STRUCTURE AND PHYSICAL PROPERTIES OF CAST AND SPLAT-QUENCHED CoCr$_{0.8}$Cu$_{0.64}$FeNi HIGH ENTROPY ALLOY†

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The article investigates the structure and physical properties of the multicomponent high-entropy alloy CoCr$_{0.8}$Cu$_{0.64}$FeNi in the cast and quenched state. The composition of the alloy under study is analyzed using the criteria available in the literature for predicting the phase composition of high-entropy alloys. These parameters are based on calculations of the entropy and enthalpy of mixing and also include the concentration of valence electrons, the thermodynamic parameter Ω, which takes into account the melting point, entropy of mixing, and enthalpy of mixing. Another important parameter is the difference in atomic radii between the alloy components δ. Cast samples of the CoCr$_{0.8}$Cu$_{0.64}$FeNi alloy of nominal composition were prepared on a Tamman high-temperature electric furnace in an argon flow using a copper mold. The weight loss during the manufacture of ingots did not exceed 1%, and the average cooling rate was ~ $10^5$ K/s. Thereafter, the cast ingot was remelted, and films were obtained from the melt. The splat quenching technique used in this work consisted of the rapid cooling of melt droplets when they collide with the inner surface of a rapidly rotating (~ 8000 rpm) hollow copper cylinder. The cooling rate, estimated from the film thickness, was ~ $10^6$ K / s. X-ray structural analysis was performed on a DRON-2.0 diffractometer with monochromatic Cu Kα radiation. Diffraction patterns were processed using the QualX2 program. The magnetic properties of the samples were measured using a vibrating sample magnetometer at room temperature. The microhardness was measured on a PMT-3 device at a load of 50 g. In accordance with theoretical predictions confirmed by the results of X-ray diffraction studies, the structure of the alloy, both in the cast and in the quenched state, is a simple solid solution of the FCC type. The lattice parameters in the cast and liquid-quenched states are 0.3593 nm and 0.3589 nm, respectively. Measurements of the magnetic properties showed that the CoCr$_{0.8}$Cu$_{0.64}$FeNi alloy can be classified as soft magnetic materials. In this case, quenching from a liquid state increases the coercivity. On quenched samples, increased microhardness values were also obtained. This can be explained by internal stresses arising during hardening.

Keywords: high entropy alloy, structure, phase composition, splat-quenching, microhardness, magnetic properties.

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The development of theories and technologies in the field of creating new materials has led to an increase in the number of elements in the composition of multicomponent alloys. In recent decades, a new class of metal compounds has been developed - the so-called multicomponent high-entropy alloys (HEAs) [1–3]. Such alloys contain at least five elements in equiatomic or close enough to equiatomic concentrations (usually from 5 to 35 at.%). The main feature of HEAs is the formation of single-phase, thermodynamically stable substitutional solid solutions with a cubic body-centered (BCC) or face-centered (FCC) lattice. Stabilization of the solid solution during crystallization is provided by the high entropy of mixing and enthalpy of mixing. Another important parameter is the difference in atomic radii between the alloy components δ.

Studies of HEAs have shown that they can form nanoscale structures and even amorphous phases [1-7]. This is due to significant distortions of the lattice, which are due to the difference in the atomic radii of the substitution elements. This also reduces the rate of diffusion processes, which decreases the growth rate of crystallites, which in turn leads to a fine crystalline structure.

Recently, it has been proposed in the literature to consider as HEAs only equimolar alloys in the structure of which there are exclusively simple solid solutions with crystalline lattices of BCC and FCC. For other alloys with high entropy but with non-equimolar component content or more complex phase composition, in which there are also ordered solid solutions and intermetallic compounds, it was proposed to introduce new terms, namely: multi-principal element alloys (MPEA), or complex concentrated alloys (CCA) [3]. However, at present, these terms are not yet common.

Casting methods are usually used as methods for producing high-entropy alloys. However, it should be noted that the formation of the structure of the solid solution, doped with many elements, should complicate the casting process, in particular, we can assume a heterogeneous distribution of elements, as well as the presence of significant internal stresses in the ingot. There is an obvious need to increase the number of melts to increase the homogeneity of the chemical composition and control the cooling rate during crystallization.

One of the widespread methods of improving the physical, chemical, mechanical and other properties of metals and alloys is quenching from a liquid state [8]. The development of quenching methods has led to a growing interest in materials with thermodynamically nonequilibrium structures worldwide. In these methods, the cooling rate of the melt reaches values above $10^4$ K/s, due to which a wide range of metastable structural states is formed in the alloys, including

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nanocrystalline and amorphous, with unique sets of properties [9]. Due to this, quenching from the liquid state is a promising method for obtaining high-entropy alloys with improved characteristics.

The properties of HEAs are determined by their elemental composition and structure. Due to the resistance to ionizing radiation, wear resistance, high hardness, and, at the same time, sufficient ductility, they can be promising materials for many fields of technology [10-17].

One of the possible applications of HEAs as not only structural but also functional materials is their use as magnetic materials. In work [18], using the density-functional theory (DFT) and a magnetic mean-field model, the possible ferromagnetic properties for a set of four- and five-component high entropy alloys were predicted. Some of these alloys look promising in terms of combining high mechanical and magnetic properties. Substances that combine the properties of several different types of materials have always been of considerable scientific interest [19,20]. This work aims to obtain a multicomponent high-entropy alloy CoCr0.8Cu0.64FeNi and to study the effect of rapid quenching from the melt on its phase composition, microhardness, and ferromagnetic properties.

EXPERIMENTAL DETAILS

The as-cast samples of CoCr0.8Cu0.64FeNi alloy with nominal composition presented in Table 1. were prepared by means of a Tamman high-temperature electric furnace in the argon gas flow using a copper mold.

Table 1. Nominal chemical composition of CoCr0.8Cu0.64FeNi alloy

<table>
<thead>
<tr>
<th>Composition of CoCr0.8Cu0.64FeNi, at. %</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.52</td>
<td>18.02</td>
<td>14.42</td>
<td>22.52</td>
<td>22.52</td>
</tr>
</tbody>
</table>

The mass losses during ingot preparation did not exceed 1% and the average rate of cooling was \( \approx 10^2 \) K/s. The as-cast ingot was thereafter remelted and the films were obtained from the melt by splat quenching (SQ) technique. A technique for splat quenching used in the present work consisted of rapid cooling of melt drops upon their collision with the internal surface of a rapidly rotating (~8000 RPM) hollow cylinder of copper. The cooling rate was estimated using the expression [8,21]

\[
V = \frac{\alpha \delta}{c \rho \delta},
\]

where \( c \) is the heat capacity of film, \( \rho \) is the film density, \( \alpha \) is the coefficient of heat transfer, \( \delta \) is the excess temperature of the film and \( \delta \) is the thickness of the film.

Taking into consideration the thickness of fabricated splat quenched films, i.e., ~40 \( \mu \)m, the estimated rate of cooling was ~10^6 K/s. The X-ray diffraction analysis (XRD) was carried out using a DRON-2.0 diffractometer with monochromatized Cu K\( \alpha \) radiation. The diffraction patterns were processed using QualX2 software [22]. The magnetic properties of the samples were measured by a vibrating sample magnetometer (VSM) at room temperature. The microhardness was examined using a tester PMT-3 at a load of 50 g.

RESULTS AND DISCUSSION

Electronic, thermodynamic and atomic-size criteria of phase formation in high-entropy alloys

There are two main criteria by which the high-entropy alloys are usually characterized. This is the entropy of mixing \( \Delta S_{mix} \) and the enthalpy of mixing \( \Delta H_{mix} \). However, to predict the phase composition of HEAs, some additional parameters were proposed [1-3]. These parameters include in particular the valence electron concentration (VEC), the thermodynamic parameter \( \Omega \), which takes into account the melting temperature, mixing entropy and the mixing enthalpy. The important parameter is an atomic-size difference between alloy components which is denoted as \( \delta \). Let's take a closer look at the above parameters.

The basic principle of HEAs is the solid solution phase stabilization by the significantly higher configurational entropy of mixing \( \Delta S_{mix} \) compared to conventional alloys. The configurational entropy of mixing during the formation of regular solution alloy can be determined as

\[
\Delta S_{mix} = -R \sum_{i=1}^{n} c_i \ln c_i,
\]

where \( c_i \) is the atomic fraction of the \( i \)-th component, \( R \) is the universal gas constant. Increasing of mixing entropy reduces the Gibbs free energy of the alloy and improves the stability of the solid solution. For the alloy where \( n \) is the number of components maximum mixing entropy is when they are mixed in equal atomic fractions.

Usually in HEAs \( \Delta S_{mix} \) value is in the range of 12-19 J/(mol·K). Due to the high mixing entropy HEAs are solid solutions typically having simple crystal structures (FCC or BCC), but to avoid the appearance of brittle intermetallic
compounds, complex microstructures and amorphous phases in the structure of alloys, some phase formation criteria are required to be completed. According to [1, 2], the \( \Omega \) parameter can be used to estimate the phase composition of HEA.

\[
\Omega = \frac{T_m \Delta S_{\text{mix}}}{\Delta H_{\text{mix}}},
\]

where \( T_m \) is the average melting temperature of alloy and \( \Delta H_{\text{mix}} \) - mixing enthalpy

\[
T_m = \sum_{i=1}^{n} c_i (T_m)_i,
\]

\[
\Delta H_{\text{mix}} = \sum_{i=1}^{n} \Omega_{ij} c_i c_j,
\]

where the regular melt-interaction parameter between \( i \)-th and \( j \)-th elements \( \Omega_{ij} = 4\Delta H_{\text{mix}}^{AB} \), and \( \Delta H_{\text{mix}}^{AB} \) - mixing enthalpy of binary liquid AB alloy. Alloy components should not have a large atomic-size difference, which is described by the parameter

\[
\delta = 100 \frac{\sum_{i=1}^{n} c_i \left( 1 - \frac{r_i}{\bar{r}} \right)^2}{},
\]

where \( \bar{r} = \sum_{i=1}^{n} c_i r_i \); \( r_i \) - the atomic radius of the \( i \)-th element.

According to [1,2] the HEA alloys for which \( \Omega \geq 1.1 \) and \( \delta \leq 6.6 \% \) can form the solid solutions without intermetallic compounds and amorphous phases. However, simple (not ordered) solid solutions form if \(-15 \text{kJ/mol} < \Delta H_{\text{mix}} < 5 \text{kJ/mol} \) and \( \delta \leq 4.6 \% \).

The other useful parameter is the valence electron concentration, \( VEC \), which has been proven useful in determining the phase stability of high entropy alloys [1,2]. \( VEC \) is defined by:

\[
VEC = \sum_{i=1}^{n} c_i VEC_i,
\]

where \( VEC_i \) - valence electron concentration (including the \( d \)-electrons) of the \( i \)-th element. As pointed in [1,2] at \( VEC \geq 8.0 \), the sole FCC phase exists in the alloy; at \( 6.87 \leq VEC < 8.0 \), mixed FCC and BCC phases will co-exist and the sole BCC phase exists at \( VEC < 6.87 \). It should be noted, however, that the exact boundaries of the valence electron concentration range, in which one should expect the formation of solid solutions based on BCC and FCC lattices are rather individual for each specific alloy. For example, the VEC criteria work on the assumption that solid solutions are the only constituents of the alloy, that is, no intermetallics or amorphous phases are formed [1,2]. In addition, the VEC criteria are most effective for HEAs containing mainly 3d or 4d transition metal elements [1,2]. Despite the above limitations, the empirical rules for predicting the phase composition of alloys are widely used in the literature and have recently been confirmed by the computational thermodynamic approach [23]. Using the data from [24], we calculated \( \Delta S_{\text{mix}}, \Delta H_{\text{mix}}, \delta, VEC, \) and \( \Omega \) of the CoCr0.6Cu0.64FeNi HEA (Table 2).

**Table 2.** Electronic, thermodynamic and atomic-size parameters of the CoCr0.6Cu0.64FeNi high-entropy alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( \Delta S_{\text{mix}}, \text{J/(mol·K)} )</th>
<th>( \Delta H_{\text{mix}}, \text{kJ/mol} )</th>
<th>( \Omega )</th>
<th>( VEC )</th>
<th>( \delta, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCr0.6Cu0.64FeNi</td>
<td>13.26</td>
<td>1.68</td>
<td>14.05</td>
<td>8.75</td>
<td>1.26</td>
</tr>
</tbody>
</table>

The analysis of these parameters shows that in CoCr0.6Cu0.64FeNi alloy the formation of a single-phase solid solution of the FCC type without intermetallic compounds should take place.

**Structure and properties of CoCr0.8Cu0.64FeNi high-entropy alloy**

The phase composition of the studied alloy and the crystal lattice parameters (Table 3) were determined from the XRD patterns (Fig. 1). An analysis of the X-ray diffraction patterns made it possible to establish the following: a single-phase FCC structure is formed in both cast and SQ samples. Thus, for this alloy, the consistency of the previously considered theoretical criteria for predicting the phase composition has been confirmed. We can also see that quenching from the liquid state does not change the phase composition of the CoCr0.8Cu0.64FeNi alloy.
Fig. 2 shows the magnetic hysteresis loops of the as-casted and splat quenched high-entropy CoCr$_{0.8}$Cu$_{0.64}$FeNi samples measured at room temperature. Both are characterized by typical ferromagnetic behavior. According to the values of coercivity $H_c$ of the samples (Table 4), they can be classified as soft magnetic materials. As can be seen from Fig. 2 and Table 4, the value of the specific saturation magnetization $M_S$ practically does not change with an increase in the cooling rate. This is because the magnetization $M$ of the alloy mainly depends on the composition and crystal structure, which are unchanged for both samples. At the same time, the coercivity value has doubled. Obviously, this is due to internal stresses arising in the material during quenching from the liquid state, as well as to the formation of a microcrystalline structure containing many defects and nanoprecipitates, which complicates the displacement of domain walls during magnetization reversal [25].

![Figure 1. XRD patterns of CoCr$_{0.8}$Cu$_{0.64}$FeNi high entropy alloy](image)

**Table 3.** The phase composition of CoCr$_{0.8}$Cu$_{0.64}$FeNi high entropy alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast CoCr$<em>{0.8}$Cu$</em>{0.64}$FeNi</td>
<td>FCC ($\alpha$=0.3593 nm)</td>
</tr>
<tr>
<td>SQ film CoCr$<em>{0.8}$Cu$</em>{0.64}$FeNi</td>
<td>FCC ($\alpha$=0.3589 nm)</td>
</tr>
</tbody>
</table>

![Figure 2. Hysteresis loops of as-cast (a) and splat-quenched (b) samples of CoCr$_{0.8}$Cu$_{0.64}$FeNi HEA](image)

**Table 4.** Magnetic characteristics of CoCr$_{0.8}$Cu$_{0.64}$FeNi high-entropy alloy

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Specific saturation magnetization $M_S$, A·m$^2$/kg</th>
<th>Coercivity $H_c$, A/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast CoCr$<em>{0.8}$Cu$</em>{0.64}$FeNi</td>
<td>35±3</td>
<td>120±10</td>
</tr>
<tr>
<td>SQ film CoCr$<em>{0.8}$Cu$</em>{0.64}$FeNi</td>
<td>32±3</td>
<td>240±20</td>
</tr>
</tbody>
</table>
Measurement of the microhardness of the SQ CoCr$_{0.8}$Cu$_{0.64}$FeNi alloy showed that the value of $H_p$ is higher than for the alloy in the as-cast state. (Table 5).

**Table 5. Microhardness of CoCr$_{0.8}$Cu$_{0.64}$FeNi high-entropy alloy**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$H_p$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast CoCr$<em>{0.8}$Cu$</em>{0.64}$FeNi</td>
<td>2200±100</td>
</tr>
<tr>
<td>SQ film CoCr$<em>{0.8}$Cu$</em>{0.64}$FeNi</td>
<td>2600±100</td>
</tr>
</tbody>
</table>

This result is not unexpected, since, taking into account the results of [21], it can be concluded that in the cast alloy in the process of segregation, a microstructure with typical morphology of dendrites and interdendritic joints is formed. In the structure of the SQ alloy, the structure of a thin conglomerate of phases is observed. Thus, the microstructure and mechanical properties of the as-cast alloy significantly differ in its more equilibrium multiphase state, while the splat quenched alloy provides higher values of hardness and strength due to internal elastic stresses.

It should be noted that the relatively low value of microhardness is specific for HEAs with an FCC lattice, which is characterized by plasticity and not very high values of hardness. At the same time, alloys with a BCC lattice have a much higher microhardness but are brittle.

**CONCLUSIONS**

In this work, a CoCr$_{0.8}$Cu$_{0.64}$FeNi high entropy alloy was obtained for the first time in the as-cast and splat quenched state. The studies carried out made it possible to establish that the alloy has an FCC structure, which is not affected by the cooling rate. The CoCr$_{0.8}$Cu$_{0.64}$FeNi HEA shows ferromagnetic properties, and quenching from a liquid state increases the coercivity practically without changing the magnetization value. An increase in the cooling rate also increases the value of the microhardness of the alloy. Thus, the splat quenched CoCr$_{0.8}$Cu$_{0.64}$FeNi alloy can be recommended for applications where the ductility characteristics of the FCC alloy together with increased microhardness values are important.

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**REFERENCES**

СТРУКТУРА ТА ФІЗИЧНІ ВЛАСТИВОСТІ ВИСОКОЕНТРОПІЙНОГО СПЛАВУ CoCr0.8Cu0.64FeNi У ЛИТОМУ ТА ЗАГАРТОВАНОМУ З РІДНИМІ СТАНАХ

О. І. Кушнерьов, В. Ф. Башев

У статті досліджено структуру та фізичні властивості багатокомponentного високоентропійного сплаву CoCr0.8Cu0.64FeNi у литому та загартованому стані. Склад досліджуваного сплаву проаналізували за використанням навіяних у літературі критеріїв для прогнозування фазового складу високоентропійних сплавів. Ці параметри базуються на розрахунках ентропії та енталпії, в яких включають концентрацію валентних електронів, термодинамічний параметр Ω, який враховує температуру плавлення, ентропію змішування та енталпію змішування. Ще одним важливим параметром є різниця в атомних радіусах між компонентами сплаву δ. Ліття зразки сплаву CoCr0.8Cu0.64FeNi номінального складу отримані за допомогою високотемпературної електричної печі Таммана в потоці аргону за допомогою мідної форми. Втрати ваги після част виготовлення злитків не перевищувала 1%, а середня швидкість охолодження становила ~ 10^2 К/с. Номінальний розплав отримували плявкі. Техніка гарчування з рідкого стану, використана в даній роботі, полягало в швидкому охолодженні крапель розплаву при зіткненні їх із внутрішньою поверхнею порожнього мідного циліндра, що обертався із великою швидкістю (~ 8000 об / хв). Швидкість охолодження, оцінена за товщиною плявкі, становила ~ 10^6 К/с.

Рентгенструктурний аналіз проводили на дифрактометрі DRON-2.0 у монохроматичному випромінюванні Cu Kα. Дифрактограми оброблялися за допомогою програми QualX2. Магнітні властивості зразків вимірювалися за допомогою вібраційного магнітометра при кімнатній температурі. Мікротвердість вимірювали на приладі PMT-3 при навантаженні 50 г. Відповідно до теоретичних прогнозів, підтверджених результатами рентгенівських досліджень, структура сплаву як у литому, так і в загартованому стані є простим твердим розчином типу ГЦК. Параметри решітки в літому та швидкоагартованому станах становлять відповідно 0.3593 нм та 0.3589 нм. Вимірювання магнітних властивостей показали, що сплав CoCr0.8Cu0.64FeNi можна класифікувати як магнітотяжкий матеріал. При цьому гарчування з рідкого стану збільшує коефіцієнтну силу зразків. На загартованих зразках також були отримані підвищені значення мікротвердості. Це можна пояснити внутрішніми напругами, що виникають під час гарчування.

Ключові слова: високоентропійний сплав, структура, фазовий склад, гарчування з рідкого стану, мікротвердість, магнітні властивості.