

Article

Multicomponent Fe-Based Bulk Metallic Glasses with Excellent Corrosion and Wear Resistances

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Abstract: In this study, new multicomponent Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Co, and Ni, denoted as Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅, respectively) bulk metallic glasses (BMGs) with excellent corrosion and wear resistances were synthesized using the J-quenching technique and fluxing treatment. The synthesized Fe-based BMGs possessed a large glass-forming ability, and the maximum diameters of the Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅ glassy alloy rods reached 5.5, 4.5, and 4.0 mm, respectively. The Fe₅₉ BMG had a wide supercooled liquid region of 65 K. Potentiodynamic tests in 3.5 wt.% NaCl solution showed that the corrosion resistances of the synthesized Fe-based BMGs were relatively better than that of the 316L stainless steel. The Fe₅₉ BMG had the highest corrosion resistance, with the lowest self-corrosion current density in the order of 10^{−8} A·cm^{−2}. Wear tests showed that the synthesized Fe-based BMGs exhibited excellent wear resistances, and the wear rate of the Fe₅₉ BMG was as low as approximately 1.73 × 10^{−15} m³·N^{−1}·m^{−1}. The rare-earth-element-free Fe-based BMGs, especially the Fe₅₉ BMG, have a low cost, large glass-forming ability, and excellent wear and corrosion resistance, which make them good candidates for wear- and corrosion-resistant coating materials.

Keywords: Fe-based bulk metallic glasses; glass forming ability; corrosion resistance; wear resistance



Citation: Zhang, G.; Sun, W.; Xie, L.; Zhang, C.; Tan, J.; Peng, X.; Li, Q.; Ma, X.; Zhao, D.; Yu, J. Multicomponent Fe-Based Bulk Metallic Glasses with Excellent Corrosion and Wear Resistances. *Metals* **2022**, *12*, 564. <https://doi.org/10.3390/met12040564>

Academic Editor: George A. Pantazopoulos

Received: 18 February 2022

Accepted: 24 March 2022

Published: 27 March 2022

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1. Introduction

Fe-based bulk metallic glasses (BMGs) have gained substantial attention in recent decades owing to their low cost and unique performance, such as high strength and hardness, excellent wear and corrosion resistance, and excellent soft magnetic properties [1–4]. The strength of Fe-based BMGs is generally higher than 2 GPa, which currently exceeds the strength of high-strength steel; in particular, the compressive fracture strength of a Fe_{33.5}Co_{33.5}Nb₆B₂₇ BMG reaches 4.84 GPa [5]. Owing to their high strength, the micro-hardness of the Fe-based BMGs is larger than that of the Zr- and Cu-based BMGs, and their wear resistance is three orders of magnitude higher than that of the Zr- and Cu-based BMGs. Additionally, owing to their unique amorphous structure, Fe-based BMGs exhibit a chemically homogeneous single phase and high atomic reactivity, which results in the formation of an extremely uniform and stable passive film on the surface of the alloys; thus, Fe-based BMGs have higher corrosion resistances compared with their crystalline alloy counterparts. For example, Li et al. reported an Fe₅₉Cr₁₂Mo_{3.5}Ni₅P₁₀C₄B₄Si_{2.5} BMG with excellent corrosion resistance, with I_{corr} and E_{corr} values of 2.47 × 10^{−7} A·cm^{−2} and −0.22 V, respectively [6].

Owing to their low cost, ultra-high strength, and excellent wear and corrosion resistance, Fe-based BMGs have been considered good candidates as wear-and corrosion-resistant coating materials [7]. It has been extensively reported that alloying elements can significantly influence the corrosion and wear properties of Fe-based BMGs. Cr and Mo are the most effective elements for providing a high passivation ability for Fe-based BMGs [8,9]. Cr can form a dense and stable hydrated chromium oxyhydroxide passive film on the surface of alloys to prevent corrosion within the alloys [10]. Generally, the higher the Cr content, the better the corrosion resistance of Fe-based BMGs. However, when the Cr content is greater than 15 at.%, further increasing the Cr content does not significantly improve the corrosion resistance of the Fe-based BMGs but increases the material cost. The effect of Mo on the protective ability of the passivation layer is weaker than that of Cr. However, Mo can promote the enrichment of Cr in the passive film, thereby enhancing the corrosion and pitting resistances of Cr-containing Fe-based BMGs. However, the excess addition of Mo is detrimental to the corrosion resistance of Fe-based BMGs [11]. Recently, it was found that the substitution of Fe with a similar element, such as Ni or Co, can produce positive effects on the glass forming ability (GFA) and the mechanical and magnetic properties of Fe-based BMGs. For example, the substitution of 20 at.% Ni for Fe in Fe₈₀P₁₃C₇ BMG resulted in an increase in the critical diameter (D_c) from 2.0 mm to 2.3 mm for full glass formation and a significant increase in room-temperature compressive plastic strain from 1.1% to 11.2% [12]. The room-temperature compressive plasticity of Fe₈₀P₁₃C₇ BMG improved from 1.1% to 3.0%, and the saturation magnetization increased from 1.45 T to 1.55 T due to the replacement of 10 at.% Fe with Co [13]. Based on the above considerations, new Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Co, and Ni) BMGs were successfully prepared in this study, and the corrosion and wear properties of the present Fe-based BMGs were systematically investigated.

2. Materials and Methods

Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Ni, and Co) alloy ingots were prepared by torch-melting a mixture of Fe₃P pieces (99.5 mass% purity), Cr powder (99.9 mass% purity), Mo powder (99.9 mass% purity), Fe powder (99.9 mass% purity), Si powder (99.99 mass% purity), boron pieces (99.95 mass% purity), graphite powder (99.95 mass% purity), Co powder (99.9 mass% purity), and Ni powder (99.7 mass% purity) under a high-purity Ar atmosphere. All the as-prepared alloy ingots had a mass of 2 g. Subsequently, the ingots were purified through a fluxing treatment at an elevated temperature of approximately 1450 K for 2–3 h under a vacuum of ~50 Pa, in which a mixture of B₂O₃ and CaO with a mass ratio of 3:1 was used as the fluxing agent. After the fluxing treatment, the alloys were subjected to the J-quenching technique [14–16]. Consequently, Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Ni, and Co) alloy rods with diameters ranging from 1.0–6.0 mm and lengths of several centimeters were prepared.

The amorphous nature of the specimens was examined using an X-ray diffractometer (XRD, Bruker D8 Discover, Bruker Inc., Karlsruhe, Germany) with Co K α radiation. The thermal behavior of the specimens was examined through differential scanning calorimetry (DSC, NETZSCH DSC 404F1, NETZSCH Inc., Selb, Germany) at a heating rate of 0.33 K/s under an Ar atmosphere. The corrosion behaviors of the specimens, as well as that of 316 stainless steel, which was used for comparison, were evaluated through electrochemical measurements (Zahner Zennium X, Zahner Inc., Kronach, Germany). This was conducted in a three-electrode cell using the glassy rod alloy specimens as the working electrode, a saturated calomel electrode as the reference electrode, and a metal platinum electrode as the counter electrode. The working face of the samples was polished to a mirror face using sandpaper, and the non-working parts were sealed with epoxy resin. The potentiodynamic polarization curves were measured in a 3.5% NaCl solution at room temperature with a potential sweep rate of 1 mV/s after immersing the specimens for approximately 30 min to stabilize the open-circuit potential. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 10 kHz to

10 mHz, using a sinusoidal potential perturbation of ± 10 mV relative to the OCP. The fitting of EIS data was operated by using the software ZSimpWin (3.60, AMETEK Inc. Middleboro, MA, USA). The surface morphology of the specimens after immersion was observed using scanning electron microscopy (SEM, SU8010). The chemical states of the surface elements of the specimens after polarization were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific Inc., Waltham, MA, USA) with a monochromatic Al K_{α} X-ray source ($h\nu = 1486.6$ eV). The binding energies were calibrated using carbon contamination with a C 1s peak value of 284.8 eV. The Vickers hardness (HV) of the specimens was measured at a load of 200 g and dwell time of 15 s using a microhardness test instrument (MT-401MVA, BangYi Co., Shanghai, China). Prior to testing, the specimens were polished to a mirror face using sandpaper and cleaned with alcohol, and the average of ten measurement values was taken as the final hardness value for each specimen. Tribological tests of the specimens were conducted under ambient conditions using a pin-on-disc tribometer (CSM, Graz, Austria) with a pin-on-disk contact geometry; a GCr15 (860HV) plate with a diameter of 60 mm was used as the counter body. A normal load of 7 N and a total sliding distance of 5000 m with a sliding speed of 1.8 m/s were adopted for all the tribological tests. The wear rate was calculated using Equation (1).

$$V = \frac{\Delta m}{PS\rho} = \frac{m_1 - m_2}{PS\rho} \quad (1)$$

where V is the wear rate, Δm is the wear mass loss, m_1 and m_2 are the masses of the sample before and after the test, respectively, S is the sliding distance of the sample, p is the load, and ρ is the density of the test sample, which was measured using density testing equipment (Micromeritics, AccuPyc-1340, Micromeritics Inc., Atlanta, GA, USA). The surface and subsurface morphologies of the worn tracks were observed using scanning electron microscopy (SEM, Hitachi s4800, Hitachi Inc., Tokyo, Japan). The topography and chemical composition of the worn surfaces were examined using energy-dispersive X-ray spectrometry (EDS HORIBA 7593-H, HORIBA Inc., Tokyo, Japan).

3. Results and Discussion

3.1. Material Preparation and Glass Forming Ability (GFA)

The XRD (X-ray diffraction) patterns of the as-prepared $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($M = \text{Fe, Ni, and Co}$) glassy alloy rods with critical diameters ($D_{\max}$) for glass formation are shown in Figure 1a. There was only a broad diffraction peak and no detectable sharp crystalline peaks in the XRD patterns of all the specimens, indicating the fully amorphous structure of the specimens [17]. Among the present Fe-based BMGs, the Fe_{59} alloy had the largest GFA with a $D_{\max}$ of 5.5 mm, and the substitution of Fe with 5 at.% Co or Ni degraded the GFA of Fe_{59} alloy; the $D_{\max}$ of $\text{Fe}_{54}\text{Co}_5$ and $\text{Fe}_{54}\text{Ni}_5$ alloys were 4.5 and 4.0 mm, respectively [17]. Figure 1b shows the DSC curves of $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($M = \text{Fe, Ni, and Co}$) BMGs at a heating rate of 0.33 K/s. The DSC (Differential scanning calorimetry) curves of all specimens exhibited a distinct glass transition, followed by a supercooled liquid region and multistep crystallization peaks. The thermal parameters associated with the glass transition temperature (T_g), crystallization temperature (T_x), and supercooled liquid region ($\Delta T_x = T_x - T_g$) are summarized in Table 1. It can be seen that the substitution of Co and Ni for Fe led to a decrease in the T_g and T_x of the Fe-based BMGs. The T_g of amorphous alloys mainly depends on the atomic bonding strength among the constituent elements, which can be evaluated through the mixing enthalpy between the constituent elements. It is suggested that the dominant short-range order unit for Fe-metalloid amorphous alloys can be characterized as solute-centered atomic clusters, in which the metallic atoms are located on the shell and the metalloid atoms are located in the center [18]. The mixing enthalpies between Fe and the metalloid elements Si, B, P, and C are -35 , -26 , -39.5 , and -50 kJ/mol, respectively; those between Co and the metalloid elements are -38 , -24 , -35.5 , and -42 kJ/mol, respectively; and those between Ni and the metalloid elements are -40 , -24 , -34.5 , and -39 kJ/mol, respectively [19]. Except

for Si, the mixing enthalpies between Fe and the metalloid elements were more negative than those between Co/Ni and the metalloid elements, which could be the reason for the decrease in the T_g and T_x of the Fe_{59} , $\text{Fe}_{54}\text{Co}_5$, and $\text{Fe}_{54}\text{Ni}_5$ alloys. It was also observed that the ΔT_x of the Fe_{59} , $\text{Fe}_{54}\text{Co}_5$, and $\text{Fe}_{54}\text{Ni}_5$ BMGs decreased. Inoue suggested that a wider ΔT_x reflects a better GFA [20], which may account for the compositional dependence of $D_{\max}$ of the Fe-based BMGs in this study. Additionally, it can be noted that the ΔT_x of the Fe_{59} BMG reaches 65 K, indicating an extremely high thermal stability.

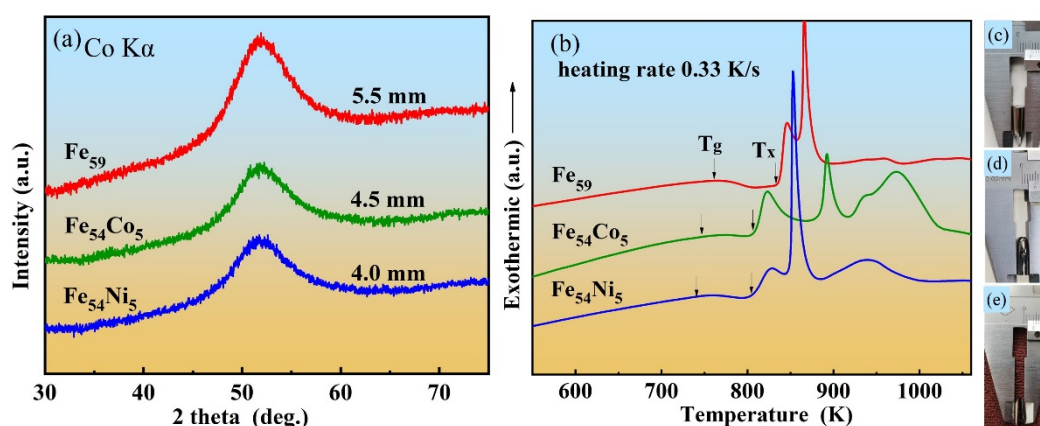


Figure 1. (a) XRD patterns and (b) DSC curves of as-prepared $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($\text{M} = \text{Fe}$, Ni , and Co) glassy alloy rods with the critical diameter ($D_{\max}$) for glass formation. Photos of (c) Fe_{59} , (d) $\text{Fe}_{54}\text{Co}_5$, and (e) $\text{Fe}_{54}\text{Ni}_5$ glassy alloy rods with the $D_{\max}$ values.

Table 1. Summary of the critical diameters for glass formation ($D_{\max}$), thermal properties, and the GFA indicators of $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($\text{M} = \text{Fe}$, Ni , and Co) glassy alloy rods determined from the DSC curves at a heating rate of 0.33 K/s (T_g : glass transition temperature, T_x : onset crystallization temperature, $\Delta T_x = T_x - T_g$).

Alloys	$D_{\max}$ (mm)	T_g (K)	T_x (K)	ΔT_x (K)
Fe_{59}	5.5	768	833	65
$\text{Fe}_{54}\text{Co}_5$	4.5	765	805	40
$\text{Fe}_{54}\text{Ni}_5$	4.0	762	800	38

3.2. Corrosion Resistance

To evaluate the corrosion resistance, electrochemical measurements of the Fe-based BMGs were performed in a 3.5 wt.% NaCl solution at room temperature. Figure 2 shows representative potentiodynamic polarization curves of the Fe_{59} , $\text{Fe}_{54}\text{Co}_5$, and $\text{Fe}_{54}\text{Ni}_5$ glassy alloy rods. The self-corrosion current density (I_{corr}) and self-corrosion potential (E_{corr}) obtained using the Tafel extrapolation method are listed in Table 2.

Table 2. Electrochemical parameters derived from potentiodynamic polarization curves and EIS analysis of the $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($\text{M} = \text{Fe}$, Co , and Ni) BMGs and 316L stainless steel (E_{corr} : self-corrosion potential, I_{corr} : self-corrosion current density, R_s : solution resistance, R_t : charge transfer resistance, R_u : charge transfer resistance, Q_t : non-ideal capacitance, Q_u : non-ideal capacitance).

Alloys	E_{corr} (V)	I_{corr} ($\times 10^{-8}$ A·cm $^{-2}$)	R_s (Ω ·cm 2)	R_t ($\times 10^6$ Ω ·cm 2)	R_u ($\times 10^6$ Ω ·cm 2)	Q_t ($\times 10^{-5}$ μF ·cm 2)	Q_u ($\times 10^{-5}$ μF ·cm 2)
Fe_{59}	0.12	8.4	1.71	0.64	1.8	3.59	9.37
$\text{Fe}_{54}\text{Co}_5$	−0.19	8.6	1.67	0.76	1.68	3.16	4.12
$\text{Fe}_{54}\text{Ni}_5$	−0.18	38.3	0.85	3.06	0.82	2.87	2.99
316L	−0.29	98.5	1.16	0.0000013	0.049	2.79	5.28

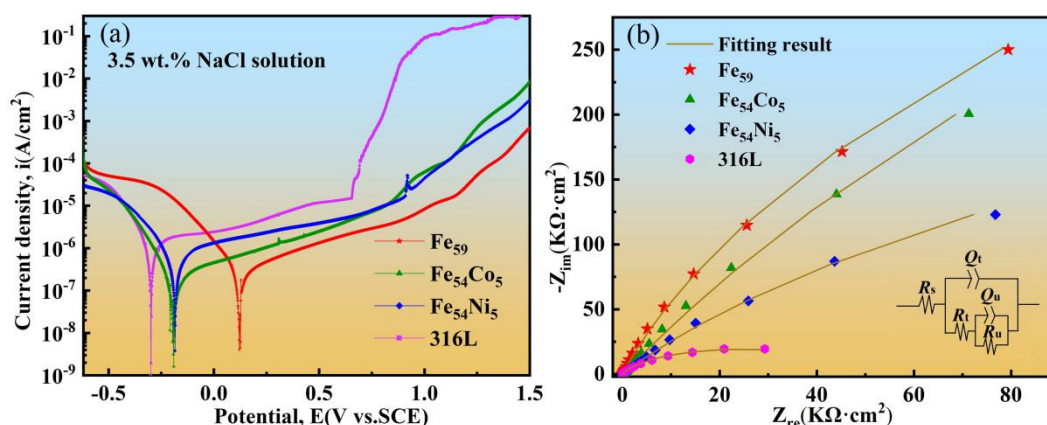


Figure 2. (a) Potentiodynamic polarization curves in 3.5 wt.% NaCl solution at room temperature for Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Ni, and Co) glassy alloy rods and 316L stainless steel; (b) Nyquist plots and the corresponding equivalent circuit (inset) for fitting the impedance spectra of Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Co, and Ni) glassy alloy rods and 316L in 3.5 wt.% NaCl solution at room temperature.

Figure 2a shows the potentiodynamic polarization curves in 3.5 wt.% NaCl solution exposed to air at room temperature for the Fe-based glassy alloy rod specimens as well as the 316L stainless steel (316L) for comparison. The self-corrosion potential (E_{corr}) and self-corrosion current density (I_{corr}) of the specimens listed in Table 2 were obtained from the potentiodynamic polarization curves using the Tafel extrapolation method. Compared with the 316L, the Fe-based BMGs exhibited a more positive E_{corr} , lower I_{corr} , and a more stable and wider passive region, indicating a relatively higher corrosion resistance and superior passive film protection. Among the Fe-based BMGs used in this study, the Fe₅₉ BMG exhibited the highest corrosion resistance, with the lowest I_{corr} and I_{pass} in the order of 10⁻⁸ and 10⁻⁷ A/cm², respectively. Further, the potentiodynamic polarization curve of the Fe₅₉ BMG had a smooth shape, as shown in Figure 2a, indicating that a stable passivation layer was formed on the surface and tiny pit corrosion occurred during the entire measurement period. However, few sharp peaks were found in the curves of the Fe₅₄Co₅ and Fe₅₄Ni₅ BMGs, as shown in Figure 2a, indicating that pit corrosion occurred during the measurement period; evidence of pit corrosion is shown in Figure 3. It is worth noting that the corrosion resistance of the Fe₅₉ BMG was better than that of most reported Fe-based BMGs, of which I_{corr} is usually in the order of 10⁻⁶–10⁻⁷ A/cm². For example, it has been reported that a Fe₃₆Cr₂₃Mo₁₀W₈C₁₅B₆Y₂ BMG possesses good corrosion resistance with an I_{corr} of 6.16×10^{-7} A·cm⁻² and E_{corr} of −0.275 V [1]. Compared with this Fe-based BMG, the Fe₅₉ BMG exhibited a lower I_{corr} but contained less Cr and Mo. This result may be related to the metalloid elements in the alloys, which can significantly influence the corrosion properties of Fe-based BMGs [4]. For example, Si can improve the passivation ability and corrosion resistance of Fe-based BMGs, which can be attributed to the formation of a dense and stable passive film rich in Si and Cr-oxides [21]. The Fe₄₃Cr₁₆Mo₁₆C₁₀B₅P₁₀ BMGs exhibited a wide passive region, indicating a higher corrosion resistance compared to that of the P-free metallic glass [22].

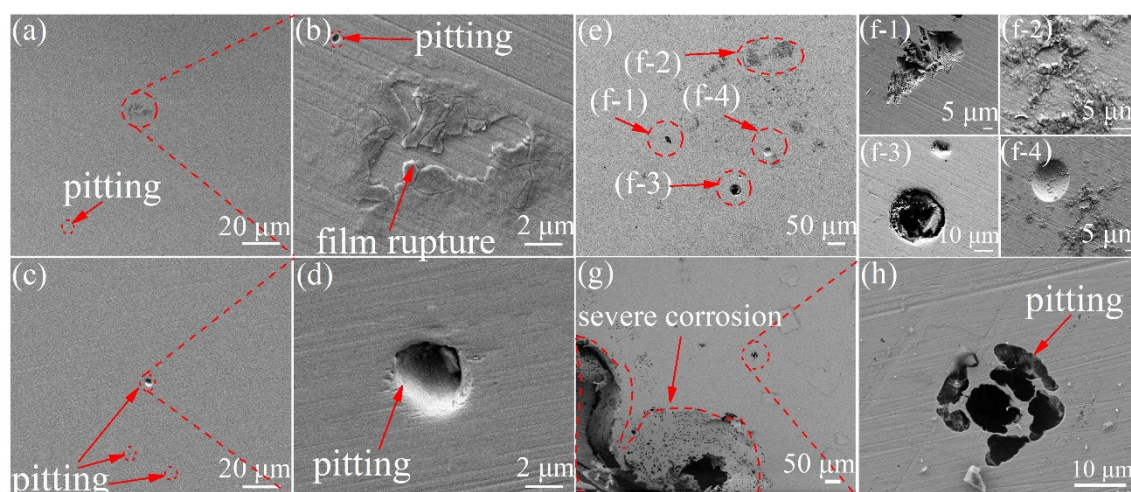


Figure 3. SEM micrographs of the electrochemical corroded surfaces of the Fe₅₉ BMG (a), Fe₅₄Co₅ BMG (c), Fe₅₄Ni₅ BMG (e), and 316L (g), respectively, and (b,d,f,h) are corresponding partial enlarged views.

Figure 2b shows the Nyquist plots of the Fe-based BMGs and 316L in 3.5 wt.% NaCl solution at room temperature. The Nyquist plots of all samples show a double capacitive loop, implying two time constants in the electrochemical measurements. The semicircle diameter in the Nyquist plots of the Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅ BMGs and 316L stainless steel decreased, implying that their corrosion resistances also decreased. An appropriate equivalent circuit for fitting the impedance spectra is shown in Figure 2b, where R_s is the solution resistance; R_t and R_u are the charge transfer resistances; and Q_t and Q_u represent the possibility of non-ideal capacitance. These fitting parameters are listed in Table 2. The R_t values of the Fe₅₉, Fe₅₄Co₅, Fe₅₄Ni₅ BMGs, and 316L stainless steel decreased. It is known that a larger R_t implies better corrosion resistance [23], and thus, the results of the EIS measurements agree well with those of the electrochemical measurements.

Figure 3 shows the SEM micrographs of the electrochemical corroded surfaces of the Fe-based BMGs and 316L specimens. There were a few pitting pits and a film rupture zone on the surface of the Fe₅₉ BMG specimen, as shown in Figure 3a,b, revealing the excellent corrosion resistance of the Fe₅₉ BMG. It can be seen in Figure 3c,d that there were pitting pits with diameters of approximately 4 μm and of a few nanometers on the surface of the Fe₅₄Co₅ BMG specimen. Compared with the Fe₅₉ and Fe₅₄Co₅ BMGs, there were more and larger pitting pits and more corrosion products on the surface of the Fe₅₄Ni₅ BMG specimen, as shown in Figure 3e,f, which could be attributed to the sharp peaks in the potentiodynamic polarization curve of the Fe₅₄Ni₅ BMG shown Figure 2a. The surface of the 316L specimen was completely damaged, covered with a thick layer of polarized product, and had huge pitting pits caused by a severe corrosion, as shown in Figure 3g,h. The observed electrochemical corroded surfaces of the specimens confirmed the results of the electrochemical and EIS measurements.

To better understand the effect of the elements on the corrosion mechanism of the Fe-based BMGs, an XPS (X-ray Photoelectron Spectroscopy) analysis was performed to characterize the chemical composition of the oxide films formed on the surfaces of the specimens after electrochemical measurement in 3.5 wt.% NaCl solution. Figure 4 shows the Fe 2p, Cr 2p, Mo 3d, Co 2p, and Ni 2p spectra of the Fe-based BMGs. The Fe 2p spectra of the specimens comprised the peaks of Fe 2p_{1/2} and 2p_{3/2} corresponding to the peaks of the metallic (Fe) and Fe²⁺, Fe_{hy}³⁺, and Fe_{ox}³⁺ oxide (Fe^{ox}) states of Fe [23–27]. The peak intensities of Fe^m in the Fe₅₄Co₅ and Fe₅₄Ni₅ BMGs were relatively higher than that of the Fe₅₉ BMG. The Cr 2p peaks represented the metallic (Cr) and Cr³⁺ and Cr⁶⁺ oxide (Cr^{ox}) states of Cr [26,28–30]. Cr⁶⁺ dissolves in water and causes the corrosion current density to increase; however, it has a self-repairing ability and can promote the formation of denser

Cr_2O_3 to prevent chloride ions from penetrating into the internal damage [31,32]. As shown in Figure 4b, the total area of the Cr 2p peaks in the Fe_{59} BMG was the largest, suggesting a higher concentration of Cr on its surface than on the $\text{Fe}_{54}\text{Co}_5$ and $\text{Fe}_{54}\text{Ni}_5$ BMGs. The Mo 3d spectrum, consisting of the Mo 3d 3/2 and 3d 5/2 peaks, corresponded to the metallic Mo and Mo^{4+} and Mo^{6+} oxide states [24,27,29,30]. The $\text{Fe}_{54}\text{Co}_5$ BMG had the highest intensity of the low-valence Mo^{4+} peak on the surface, followed by the Fe_{59} and $\text{Fe}_{54}\text{Ni}_5$ BMGs. The Fe_{59} BMG had the highest intensity of the high-valence Mo^{6+} peak in the surface film, followed by the $\text{Fe}_{54}\text{Co}_5$ and $\text{Fe}_{54}\text{Ni}_5$ BMGs. Mo can promote the enrichment of Cr in the passive film and, consequently, enhance the corrosion resistance of amorphous alloys [33–35]. The Co 2p spectrum consisted of the metallic Co (Co^m), $\text{Co}_{\text{hy}}^{2+}$, and $\text{Co}_{\text{ox}}^{2+}$ peaks, as shown in Figure 4d. The Ni 2p spectrum consisted of the peaks corresponding to the metallic Ni (Ni), Ni^{2+} , and Ni^{3+} , as shown in Figure 4e. It is known that Co and Ni are more effective in providing a high passivation ability for alloys compared with Fe; however, the corrosion resistance of the Fe-based BMGs in this study decreased with the substitution of Co and Ni for Fe. This could be due to the small amount of crystallization in the $\text{Fe}_{54}\text{Co}_5$ and $\text{Fe}_{54}\text{Ni}_5$ BMGs owing to the lower GFA, which degraded their corrosion resistance.

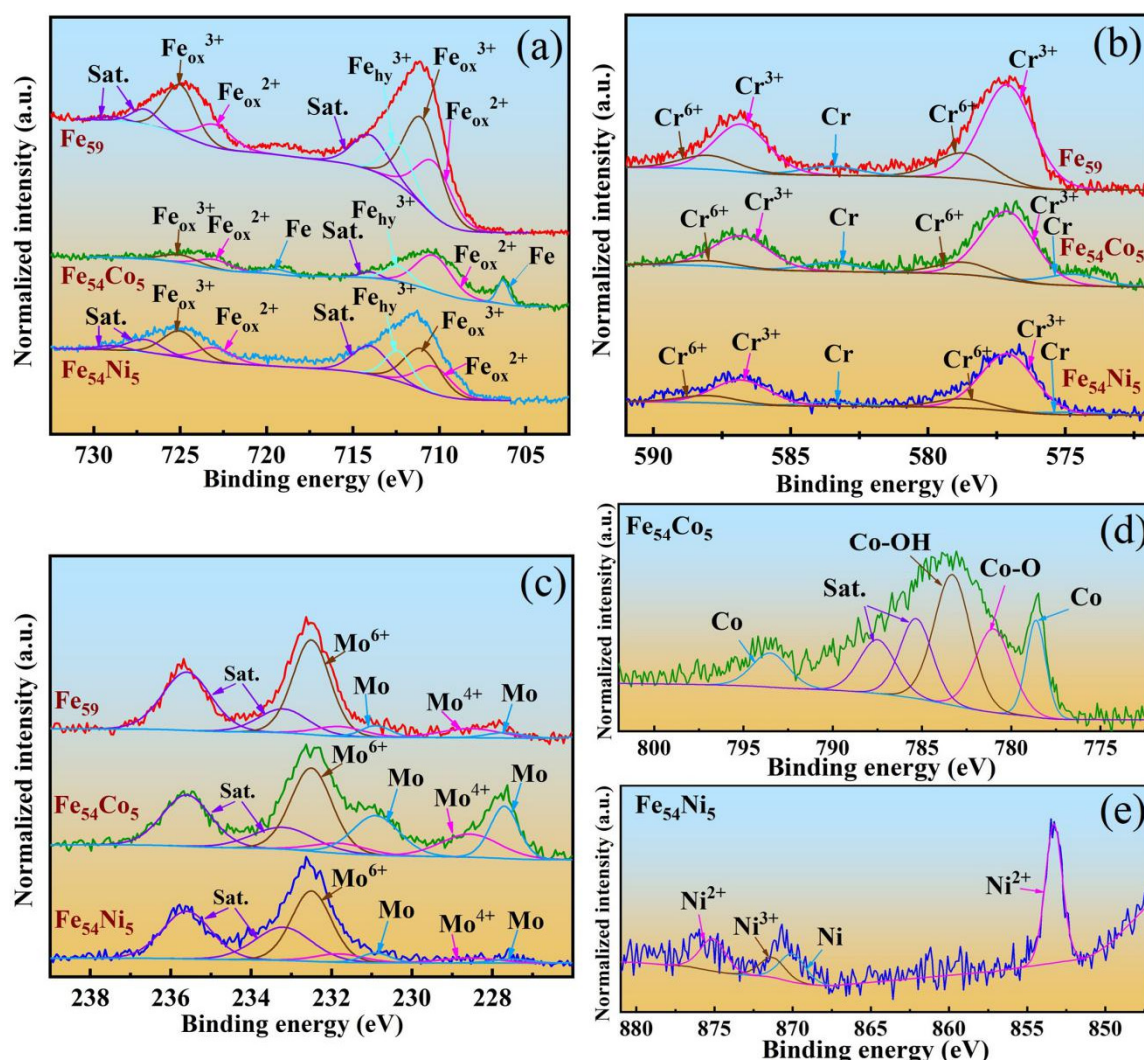


Figure 4. XPS spectra of Fe 2p (a), Cr 2p (b), Mo 3d (c), Co 2p (d), and Ni 2p (e) in the passive films on the surface of the $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ (M = Fe, Co, and Ni) glassy alloy rod specimens after electrochemical measurements in a 3.5 wt.% NaCl solution.

The outstanding corrosion resistance of amorphous alloys is primarily influenced by the stability of a uniform passive film. Figure 4b,c show that the Cr^{ox} and Mo^{ox} fractions in

the Fe₅₉ and Fe₅₄Co₅ BMGs in the surface film after the electrochemical test were apparently higher than those in the Fe₅₄Ni₅ BMG. The enrichment of Cr^{ox} and Mo^{ox} was beneficial for the modification of the passive film quality of the BMGs and thus improved the corrosion resistance. The XPS results for the Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅ BMGs were consistent with the SEM morphology of the samples after the electrochemical test, as shown in Figure 3, in which the Fe₅₄Ni₅ BMG exhibited a more severely corroded surface than the Fe₅₉ and Fe₅₄Co₅ BMGs.

3.3. Microhardness and Wear Resistance

The measured microhardness values (HV0.2) of the Fe-based BMG specimens are listed in Table 3 and shown in Figure 5a. The Fe-based BMGs exhibited extremely high microhardnesses, exceeding 1000 HV0.2. The microhardness values of the Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅ BMGs decreased in turn. Similar to the T_g of amorphous alloys, the hardness of the alloys depends on the atomic bonding strength between the constituent elements; therefore, the microhardness has a similar change trend as the T_g of the synthesized Fe-based BMGs.

Table 3. Density, average microhardness, average COF, and wear rate of the Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Ni, and Co) BMGs.

Alloys	Density (g/cm ³)	Average HV0.2	Average COF	Wear Rate (×10 ^{−15} m ³ /N·m)
Fe ₅₉	6.62 ± 0.02	1105 ± 31	0.716 ± 0.034	1.73 ± 0.20
Fe ₅₄ Co ₅	6.83 ± 0.02	1098 ± 17	0.795 ± 0.059	6.18 ± 0.28
Fe ₅₄ Ni ₅	6.79 ± 0.01	1024 ± 22	0.727 ± 0.018	5.05 ± 0.24

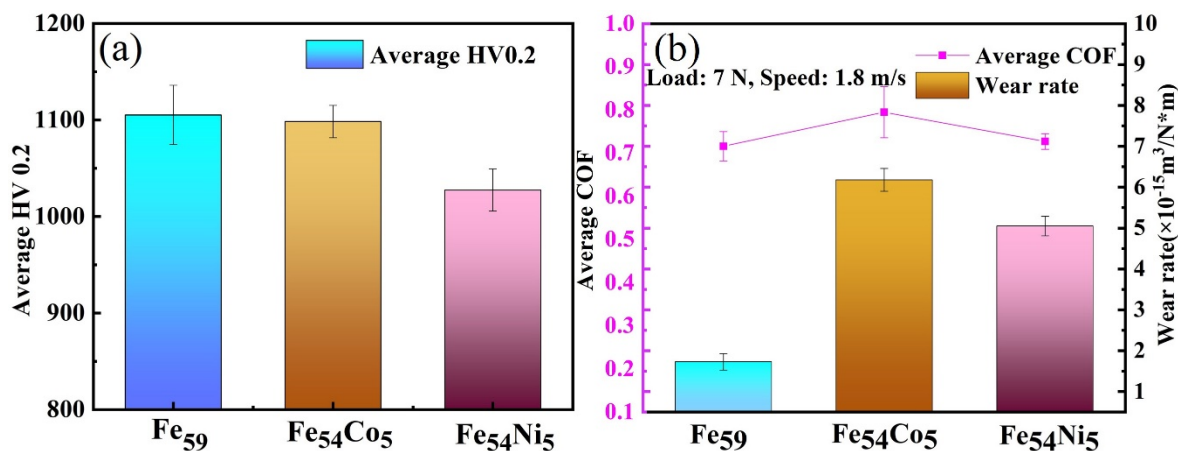


Figure 5. (a) Microhardness, (b) average coefficient of friction (COF), and wear rate of the Fe₅₄M₅Cr₁₅Mo₆Si₂B₄P₁₀C₄ (M = Fe, Ni, and Co) BMGs.

Friction and wear tests of the Fe-based BMGs were performed using pin-on-disk experiments, which were run against a GCr15 plate with a diameter of 60 mm and a hardness of 860 HV under a constant normal load of 7 N, a rolling speed of 1.8 m/s, and a sliding distance of 5000 m. The obtained average steady-state coefficient of friction (COF) and the wear rate, which is calculated by Equation (1), of the Fe-based BMG specimens are listed in Table 3 and shown in Figure 5b. Among the Fe-based BMGs, the Fe₅₉ BMG had the smallest wear rate of $1.73 \times 10^{-15} \text{ m}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, followed by the Fe₅₄Ni₅ BMG with a wear rate of $5.05 \times 10^{-15} \text{ m}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$; the Fe₅₄Co₅ BMG had the largest wear rate of $6.18 \times 10^{-15} \text{ m}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$. Furthermore, the wear rate of the Fe₅₉ BMG was relatively lower than those of the Fe₅₄Co₅ and Fe₅₄Ni₅ BMGs. The COF values for the Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅ BMGs under dry friction conditions were 0.716, 0.795, and 0.727, respectively. It was clear that the wear rates of the Fe-based BMG specimens exhibited an obvious

positive association with their COF under dry sliding conditions [36]. It should also be noted that the wear rates of the $\text{Fe}_{54}\text{Co}_5$ and $\text{Fe}_{54}\text{Ni}_5$ BMGs were negatively correlated, but not inversely proportional, with the microhardness. This indicates that the wear resistance of the Fe-based BMGs cannot be simply determined by their hardness, as predicted by the Archard equation.

Figure 6 shows the SEM (Scanning electron microscope) images of the worn areas of the Fe_{59} , $\text{Fe}_{54}\text{Co}_5$, and $\text{Fe}_{54}\text{Ni}_5$ BMGs. An EDS mapping test was performed on typical regions of the worn surfaces; their chemical compositions are summarized in Figure 6c,f,i. The worn surfaces of Fe_{59} exhibited various ploughed grooves parallel to the sliding direction, with different widths and depths, which are typical features corresponding to the abrasive-wear mechanism. In addition, as shown in Figure 6a,b, the worn surface of the Fe_{59} BMG was covered with tribo-patches, in which a high fraction of oxygen was observed through EDS (Energy Disperse Spectroscopy) mapping analysis, as shown in Figure 6c. This result demonstrates the oxidation of the tribo-patches of the Fe_{59} BMG during the sliding process. The worn surface of $\text{Fe}_{54}\text{Co}_5$, as shown in Figure 6d,e, exhibited a smooth morphology covered with a uniform oxide film (Figure 6f), including some small tribo-patches, indicating an oxidation wear mechanism. As shown in Figure 6g,h, the worn morphology of the $\text{Fe}_{54}\text{Ni}_5$ BMG exhibited much wear debris with grain-like wear particles, which resulted from a brittle failure characteristic, and many tribo-patches with diverse widths and lengths, indicating an adhesive wear mechanism.

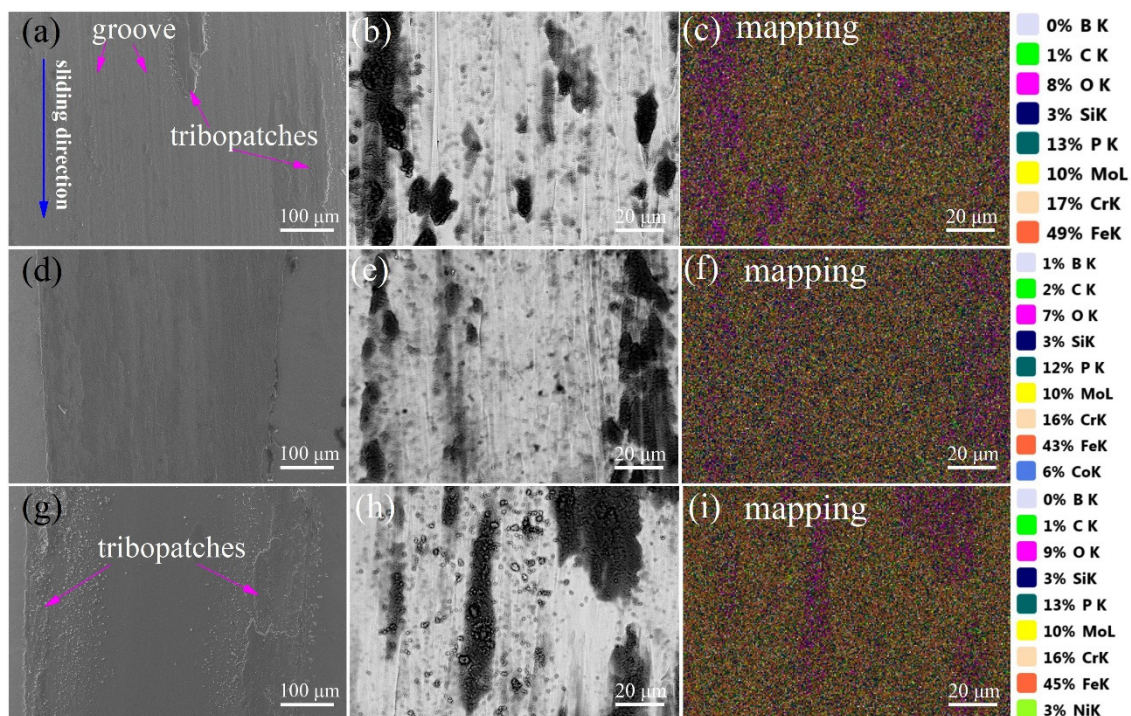


Figure 6. SEM images of wear surface morphology and EDS mapping of the Fe_{59} (a–c), $\text{Fe}_{54}\text{Co}_5$ (d–f), and $\text{Fe}_{54}\text{Ni}_5$ (g–i) glassy alloy rod specimens.

4. Conclusions

In this study, a new series of rare-earth-element-free $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($\text{M} = \text{Fe}$, Ni , and Co) BMGs were prepared, and the effects of Fe, Co, and Ni contents on the thermal stability, corrosion, and wear resistances of the Fe-based BMGs were investigated. The main results are as follows.

- (1) $\text{Fe}_{54}\text{M}_5\text{Cr}_{15}\text{Mo}_6\text{Si}_2\text{B}_4\text{P}_{10}\text{C}_4$ ($\text{M} = \text{Fe}$, Ni and Co) bulk glassy alloy rods were successfully prepared using the J-quenching and fluxing techniques. The D_{max} of the Fe_{59} , $\text{Fe}_{54}\text{Co}_5$, and $\text{Fe}_{54}\text{Ni}_5$ alloys reached 5.5, 4.5, and 4.0 mm, respectively.

- (2) The Fe-based BMGs exhibited high thermal stability, and the ΔT_x of the Fe₅₉ BMG reached 65 K. The T_g , T_x , and ΔT_x of the Fe-based BMGs decreased when Co and Ni substituted for Fe.
- (3) Electrochemical and EIS tests showed that, compared with 316L stainless steel, the Fe-based BMGs exhibited excellent corrosion resistance in a 3.5% NaCl solution with very low I_{corr} in the order of 10^{-8} – 10^{-7} A/cm². Among the Fe-based BMGs, the Fe₅₉ BMG exhibited the highest corrosion resistance with the highest positive E_{corr} , the lowest I_{corr} , and the most stable and widest passive region.
- (4) Friction and wear tests showed that the COF values of the Fe₅₉ (0.716), Fe₅₄Co₅ (0.795), and Fe₅₄Ni₅ (0.727) BMGs under the dry-friction condition had slight differences. Among the Fe-based BMGs, the Fe₅₉ BMG had the lowest wear rate of 1.73×10^{-15} m³.N⁻¹.m⁻¹, followed by the Fe₅₄Ni₅ BMG with a wear rate of 5.05×10^{-15} m³.N⁻¹.m⁻¹ and the Fe₅₄Co₅ BMG with a wear rate of 6.18×10^{-15} m³.N⁻¹.m⁻¹. SEM observation of the wear surface morphology indicated that the wear mechanisms of the Fe₅₉, Fe₅₄Co₅, and Fe₅₄Ni₅ BMGs were abrasive and oxidation, oxidation, and adhesive and oxidation, respectively.
- (5) The rare-earth-element-free Fe-based BMGs, particularly the Fe₅₉ BMG, showed potential as a coating material, owing to its combined advantages (low cost, large GFA, and excellent wear and corrosion resistances).

Author Contributions: Conceptualization, G.Z., Q.L. and W.S.; methodology, G.Z. and J.T.; validation, G.Z., Q.L. and W.S.; formal analysis, G.Z.; investigation, G.Z. and L.X.; resources, Q.L. and D.Z.; data curation, Q.L.; writing—original draft preparation, G.Z.; writing—review and editing, G.Z., Q.L., W.S., C.Z., X.P., X.M. and J.Y.; visualization, G.Z.; project administration, Q.L. and W.S.; funding acquisition, G.Z., Q.L. and W.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the University Science Research Planning Project of Xinjiang Uygur Autonomous Region, grant number XJEDU2021Y008, the key University Science Research Planning Project of Xinjiang Uygur Autonomous Region, grant number XJEDU2021I003, the Tianshan Innovation Team Program of Xinjiang Uygur Autonomous Region, grant number 2020D14038, the Xinjiang Autonomous Region Key Laboratory Open Fund, grant number 2020520002 and the “Talent Projects” of Urumqi Key Training Object.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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