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METAL MATRIX COMPOSITES PREPARED BY POWDER METALLURGY ROUTE
KOMPOZITY S KOVOVOU MATRICÍ PŘIPRAVENÉ CESTOU PRÁŠKOVÉ METALURGIE

DOCTORAL THESIS
DIZERTAČNÍ PRÁCE

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1 Introduction

Conventionally, the alloy design, alloy production, and alloy selection are almost strictly confined to single element based or one compound alloy concept [1]. Consequently, this alloy concept imposes a significant limit to the degrees of freedom in alloy’s composition and thus limits the development of special microstructure and properties. In the last decade, it has become particularly obvious that materials science and alloy engineering are still not fully explored due to an appearance of new class of alloys – usually called High entropy alloys (HEA) paying respect to the original work of J. W. Yeh and Cantor [1]. This exclusively new class of alloys caught significant scientific attention for the novelty of its approach to alloy design, as they do not contain a single base element, but rather at least 5 elements in very close atomic portions. HEAs became a base for the new group of alloys with concentrated solid solutions microstructures called Medium entropy alloys (MEA) that usually contains only 3 elements. HEAs and MEAs such as CoCrNiFeMn and CoCrNi, exhibit remarkable combinations of properties as presented in Fig. 1.

Fig. 1 Influence of temperature on tensile properties a fracture toughness of a, b) CoCrFeMnNi alloy and c, d) CoCrNi alloy, showing simultaneous increase in strength and ductility with decreasing temperature [Gludovatz, Nature 2014].

Composites are another group of materials which is gradually receiving substantial scientific and industrial attention. They represent combined materials containing at least two components with remarkably different properties. As such, they pose a way to solve some of the most challenging engineering problems [2, 3], where classic alloys meet their service limits.

The previously mentioned HEA systems could be produced by traditional casting manufacturing route. Powder metallurgy (PM) manufacturing route may be employed for these
alloys preparation as an additional method. Especially the combination of mechanical milling (MA) of elementary powder mixtures, followed by pressure or field assisted densification, has yielded the most promising results in the preparation of the full density high entropy materials [4]. The nature of PM process may solve several problems usually associated with traditional casting preparative, e.g. segregation problems, chemical heterogeneity etc. PM alloys usually possess higher strengths than their cast counterparts, stemming from fine grained microstructure [5]. PM manufacturing route is also possessing another advantage; namely relatively easy and efficient production of wide scope of advanced materials, including composites, that would be extremely demanding to produce by the conventional metallurgical methods [6].

Accordingly, the metal matrix composites with high or medium entropy alloy matrix phase can be produced. The creation of composite materials with HEA alloy as the matrix may result in a completely new branch of advanced materials.

In this manner, this work will be dedicated to study of feasibility and challenges of subsequent production of HEA and their respective composites by PM route as well as the property characterization of these materials.

2 Aim of the work

HEAs are unquestionably perspective materials for applications bearing a wide variety of interesting properties. In most cases these new materials are being manufactured by traditional casting procedures and studied in as cast state. However, due to relatively complicated chemical compositions, additional issues with casting may arise (elements segregation, structural inhomogeneity etc.). For instance, it is extremely complicated to prepare alloy containing high amounts of aluminum and chromium (melting point difference 1247 ºC). In this particular case, excessive evaporation of aluminum can take place; consequently the final chemical composition of the material may be significantly altered (especially in industrial scale production in induction or arc melting furnaces).

Consequently, powder metallurgy route may be an alternative way of production of various HEAs, with perfect chemical homogeneity and the abundance of casting defects. Additionally, powder metallurgy would enable a very feasible way of MMCs manufacturing with HEAs or MEAs as a matrix material. Therefore, the objectives of dissertation thesis were given as:

1. Investigate the aspect of mechanical alloying process for production of HEA powders
2. Confirm the possibility of production of ductile bulk HEAs and MEAs by powder metallurgy route, especially by the combination of mechanical alloying and spark plasma sintering.
3. Microstructural and phase characterization of produced materials
4. Characterization of basic mechanical properties of bulk materials (hardness, strength, ductility).
5. Explore the possibility of MMCs production with previously obtained HEAs or MEAs as a matrix material.
3 Experimental

3.1 Experimental materials preparation

All the experimental powder materials in this study were prepared by feedstock elemental powder processing by mechanical alloying (supplied by GTV VerschleibSchutz GmbH Germany and Sigma Aldrich with chemical purities over 99 wt. %). The process was carried out in an in-house made EN 1.2379 (X120CrMoV 12-1) hardened tool steel vial, into which the powders were sealed together with hardened EN 1.3505 (100Cr6) steel balls with 15 mm diameter. The sealed vial was then placed in a high energy planetary ball milling (Fritsch Pulverisette 6). The selected milling time was in range of 30-35 hours for all powders with 250 RPM milling speed. After the milling, the powder were removed from the milling vial and dried on air. The mechanically alloyed powders were subsequently densified by SPS technology to obtain bulk alloy materials. The parameters of mechanical alloying process and SPS utilized for the preparation of experimental materials were different for different composition as they were chosen according to processing parameters optimization. The SPS densification properties were selected in the interval of 950 – 1180 °C with the dwell time of 8-10 minutes. The SPS was performed in vacuum.

3.2 Methods of property characterization

Preparation of bulk and powder samples for microstructural observation was done by traditional grinding and polishing methods. Scanning electron microscopy (SEM) X-ray diffraction analysis (XRD), Transmission electron microscopy (TEM) Differential scanning dilatometry (DSC) methods has been used for phase and microstructural characterization. Subsequently, Vickers Indentation experiments, bending tests and tensile tests have been performed for mechanical characterization.

Vickers hardness measurements were performed according to ISO 6507-1:2005, Bending was then measured using three-point bending jig on Zwick Z020 universal tensile test machine, with the loading span of 18 mm and a crosshead speed of 1 mm.min-1 with samples had the dimension of approximately 22 × 6 × 4 mm. Samples were polished to mirror finish, to decrease the influence of surface roughness on the measured values. The 4 × 22 mm face of these samples corresponded to the direction perpendicular to the SPS pressing direction.

The tensile strength test was performed using cylindrical samples with a two different types of geometry. First geometry had a gauge length of 12.5 mm and 3.5 mm in diameter, tested with speed of 0.2 mm.min^{-1} (i.e., strain rate of 0.25 10^{-4} according to EN ISO 6892). Second geometry had a gauge length of 7.6 mm with 2 mm in diameter. Heat treatment experiments on AlCoCrNiFeNiTi_{0.5} alloy were executed with 2 hours dwell time on 1100 °C and 1250 °C. After the end of dwell time samples were removed and cooled in water to prevent phase changes.
3.3 AlCoCrFeNiTi$_{0.5}$ alloy

3.3.1 AlCoCrFeNiTi$_{0.5}$ alloy A bulk

The XRD pattern of the AlCoCrFeNiTi$_{0.5}$ alloy A prepared from powders milled with 250 RPM, 24 h and 15 mm balls is presented in Fig. 2b. The milled powder pattern is added for better comparison. Only the peaks attributed to a BCC solid solution phase with 2.87 Å lattice parameter (i.e. close to Cr and Fe) are visible in the milled powders.

Apparently, the BCC phase formed by mechanical alloying process is highly unstable, and upon high temperature exposure during SPS densification (short, but dramatic increase in diffusion rates), subsequent phase transformation to more stable products takes place; the mixture of 4 phases is observed in the bulk alloy pattern – B2 NiAl-like bearing lattice parameter of 2.89 Å phase with clearly visible superlattice (100) peak, a disordered FCC phase with lattice parameter of 3.59 Å, a tetragonal σ phase with a=8.81 Å, c=4.56 Å, and lastly an evident FCC structured phase closely resembling titanium carbide (TiC). As compared to milled powder pattern, the peaks are much sharper, suggesting the increase in crystallite size of the phases. The calculated volume fraction of phases by Rietveld method are 42.2 % of FCC phase, 42.3 % of B2 phase, 9.9 % of σ phase and 5.7 % of TiC.

![Fig. 2 – XRD pattern of a) AlCoCrFeNiTi$_{0.5}$ powder milled with 250 RPM, 24h and 15mm balls b) bulk alloy A after SPS](image)

The appearance of TiC phase is very interesting, especially considering that no intentional addition of carbon to the powders was made. Its presence is attributed to the addition of methanol (CH$_3$OH) to the powders as a PCA. During the milling process, methanol was most likely trapped between the powder particles that were cold welded together. Subsequently it decomposed and dissolved to the lattices of the powders. After the sintering, the high affinity of carbon to titanium resulted in the formation of the TiC phase.
As analyzed by SEM observations, full density material has been obtained by SPS with only few pores present.

The results of TEM observation and diffraction analysis (Fig. 3) are in good agreement with the results from XRD analysis. The microstructure is composed of the two major phases, i.e. FCC high entropy solid solution phase enriched in iron and chromium (visible as lighter contrast phase in SEM BSE micrographs) and an ordered B2 phase enriched in nickel and aluminum (darker grey phase). Small black dots correspond to nano-sized dispersion of in-situ formed TiC. In the SEM micrographs, it is impossible to distinguish tetragonal σ phase, due to its very close chemical composition with FCC phase, as seen in Table 1. However, its presence was revealed by electron diffraction (Fig. 3 e). As a consequence of powder surfaces contamination by air exposure, aluminum oxide particles were identified. From the present elements, aluminum has the highest affinity to oxygen. Therefore, other oxides present before milling on original elemental particles surfaces (chromium, titanium etc.), transformed during sintering to the oxide with highest thermodynamic stability - aluminum oxide.

Table 1 TEM EDS chemical composition of the phases present in AlCoCrFeNiTi0.5 A alloy after SPS (atomic %)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>1.8</td>
<td>0.7</td>
<td>26.3</td>
<td>31.3</td>
<td>24.6</td>
<td>15.4</td>
</tr>
<tr>
<td>B2</td>
<td>24.9</td>
<td>5.2</td>
<td>4.1</td>
<td>11.6</td>
<td>24.1</td>
<td>30.2</td>
</tr>
<tr>
<td>σ phase</td>
<td>-</td>
<td>-</td>
<td>26.4</td>
<td>34.6</td>
<td>31.8</td>
<td>6.1</td>
</tr>
</tbody>
</table>

![Fig. 3 TEM micrographs of AlCoCrFeNiTi0.5 bulk alloy A a), b) microstructure with marked phases](image)

**AlCoCrFeNiTi0.5 Bulk Alloy A Bending Test**

Room temperature bending strength (Rmb) was measured on 2 samples (2 of them in state after SPS, while the other 2 after heat treatment at 1250 °C). The summarization of results is presented in Fig. 4 and Table 2 respectively.
The first visible feature common for all bending curves is the absence of any plastic deformation before the fracture, which is typical for brittle fracture behavior. The samples were broken by cleavage in the elastic loading region as seen from stress – displacement curve (line).

The strength values of the first two specimens, corresponding to the state of alloy A directly after SPS exhibit extremely different values. This phenomenon is typical for materials with brittle fracture mode (similar to ceramic materials). It is associated with the defect driven fracture, as the crack growth occurs rapidly with small energy dissipation. Most probably, pore, or some other type of microstructural defect was present in sample 2, causing the premature failure.

Even if the values of bending strength are relatively high, the alloy A unfortunately exhibited unsatisfactory level of ductility, due to pure brittle fracture behavior.

Fig. 4 Stress – deflection curves from three-point bending test of AlCoCrFeNiTi<sub>0.5</sub> bulk alloy (the sample annotations 1-2 correspond to the ones illustrated in Table 2

<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>( R_{mb} ) (MPa)</th>
<th>( E ) (GPa)</th>
<th>Max. deflection (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 after SPS</td>
<td>1275</td>
<td>99.4</td>
<td>0.2</td>
</tr>
<tr>
<td>2 after SPS</td>
<td>820</td>
<td>98.4</td>
<td>0.156</td>
</tr>
</tbody>
</table>

3.4 **Co<sub>1.5</sub>Ni<sub>1.5</sub>CrFeTi<sub>0.5</sub> alloy**

The microstructure of the corresponding cast alloys from the previous studies [7] was presented as a mixture of FCC solid solution phase and an ordered \( \gamma' \) phase (L\(1\)\(_{2}\) lattice type) or \( \eta \) phase (D\(0\)\(_{24}\) lattice type). Therefore the alloy should provide adequate ductility derived from the presence of FCC solid solution and strength due to the dispersion of coherent intermetallic phase.
### 3.4.1 Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ alloy bulk

XRD patterns of the bulk Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ alloy after SPS densification are provided in Fig. 5 together with the XRD patterns of milled powder, that were utilized in sintering process. Upon high temperature exposure during SPS densification, the phases present in the powders were transformed to a thermodynamically more stable, FCC solid solution of all elements present within a single lattice bearing, parameter of 3.57 Å. The diffraction peaks are much sharper (as compared to the milled powders), suggesting an increase in the crystallite size.

As compared to cast alloys, the lower processing temperature of SPS densification caused the alteration of diffusion kinetics that may have resulted in different phase composition, as it was already observed in AlCoCrFeNiTi$_{0.5}$.

![XRD pattern](image)

**Fig. 5** XRD pattern of a) Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ MA powder b) Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ sintered bulk alloy

The microstructure of the alloy in BSE SEM mode is demonstrated in Fig. 6. The first striking microstructural feature visible on the images is the extremely fine grain size of the present, single FCC phase. The size of the most grains was measured to be well under 1 μm (as measured later by EBSD). Fine annealing twins are present within the grains, suggesting the possibility of low stacking fault energy (SFE) levels of the present FCC phase.

Second visible microstructural components are the black contrast dots. These black areas do not pertain to porosity, as 100% density of the bulk material was observed (no pores were observed by SEM and the density measured by Archimedes method exceeded 100 % of the theoretical one, that is 7.80 g cm$^{-3}$). Instead, they represent oxides with diverse sizes revealed by the EDS measurement to be mostly containing Al and Ti elements.

The extremely fine grain sized nature of the produced bulk alloy (later quantified by the EBSD) is the result of extreme grain. The processing time of SPS densification is short enough to prevent excessive grain coarsening during the high temperature dwell time. The oxide particles may have played a significant role in the grain growth suppression too, due to their pinning effect on moving grain boundaries.
FIG. 6 SEM micrographs in back scattered mode (BSE) of Co_{1.5}Ni_{1.5}CrFeTi_{0.5} bulk alloy in different magnification with Al and Ti oxide particles by red arrows

For more accurate determination of the phase composition and consecutive grain orientation and size analysis, EBSD measurement has been performed with the results presented in Fig. 7. The microstructure is composed of sole FCC phase grains (with corresponding Kikuchi diffraction pattern presented in Fig. 7 c), with lattice parameter matching the parameter measured by XRD analysis - 3.57 Å. The orientation map and attached pole figures reveal the lack of any preferential orientation of the FCC phase grains.

The determined average grain size is - as expected – extremely small, 1.05 μm. This value is on the boundary lying between the nano and fine-grained materials (1 μm is usually taken as the limit grain size, under which the materials are referred to as nano grained). The size distribution presented in Fig. 7 b is pointing out to relatively non–uniform grain size, e.g. 80% of the present grains is bearing the diameter bellow 0.5 μm, with few larger grains of higher diameter, that increase the total value of average grain size, calculated as a weighted average value.

A large volume of annealing twins was detected by the EBSD method as well. Twining boundaries with typical miss-orientation angle of 60° are highlighted by wider black lines in Fig. 7 a. It should be noted, that the apparent density of the twins appears somewhat lower with respect to the images in Fig. 6 b and d, as the finest twins are not highlighted due to resolution constraints.

For the purposes of deep microstructural analysis, especially focused on the evidence of the single phase nature of the bulk alloy, TEM observation has been performed. The results are demonstrated in Fig. 8. The observation confirmed the previous findings i.e. the microstructure of the alloy is composed of single FCC phase and oxide inclusions of diverse size and chemical nature.
Fig. 7 SEM EBSD analysis results of Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ bulk alloy representing a) color orientation map with pole figure revealing single phase FCC bulk material with twin boundaries denoted by black lines showing no significant preferred orientation of grains b) grain size distribution c) diffraction pattern corresponding to FCC phase.

The observed oxides may be divided in two categories (observed by both, SEM and TEM). Grain boundary oxides and the oxides dispersed inside the FCC grains, respectively. Grain boundary oxides are in general much coarser. The reason for this is the significantly higher diffusion flow on the grain boundaries as compared to the diffusion inside the grains. The higher diffusion rates generate more favorable condition for the consecutive coarsening of oxide particles during the high temperature exposure. On the contrary, the oxides present inside the individual grains form homogenous dispersion of extremely fine particles (highlighted by yellow circular area in Fig. 8 b). Such particles act as obstacles for the movement of dislocations i.e. provide Orowan strengthening effect. The arrangement of dislocation loops pinned on the oxide particles is observed on several places in the microstructure (denoted by red arrows in the images of Fig. 8).
As observed by TEM EDS analysis, the microstructure is chemically very homogenous with all elements evenly distributed in the FCC grains. The oxides of diverse sizes present in the microstructure are revealed to contain Ti and Al elements – corresponding to SEM findings. The higher fraction of oxide particles belongs to Ti.

![TEM micrographs](image)

Fig. 8 TEM micrographs of Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ bulk alloy with dislocation loops and nano-size twins denoted by red and yellow arrows respectively a), c) FCC grain microstructure b) oxide dispersion in coarser FCC grain d) dark contrast image with denoted twins starting on grain boundary

**Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ alloy tensile test**

The good level of ductility possessed by the alloy observed during the bend test enabled to assess the alloy on the account of its performance in regular tensile test. The measurement of tensile properties provides a credible data readily comparable with the commercial alloys, and other HEA systems as well.

The excellent strength properties, in combination with good ductility (for the materials of this strength level) originate from combination of strengthening mechanisms present in the material. The most pronounced effect on the increase in strength should originate from the extremely fine grain size of the material. The inherently ductile, fine grained FCC phase provides
the ductility, while the significant amount of grain boundaries acts as obstacles for the consecutive dislocations movement during mechanical loading and thus provide increased strength. Due to high value of atomic size misfit $\delta$ (5.04 %), FCC phase should possess high strength on its own accord, as a consequence of extreme substitutional strengthening – inherent property to all single phase HEAs. The presence of hard oxides particles should also play a role in the high strength properties directly thanks to Orowan strengthening mechanism, and indirectly by the grain growth suppression.

Strain hardening coefficient determined by usual hardening analysis has relatively low value of 0.11. Low strain hardening is also exhibited by relatively small difference in the respective values of $R_{p0.2}$ (0.2% proof strength) and ultimate tensile strength $R_m$: only 76 MPa. The reason for this behavior is that the alloy is already extensively strengthened prior to mechanical testing (as proved by the high $R_{p0.2}$ value of 1308 MPa). The already high proof strength of the alloy has a deleterious effect on any additional strain hardening, as the dislocation density is already high (dislocation forming the grain boundaries as well as GNDs around oxides), with the new dislocations formed during tensile test unable to pass through the lattice.

Fig. 9 representative engineering stress – strain curves from tensile test of Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ bulk alloy at room temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{p0.2}$ (MPa)</th>
<th>$R_m$ (MPa)</th>
<th>Elastic modulus $E$ (GPa)</th>
<th>Elongation to fracture $\varepsilon_f$ (%)</th>
<th>Strain hardening coefficient $n$ (1)</th>
<th>Reduction $Z$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1308</td>
<td>1384</td>
<td>216</td>
<td>4.01</td>
<td>0.11</td>
<td>5.04</td>
</tr>
</tbody>
</table>
Fig. 10 demonstrates the results of the fractographic and microstructural analysis of the ruptured tensile specimen. In general, the features observed on the fracture surface are identical (Fig. 10 a, b, c) with the previously presented bending test samples. The initiation site of the starting crack, denoted by red arrow in Fig. 10 a, is located on the surface of the specimen. The sample exhibited a rather ductile fracture behavior, as the fracture dimples are observed again on the whole fracture surface.

The microstructure of the polished cross section of broken tensile specimen from the vicinity of the crack reveals the extensive level of localized plastic deformation near in the vicinity of the crack (presented in Fig. 10 e). The original microstructure with well-defined fine grain boundaries prior to tensile testing has been broken down to such extent, that the original grain boundaries are not visible. The white – dark contrast in the BSE mode suggests the extensive dislocation activity, taking place before the onset of cracking. Fine deformation twins are present at several places of the sample (denoted by yellow arrow in Fig. 10 e). In particular, the area delimited by an yellow rectangle shows a place, plastically deformed by dislocation glide (visible from dark – white – grey contrast from left to right) crossed by a number of twins with the same direction. The green arrow is pointing out to a long deformation twin, connected to multiple shorter deformation twins with different orientation – suggesting, that at least two separate twinning systems has been activated. The yellow arrow in the Fig. 10 e points out to the place, where the several smaller twins are crossing longer twin with different orientation. In this particular case, it seems that the twins are not able to penetrate each other, which may serve as an additional strengthening phenomenon contributing to the overall strength of the alloy. The analysis of the deformation twins has not been carried out due to the resolution constraints of the SEM EBSD method as a consequence of their extremely small thickness.

It seems that the plastic deformation in the alloy is carried out by a combination of dislocation glide and deformation twinning. In the most deformed FCC grains dislocation structures formed by both dislocation glide and deformation twinning are observed [8]. The grains that were in less favorable orientations are deformed only by the usual dislocation glide. The deformation twining explicitly acts as an additional deformation mechanism, activated at higher strain levels.

The black dots present in the microstructure, corresponding to oxide inclusions, appear to be well bonded to the FCC matrix, as there is no visible decohesion or crack initiation on the oxide/FCC grain boundaries in the severely plastically deformed material, as observed in the bend test specimen previously.
Fig. 10 SEM micrographs of a, b, c) fracture surfaces of Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ bulk alloy tensile specimen, initiation site location is denoted by red arrow d) view of the polished section perpendicular to fracture surface of specimen e) the deformed microstructure from the vicinity of the crack in with twins denoted by yellow arrow

3.5 CoCrNi alloy

The alloy composition selected for this study has been utilized with the respect to previous studies on cast materials, presented in the literature, that are pointing out to the tremendous potential of the alloy [9]. Thereby, the production of this alloy by PM route has been studied.

3.5.1 CoCrNi alloy bulk

The results of XRD analysis of the bulk CoCrNi alloy after SPS densification are provided in Fig. 11 together with the patterns of the milled powders, before the start of the sintering process. The major phase was an FCC solid solution with lattice parameter of 3.57 Å comprising 94.4 % of the bulk microstructure. In contrast to the expectations of pure single face microstructure, the minor BCC solid solution with 2.90 Å lattice parameter and 5.6 % fraction appeared as well. The
peaks of the phases are much sharper and thinner as a consequence of bigger crystallite sizes. The Co-based HCP phase, observed in the milled powders, was not detected in the XRD pattern, as Co element probably dissolved in FCC solid solution.

Calculated values of $\delta$, $\Delta H_{\text{mix}}$, $\Delta S_{\text{mix}}$, $\Omega$ and VEC are 0.36 %, -4.8 kJ mol$^{-1}$, 9.13 K$^{-1}$ mol$^{-1}$, 3.53 and 8.33 respectively (formation of single solid solution microstructure predicted for $\delta \leq 4$ %, $-10 \leq \Delta H_{\text{mix}} \leq 5$ kJ.mol$^{-1}$, $\Delta S_{\text{mix}} > 13.38$ J.mol$^{-1}$ and $\Omega > 1$). Theoretical density calculated by rule of mixture of CoCrNi composition is 8.28 g cm$^{-3}$. Considering the parameters, the formation of additional phase may have been expected – the value of $\Delta S_{\text{mix}}$ didn’t reach the proposed minimum. It is an inevitable consequence of the alloy composition, provided that only three elements (Co, Cr and Ni) do not sufficiently increase the $\Delta S_{\text{mix}}$ values.

Fig. 11 XRD pattern of a) CoCrNi mechanically alloyed powder b) CoCrNi sintered bulk alloy

Fig. 12 reveals the microstructures of the bulk CoCrNi alloy. The bulk material was densified to full density, i.e. no porosity has been observed throughout the whole cross-section. However, the density measured by Archimedes method reached 99 % of the theoretical given by the rule of mixture (not 100 %). This small discrepancy is caused by accuracy and scatter of the Archimedes method, as well as the inaccuracy of the calculation by the rule of mixture, that does not take in account the difference in lattices of used elements.

Layers of different phases or elements, that were present in the powder particles before the SPS were not observed, as mentioned in the preceding paragraph.

The most of the microstructure is composed of the grains corresponding to the major FCC phase, with high density of very fine annealing twins. The secondary phase observed solely at the FCC grain boundaries (denoted by red arrow in Fig. 12 c) should correspond to minor BCC phase detected by in the XRD patterns. The phase was too small to perform reliable accurate EDS measurement, however it seems it contains Cr as the base element. Considering the morphology
and the emplacement of the phase, it is almost certain that it formed by the secondary precipitation process from the parental FCC phase. It is not clear if it formed during dwell time on the sintering temperature or the subsequent cooling after the SPS process. It seems that the later should be the best assumption, as the cooling time of the hot graphite die in the vacuum chamber of the SPS machine (reduced heat transfer conditions) is by far longer, that relatively short heating and dwell time - see paragraph.

The black dots present in the microstructure in Fig. 12 b, c pertain to oxide particles. Their size distribution is relatively wide. The ones possessing the largest sizes are usually observed on the grain boundaries, as they naturally represent areas, where the diffusion kinetics is greatly enhanced, with respect to the rest of the microstructure. The oxides measured by the EDS analysis corresponded to the Cr and Al based oxides. The origin of the oxide phases in the microstructure is similar to the origin of oxides in Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$ alloy - they emerge as a consequence of the surface contamination of elemental powders by air atmosphere prior to start of milling process. Subsequently they remain in the milled powders and produced bulks due to their high thermal and chemical stability.

Consecutive EBSD analysis has been performed to better evaluate the grain size of the major FCC phase. The average grain size of the major FCC phase was determined to be 4.11 μm (size distribution in Fig. 13 b). The grains do not show any preferential orientation, similarly as in the case of Co$_{1.5}$Ni$_{1.5}$CrFeTi$_{0.5}$. However even though the same processing equipment was used, the average grain size is almost 4-times larger.
Fig. 13 SEM EBSD analysis results of CoCrNi bulk alloy representing a) color orientation map with pole figure revealing FCC phase with twin boundaries denoted by black lines showing no significant preferred orientation of grains b) grain size distribution c) diffraction pattern corresponding to FCC phase

On one hand, the increased grain size may be the influence of increase in sintering temperature (30 °C). On the other, the presence of only three elements i.e. decrease in configurational entropy could decrease the sluggish diffusion effect in the CoCrNi alloy. Due to the very small size, the intergranular minor phase has not been detected, due to the resolution limit of performed EBSD analysis as well as the oxide phases.

To better evaluate the nature of the microstructure and BCC intergranular phase, TEM analysis has been carried out, with the results present in Fig. 14. Dislocations pinned by oxide particles are denoted by red arrow, suggesting pronounced effect of dispersion strengthening. The annealing twins present in the microstructure of the SPSed CoCrNi alloy are extremely fine, much finer as compared to Co1.5Ni1.5CrFeTi0.5 alloy - pointing out to relatively lower values of SFE of CoCrNi alloy. Additionally, notable feature was observed in the TEM imaging (denoted by green arrow in Fig. 14 b). The feature may represent the stacking fault parallelepiped, as observed previously by Zhang in CoCrFeMnNi high entropy alloy [10]. This volume structural defect is
supposed to be formed by the simultaneous movement of partial dislocations on two active \{111\} planes and their subsequent intersection, forming an obstacle around which entangling of dislocations occurs. This defect structure should be retarding the dislocation movement, and thereby increasing the strength and strain hardening capacity of the alloy [10].

Fig. 14 TEM micrographs of a) FCC grains containing dislocation arrays pinned by oxides (red arrow) and very fine twins (yellow arrow) b) dislocation networks pinned by oxide particles and stacking-fault parallelepiped structure (denoted by green arrow) formed by slip on multiple 111 planes c) single FCC grain containing d) corresponding SAED pattern of FCC phase in 011 pole axis

The intergranular phase TEM analysis is presented in Fig. 15. The phase is denoted by green arrow at the grain boundaries of the major FCC phase grains. The selected area diffraction pattern analysis of the feature (presented in Fig. 15 b with elemental mapping in c) revealed the phase is bearing a BCC crystal lattice. The phase possesses chemical composition of almost pure Cr element, as observed by the point EDS measurement and corresponding elemental mapping. The chemical composition and lattice of the phase perfectly corresponds to the nature of Cr-based BCC phase revealed previously by XRD and SEM analyses.
Fig. 15 TEM analysis of BCC phase that precipitated at FCC grain boundaries a) image micrograph of the precipitate (denoted by green arrow) with corresponding point EDS composition measurement b) corresponding SAED pattern in 111 pole axis revealing BCC lattice c) EDS elemental distribution maps

CoCrNi alloy tensile test

Room temperature tensile strength was measured on 3 samples only with results presented in Fig. 16 with samples of 7.6 mm gauge length. The CoCrNi alloy exhibited an excellent combination of tensile strength and ductility. The very low scatter of the presented values is especially worth mentioning, pointing out to very a good homogeneity of the obtained bulk material throughout the whole cross section. The values of elastic constants $E = 222$ GPa and $\nu = (0.30 \pm 0.01)$ were obtained from the resonant ultrasound spectroscopy measurements (RUS), not from the tensile testing procedure, for increased accuracy of the method. The strain hardening exponent values showed a smooth change from 0.1 to 0.28. The strain hardening rate changed smoothly, without any sudden discontinuities, suggesting no sudden change in deformation mechanism. Therefore, deformation twinning and dislocation slip is probably employed simultaneously, depending on the grain orientations.

SEM fractographic analysis of the ruptured tensile specimens is displayed in Fig. 17. Almost typical ductile fracture behavior was observed, i.e. fracture process initiated approximately in the geometrical middle of the tensile specimens and ended with shear tearing at the specimen edges, denoted by red arrow. Nucleation, growth and coalescence of fine microvoids is responsible for the morphology observed in Fig. 17 b and c. Oxide inclusions were located in the middle of majority of the ductile dimples as illustrated by yellow arrow. In Fig. 17 d, e and f, polished cross-section of broken tensile specimen is presented. The microstructure from the vicinity of fracture surface is showing signs of significant dislocation activity, as a consequence of plastic deformation process that is usually most extensive near the crack tip. Dislocation cells were formed by the dislocation pile – up, as observed by the change of dark grey / light grey contrast in the Fig. 17 e, d (denoted by green arrow).
Fig. 16 Representative engineering stress - strain curve from tensile test of CoCrNi bulk alloy at room temperature

Table 4 Average tensile strength test results of CoCrNi bulk alloy

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{p0.2}$ (MPa)</th>
<th>$R_m$ (MPa)</th>
<th>Elastic modulus E (GPa)</th>
<th>Elongation to fracture $A_t$ (%)</th>
<th>Strain hardening coefficient $n$ (-)</th>
<th>Reduction $Z$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td>652±0.58</td>
<td>1024±6</td>
<td>222</td>
<td>25.9±0.7</td>
<td>0.1 – 0.28</td>
<td>21.5±1.4</td>
</tr>
</tbody>
</table>

3.6 CoCrNi / boride

Fig. 18 depicts the representative microstructures of the CoCrNi / boride composite. The microstructure is not completely porous free – most probably a consequence of lower sintering temperature and different SPS setup (sintering temperature of 950 °C only was used as compared to 1180 °C for CoCrNi due to problem with powder melting if higher sintering temperatures were tested). The lower processing temperature is probably a reason for the obtained extremely small grain size. The grain size could have been further suppressed by present borides and oxides. The microstructure is composed of FCC phase grains, with significant amount of Cr$_5$B$_3$ boride and remaining carbides. The grains of the Cr$_5$B$_3$ are located between the FCC grains and compose around 30 volume % of the microstructure (as measured by the image analysis). Even though only 7.5 volume % of B$_4$C was added, the reaction with Cr caused, that the total volume amount of Cr$_5$B$_3$ is higher. The black dots (denoted by green arrow) located on the grain boundaries of all phases were determined to be oxides and carbides. Oxides formed as a consequence of powder contamination by oxygen. The carbides probably appear in the microstructure due to the reaction of remaining C from B$_4$C with chromium.

The measured hardness of the microstructure is 467 HV0.3 – evidently higher than 303 HV for the pure CoCrNi bulk alloy.
CoCrNi / boride composite tensile test

Ultimate Tensile stress ($R_m$) of the composite was measured at room temperature. The evaluation of results is presented in Table 5 and Fig. 19 respectively. The presence of Cr$_5$B$_3$ boride particles resulted in the dramatic increase of tensile strength properties (as compared to pure CoCrNi); the values of both yield strength $R_{p0.2}$ and ultimate tensile strength $R_m$ are surpassing 1400 MPa. However, very low strain hardening is also observed where the difference in the measured values of $R_{p0.2}$ and $R_m$ reached 7 MPa only. The total ductility value has been significantly reduced – it reached only 1.86 % as a consequence of the pronounced strengthening. The elastic modulus determined from elastic part of tensile curve remained relatively unchanged as compared to the pure CoCrNi alloy. It seems that the appearance of boride particles did not have significant influence on elastic properties.
Fig. 18 SEM micrographs in BSE mode of CoCrNi/boride bulk composite showing FCC grains denoted by yellow arrow, Cr$_5$B$_3$ boride particles denoted by red arrow and oxides by green arrow respectively.

Fig. 19 engineering stress – strain curves from tensile test of CoCrNi/ $B_4C$ composite at room temperature.
Table 5 Average tensile strength test results of CoCrNi / boride composite bulk alloy

<table>
<thead>
<tr>
<th>Sample</th>
<th>R_p0.2 (MPa)</th>
<th>R_m (MPa)</th>
<th>Elastic modulus E (GPa)</th>
<th>Elongation to fracture A_t (%)</th>
<th>Reduction Z (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1425</td>
<td>1432</td>
<td>226</td>
<td>1.86</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The fracture was initiated on the relatively large, brittle particle (as compared to the rest of microstructural features). The EDS analysis revealed that the particle is composed almost solely of pure Cr element. Most probably, some small amount of Cr element particle has not been milled, and remained in the microstructure, same as in the case of Co_{1.5}Ni_{1.5}CrFeTi_{0.5}. Apart from the crack initiating inclusion, the morphology of the fracture surface is a mixture of ductile and brittle fracture behavior. The surface is composed from very fine ductile dimples, formed by adjacent microvoids coalescence, but without visible inclusions present at the dimple bottoms. However, the fracture surface contains ridges retracting towards the fracture initiation site – typical for brittle fracture behavior. In general, considering the low value of tensile ductility, the fracture should be referred to as brittle in nature with transgranular character.

In spite of that, the absence of hard boride particles or other ceramic particles in the bottoms of the dimples suggests that the dimples formed predominantly by ductile tearing of FCC phase i.e. not by FCC / boride interphase decohesion. Probably, the dimples formed and subsequently grew at the places of the highest stress concentration triaxiality between narrowly spaced angular boride particles [11]. At such places, the local stress overcomes the cohesive strength of the FCC phase and new free surface in the form of void is created. The cohesive strength of the FCC phase atoms is evidently lower that the interphase cohesive strength between boride and FCC phase. Therefore, the interphase between in situ formed Cr_{3}B_{3} borides must be inherently strong, which is the basic requirement for ductile composites with high ceramic content.

4 Discussion

In the presented study, various issues considering the preparation and feasibility of HEA alloys, as well as MMCs with HEA as a matrix phase production by the means of PM manufacturing route has been investigated. The microstructures, response to mechanical loading and other selected properties of these progressive materials were characterized, to evaluate their potential for future development and application. In the following paragraphs, the main findings of the work will be discussed, regarding the varied prospects of the topic and the field.

4.1 Comparison of the mechanical properties

PM AlCoCrFeNiTi_{0.5} shower rather poor mechanical properties, compared to the rest of the produced materials. Considering all its properties, it seems that the alloy could find an application as the tool material, either used as a bulk, or coating. For the application as a traditional, load bearing structural material, the ductility and damage resistance properties does not seems satisfactory at the moment, in the light of results obtained herein and the published works [3, 12, 13].
The comprehensive comparison of the mechanical properties obtained by tensile test of the PM alloys \(\text{Ni}_{1.5}\text{Co}_{1.5}\text{CrFeTi}_{0.5}\), \(\text{CoCrNi}\) and \(\text{CoCrNi/boride}\) composite produced in this work, with the available published results of alloys produced by casting is presented in Fig. 20 - the data for comparison has been taken from references [9, 14-25].

It is obvious that in terms of room temperature tensile properties, many of the HEAs easily outperform the steels. In addition, they usually possess excellent secondary properties, especially corrosion resistance given by the passivating influence of Cr and Al element in their compositions.

Comparing the properties of the produced PM \(\text{CoCrNi}\) and PM \(\text{Co}_{1.5}\text{Ni}_{1.5}\text{CrFeTi}_{0.5}\) alloy, one can see that the latter possesses much higher strength properties, but its ductility is significantly lower. In fact, the whole set of available results from mechanical testing are supporting this claim, especially the fractographic analysis. The increase in the strength is most probably associated with multiple strengthening phenomena acting concurrently. One of them emerges from the average grain size of the \(\text{Co}_{1.5}\text{Ni}_{1.5}\text{CrFeTi}_{0.5}\) alloy being approximately \(\frac{1}{4}\) of the \(\text{CoCrNi}\). The significantly reduced grain size of the 5 elements alloy may be associated to slower diffusion kinetics – sluggish diffusion effect intrinsic to all HEAs, induced by the presence of 5 elements as compared to only 3 in \(\text{CoCrNi}\). The increase in grain size should not be notably affected by the slightly higher sintering temperature used for \(\text{CoCrNi}\) alloy preparation, as the total difference was only 30 °C.

Another phenomenon greatly affecting the total strength is much more pronounced atomic size mismatch \(\delta\) - 5.04% of \(\text{Co}_{1.5}\text{Ni}_{1.5}\text{CrFeTi}_{0.5}\) alloy, in contrast to \(\delta\) value of 0.36% in 3 element \(\text{CoCrNi}\) alloy.

The introduction of hard boride particles of in-situ formed \(\text{Cr}_5\text{B}_3\) - result of \(\text{B}_4\text{C}\) reaction with present Cr – caused more than two-fold increase in the ultimate tensile strength and hardness of PM \(\text{CoCrNi} / \text{boride}\) composite, but notably decreased the total elongation i.e. to only 1.86%.
However, it is very interesting to note that the interface between the reinforcement boride and the matrix FCC phase exhibited very high bonding strength, as no direct interfacial decohesion has been observed in fracture surfaces. Instead, the ductile tearing of the FCC matrix phase has been observed, probably at the places of high stress triaxiality, which is a requirement for ductile fracture behavior [11].

The $\text{Co}_{1.5}\text{Ni}_{1.5}\text{CrFeTi}_{0.5}$ is closely matching the CoCrNi / boride composite in terms of strength. On the other hand it exhibits the tensile elongation exceeding 4 %. Therefore, in the overall comparison, the $\text{Co}_{1.5}\text{Ni}_{1.5}\text{CrFeTi}_{0.5}$ alloy comes on top of all materials produced in this study.

5 Conclusions

The presented work has been focused on preparation and feasibility of production of medium and high entropy alloys and their composites by utilization of powder metallurgy processes; namely a combination of mechanical alloying and spark plasma sintering. The properties of the manufactured materials have been evaluated; with a special focus on their prospective mechanical response. The main results of the work can be summarized as follows:

1. The HEAs and MEAs powders with extremely fine crystallite sizes can be produced by mechanical alloying of elemental powders.
2. The presence of process control agent containing carbon is important to prevent agglomeration of powders. However, it may cause the formation of in-situ carbides after mechanical alloying.
3. The mechanically alloyed powders can be readily densified to full density bulk materials by spark plasma sintering process.
4. The manufactured bulks possess very fine grain sizes and isotropic properties.
5. The oxides present at the surfaces of powders are retained and produce homogenous dispersion after the mechanical alloying process that is retained in the final bulks.
6. The best mechanical properties have been attributed to the $\text{Co}_{1.5}\text{Ni}_{1.5}\text{CrFeTi}_{0.5}$, exhibiting the ultimate tensile strength $R_m$ of 1384 MPa and 4% of tensile elongation.
7. For the use as a matrix for composite materials, the PM CoCrNi alloy possessed best properties with ultimate tensile strength $R_m$ of 1024 MPa and 26% tensile elongation (as compared to reported $R_m$ of 890 MPa and 72% in wrought state).
8. CoCrNi alloy reinforced by in-situ formed Cr boride exhibited an exceptional increase in strength properties at the expense of plasticity.

References:


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- General work in powder metallurgy field,

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- Origin Lab;
- DS Catia;
- DS Solid Work
Abstract

Conventionally, the alloy design, alloy production, and alloy selection are almost strictly confined to single element or one compound concept. Consequently, this alloy concept imposes a significant limit to the degrees of freedom in alloy’s composition and thus limits the development of special microstructure and properties. In the last decade, it has become particularly obvious that materials science and alloy engineering are still not fully explored due to an appearance of new class of alloys – usually called high entropy alloys (HEA). This exclusively new class of alloys caught significant scientific attention for the novelty of its approach to alloy design, as they do not contain a single base element, but rather at least 5 elements in very close atomic portions. In the recent years medium entropy alloys (MEA) appeared as a variant of HEAs with only three or four elements. The work is contributed to the research of feasibility of production of HEA and MEA alloys and composites by utilization of powder metallurgy (PM) manufacturing route, the combination of mechanical milling (MA) of elementary powders, followed by pressure or field assisted densification.

Altogether three compositions have been studied: AlCoCrFeNiTi0.5, Co1.5Ni1.5CrFeTi0.5 and CoCrNi, as well as B4C metal matrix composite (MMC) with CoCrNi as matrix phase. Deep microstructural and mechanical analyses including transmission electron microscopy and tensile testing have been performed. During the whole study, the problems with the contamination of powders with oxygen have been observed, however the oxides formed relatively homogenous dispersion in all manufactured materials and they did not impair significant mechanical property reduction.

AlCoCrFeNiTi0.5 exhibited relatively high hardness over 800 HV, but rather low ductility. The attempt has been made to improve the ductility with heat treatment procedure, but to no avail. The formation of in-situ TiC dispersion has been recorded, due to the utilization of carbon containing methanol as a process control agent during milling, that reacted with the present elemental Ti. In this manner metal matrix composite has been effectively produced. Additionally, the same procedure, the milling in the controlled amount of carbon containing medium, may be used also to produce other advanced composites with dispersion of in-situ formed TiC.

On the other hand, CoCrNi alloy possessed very high tensile ductility (26%) and ultimate strength over 1000 MPa. Microstructure was composed of major FCC phase and BCC precipitates. The CoCrNi alloy has been due to the high ductility chosen as the best candidate for the subsequent production of metal matrix composites. The introduction of B4C resulted in the displacement reaction of Cr element with B4C, resulting in the formation of Cr3B3 boride phase. The composite possessed nano-grained microstructure and high tensile strength over 1400 MPa. However, the tensile ductility decreased to 1.9%.

The AlCoCrFeNiTi0.5 alloy achieved the best combination of tensile ductility (4%) and remarkable strength over 1300 MPa, bearing pure FCC microstructure with extremely fine grain size.

Therefore, the PM production route has proven to be a feasible way for the production of HEAs and MEAs, as well as HEA and MEA based metal matrix composites with remarkable combination of mechanical properties. Furthermore, the utilization of PM process offers a control of microstructure features and material design freedom by a simple change of process parameters, unmatched by any other manufacturing method.
Abstract

Ve všeobecnosti, poznatky o design slitin, jejich výrobě a výběru legujúcich prvků sú omezené na slitiny s jedním základním prvkem. Tento fakt ale výrazně limituje možnosti a volnost výběru prvků pro dosáhnutí speciálních vlastností a mikrostruktúr. V posledních dekádach se ukázalo, že materiálová věda a inžinýrství nejsou ještě zdaleka prozkoumané v důsledku objevu nové třídy materiálů nazvané vysoko entropické slitiny (HEA high entropy alloys). Jejich objev upoutal pozornost vědecké komunity. Základní koncept pro jejich design je, že namísto jednoho, nebo dvou základních prvků obsahují minimálně 5 prvků v podobných atomových koncentracích. V posledních letech se objevilá skupina materiálů odvozená od HEA, nazvaná slitiny so strednou entropiou (MEA medium entropy alloys). Na rozdíl od HEA ale obsahují 3, nebo 4 prvky. Táto práca je věnovaná studiu přípravy a charakterizací HEA, MEA a jejich kompozitů s pomocí metod práškové metalurgie.

V této práci byly dohromady zkoumány tři kompozice: AlCoCrFeNiTi0.5, Co1.5Ni1.5CrFeTi0.5 a CoCrNi, kompozity s kovovou matricí (MMC metal matrix composites) vyztužené částicemi B₄C s CoCrNi jako matrici. Hloubková mikrostruktúrní a mechanická analýza těchto materiálů byla provedena pomocí metod rastrovací a transmisní elektronové mikroskopie spojené s tahovými a ohybovými zkouškami. V průběhu celé studie se objevovaly problémy s kontaminací kyslíkem, co se projevilo vznikem značného množství oxidů v připravených materiálech.

U slitiny AlCoCrFeNiTi0.5 byla naměřena tvrdost přesahující 800 HV. Její houževnatost ale byla velice omezena. V její mikrostrukturu byly identifikovány částice in-situ TiC v důsledku přítomnosti organického, anti-aglomeráčního činidla (metanolu) v mleci misce. Tato reakce může být použita v budoucnu k přípravě MMC se záměrnou disperzí TiC.

Na druhé straně, slitina CoCrNi ukázala vysoké hodnoty tažnosti (26%) a meze pevnosti přes 1000 MPa. Mikrostruktura obsahovala majoritní FCC fázi s BCC precipitáty. Tahle slitina byla z důvodu vysoké tažnosti zvolena pro přípravu kompozitu s výztuží B₄C. V průběhu slinování ale došlo k reakci mezi přítomným Cr a B₄C, které výsledkem byl Cr₅B₃ borid. Tento kompozit mel pevnost v tahu 1400 MP a extrémne jemnozrnnou strukturu. Celková tažnost ale klesla na 1.9 %.

Slitina AlCoCrFeNiTi0.5, která mela strukturu složenou jen z FCC tuhého roztoku dosáhla nejlepší kombinaci mechanických vlastností s pevností přesahující 1300 MPa a dostatečnou tažností 4%.

Prášková metalurgie se ukázala jako vhodná metoda pro přípravu HEA a MEA slitin a jejich kompozitů, s dobrou kombinací pevnosti a tažnosti. Tato metoda dovoluje měnit mikrostruktúrní parametry připravených materiálů jednoduchou úpravou parametrů procesu.