be post-processed thermally [11] or thermomechanically [10]. Advanced methods, including powder metallurgy [5, 8] and subsequent compaction with e.g. hot isostatic pressing (HIP) [4], spark plasma sintering (SPS) [7], or additive manufacturing [13], are used to obtain a more refined and homogeneous microstructure without a need for further processing.

Mechanical properties and phase composition of CoCrFeNiTix alloy are strongly dependent on the amount of Ti [16]. The increasing amount of Ti increases the number of secondary phases formed within the FCC solid solution originating from CoCrFeNi [12]. Solid solution strengthening and formation of hard secondary phases are the two main factors affecting the mechanical properties. The more Ti the alloy contains the higher the hardness and ultimate compressive strength (UCS) whereas the ductility decreases. The CoCrFeNiTi-based alloy is also subject to corrosion resistance tests, which, considering pitting resistance, achieved better results than Ni-based superalloys exposed to the same environment [2]. Up to these days, the CoCrFeNiTix alloy is prepared mostly by arc melting [12, 17] or additive manufacturing [2, 6]. There are almost no scientific reports of this alloy group being prepared by mechanical alloying, which will undoubtedly further increase the overall properties due to microstructural refinement and deformation of the crystallographic lattice of present phases. The closest mention came from Haq et al. [3] who prepared a core-shell structured CoCrFeNiTi alloy via mechanical alloying and consequential annealing in a precisely controlled atmosphere N2/Ar.

The attention given to the equimolar CoCrFeNiTi alloy is almost none compared to the CoCrFeNiMn, thus this paper provides elemental information on the phase composition and mechanical properties of this alloy prepared with mechanical alloying and spark plasma sintering.

2 Experiment

The CoCrFeNiTi alloy was prepared by mixing pure powders of individual elements each having a purity at least of 99.5% or higher. The powder mixture (20 g in total) was put into a stainless steel milling vessel together with milling balls, both made from AISI 420 stainless steel. The powder to milling ball

weight ratio was 1:15. To prevent excessive cold welding, 4 wt. % of n-heptane was added as a process control agent (PCA). Finally, the vessel was sealed and flushed with argon (99,996 % purity) with a flow rate of 2l/min for at least 2 min to prevent oxidation during the process. The mechanical alloying was performed in a planetary ball mill Retsch PM-100. The time of the alloying itself was 8 h, but after every 30 min interval the process was interrupted for a 10 min cool-down period and then it continued for another 30 min with spinning in opposite direction, so the whole process took 10 h and 30 min. The rotation speed was 400 rpm.
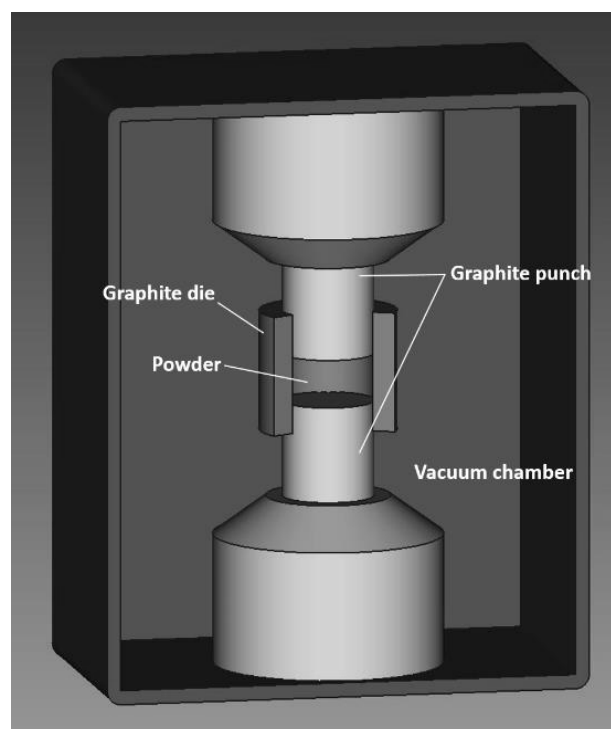

Fig. 1 *Schematic model of the SPS chamber*

The 10 g of MA powder alloy was then compacted in the spark plasma sintering machine FCT Systeme HP D-10 (Fig. 1). The compaction took place at 1000 °C achieved by the heating rate of 200 °C min^{-1}. After reaching 1000 °C the powder was compressed with a pressure of 48 MPa for 1 min and remained compressed at the temperature for another 9 min followed by rapid cooling and relieving of the pressure.

The chemical and phase composition was determined by X-ray fluorescence spectroscopy (XRF, PANalytical Axios) and X-ray diffraction spectrometry (XRD, PANalytical X'Pert PRO, Cu K$_\alpha$ = 1.54060 Å). The prepared sample was observed with light microscopy (LM, Nikon ECLIPSE MA 200) and scanning electron microscopy (SEM, Tescan Lyra) with an energy dispersion spectrometer (EDS, OXFORD Instruments INCA 350, 80 mm²). For this purpose, the specimen was etched in Aqua regia (1:3

molar mixture of HNO₃ and HCl) further diluted with distilled water in a ratio of 1:1.
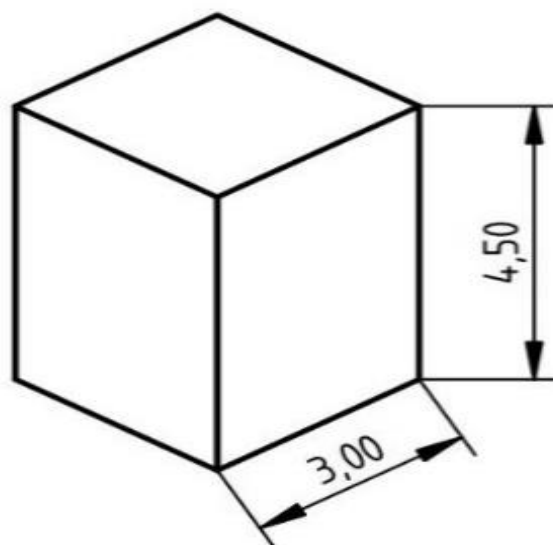

Fig. 2 *Scheme of a specimen used for the compressive stress-strain tests*

The evaluation of mechanical properties included hardness measurements, compressive tests and wear tests. Vickers hardness was measured according to ČSN EN ISO 6507-1 with a load of 30 kg, 10s dwell time on at least 10 individual places providing sufficient data used to determine the average value and 95% confidence interval. Compressive tests were carried out on cuboidal specimens with a height of 1,5x the dimension of the base (Fig. 2). The strain speed was set to $1 \cdot 10^{-3}$ s^{-1}. The wear resistance test was performed on TRIBOtester, TRIBOtechnic. An Al₂O₃ ball with a 6 mm in diameter loaded with 5 N was used for the test. The test took place in a linear mode within the 5mm track, the speed of the ball was set to 15 mm s^{-1} and the total length of the slide was 20 010 mm.

3 Results and discussion

3.1 Chemical and phase composition, microstructure

The chemical composition of the alloy determined with the XRF analysis, which results are shown in Tab. 1, is in good agreement with the intended equiatomic composition. A slightly higher amount of Fe may be caused due to the abrasive behaviour of the prepared alloy to the mill vessel causing contamination of the alloy.

Tab. 1 *Chemical composition of CoCrFeNiTi alloy after 8h of MA*

Element	Co	Cr	Fe	Ni	Ti
At. %	19.5	18.6	21.9	20.9	19.1

Results from the XRD analysis are shown in Fig. 3. The pattern of the MA powder alloy shows that the

microstructure is composed of a solid solution with FCC crystallographic lattice, which corresponds well with other works concerning the CoCrFeNiTi alloy microstructure [16]. The broad peak in the MA powder implies a very fine particle size of the powder and lattice stress strains imposed during the MA. On the other hand, the SPS compaction resulted in a partial disintegration of the FCC solid solution into HCP Laves phases identified as $TiCo_2$. This was accompanied by a narrowing of the (111) peak of the FCC solid solution due to Ti depletion which is known to have the highest atomic radii (0.147 nm) compared to Co (0.125 nm), Cr (0.128 nm), Fe (0.126 nm) or Ni (0.124 nm) elements [12]. Due to high deformation stresses introduced in crystal lattice during MA, it is hard to precisely determine the exact phases which may become isomorphic. Besides the mentioned phases it was also detected an insignificant existence of carbides in the structure of compacted alloy, which were formed during the SPS process due to a reaction with the graphite foil surrounding the powder during sin-

tering. Another source of carbon is the mechanical alloying process itself which is done using n-heptane as PCA, which may result in supersaturation of the FCC solid solution by carbon. On the contrary, a $CoCrFeNiTi_{0.6}$ alloy prepared by the vacuum arc melting and subsequent aging in the work of Zhao [17] et al. showed a dendritic microstructure composed of the primary FCC solid solution with (Cr, Fe)-rich σ and (Ni, Ti) η-phases. Furthermore prolonged aging time resulted in an increase in the volume fraction of secondary phases in the interdendritic regions. Thus, this demonstrates the importance of chosen preparation method which is responsible for significantly different microstructural appearance and phase compositions. Stress strains introduced into the crystallographic lattice during the MA process along with the increased dislocation density result in the nanocrystalline but metastable microstructure of the material. The rapid SPS compaction with high cooling velocities partially disintegrates the former FCC solid solution into more stable phases, although the rapid heating and cooling may still preserve its metastable character.
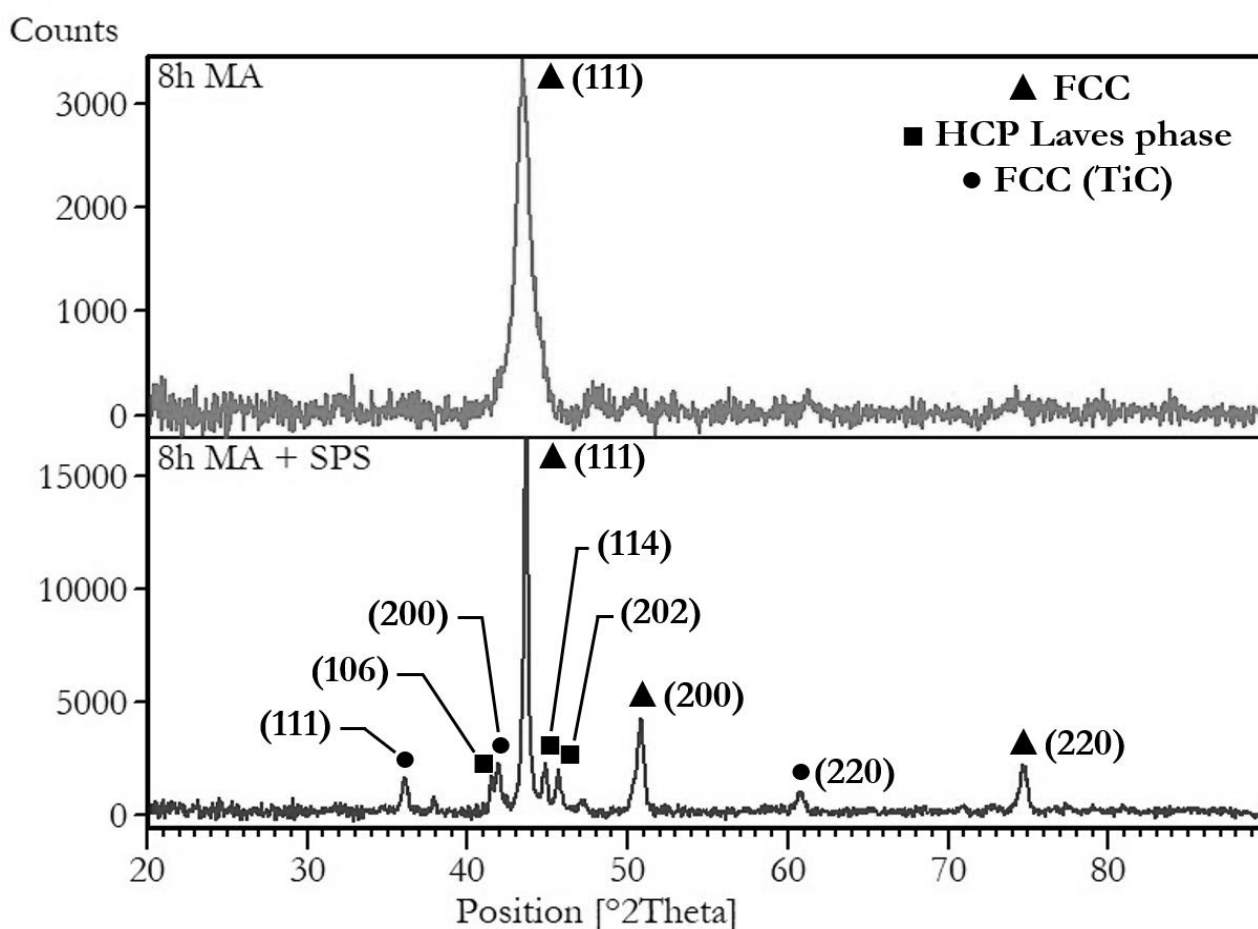

Fig. 3 *XRD patterns of CoCrFeNiTi alloy – upper pattern for the 8h MA powder alloy and the lower pattern for SPS compacted alloy*

The MA powder (Fig. 2a) had a uniform microstructure without any traces of lamellar structure from the mechanical alloying. There are only visible

internal voids as a result of the repeating cold-welding during the MA process. The homogeneity of the microstructure is preserved throughout the SPS

compaction as can be seen in Fig. 2b. There is only difference caused by the newly formed particles of brighter colour identified by the XRD as Laves phases. The porosity of powder particles was dramatically reduced during the SPS ending in low tenths of a per cent in the compacted specimen. The detailed SEM micrograph showing the microstructural refinement is shown in Fig. 2c where phases with dimensions ranging from tenths to a few hundreds of nm in diameter are marked with yellow arrows.
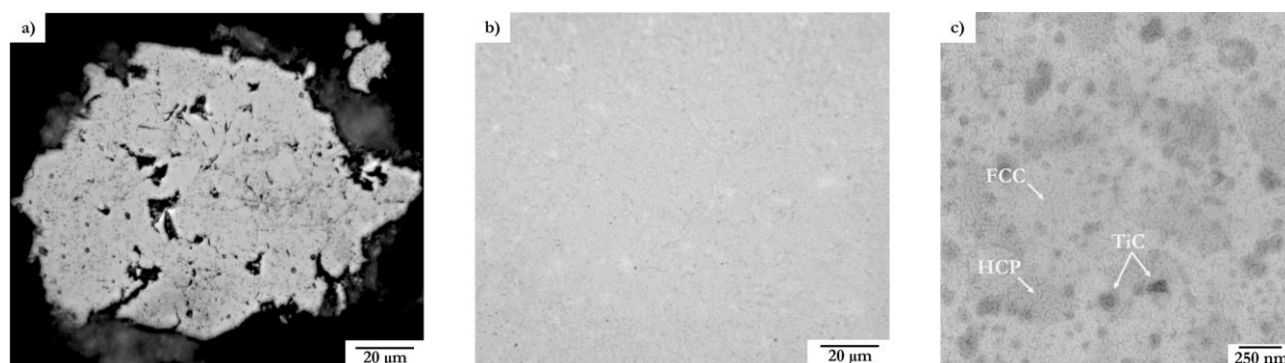

Fig. 4 Micrographs of the CoCrFeNiTi alloy showing: a) powder alloy after 8h MA (LM), b) compact alloy (LM), c) detailed insight of the compact (SEM)

The homogeneity of microstructure was further confirmed with SEM+EDS element distribution maps (Fig. 3). It can be seen that all elements are well distributed within the microstructure of the alloy. Furthermore, it was discovered that the slightly dark-grey places enriched in Ti could refer to a Laves phase or carbide particle. The chemical composition of little rounded particles (dark grey) present in the preview was not quantified due to their small dimensions and the physical limitations of the EDS detector. It can be presumed that they are pores whose presence was caused by etching.
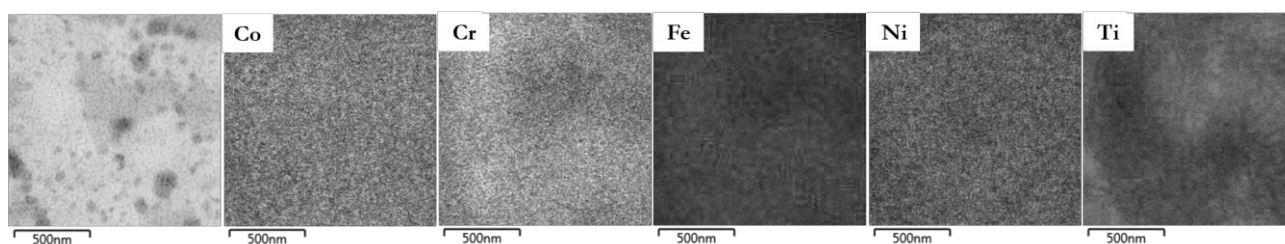

Fig. 5 SEM + EDS element distribution maps of compact CoCrFeNiTi

3.2 Mechanical properties

Fundamental investigation of the mechanical properties, including hardness, and compressive tests are summarized in Tab. 2. The alloy achieved a good hardness of 757 ± 18 HV 30 and an ultimate compressive strength of 1340 MPa.

Tab. 2 Mechanical properties of CoCrFeNiTi alloy

CYS [MPa]	UCS [MPa]	Compressive strain [%]	HV 30
-	1340	3.5	757 ± 18

Where:
CYS…Compressive yield strength,
UCS…Ultimate compressive strength,
HV…Vickers hardness.

Although it reached a good value of strength no plastic deformation occurred during the test pointing out a brittle behaviour of the alloy because of what the compressive yield strength could not be determined. Total compressive strain until the failure was 3.5 %. The brittle behaviour corresponds with the findings of Shun et al. [12] describing the influence of Ti content on the plasticity of the alloy. With increasing content of Ti (from 0 up to 11 at. %) within the alloy, the hardness of the alloy increased at the expense of ductility. On the other hand, the CoCrFeNiTi$_{0,5}$ alloy prepared with arc melting reached the hardness value of 515 HV 1, which is significantly lower than the value reached by the CoCrFeNiTi alloy prepared in this work. The reason for this is that with higher Ti content in the equiatomic alloy rises a volume fraction of a hard Laves phase, which contributes to the overall hardness as well as brittleness of the alloy. Higher Ti content with the combination of MA resulted in a well-refined microstructure reaching hardness by more than 200 HV higher. Among these results, the tribological properties of the material were examined. A profile of the worn track in the material is shown in Fig. 4 with a maximum depth of the track nearly

reaching 9 μm. The average value of a friction coefficient was 0.61 and it was stable during the measurement without bigger deviations. The wear rate of the sample reached $1.19 \cdot 10^{-4}$ mm³·N⁻¹·m⁻¹. The main factor of the wear was an adhesive mechanism, however, Laves phases and carbide particles loosened during the test probably intensified the wear with an abrasive mechanism which suggests the characteristic shape corresponding to intensive ploughing and formation of deep grooves.
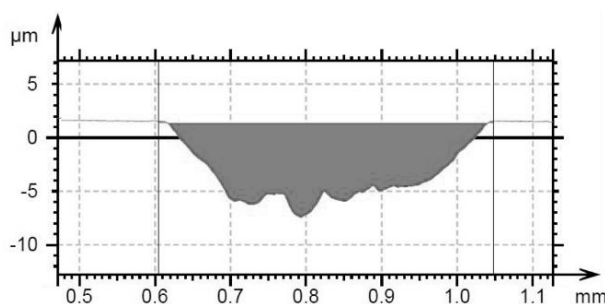

Fig. 6 *Profile of the worn track*

4 Conclusion

The compact CoCrFeNiTi alloy was successfully prepared using the combination of MA and SPS. The chosen fabrication route resulted in ultrafine-grained homogeneous microstructure with low porosity composed mainly of FCC solid solution with a small volume fraction of Laves phases. Besides the mentioned phases a really small amount of carbides was present which were formed due to the direct contact with graphite die during the SPS process. The alloy achieved a high hardness of 757 ± 18 HV 30 and UCS of 1340 MPa. The high content of Ti was the reason for the brittle behaviour of the alloy. The high hardness of the alloy resulted in good tribological properties of the material. The total wear rate was $1.19 \cdot 10^{-4}$ mm³·N⁻¹·m⁻¹ with the coefficient of friction reaching 0.61. The wear was mainly caused by the adhesive wear with the contribution of the abrasive mechanism.

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