MICROSTRUCTURE, PHASE FORMATION, AND PROPERTIES OF MELT-QUENCHED $CoCr_{0.8}Cu_{0.64}FeNi$ HIGH-ENTROPY ALLOY

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This paper explores the $CoCr_{0.8}Cu_{0.64}FeNi$ high-entropy alloy. Different criteria, such as the valence electron concentration, the Ω parameter, and the atomic size difference δ, are used to estimate the phase composition of the alloy. As-cast samples of the alloy are made by melting the components in a high-temperature Tamman furnace in an argon flow and solidifying them in a copper mold. The weight loss during the ingot production is minimal, and the average cooling rate is about 10^2 K/s. Melt-quenched samples are made by remelting the cast ingot and rapidly cooling the melt droplets on the inner surface of a fast rotating (about 8000 rpm) hollow copper cylinder. The cooling rate, estimated from the film thickness, is about 10^6 K/s. X-ray diffraction is used to analyze the structure of the samples on a DRON-2.0 diffractometer with monochromatic Cu *Kα* radiation. Magnetometry is used to measure the magnetic properties of the samples at room temperature. The results confirm the theoretical predictions that the structure of the alloy, in both states, is an FCC solid solution. The lattice parameters in the as-cast and melt-quenched states are 0.3593 nm and 0.3589 nm, respectively. The results also show that the $CoCr_{0.8}Cu_{0.64}FeNi$ alloy is a soft magnetic material, but its coercivity and microhardness increase after quenching due to internal stresses.

Keywords: high-entropy alloy**,** microstructure, phase composition, melt-quenching, microhardness, magnetic properties.

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1. Introduction

High-entropy alloys (HEAs) are a new class of metallic materials that have attracted a lot of attention in recent years [1-4]. Unlike conventional alloys, which are based on one or two dominant elements with minor additions of other elements, HEAs consist of five or more elements in equal or near-equal proportions. 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 the components in the melt.

One of the widespread methods of improving the physical, chemical, mechanical and other properties of metals and alloys is quenching from a liquid state. The development of quenching methods has led to 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 nanocrystalline and amorphous, with unique sets of properties [5, 6]. Due to this, quenching from the liquid state is a promising method for obtaining HEAs with improved characteristics.

One of the possible applications of HEAs as not only structural but also functional materials is their use as magnetic materials. In work [7], 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. This work aims to obtain a multicomponent high-entropy alloy $CoCr_{0.8}Cu_{0.64}FeNi$ and to study the effect of rapid quenching from the melt on its phase composition, microhardness, and ferromagnetic properties.

2. Experimental details

The as-cast samples of $CoCr_{0.8}Cu_{0.64}FeNi$ alloy with a nominal composition of 22.52 at.% Co, 18.02 at.% Cr, 14.42 at.% Cu, 22.52 at.% Fe, and 22.52 at.% Ni were prepared with a Tamman high-temperature electric furnace in the argon gas flow using a copper mold. The mass losses during ingot preparation did not exceed 1% and the average rate of cooling was ~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 the 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 of the films was calculated from the film thickness as described in [21]. Taking into consideration the thickness of fabricated SQ films, i.e., ~40 µm, 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 *Kα* radiation. The diffraction patterns were processed using QualX2 [8] and Fityk [9] software. 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 100 g.

3. Results and discussion

In our previous works [6, 10], the parameters commonly used to predict the phase composition of high-entropy alloys were described. They include entropy of mixing of components ΔS_{mix}, enthalpy of mixing ΔH_{mix}, thermodynamic parameter Ω, topological parameter δ, which characterizes the difference in atomic radii of alloy components and concentration of valence (*s* + *d*) electrons per one atom (VEC).

As pointed out in [1, 2], the sole FCC phase exists in the alloy at VEC ≥ 8.0, mixed FCC and BCC phases co-exist at 6.87 ≤ VEC < 8.0, and the sole BCC phase exists at VEC < 6.87. We calculated ΔS_{mix}, ΔH_{mix}, δ, VEC, and Ω using the data from [18] (Table 1).

Table 1

Electronic, thermodynamic, and topological parameters of the $CoCr_{0.8}Cu_{0.64}FeNi$ high-entropy alloy

Alloy	ΔS_{mix}, J/(mol·K)	ΔH_{mix}, kJ/mol	Ω	VEC	δ, %
$CoCr_{0.8}Cu_{0.64}FeNi$	13.26	1.68	14.05	8.75	1.26

The analysis of these parameters shows that in $CoCr_{0.8}Cu_{0.64}FeNi$ HEA the formation of a single-phase FCC solid solution without intermetallic compounds should take place.

The phase composition of the studied alloy and the crystal lattice parameters (Table 2) were determined from the XRD patterns (Fig. 1). An analysis of the XRD patterns made it possible to establish the following: a single-phase FCC structure is formed in both cast and SQ samples. The lattice parameters in the as-cast and SQ states are 0.3593 nm and 0.3589 nm, respectively. 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 melt quenching does not change the phase composition of the $CoCr_{0.8}Cu_{0.64}FeNi$ alloy.

Typical dendritic structures were observed in the as-cast sample of $CoCr_{0.8}Cu_{0.64}FeNi$ HEA (Fig. 2 a). At the same time, the microstructure of the SQ film (Fig. 2 b) is a finely dispersed structure. Observed transformation may be explained by the following: increasing of cooling rate (up to 10^6 K/s) leads to the degeneracy of dendritic structure and formation of the plane front of crystallization with finely dispersed structure occurrence.

Both the as-cast and SQ samples of the $CoCr_{0.8}Cu_{0.64}FeNi$ HEA are characterized by typical ferromagnetic behavior. According to the values of coercivity H_c of the samples (Table 2), they can be classified as soft magnetic materials. As can be seen from Table 2, thevalue 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 melt, 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 [4].

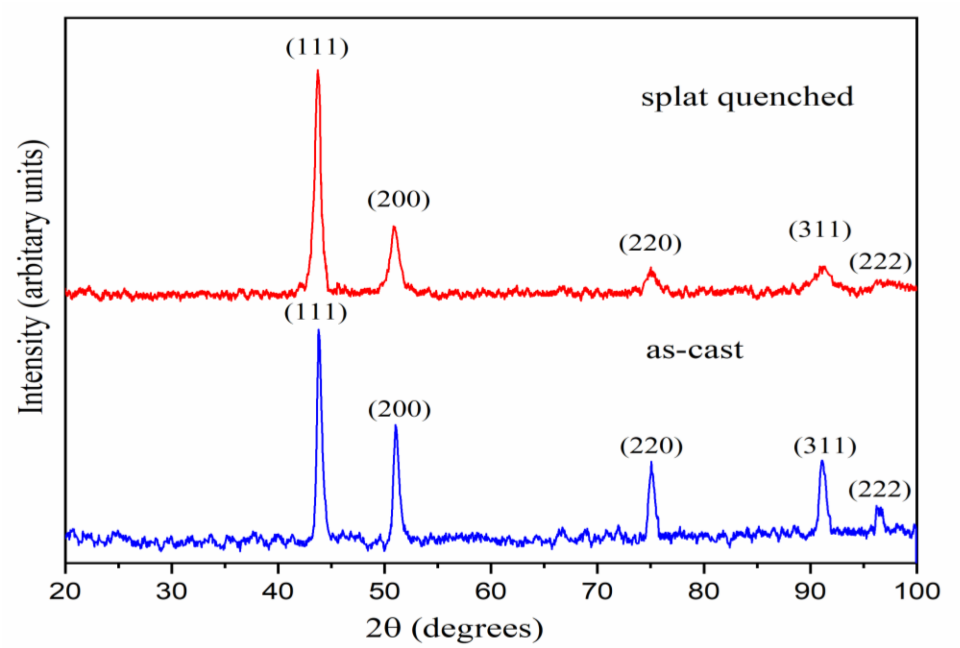
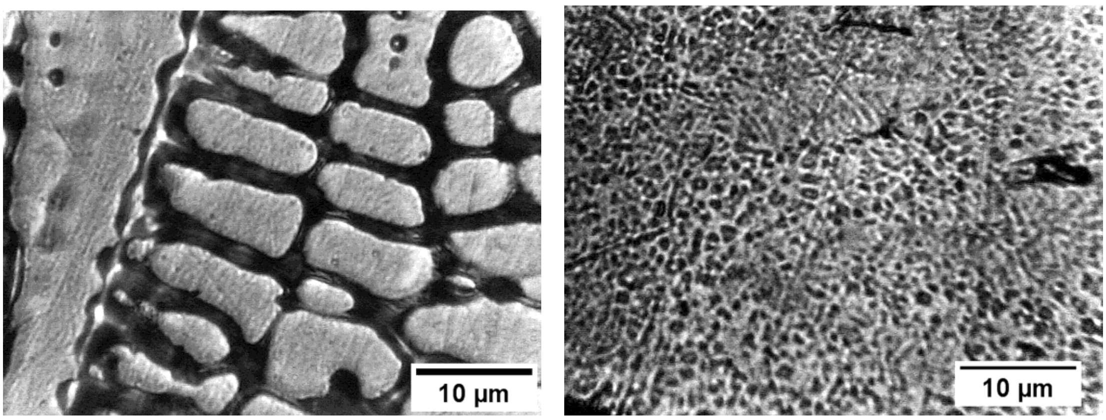


Fig. 1. XRD patterns of $CoCr_{0.8}Cu_{0.64}FeNi$ high-entropy alloys.



(a) (b)

Fig. 2. Optical micrographs of the cross-section of as-cast (a) and SQ (b) samples of $CoCr_{0.8}Cu_{0.64}FeNi$ HEA.

Table 2

Magnetic characteristics and microhardness of $CoCr_{0.8}Cu_{0.64}FeNi$ high-entropy alloys

Alloy	Specific saturation magnetization M_S, A·m^2/kg	Coercivity H_c, A/m	H_μ, MPa
As-cast $CoCr_{0.8}Cu_{0.64}FeNi$	35±3	120±10	2200±100
SQ film $CoCr_{0.8}Cu_{0.64}FeNi$	33±3	240±20	2600±100

Microhardness measurement of SQ $CoCr_{0.8}Cu_{0.64}FeNi$ alloy film has showed that the value of H_μ is higher than for the alloy in the as-cast state. (Table 2). This result is not unexpected, since, in the as-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 SQ alloy provides higher values of hardness and strength due to internal elastic stresses. It should be noted that the relatively low value of H_μ 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 H_μ but are brittle.

4. Conclusions

In this work, a $CoCr_{0.8}Cu_{0.64}FeNi$ HEA was obtained for the first time in the as-cast and melt-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 melt 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 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.

References

1. **Srivatsan, T. S.** High entropy alloys. Innovations, advances, and applications / T. S. Srivatsan, M. Gupta. – Boca Raton : CRC Press, 2020. – 758 p.

2. **Brechtl, J.** High-entropy materials: theory, experiments, and applications / J. Brechtl, P. K. Liaw. – Cham : Springer International Publishing, 2021. – 774 p.

3. **Xiang H.** High- entropy materials. From basics to applications / H. Xiang, F.-Z. Dai, Y. Zhou. – Weinheim, Germany : Wiley – VCH GmbH, 2023. – 272 p.

4. **Miracle, D. B.** A critical review of high entropy alloys and related concepts / D. B. Miracle, O. N. Senkov // Acta Materialia. – 2017. – Vol. 122. – P. 448 – 511.

5. **Kushnerov, O. I.** Structure and properties of nanostructured metallic glass of the Fe–B–Co–Nb–Ni–Si high-entropy alloy system / O. I. Kushnerov, V. F. Bashev, S. I. Ryabtsev // Springer Proceedings in Physics. – 2021. – Vol. 246. – P. 557 – 567.

6. **Kushnerov, O. I.** Structure and physical properties of cast and splat-quenched CoCr0.8Cu0.64FeNi high entropy alloy / O. I. Kushnerov, V. F. Bashev // East European Journal of Physics. – 2021. – No. 3. –P. 43 – 48.

7. **Körmann F.** “Treasure maps” for magnetic high-entropy-alloys from theory and experiment / F. Körmann, D. Ma, D. D. Belyea, M. S. Lucas, C. W. Miller, B. Grabowski, M. H. F. Sluiter // Applied Physics Letters. – 2015. – Vol. 107, No. 14. – P. 142404.

8. **Altomare, A.** Key features of Qualx2.0 software for qualitative phase analysis / A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni, R. Rizzi // Powder Diffraction. – 2017. – Vol. 32, No. S1. – P. S129 – S134.

9. **Wojdyr, M.** Fityk: a general-purpose peak fitting program / M. Wojdyr // Journal of Applied Crystallography. – 2010. – Vol. 43, No. 5–1. – P. 1126 – 1128.

10. **Polonskyy, V. A.** Structure and corrosion-electrochemical properties of Fe-based cast high-entropy alloys / V. A. Polonskyy, V. F. Bashev, O. I. Kushnerov // Journal of Chemistry and Technologies. – 2020. – Vol. 28, No. 2. – P. 177 – 185.

11. **Takeuchi, A.** Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element / A. Takeuchi, A. Inoue // Materials Transactions. – 2005. – Vol. 46. – P. 2817 – 2829.