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HIGH ENTROPY $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ METALLIC GLASS WITH SOFT MAGNETIC PROPERTIES

The new multicomponent high-entropy alloy of Fe-B-Co-Nb-Ni-Si system in the as-cast and splat-quenched state is developed. The simple solid solution with a face-centered cubic structure together with Fe_2B phase is obtained in the as-casted alloy. The value of lattice parameters of the investigated alloy indicates that the face-centered solid solution is formed on the base of the γ-Fe lattice. The splat-quenched alloy consists of fully glassy phase. The $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ high entropy metallic glass fabricated by splat-quenched technique possesses good soft magnetic properties with low coercivity and high saturation magnetization together with the high microhardness value.

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

1. Introduction

The first papers related to the designing and complex study of a new class of materials, i.e. the so-called high-entropy (HE) multicomponent alloys, were published in 2004. As a rule, these compositions comprise 5–13 principal elements, the concentrations of which are equiatomic or close to equiatomic (5–35%) [1]. Choosing a number of components and their concentration allows one to achieve increased entropy of mixing, which remains not only in the melt but after solidification. Because of the high entropy, usually simple substitutional solid solutions with BCC or FCC crystal lattices are formed during the solidification of multicomponent alloys. At the same time, the purposeful selection of components allows one to obtain the structure of HE alloys, which is a combination of a simple solid solution characterized by high plasticity and intermetallic compounds (σ phase, Laves phases) characterized by high hardness [1]. The HE alloys (HEAs) are characterized by unique structures and a number of useful operational characteristics, such as hardness, wear-resistance, resistance to oxidation, corrosion, and ionizing radiation, high thermal stability, and biocompatibility [1–6]. Thus, the HE alloys show promise as materials for application in electronics, atomic power engineering, transportation equipment, space-rocket hardware, medicine etc.

In contrast to HEAs, metallic glasses (MGs), known as another type of advanced materials, usually contain more than two kinds of elements but only one, sometimes two principal constituents. Due to their considerably different characteristics in structure and composition rules, the HEAs and MGs have been studied independently until the HEAs with an amorphous structure, namely high entropy metallic glasses (HE-MGs) were successfully synthesized [1]. The developed HE-MGs provide a new strategy of design and synthesis of MGs. The high entropy metallic glasses possess excellent mechanical and physical properties inherited from the advantages of both HEAs and MGs and show great potential for practical applications [7]. In particular, MGs usually possess excellent soft magnetic properties including low power loss and high saturation magnetization. Till now, series of HE-MG systems have been synthesized [1, 7-10]. This paper is intended to improve the previously synthesized soft magnetic $Fe_{25}Co_{25}Ni_{25}(B, Si)_{25}$ and $Fe_{25}Co_{25}Ni_{25}(P, C, B)_{25}$ HE-MGs [7-9]. As a result, a new $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ HE-MG which possesses good mechanical and soft magnetic properties was developed.

2. Experimental procedure

The as-cast alloy ingot with a nominal composition of $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ (in at. %) was prepared in a laboratory Tamman furnace in the flow of argon using a copper mold (the average cooling rate is ~10^2 K/s). The mass losses during melting did not exceed 1%. The quenching was performed by splat cooling technique; in this case, cooling is achieved via the collision of melt drops with the internal surface of a rapidly rotating copper cylinder. To estimate the cooling rate, we used the procedure suggested in [11] and the expression (1)

$$V = \frac{\alpha \vartheta}{c \rho \delta}, \qquad (1)$$

where α is the heat transfer coefficient, ϑ is the excess temperature of the film, c is the heat capacity of film material, ρ is the density of film material, and δ is the film thickness. Taking into account the thickness of splat-quenched films, i.e. ~50 µm, the estimated cooling rate was ~10^6 K/s. The X-ray phase diffraction (XRD) analysis was performed with using a DRON-2.0 diffractometer and Cu *Kα* monochromatized radiation. The patterns were processed using a QualX [12] and FullProf software [13]. The microhardness was measured using a PMT-3 tester at a load of 200 g. The magnetic properties of the films were measured by a vibrating sample magnetometer (VSM) at room temperature with the magnetic field applied parallel to the film plane. The coercive force (H_C) was measured with a B–H loop tracer.

3. Results

The phase composition of the investigated alloys and crystal lattice parameters (Tab.1) were determined from the XRD patterns (Fig. 1).

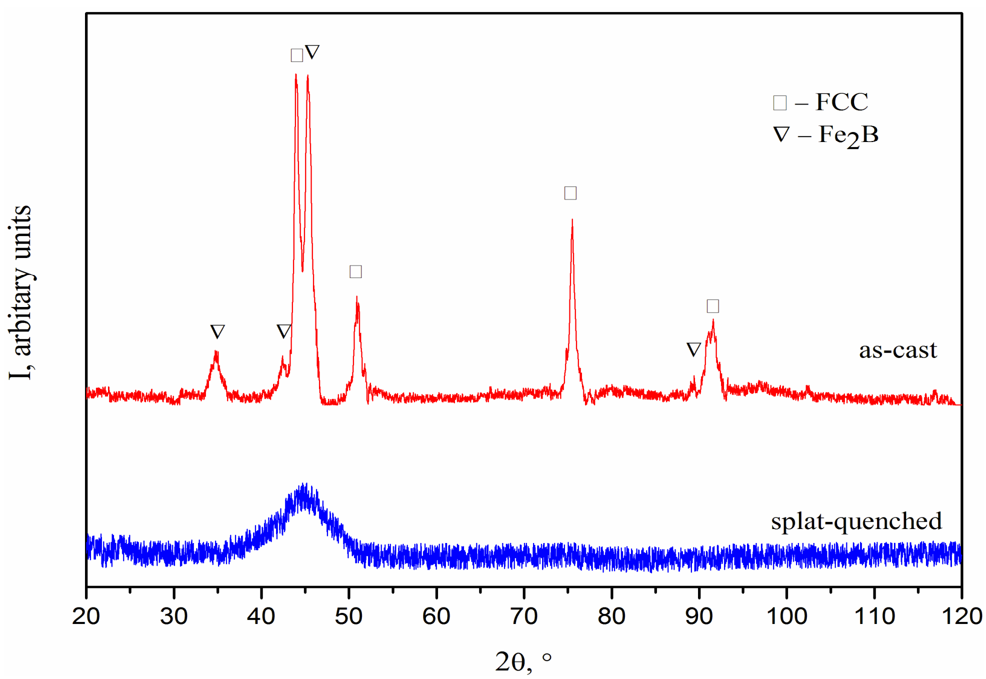

Fig.1. XRD patterns of as-cast ingots and splat-quenched films of $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ HEA.

Table 1

Phase composition, microhardness (H_μ), saturation magnetization (M_S) and coercive force (H_C) of investigated alloys

Alloy	Phase composition	H_μ, MPa	M_S, Am^2/kg	H_c, A/m
As-cast $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$	FCC (a=0.3574 nm) + Fe_2B	9000±400	71±7	1200±100
Splat-quenched $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$	fully glassy phase	8500±400	74±7	40±4

For the as-cast sample of $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ HEA, the structure is composed of a simple FCC phase and Fe_2B phase. For the splat-quenched $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ alloy the XRD pattern consists only of a broad diffraction maximum without any distinct crystalline peaks, indicating a fully glassy structure.

The estimation of lattice parameters allows us to assume that the FCC structure is formed based on γ iron (the extrapolated lattice parameter of γ iron at room temperature is a = 0.3572 nm [14]). Fig. 2 shows the room temperature hysteresis loops of the as-cast $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ HEA and splat-quenched (SQ) metallic glass. In accordance with the measured values of coercive force H_C (Tab.1), the SQ alloy exhibits a typical soft magnetic hysteresis characteristic, while H_C of the as-cast HEA is about 30 times greater. So the transformation of the $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ alloy from the crystalline to the amorphous state has been shown to result in shifting the magnetic characteristics from hard magnetic to the soft magnetic side. Both as-cast and SQ samples demonstrate high microhardness values (Tab.1) indicating good mechanical properties of alloys.

4. Discussion

High-entropy alloys are usually characterized by the entropy of mixing ΔS_{mix} and mixing enthalpy ΔH_{mix}. But in order to describe the phase composition of HEA's, some empirical criteria were proposed, namely, an atomic-size difference which is described by the parameter δ, valence electron concentration *VEC*, and the thermodynamic Ω parameter, correlates the melting point, entropy of mixing, and the enthalpy of mixing. The definitions of these parameters were considered in many papers [15]. Recently it has been established that the difference in atomic sizes affects the topological instability of atomic packing [16]. It was suggested that atoms with the maximum and minimum radii play a crucial role in determining the stability of the packing in high-entropy alloys. The solid angles of packing for the atoms with the smallest ω_S and highest ω_L sizes were chosen [16] to describe the effects of the atomic packing in HEA's quantitatively.

$$\omega_S = 1 - \sqrt{\frac{(r_S + \bar{r})^2 - \bar{r}^2}{(r_S + \bar{r})^2}} , \tag{2}$$

$$\omega_L = 1 - \sqrt{\frac{(r_L + \bar{r})^2 - \bar{r}^2}{(r_L + \bar{r})^2}} . \tag{3}$$

Here r_S and r_L are the atomic radii of smallest and largest atoms respectively, $\bar{r} = \sum_{i=1}^{n} c_i r_i$, r_i is the atomic radius, and c_i is the atomic fraction of the i-th component.

Then, the normalized parameter of packing state was defined as the ratio between the solid angles for the atoms with smallest and largest sizes

As pointed out in [16], the critical value of $\gamma = 1.175$ can distinguish the simple solid solution alloys and alloys with intermetallic compounds or MG.

$$\gamma = \frac{\omega_S}{\omega_L}. \qquad (4)$$

Using the data from [17-19], we calculated ΔS_{mix}, ΔH_{mix}, δ, VEC, Ω and γ of the $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ HEA (Tab. 2).

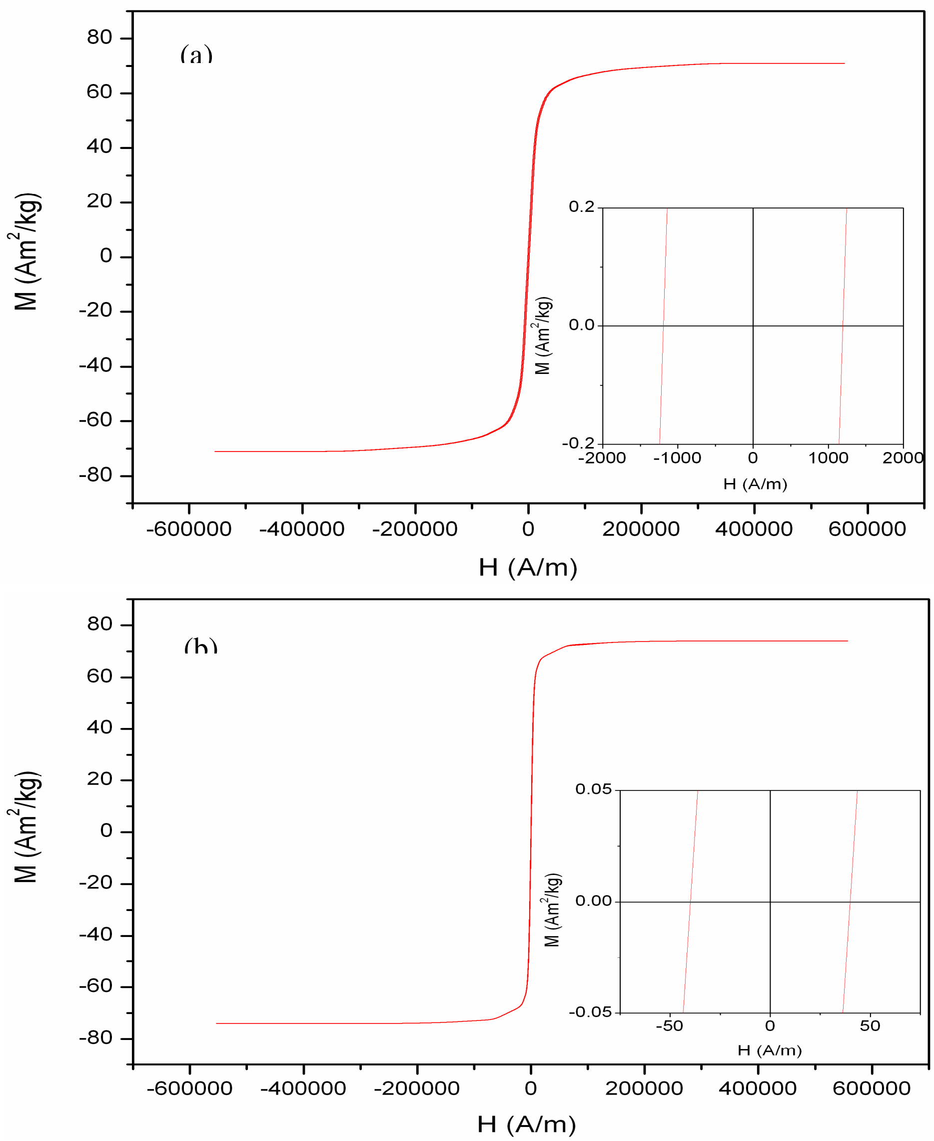

Fig.2. Hysteresis loops of as-cast (a) and splat-quenched (b) samples of $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ HEA.

According to [20], high entropy metallic glasses can form when δ, ΔH_{mix} and ΔS_{mix} simultaneously satisfy δ ≥ 9, -49 ≤ΔH_{mix} ≤ -5.5 kJ/mol, and 7 ≤ΔS_{mix} ≤ 16 J/(mol·K). The parameter Ω≤1.1 also indicates the ability to form MG or intermetallic compounds. It is seen from Tab. 2 that the $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ alloy fully satisfies all above-mentioned criteria, and the phase selection rules determined by ΔS_{mix}, ΔH_{mix}, δ, Ω, and γ are suitable for predicting the phase composition in high entropy alloys. As indicated in [7], the δ is a critical parameter for amorphous or solid solution phase formation. The necessity of a large δ to form the amorphous phase originates from the requirement of the sufficient atomic-level stress to destabilize the solid solution phase [7]. In addition, a large δ and negative ΔH_{mix} would improve the local packing efficiency and restrain the long-range diffusion of atoms. The crystalline phase formation will be suppressed during the cooling process, which leads to a high glass forming ability [7].

The H_c of the SQ films of the investigated alloy (HE-MG) reaches a relatively low value of 40 A/m, which is much smaller than in the crystallized as-cast alloy. The origin of the lower H_c can be attributed to the low number density of the domain-wall pinning sites, resulting from the high degree of amorphicity and structural homogeneity proceeding from the high glass forming ability [7]. Such behavior is typical for alloys in the amorphous state [21].

The higher values of microhardness observed in the as-cast crystalline alloy can be explained by the presence of precipitates of the brittle Fe_2B compound, which have a high hardness. At the same time, a homogeneous metallic glass without such precipitates has a lower microhardness but more ductile.

5. Conclusions

In this study, a new soft magnetic $Fe_{25}B_{17.5}Co_{21.35}Nb_{3.65}Ni_{25}Si_{7.5}$ alloy (HE-MG) was synthesized by the means of splat-quenching technique. The HE-MG exhibits low H_C of 40 A/m, the high saturation magnetization of 74 A·m^2/kg, and high microhardness value of 8000 MPa. The newly developed HE-MG with good soft magnetic and mechanical properties might be used for both scientific and engineering applications.

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References

1. High-entropy alloys. Fundamentals and Applications [Text]/ ed. M. C. Gao, ed. J.-W. Yeh, ed. P. K. Liaw, ed. Y. Zhang. – Springer International Publishing, 2016. – 516 p.

2. **Firstov, G. S.** High entropy shape memory alloys[Text] / G. S. Firstov, T. A. Kosorukova, Y. N. Koval, V. V Odnosum // Materials Today: Proceedings. – 2015. – V. 2. – P. S499–S503.

3. **Bashev, V. F.** Structure and properties of high entropy $CoCrCuFeNiSn_x$ alloys [Text] / V. F. Bashev, O. I. Kushnerov // The Physics of Metals and Metallography. –2014. –V. 115, No. 7,– P. 692–696.

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

5. **Wang, S.** TiZrNbTaMo high-entropy alloy designed for orthopedic implants: as-cast microstructure and mechanical properties [Text]/ S. Wang, J. Xu // Materials Science and Engineering: C. – 2017. – Vol. 73.– P. 80–89.

6. **Pogrebnjak, A. D.** Irradiation resistance, microstructure and mechanical properties of nanostructured (TiZrHfVnBTa)N coatings [Text] / A. D. Pogrebnjak, I. V. Yakushchenko, O. V. Bondar, V. M. Beresnev, K. Oyoshi, O. M. Ivasishin, H. Amekura, Y. Takeda, M. Opielak, C. Kozak // Journal of Alloys and Compounds. – 2016. – Vol. 679. – P. 155–163.

7. **Li, Y.** New soft magnetic $Fe_{25}Co_{25}Ni_{25}(P,C,B)_{25}$ high entropy bulk metallic glasses with large supercooled liquid region [Text]/ Y. Li, W. Zhang, T. Qi // Journal of Alloys and Compounds. – 2017. – Vol. 693. – P. 25–31.

8. **Qi, T.** Soft magnetic $Fe_{25}Co_{25}Ni_{25}(B,Si\ )_{25}$ high entropy bulk metallic glasses[Text] / T. Qi, Y. Li, A. Takeuchi, G. Xie, H. Miao // Intermetallics. – 2015. –V. 66. – P. 8–12.

9. **Wei, R.** Soft magnetic $Fe_{26.7}Co_{26.7}Ni_{26.6}Si_9B_{11}$ high entropy metallic glass with good bending ductility [Text]/ R. Wei, J. Tao, H. Sun, C. Chen, G. W. Sun, F. S. Li // Materials Letters. – 2017. – Vol. 197. – P. 87–89.

10. **Ding, J.** High entropy effect on structure and properties of (Fe,Co,Ni,Cr)-B amorphous alloys [Text]/ J. Ding, A. Inoue, Y. Han, F. L. Kong, S. L. Zhu, Z. Wang, E. Shalaan, F. Al-Marzouki // Journal of Alloys and Compounds. – 2017. – Vol. 696. – P. 345–352.

11. **Miroshnichenko, I. S.**, Quenching from the Liquid State [Text]/ I.S. Miroshnichenko. – Metallurgiya, Moscow, 1982. –168p. [in Russian].

12. http://www.ba.ic.cnr.it/softwareic/qualx/

13. https://www.ill.eu/sites/fullprof/index.html.

14. **Ruhl, R.C**. Splat quenching of iron-carbon alloys [Text]/ R.C. Ruhl, M. Cohen // Trans Met Soc AIME. -1969. -V. 245, № 2. -P. 241–251.

15. **Bashev, V. F.** Structure and properties of cast and splat-quenched high-entropy Al–Cu–Fe–Ni–Si alloys / V. F. Bashev, O. I. Kushnerov // Physics of Metals and Metallography. – 2017. – Vol. 118, No. 1. – P. 39–47.

16. **Wang, Z.** Atomic-size effect and solid solubility of multicomponent alloys [Text]/ Z. Wang, Y. Huang, Y. Yang, J. Wang, C. T. Liu // Scripta Materialia. – 2015. – V. 94. – P. 28–31.

17. **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 [Text]/A. Takeuchi, A. Inoue// Materials Transactions.–2005. –V. 46 –P. 2817-2829.

18. **Li, W.K.** Advanced Structural Inorganic Chemistry [Text]/W.K. Li, G.D. Zhou, T.C.W. Mak. –New York: Oxford University Press, 2008. –688 p.

19. **Troparevsky, M. C.** Criteria for predicting the formation of single-phase high-entropy alloys [Text] / M. C. Troparevsky, J. R. Morris, P. R. C. Kent, A. R. Lupini, G. M. Stocks // Physical Review X. – 2015. – V. 5, No. 1. – P. 0110141-1–011014-6.

20. **Guo, S**. Phase stability in high entropy alloys: Formation of solid-solution phase or amorphous phase [Text]/S. Guo, C.T.Liu// Progress in Natural Science: Materials International.–2011.–V. 21, Iss. 6, –P. 433–446

21. **Gulivets, A. N.** Multilayer compound Co-P films with controlled magnetic properties [Text]/ A. N. Gulivets, V. A. Zabludovsky, E. P. Shtapenko, A. I. Kushnerev, M. P. Dergachov, A. S. Baskevich // Transactions of the IMF. – 2002. – Vol. 80, No. 5. – P. 154–156.

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