

Article

Effect of Nickel Alloying on the Glass-Forming Ability and Corrosion Resistance of a Pt-Pd-Cu-P Bulk Metallic Glass

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Abstract

This study systematically investigates the effect of substituting Copper (Cu) with Nickel (Ni) on the glass-forming ability (GFA) and corrosion resistance of a Pt-based bulk metallic glass (BMG). We demonstrate that a minor substitution of 5 at.% Ni for Cu in the $\text{Pt}_{40}\text{Pd}_{20}\text{Cu}_{20}\text{P}_{20}$ base alloy significantly enhances both properties. The GFA is markedly improved, as evidenced by the supercooled liquid region (ΔT_x) widening from 68 K to 91 K. The optimized $\text{Pt}_{40}\text{Pd}_{20}\text{Cu}_{15}\text{Ni}_5\text{P}_{20}$ alloy exhibits a compressive fracture strength of 1.38 GPa. Electrochemical tests in a 3.5 wt.% NaCl solution reveal a substantial improvement in corrosion resistance. Compared to the Ni-free baseline alloy, the passive film resistance (R_f) and charge-transfer resistance (R_{ct}) of the Ni-containing alloy are enhanced by factors of 2.75 and 2.60, respectively. This superior performance is attributed to a synergistic effect wherein Ni alloying both stabilizes the amorphous structure and promotes the formation of a more robust passive film. This work presents a viable strategy for designing cost-effective, high-performance multi-component BMGs for applications in aggressive chloride environments.

Keywords: bulk metallic glass; glass-forming ability; pitting corrosion; electrochemical impedance spectroscopy; passive film



Academic Editors: Jose Manuel Torralba and Jiro Kitagawa

Received: 2 September 2025

Revised: 12 October 2025

Accepted: 14 October 2025

Published: 25 October 2025

Citation: Ao, P.; Song, S.; Liu, H.; Liu, L.; Liao, L. Effect of Nickel Alloying on the Glass-Forming Ability and Corrosion Resistance of a Pt-Pd-Cu-P Bulk Metallic Glass. *Metals* **2025**, *15*, 1188. <https://doi.org/10.3390/met15111188>

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1. Introduction

Bulk metallic glasses (BMGs), characterized by their long-range disordered atomic structure, represent a paradigm shift from traditional crystalline alloys. The absence of microstructural defects such as grain boundaries, dislocations, and precipitates endows them with a unique combination of properties, including near-theoretical strength, high elastic strain limits, and exceptional chemical homogeneity [1–5]. This inherent structural uniformity makes BMGs particularly resistant to localized corrosion phenomena, such as pitting, which typically initiate at the chemically active sites prevalent in crystalline materials [6–8]. Consequently, BMGs are prime candidates for demanding applications where both mechanical robustness and long-term stability in aggressive environments are paramount.

Among the vast family of BMGs, systems incorporating noble metals like Platinum (Pt) and Palladium (Pd) are of particular interest [9–11]. These elements impart exceptional chemical inertness and catalytic activity, making Pt- and Pd-based BMGs highly attractive for biomedical devices [12], luxury goods [10], and electrocatalysis [13]. Prototypical systems such as Pt-Cu-P and the landmark Pd-Cu-Ni-P have demonstrated remarkable glass-forming ability (GFA), enabling the fabrication of bulk amorphous parts with thin

dimensions [14–16]. However, the widespread application of these high-performance materials is often constrained by two key factors: the high cost of noble metals and the perpetual challenge of further enhancing their GFA to enable the manufacturing of larger and more complex components [17,18].

A promising strategy to address these challenges is through multi-component alloying, often termed the “confusion principle,” where the addition of new elements can frustrate crystallization and stabilize the amorphous phase [19–21]. Nickel (Ni), a cost-effective transition metal, presents a particularly compelling case as an alloying element. Ni is known to exhibit strong negative heat when mixing with metalloids like Phosphorus (P) and other constituent elements, which is a favorable thermodynamic indicator for glass formation [22,23]. Furthermore, Ni plays a crucial role in the passivation behavior of many corrosion-resistant alloys. It can significantly alter the chemistry and electronic properties of the surface passive layer (e.g., by forming stable NiO/Ni(OH)₂ species), thereby offering a powerful lever to control pitting susceptibility and repassivation kinetics [24]. While the role of Ni in the celebrated Pd-Cu-Ni-P system is well-established, its specific effect as a substitute for a primary component like Cu in a Pt-Pd-Cu-P quinary system remains unexplored.

Inspired by this, in this study, by regulating the content of Ni, the influence of Ni on the Pd-Cu-Ni-P alloy was investigated. The addition of 5 at.% Ni was found to significantly enhance the glass-forming ability and thermal stability, increasing the supercooled liquid region width (ΔT_x) from 68 K to 91 K. The optimized alloy exhibited a compressive fracture strength of 1.38 GPa. Impressively, this HE-MG not only retains excellent bending ductility after stress-relief annealing but also exhibits enhanced corrosion resistance in a 3.5% NaCl solution. The resistance of the passivation film and the charge transfer resistance were increased by 2.75 times and 2.60 times, respectively, implying the significant enhancement of corrosion resistance.

2. Materials and Methods

2.1. Alloy Fabrication

Amorphous alloy ribbons were fabricated in two sequential stages: first, to optimize the base composition of the quaternary Pt-Pd-Cu-P system, and second, to systematically investigate the effect of Ni addition on the optimized composition. For all alloys, master ingots were prepared from high-purity elements (Pt 99.9%, Pd 99.9%, Cu 99.99%, Ni 99.99%, P 99.5%) by arc-melting in a high-purity argon atmosphere. Each ingot was remelted four times to ensure chemical homogeneity. Amorphous ribbons were then produced from these ingots via single-roller melt-spinning. All subsequent characterization was performed on these as-spun ribbons.

Stage 1: Optimization of the Quaternary Base Alloy

In the initial stage, a broad range of quaternary alloys within the Pt-Pd-Cu-P system was fabricated to screen for the optimal glass-forming composition. This screening involved systematically varying the atomic ratios of Pt, Pd, and Cu. Based on a comprehensive analysis of their thermal properties, the composition Pt₄₀Pd₂₀Cu₂₀P₂₀ was identified as exhibiting a superior combination of glass-forming ability and thermal stability and was selected as the base alloy for the subsequent stage.

Stage 2: Investigation of Ni Alloying Effects

In the second stage, the effect of Ni was investigated by substituting Cu in the optimized base alloy, yielding a series of quinary compositions with the formula Pt₄₀Pd₂₀Cu_(20-x)Ni_xP₂₀ (where $x = 0, 2.5, 5, 5.5, 7.5, 10$, and 15 at.%). For clarity, these samples are hereafter designated Ni-0, Ni-2.5, Ni-5, etc., corresponding to their Ni content.

2.2. Experimental Procedure

The amorphous nature of the as-spun ribbons was verified by X-ray diffraction (XRD) using a Rigaku D/Max-2200/PC diffractometer (Tokyo, Japan) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scans were performed over a 2θ range of $20\text{--}80^\circ$ at a speed of $5^\circ/\text{min}$.

Thermal analysis was conducted to determine the characteristic temperatures of the alloys. The glass transition temperature (T_g) and the onset of crystallization (T_x) were measured using a Perkin-Elmer DSC-6 differential scanning calorimeter (DSC, Waltham, MA, USA). Samples of approximately 15 mg were heated at a constant rate of 40 K/min under a flowing pure argon atmosphere. The melting point (T_m) and liquidus temperature (T_l) were determined using a separate differential thermal analyzer (DTA) (Shimadzu Corporation, Kyoto, Japan) capable of reaching higher temperatures, under identical heating rates and atmospheric conditions. The supercooled liquid region is defined as $\Delta T_x = T_x - T_g$.

Uniaxial compression tests were performed on the $\text{Pt}_{40}\text{Pd}_{20}\text{Cu}_{15}\text{Ni}_5\text{P}_{20}$ (Ni-5) alloy to evaluate its mechanical properties, including sample dimensions (cylindrical rods with a 2:1 aspect ratio) and strain rate ($1 \times 10^{-4} \text{ s}^{-1}$). Tests were carried out on a Zwick/Roell Z100 servo-electric frame (Ulm, Germany) at room temperature. Cylindrical specimens with a diameter of 3 mm and length 6 mm (aspect ratio 2:1, in accordance with ASTM E9-19) were machined from the as-cast rods by slow-speed diamond cutting and subsequently ground with 2000-grit SiC paper to ensure parallel end faces (parallelism within $\pm 5 \text{ }\mu\text{m}$). A constant engineering strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ was imposed under displacement control. The fracture surfaces of the compressed samples were examined using scanning electron microscopy (SEM) (Zeiss, Oberkochen, Germany) to identify the deformation and fracture mechanisms.

Electrochemical measurements were conducted in a 3.5 wt.% NaCl aqueous solution at ambient temperature using a standard three-electrode cell configuration. The alloy ribbon served as the working electrode, a platinum mesh as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to each measurement, the working electrode was mechanically polished, cleaned, and then stabilized at its open-circuit potential (OCP) for 60 min.

Potentiodynamic polarization curves (PPC) were recorded by scanning the potential from -250 mV to $+1200 \text{ mV}$ versus OCP at a scan rate of 1 mV/s . Electrochemical impedance spectroscopy (EIS) was performed at the OCP over a frequency range from 100 kHz to 10 mHz with a 10 mV (rms) sinusoidal perturbation. The resulting EIS data were fitted to an equivalent electrical circuit (EEC) model to extract quantitative parameters. Mott-Schottky analysis was conducted by scanning the potential in the passive region at a frequency of 1 kHz to characterize the semiconductor properties of the passive film [25].

3. Experiment Result

3.1. Optimization of the Composition of Pt-Pd-Cu-P Amorphous Alloys

In order to understand the structure and characteristics of the samples. A systematic compositional screening was performed on the Pt-Pd-Cu-P quaternary system to optimize its GFA. The amorphous nature of the as-spun ribbons was confirmed via XRD. As presented in Figure 1a, the patterns for representative compositions, including $\text{Pt}_{24}\text{Pd}_{32}\text{Cu}_{24}\text{P}_{20}$, $\text{Pt}_{32}\text{Pd}_{16}\text{Cu}_{32}\text{P}_{20}$, and $\text{Pt}_{48}\text{Pd}_{16}\text{Cu}_{16}\text{P}_{20}$, each exhibit a single, broad diffraction halo centered at approximately $2\theta \approx 40^\circ$, with no discernible Bragg peaks corresponding to crystalline phases.

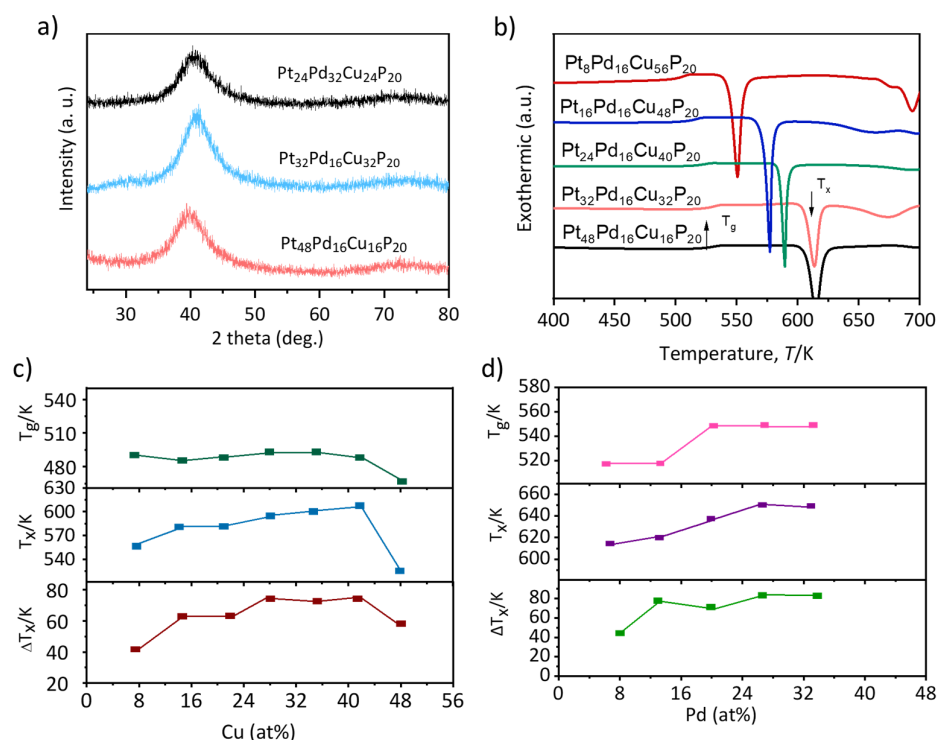


Figure 1. (a) XRD patterns and (b) DSC curves of $Pt_{80-x-y}Pd_xCu_yP_{20}$ ($x = 8-56\%$, $y = 8-56\%$) ribbons. (c) As the Cu content varies in $Pt_{16}Pd_{64-x}Cu_xP_{20}$ ($x = 8-56\%$), changes occur in the glass T_g , T_x , and ΔT . (d) The changes in the Pt content for $Pt_{16}Pd_{64-x}Cu_xP_{20}$ ($x = 8-56\%$).

The thermal behavior of the alloys was characterized by DSC, as shown in Figure 1b. The DSC traces universally display a distinct glass transition followed by a single exothermic crystallization event. The T_g and T_x were found to be in the ranges of 500–550 K and 550–600 K, respectively. This yields a supercooled liquid region ($\Delta T_x = T_x - T_g$) of approximately 50 K, indicating a favorable thermal stability window for potential thermo-plastic forming.

To further refine the GFA, the influence of individual constituent elements was investigated. For the $(Pt_{16}Pd_{64-x}Cu_x)P_{20}$ series (Figure 1c), it was observed that while the Cu content had a minimal effect on T_g , it systematically elevated T_x . Consequently, the supercooled liquid region was widened, reaching a maximum for Cu concentrations between 32 and 48 at.%, which underscores the critical role of Cu in enhancing the thermal stability of the undercooled liquid. In contrast, for the $(Pt_{64-x}Pd_xCu_{16})P_{20}$ series (Figure 1d), the partial substitution of Pt with Pd resulted in a concurrent increase in both T_g and T_x . However, this led to a relatively stable ΔT_x across the tested compositional range, suggesting that the Pt/Pd ratio has a less pronounced effect on the width of the supercooled liquid region in this specific series.

3.2. The Study of Structural Transformation of Amorphous Crystals

To contextualize the impact of Ni substitution, the GFA landscape of the parent Pt-Pd-Cu-P quaternary system was first surveyed. DSC traces (Figure 2a) reveal a pronounced compositional dependence of the super-cooled-liquid region width (ΔT_x). A broad GFA domain is identified, with ΔT_x attaining a maximum of 84 K at 16–48 at.% Pt, 16–32 at.% Pd and 16–32 at.% Cu. In Pd- or Cu-rich regimes, ΔT_x declines markedly, signaling deteriorated GFA. The left panel of Figure 2b systematically maps the correlation between alloy composition and ΔT_x , whereas the right panel denotes compositions that yield bulk-amorphous rods upon water quenching, corroborating the general rule that wider ΔT_x

implies superior GFA and thermal stability. Additionally, the DTA melting trace of the base alloy (Figure 2c) exhibits a single, sharp endothermic peak, evidencing a near-eutectic composition and intrinsically high glass-forming propensity.

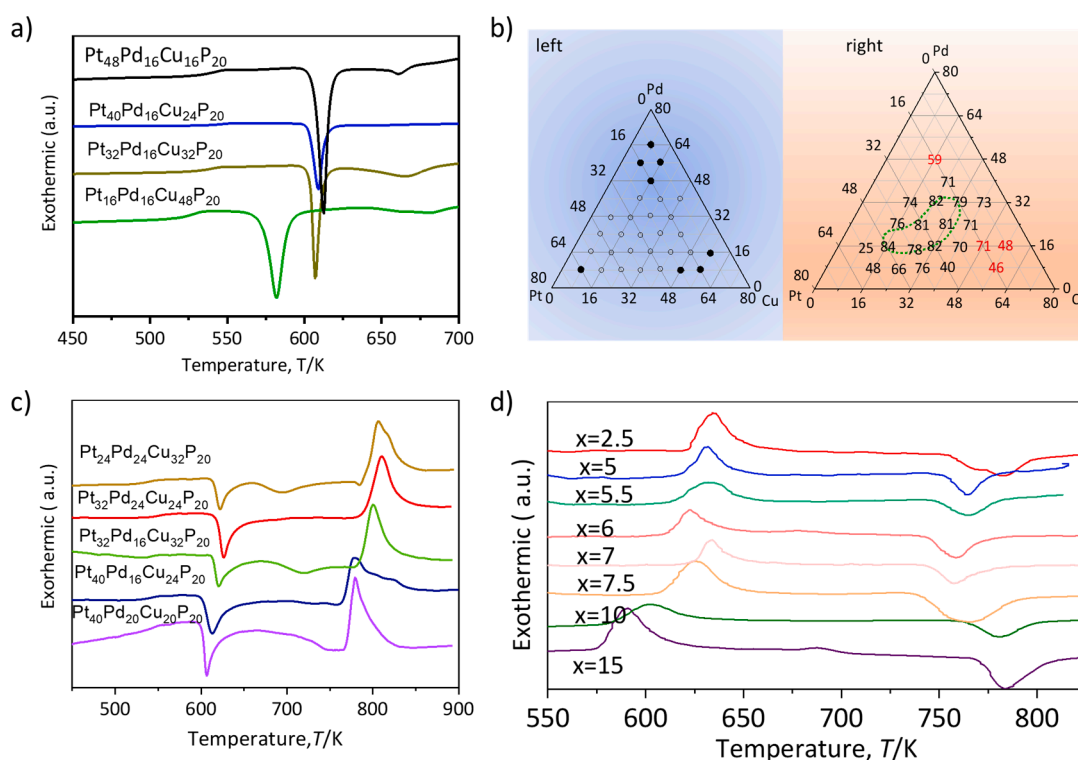


Figure 2. (a) The DSC (Differential Scanning Calorimetry) curve of Pt-Pd-Cu-P bulk amorphous alloy. (b) The temperature of the supercooled region in the Pt-Pd-Cu alloy varies with composition changes (left) and the composition range for the formation of large amorphous phases of Pt-Pd-Cu alloy (right). (c) DSC curve of Pt_{80-x-y}Pd_xCu_yP₂₀, (d) DTA curves of Pt-Pd-Cu-P-Ni alloy.

The thermal properties of the resulting PtPdCu_(20-x)Ni_xP ($x = 0-15$ at.%) alloy series are summarized in Table 1, with representative DTA curves shown in Figure 2d and Table 1. It reveals a pronounced enhancement in the thermal stability of the supercooled liquid upon Ni addition. The Ni-0 base alloy exhibits a supercooled liquid region width ($\Delta T_x = T_x - T_g$) of 68 K. Upon substitution with 5 at.% Ni (the Ni-5 alloy), ΔT_x increases substantially to a maximum of 91 K, representing a 34% improvement. A wider ΔT_x signifies a greater resistance to crystallization upon heating, which is a direct indicator of enhanced GFA.

Table 1. T_g , T_x , T_m , T_l of Pt-Pd-Cu-P-Ni alloys and parameter values characterizing GFA.

	T_g	T_x	ΔT_x	T_m	T_l	T_{rg}
Pt ₄₀ Pd ₂₀ Cu ₂₀ P ₂₀	533	601	68	767	823	0.65
Pt ₄₀ Pd ₂₀ Cu ₁₅ Ni ₅ P ₂₀	531	622	91	756	784	0.69
Pt ₄₀ Pd ₂₀ Cu ₁₃ Ni ₇ P ₂₀	546	625	79	747	810	0.67
Pt ₄₀ Pd ₂₀ Cu ₁₀ Ni ₁₀ P ₂₀	520	586	66	769	800	0.65
Pt ₄₀ Pd ₂₀ Cu ₅ Ni ₁₅ P ₂₀	508	577	69	772	806	0.63

To further quantify the GFA from a thermodynamic perspective, the reduced glass transition temperature ($T_{rg} = T_g/T_l$) was calculated. This parameter, which normalizes the glass transition temperature against the liquidus temperature, is considered a more robust indicator of GFA. As detailed in Table 1, the T_{rg} value also peaks at 0.69 for the Ni-5 composition, corroborating the trend observed with ΔT_x and confirming that this

composition possesses the highest GFA within the investigated series. Further evidence for the optimal nature of the 5 at.% Ni composition is found in the alloy's melting behavior, as observed in the DTA traces (Figure 2d). For the Ni-5 alloy, the melting event is characterized by the sharpest endothermic peak, and the temperature interval between crystallization and melting is minimized. Such features are characteristic of a composition near a deep eutectic, which kinetically and thermodynamically favors the suppression of crystallization and promotes glass formation. The collective analysis of ΔT_x , T_{rg} , and DTA melting characteristics consistently indicates that a 5 at.% substitution of Cu with Ni is the optimal modification for maximizing the glass-forming ability of this alloy system. This enhancement can be partially attributed to the increase in the configurational entropy of mixing (ΔS_{mix}) upon introducing a fifth element, which thermodynamically favors the formation of a disordered amorphous state over a competing crystalline phase.

Further XRD characterization (as shown in Figure 3) of Ni-5 revealed a pronounced broad diffuse halo centered at approximately $2\theta \approx 40^\circ$, and no sharp Bragg peaks corresponding to any known crystalline phases were observed across the entire scan range, indicating that the sample is amorphous (lacking long-range crystalline order).

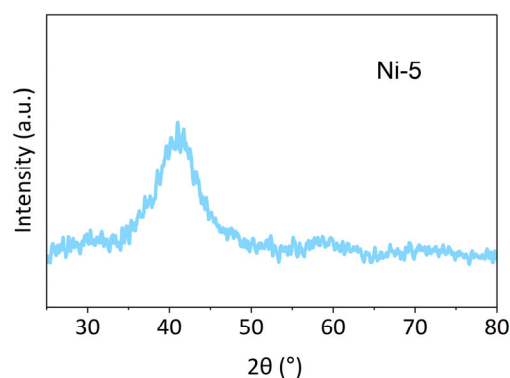


Figure 3. XRD patterns of the Ni-5 sample.

4. The Study of the Properties of Pt-Pd-Cu-P-Ni Alloys

4.1. The Performance of Mechanical Property for Pt-Pd-Cu-Ni-P Alloys

The compressive stress–strain curve for the optimized Ni-5 alloy is shown in Figure 4. Compared to its initial as-cast state, a slight increase in compressive fracture strength is observed, accompanied by a modest reduction in fracture strain as the heat treatment temperature rises. This subtle change can be attributed to the minor adjustments in the alloy's microstructure following heat treatment. The data clearly show that the as-cast high-entropy alloys exhibit a strength of 1.38 ± 0.2 GPa, although their plasticity is somewhat limited at 4.4%.

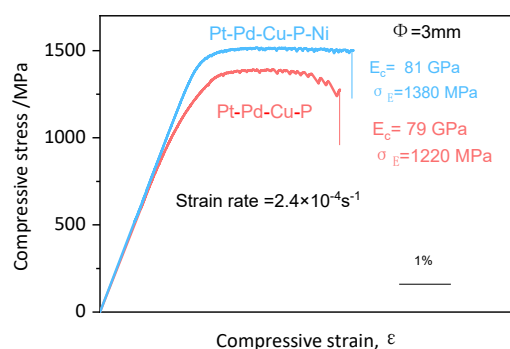


Figure 4. The stress–strain curve of the Pt-Pd-Cu-P-Ni amorphous alloy.

The fracture surface morphology of the compressed Ni-5 sample was examined by SEM (Figure 5). The surface is dominated by a dense network of vein-like patterns (Figure 5a), which is a characteristic fracture feature of BMGs that have undergone plastic deformation. These patterns arise from the localized softening and viscous flow of material within the shear band just prior to catastrophic failure. Examination of the sample's side surface (Figure 5b) reveals the presence of multiple, well-defined shear bands, which are the primary carriers of plastic deformation in amorphous alloys. The operation of these multiple shear bands before one becomes critical is consistent with the observed macroscopic plasticity of 4.4%.

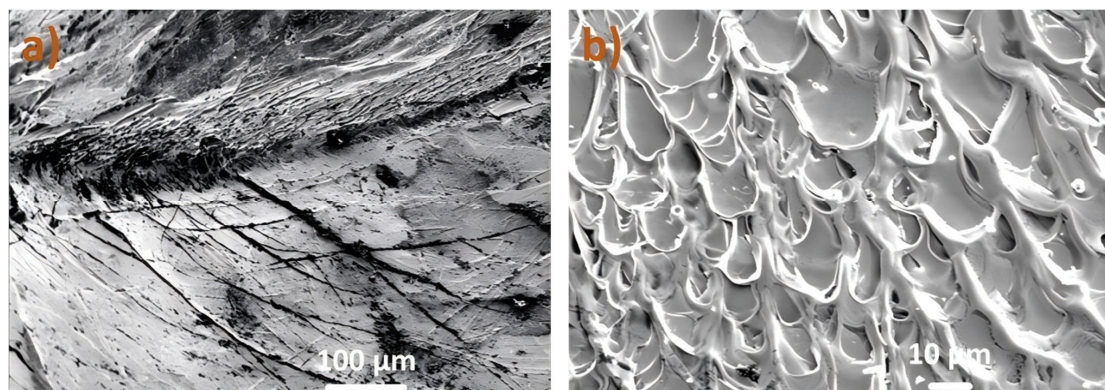


Figure 5. SEM images of the Pt-Pd-Cu-P-Ni amorphous alloy's surface at different scales from the compression test. (a) Sample surface morphology. (b) Sample side morphology.

4.2. Electrochemical Corrosion Performance

4.2.1. Potentiodynamic Polarization Curves

Based on its excellent structural properties, the corrosion performance of the alloys was evaluated primarily through electrochemical testing, encompassing both anodic and cathodic processes. Potentiodynamic polarization curves (PPC) were employed to characterize the electrochemical behavior of these alloys in a 3.5% NaCl solution. According to the data presented in Figure 6 and Table 2, as the Ni content increases, the corrosion potential of the alloys gradually rises, indicating a significant improvement in their stability in corrosive environments. Specifically, the corrosion potential of the Ni-0 alloy is 378 ± 21 mV, with a corrosion current density of 3.6×10^{-4} A/cm²; for the Ni-5 alloy, the corrosion potential is 485 ± 13 mV, with a corrosion current density of 3.1×10^{-4} A/cm². The addition of Ni significantly enhances the corrosion potential of the alloy, thereby improving its corrosion stability. Overall, the increase in Ni content effectively enhances the corrosion resistance of the alloys, particularly by raising the corrosion potential, which leads to a marked improvement in their stability in corrosive environments.

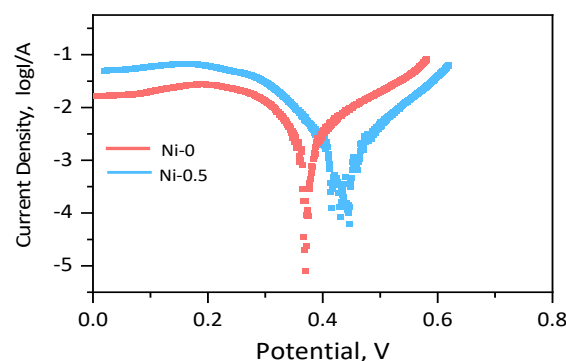


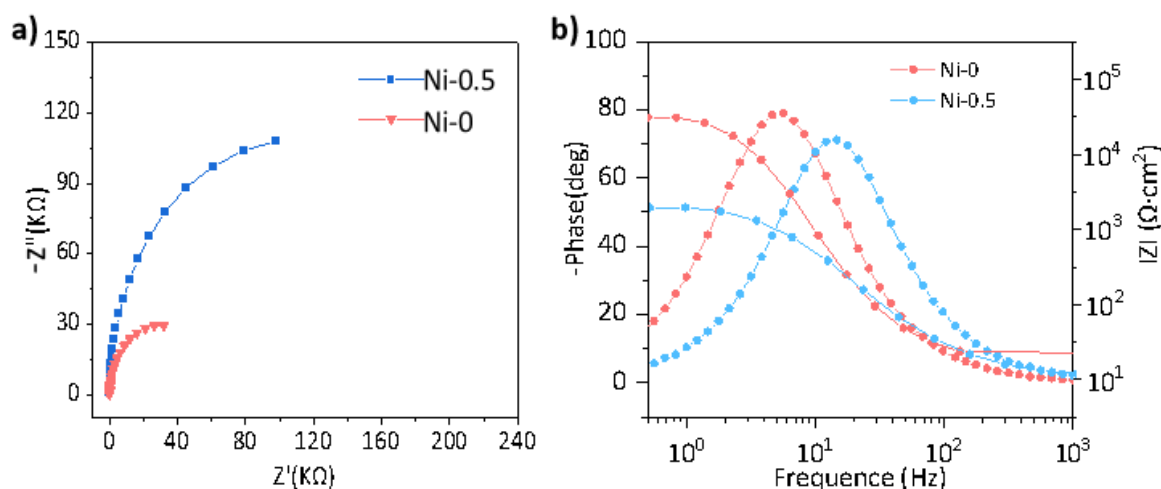
Figure 6. PPCs of Pt-Pd-Cu-Ni-P and Pt-Pd-Cu-P immersion corrosion test.

Table 2. Electrochemical parameters derived from polarization tests of cast HEAs in a 3.5 wt.% NaCl solution.

Material	E_{corr} (mV _{SCE})	I_{corr} (A/cm ²)
Ni-0	378 ± 21	3.6×10^{-4}
Ni-5	485 ± 13	3.1×10^{-4}

4.2.2. Electrochemical Impedance Spectroscopy (EIS)

To elucidate the intrinsic electrochemical corrosion mechanism of the alloys, we systematically investigated their steady-state response in a NaCl solution using electrochemical impedance spectroscopy (EIS). The EIS analysis (Figure 7) reveals that the Ni-5 alloy exhibits superior corrosion resistance compared to the Ni-0 baseline, a performance primarily attributed to the exceptional chemical stability and structural integrity of its surface passivation layer. This conclusion is directly substantiated by the impedance response. In the Nyquist plot (Figure 7a), the Ni-5 alloy displays a significantly enlarged capacitive arc, indicating a remarkably high polarization resistance. This is further corroborated in the Bode plot (Figure 7b), where its low-frequency impedance modulus ($|Z|_{0.01\text{Hz}}$) exceeds that of the Ni-0 alloy by more than an order of magnitude to reach a level of $10^4 \Omega \cdot \text{cm}^2$. Concurrently, its broader phase angle peak approaching -90° signifies the formation of a dense and near-ideal capacitive passive interface.

**Figure 7.** (a) Nyquist and (b) Bode plots for Ni-0 and Ni-5.

To quantitatively deconvolute the contributions of the interfacial processes to the impedance, the data were fitted using a physically meaningful equivalent electrical circuit (EEC) model of Figure 8 (see Table 3 for fitting parameters). The results precisely unveil the origin of the performance disparity: the passive film resistance ($R_f = 4.53 \times 10^4 \Omega \cdot \text{cm}^2$) and charge-transfer resistance ($R_{ct} = 4.92 \times 10^5 \Omega \cdot \text{cm}^2$) of the Ni-5 alloy are 2.75- and 2.60-fold higher, respectively, than those of the Ni-0 alloy. The marked increase in R_f indicates a dense, low-defect passivation film acting as a formidable physical barrier that effectively suppresses the ingress of chloride ions. Meanwhile, the concurrent elevation in R_{ct} implies that charge-transfer processes at the film/electrolyte interface, including anodic dissolution and cathodic reactions, are severely kinetically hindered.

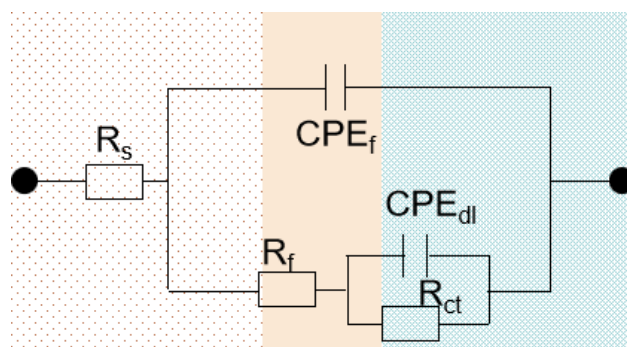


Figure 8. An equivalent circuit model used to fit the EIS data of HEAs.

Table 3. The parameters of the equivalent electrical circuit used for the electrochemical impedance spectroscopy analysis of the alloys.

Material	R_s ($\Omega \cdot \text{cm}^2$)	R_f ($10^4 \cdot \Omega \cdot \text{cm}^2$)	R_{ct} ($10^5 \cdot \Omega \cdot \text{cm}^2$)
Ni-0	10.14	1.65	1.89
Ni-5	13.23	4.53	4.92

The corrosion mechanism of the alloy is strongly linked with the semiconductor properties of the passive layer. As shown in Figure 9, the Mott–Schottky plots exhibit positive slopes, unequivocally confirming the n-type semiconducting character of the passive film. With increasing Ni additions, the absolute slope monotonically decreases [26].

$$d = \sqrt{\frac{2\epsilon\epsilon_0(E - E_{fb} - KT/b)}{eN_D}} \quad (1)$$

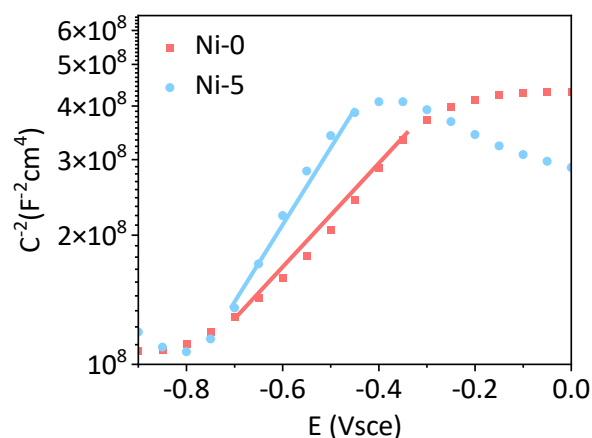


Figure 9. Mott–Schottky plots of the passive layers of alloys.

Here, ϵ is the relative dielectric constant of the passive film (taken as 15.6), ϵ_0 the vacuum permittivity ($8.85 \times 10^{-14} \text{ F cm}^{-1}$), e the elementary charge ($1.602 \times 10^{-19} \text{ C}$), E_{fb} the flat-band potential, K Boltzmann’s constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), and T the absolute temperature [27]. According to the Mott–Schottky relation, the slope is inversely proportional to the donor density; consequently, the observed decrease in slope (Equation (1)) demonstrates that Ni incorporation increases the passive-film thickness.

The significant enhancement in corrosion resistance of the Ni-5 alloy compared to its Ni-0 counterpart in a NaCl solution can be attributed to the formation of a highly uniform amorphous structure. This structure, which features long-range atomic disorder

and short-range chemical ordering, effectively eliminates conventional defects such as grain boundaries that typically serve as primary initiation sites for corrosion. As a result, the Ni-5 alloy exhibits significantly reduced corrosion, with the formation of a largely intact passive film (Figure 10b), while the Ni-0 alloy experiences severe corrosion and localized surface spalling (Figure 10a). Therefore, the role of Ni is twofold: it contributes thermodynamically to the formation of this uniform amorphous substrate and chemically enhances the stability and protective capacity of the overlying passive film. This synergy between an advanced structure and beneficial composition ultimately leads to superior corrosion resistance.

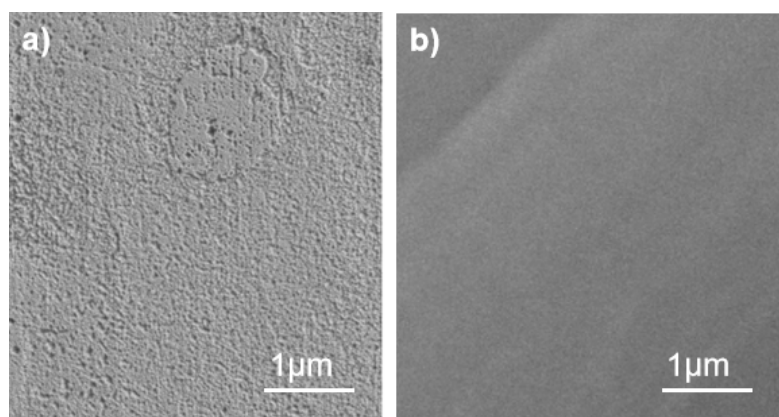


Figure 10. SEM images of (a) Ni-0 and (b) Ni-5 inclusions for corrosion morphology after immersion.

5. Discussions

5.1. Mechanism of Enhanced Glass-Forming Ability

The substitution of 5 at.% Cu with Ni leads to a remarkable improvement in GFA, as evidenced by the significant increase in ΔT_x and T_{rg} . This can be understood through the established empirical rules for BMG formation, which emphasize the roles of atomic size mismatch, negative heats of mixing (ΔH_{mix}), and multi-component “confusion”.

As shown in Table 4, Ni has an atomic radius (1.28 Å) similar to Cu (1.27 Å) but different from Pt (1.77 Å), Pd (1.69 Å), and P (0.98 Å). The introduction of Ni maintains the significant atomic size differences within the five-element system, which frustrates the efficient atomic packing required for crystallization. More importantly, Ni exhibits strong negative heats of mixing with Pt (−8 kJ/mol), Pd (−10 kJ/mol), and P (−5 kJ/mol). These strong, attractive interactions between dissimilar atom pairs increase the viscosity of the undercooled liquid and raise the energetic barrier for the atomic rearrangement necessary for crystal nucleation and growth, thereby stabilizing the disordered amorphous phase. The addition of a fifth component also increases the configurational entropy of the system, which thermodynamically favors the disordered glassy state over competing crystalline phases, an effect often termed the “confusion principle”. The peak GFA at 5 at.% Ni suggests that this composition achieves an optimal balance of these thermodynamic and kinetic factors, likely positioning it closer to a deep eutectic in the quinary phase space.

Table 4. Properties of selected alloying elements (Adapted from Ref. [28]).

	Pt	Pd	Cu	P	Ni				
Atomic radius	1.77	1.69	1.27	0.98	1.28				
Group element	Pt-Cu	Pt-P	Pd-Cu	Pd-P	Pt-Pd	Cu-P	Pt-Ni	Pd-Ni	Ni-P
Radius difference (%)	29	45	26	42	4.5	22	28	24	23
ΔH (J/mol)	−12	−26	−14	−28	2	−9	−8	−10	−5

5.2. Unifying the Corrosion Mechanism

Defects as Facilitators of Repair: According to the Point Defect Model (PDM), point defects such as oxygen vacancies (the likely source of n-type behavior) are the primary charge carriers for ionic transport through the passive film. While a high defect density might imply a less-perfect insulator, it can also provide more pathways for ionic diffusion. A higher donor density (N_D) can therefore lead to a higher ionic flux and, consequently, a faster film growth and repair rate [29,30]. Additionally, in an aggressive chloride environment, a passive film is not a static barrier. It is under constant attack, leading to localized breakdown events. The overall corrosion resistance of the material is determined less by the film's initial perfection and more by its ability to rapidly repair these local breaches.

Thus, while Ni promotes interfacial charge transfer kinetics, its primary role is to stabilize the passive film electronically and structurally, shifting the corrosion mechanism toward a more controllable, passivation-dominated regime. This agrees with EIS and PDP data which corroborate this interpretation. The highest-Ni alloy displays ultimately degrading corrosion resistance.

6. Conclusions

The partial substitution of Cu with 5 at.% Ni in the Pt₄₀Pd₂₀Cu₂₀P₂₀ base alloy significantly improves its GFA. The supercooled liquid region (ΔT_x) is widened from 68 K to 91 K, and the reduced glass transition temperature (T_{rg}) increases from 0.65 to a peak of 0.69, indicating enhanced thermal stability of the undercooled liquid. The optimized Ni-5 alloy possesses robust mechanical properties, with a compressive fracture strength of 1.38 GPa and fracture morphology indicative of a ductile failure mode in a 3.5 wt.% NaCl solution compared to the Ni-free alloy. This is evidenced by a significant corrosion potential, which significantly increases in both passive film resistance (2.75-fold) and charge-transfer resistance (2.60-fold). A novel corrosion resistance mechanism is proposed to resolve the apparent contradiction between superior performance (EIS) and higher defect density (Mott–Schottky). We conclude that Ni incorporation endows passive films with enhanced self-healing capabilities, leading to greater dynamic stability in a chloride-rich environment.

Author Contributions: Conceptualization, P.A. and L.L. (Luliang Liao); Software, P.A., S.S., H.L. and L.L. (Lei Liu); Formal analysis, S.S. and L.L. (Lei Liu); Data curation, S.S., H.L. and L.L. (Luliang Liao); Writing—original draft, P.A.; Writing—review & editing, L.L. (Luliang Liao); Funding acquisition, P.A. and L.L. (Luliang Liao). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science and Technology Program of Education Office of Jiangxi Province (grant numbers: GJJ212312 and GJJ202321).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

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

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