A high-resolution compositional map of glass-forming ability (GFA) in the Ni–Cr–Nb–P–B system is experimentally determined along various compositional planes. GFA is shown to be a piecewise continuous function formed by intersecting compositional sub-surfaces, each associated with a nucleation pathway for a specific crystalline phase. Within each sub-surface, GFA varies exponentially with composition, whereas exponential cusps in GFA are observed when crossing from one crystallization pathway to another. The overall GFA is shown to peak at multiple exponential hypercusps that are interconnected by ridges. At these compositions, quenching from the high-temperature melt yields glassy rods with diameters exceeding 1 cm, whereas for compositions far from these cusps the critical rod diameter drops precipitously and levels off to 1 to 2 mm. The compositional landscape of GFA is shown to arise primarily from an interplay between the thermodynamics and kinetics of crystal nucleation, or more precisely, from a competition between driving force for crystallization and liquid fragility.

The glass-forming ability, or GFA, of a liquid metal alloy is not an intrinsic material attribute, but rather defined by the absence of a viable crystallization pathway as the liquid is under-cooled below its thermodynamic melting temperature (1, 2). Crystallization is typically triggered by nucleation of a particular crystalline phase, followed by other competing phases, often catalyzed by the presence of the first phase. Crystal nucleation rates depend not only on temperature, pressure, and alloy composition, but also on extrinsic factors such as the presence of chemical impurities, trace crystalline debris (e.g., oxide inclusions), container wall effects, or shear flow conditions in the liquid, to name a few (3–7). Variations in these extrinsic factors often lead to inconsistent and nonreproducible GFA.

The classical nucleation theory of crystals in undercooled liquids was originally developed by Turnbull (1) to account for the substantial undercooling observed in elemental liquid metals. He later extended his theory to explain metallic glass formation in rapidly cooled low melting eutectic Au–Si and Au–Ge–Si alloys (8, 9). Below the liquidus temperature \( T_L \), the liquid viscosity, \( \eta(T) \), rises steeply with falling temperature. A liquid ultimately freezes at a glass transition temperature \( T_g \) where the viscosity reaches a solid-like value of \( \sim 10^{12} \) Pa·s. Turnbull considered the “reduced glass transition temperature” \( T_g' = T_g / T_L \) as a characteristic material parameter. He argued that crystal nucleation rates should fall precipitously as \( T_g' \) increases, becoming immeasurably small for \( T_g' \approx 2/3 \). This is widely referred to as Turnbull’s criteria for bulk glass formation; it has been proven to be a valuable, albeit rough, guide in the development of bulk metallic glasses (10–12).

In the present work, a systematic experimental approach is developed to quantify the intrinsic dependence of GFA on composition for near-eutectic multicomponent metal alloys. The optimization of GFA for quinary Ni–Cr–Nb–P–B alloys is presented as a case study wherein bulk glasses of centimeter thickness are achieved. This quinary system is based on the low melting binary Ni$_{36}$P$_{60}$ eutectic alloy with small additions of Cr and Nb as substitutes for Ni, and B as a substitute for P. Binary Ni–P and ternary Ni–Cr–P alloys have long been known to form glassy ribbons of 20 to 40-μm thickness on quenching from the melt at cooling rates of \( 10^5 \) to \( 10^6 \) K/s using rapid melt quenching approaches such as planar flow casting (13, 14). Following the discovery of bulk metallic glasses, Hashimoto and coworkers (15) as well as Inoue and coworkers (16) investigated bulk glass formation in quinary Ni–Cr–Nb–P–B alloys and identified specific alloy compositions capable of forming metallic glass rods with diameters of 1 to 2 mm. In the current investigation, by using an efficient and reproducible GFA assessment and optimization strategy, we report that maximum attainable metallic glass rod diameters in the same Ni–Cr–Nb–P–B system are an order of magnitude larger (1–2 cm) than reported in prior work.

To accurately quantify the intrinsic composition dependence of GFA requires (i) precisely controlling alloy composition and impurity content, (ii) quantitatively and reproducibly determining GFA at a specific composition by controlling the sample cooling history, and (iii) minimizing the influence of extrinsic factors such as heterogeneous nucleation sites (foreign oxide inclusions, the container wall, etc.) and melt flow conditions during cooling. In this work, alloys with precisely controlled composition were produced from high-purity starting elements. GFA was determined by melting the alloys in silica tubes and subsequently water quenching to form metallic glass rods. The silica tubes exhibit no detectable reaction with the present alloys. Moreover, being a glass, the silica tube is not expected to induce heterogeneous nucleation at the inner wall. Finally, the melt being confined inside the tube during quenching does not undergo significant shear flow. As such, the cooling history of the sample is governed almost solely by conduction without any significant convection, and is therefore expected to be reproducible. GFA is characterized by a critical rod diameter, \( d_{cr} \), defined as the largest diameter rod that can be quenched into a fully glassy structure without detectable crystallinity, as verified by X-ray diffraction. Additional details on the alloy preparation, characterizations, and data analysis can be found in Supporting Information S1.

**Significance**

This paper reports and explains the exponential dependence of crystal nucleation rates on alloy composition for an undercooled liquid. It is shown that maxima in alloy glass-forming ability (GFA) take the form of exponential hypercusps in composition space. The approach is illustrated by optimizing the composition of a five-component nickel–chromium-base metallic glass to achieve order-of-magnitude improvements in GFA over prior work. Variations in GFA are shown to arise from the interplay between alloy-melting behavior and the liquid rheology.


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cooling history, and determination of GFA are presented in Materials and Methods.

The quinary Ni–Cr–Nb–P–B system has a 4D composition space with independent variables, \(w, x, y, z\), and \(w\), where composition is expressed as \(\text{Ni}_{100-w-x-y-z} \text{Cr}_w \text{Nb}_y \text{P}_{z} \text{B}_w\). The variables are in atomic percentages. In Fig. 1A, we present a detailed 2D GFA contour map associated with composition variation along 2 degrees of freedom, \(w\) and \(x\), while keeping \(y\) and \(z\) constant at 16.5 and 3, respectively. This high-resolution contour map is based on the measured \(d_{cr}\) for 42 alloys. Two distinct local maxima with \(d_{cr} \geq 10\) mm are clearly evident in the contour map. More specifically, along the compositional line \(x = 4.0625 - 0.125w\) (where \(y\) and \(z\) are held constant at 16.5 and 3), a ridge interconnecting the two peaks is observed in the GFA landscape. The compositional dependence of GFA along this compositional line is presented in Fig. 1B. Along this ridge and within 4.5 < \(w\) < 10.5 (which corresponds to 2.75 < \(x\) < 3.5), \(d_{cr}\) is found to vary between 8 and 10 mm, whereas a precipitous dip in the GFA is observed for \(w < 4.5\) and \(w > 10.5\). At \(w = 5.6\) and 8.5 (corresponding to \(x = 3.4\) and 3), the compositions \(\text{Ni}_{86.5} \text{Cr}_{7.5} \text{Nb}_{13} \text{P}_{16.5} \text{B}_3\) and \(\text{Ni}_{80} \text{Cr}_{9.5} \text{Nb}_{19.5} \text{B}_3\) are seen to exhibit local maxima with \(d_{cr} \geq 10\) mm.

In Fig. 2A we present a second 2D GFA contour map associated with composition variation in the \(x\)–\(z\) plane. This map was generated from GFA data on 58 separate alloy compositions. Another ridge in the GFA landscape is identified in this compositional plane along the compositional line \(x = z\) where the sum of transition metals \((w + x)\) and metalloids \((y + z)\) are held constant at 11.5 and 19.5, respectively. The GFA compositional dependence along this line is presented in Fig. 2B. Along this ridge with \(3 < (x, z) < 4\), \(d_{cr}\) varies between 9 and 10 mm, whereas it gradually degrades outside this range. A ridge in GFA along \(x = z\) suggests that the GFA dependence on Nb and B contents is strongly correlated. This suggests Nb and B atoms tend to occupy associated sites in the short-range configurational order of the glass structure. It is also worth noting that another shallower peak is identified in this 2D plane, isolated from the \(x = z\) ridge near \(x = 2\) and \(z = 5\), where \(d_{cr} \approx 7\) mm.

None of the local maxima identified in the compositional planes of Figs. 1 and 2 necessarily represent a global maximum for the overall GFA. Other higher maxima, including an absolute global maximum, may exist in the 4D composition space along different planes; however such maxima are not expected to be far from the common peaks appearing in the planes of Figs. 1A and

![Fig. 1.](image)

![Fig. 2.](image)
24. If a global GFA maximum exists in the current compositional neighborhood it would be hard to predict given the steepness of the GFA composition maps. In the present work, alloys with an even higher GFA have in fact been discovered for compositions in the neighborhood surrounding Ni$_{68.6}$Cr$_{8.7}$Nb$_3$P$_{16}$B$_{3.2}$Si$_{0.5}$. For example, a six-component alloy Ni$_{68.6}$Cr$_{8.7}$Nb$_3$P$_{16}$B$_{3.2}$Si$_{0.5}$, which includes a minority addition of Si in its metallloid moiety, demonstrates $d_{cr} \approx 20$ mm when processed by a high-temperature fluxing process (Materials and Methods). A fully amorphous 17-mm-diameter rod of Ni$_{68.6}$Cr$_{8.7}$Nb$_3$P$_{16}$B$_{3.2}$Si$_{0.5}$, along with an X-ray diffraction pattern and a calorimetric scan verifying its amorphous structure, are shown in Fig. 3.

To map the detailed compositional dependence of GFA in the neighborhood of a peak, we evaluated the GFA along a family of straight lines in the composition space that intersect the peak, where each line is referred to as an “alloy series.” The detailed compositional dependence of GFA for four alloy series (labeled I–IV) intersecting the common composition Ni$_{68.6}$Cr$_{8.7}$Nb$_3$P$_{16}$B$_{3.2}$Si$_{0.5}$ is presented in Fig. 4. Series I–IV respectively correspond to varying $w, x, z$, and $(y + z)$ around the composition Ni$_{68.6}$Cr$_{8.7}$Nb$_3$P$_{16}$B$_{3.2}$Si$_{0.5}$, which corresponds to a local maximum in GFA in the 4D compositional space. For series I–IV one observes a steeply rising GFA followed by a rapidly decaying GFA as the peak at $d_{cr}$ is traversed. These GFA functions along the composition lines generally consist of piecewise continuous curves, or branches. The curves meet at cusps. It was observed that the individual branches of the GFA map have a roughly exponential dependence on composition (see SI Materials and Methods for a list of the exponential fitting parameters). We argue below that the atomic rearrangement and formation of a critical nucleus within a liquid are both thermally activated processes with associated barrier heights that should depend linearly, to leading order, on composition. As such, an exponential dependence of GFA on composition ensues.

From transition state theory, the nucleation of a phase $\alpha$ ($\alpha$ refers to one of the competing crystalline phases) is expected to be an activated process involving the crossing of a temperature and composition dependent nucleation barrier, $\Delta G_n(T, c)$ (5, 6, 8, 9). The rate at which atomic configurations are sampled in an undercooled liquid is taken to be proportional to the liquid fluidity, or inverse viscosity $\nu^{-1}$. Viscous flow is taken to be an activated process that may be characterized by a temperature and composition dependent barrier, $W(T, c)$ (17, 18). The characteristic time for the nucleation of an $\alpha$-crystal takes the general form

$$\tau_\alpha = \nu^{-1} \exp\left[\frac{W(T, c) + \Delta G_n(T, c)}{kT}\right],$$

where $\nu$ is an attempt frequency taken to be a characteristic atomic vibrational frequency in the liquid. For a fixed $c$, a plot of $\ln \tau_\alpha$ vs. $T$ produces the well-known C-shaped time-temperature-transformation (TTT) diagram for the $\alpha$-crystal nucleation. Below the $\alpha$-liquidus temperature where the crystal becomes thermodynamically stable, competition between a rising $W$ vs. a falling $\Delta G_n$ determines the TTT diagram. The TTT diagram exhibits a minimum crystallization time scale, $\tau_{\alpha,p}$, at an associated “nose” temperature, $T_{\alpha,nose}$, for which the nucleation time is minimized. One obtains $\tau_{\alpha,p}$ and $T_{\alpha,nose}$ by requiring $d\ln \tau_\alpha/dT = 0$ at fixed $c$. Assuming $\tau_{\alpha,p}$ to be a well-behaved function of $c$ and expanding $\ln \tau_\alpha$ vs. $c$ in a Taylor series around an initial composition $c_0$, one obtains the compositional dependence of $\tau_{\alpha,p}$ for a small compositional change, $c - c_0$, to leading order as

$$\ln \tau_{\alpha,p}(c) - \ln \tau_{\alpha,p}(c_0) \approx \lambda_{\alpha}(c - c_0),$$

where $\lambda_{\alpha} = \nabla_\alpha \ln \tau_{\alpha,p}(c)$ refers to the partial derivative of the inverse crystallization time with respect to composition evaluated at the nose temperature $T_{\alpha,nose}$. Eq. 2 predicts that for the $\alpha$-crystallization pathway, $\ln \tau_{\alpha,p}$ should vary exponentially with $c$ for small compositional displacements, $c - c_0$. The exponential composition dependence is a consequence of crystal nucleation being a thermally activated process. The minimum crystallization time, $\tau_{\alpha,p}$, is a fundamental measure of GFA. According to the Fourier heat flow equation, one expects the time scale for cooling a molten sample to scale with the square of the lateral dimension of the sample, i.e., $\tau_{\alpha} \propto d_{cr}^2$. Accordingly, a GFA composition map that reflects the composition variation of $\tau_{\alpha,p}$ can be constructed by mapping $d_{cr}$ as a function of composition. This map would reflect the composition variation of $\tau_{\alpha,p}$ for the $\alpha$-crystallization event where such event has the shortest (i.e., the limiting) crystallization time. Collectively considering the set of all competing crystallization pathways for the various crystalline phases (e.g., $\alpha, \beta, \gamma$, etc.), a global GFA composition map is constructed determined at each composition by the competing phase which has the shortest crystallization time. The overall GFA map will consist of piecewise
continuous exponential subsurfaces, indexed by α, β, γ, etc., which intersect to form exponential cusps at compositions associated with the cross-over in the nucleation pathway (e.g., from α to β, etc.).

According to Eq. 1, GFA is determined by the competition of two thermally activated processes: that of forming the critical nucleus of the crystalline phase and that of configurationally rearranging the liquid, having respective activation barriers $W(T^*, c)$ and $\Delta G_a(T^*, c)$. In our analysis, we only assume that these barriers are smooth functions of temperature and composition. The rising $\eta$ with increasing undercooling can be well described by the liquid fragility parameter $m$, defined as $m = d(\log \eta)/d(T_g/T)$ together with the value of $T_g$ (19). To lowest order, the driving force for crystallization with increasing liquid undercooling scales with $1 - T/T_L$, so that $\Delta G_a$ scales according to $(1 - T/T_L)^{-2}$ for modest undercooling (2). So at the Kauzmann temperature $T_K$ where the entropy of the liquid is assumed to match the entropy of the crystal (also referred to as the ideal or thermodynamic glass transition) (20), the leading term in $\Delta G_a$ would be of order $(1 - T_K/T_L)^{-2}$. Here we assume that the calorimetric glass transition temperature $T_K$, which is readily accessible experimentally, adequately approximates $T_g$. As such, the leading term in $\Delta G_a$ is taken here to be of order $(1 - \tau_g)^{-2}$. Both $\tau_g$ and $m$ are experimentally accessible material properties that provide a quantitative measure of the respective activation barriers along with their variation with composition. One can describe mathematically the dependence of the crystallization time scale $\tau_g$ on the independent parameters $\tau_g$ and $m$ by examining the dependence of the activation barriers $W(T, c)$ and $\Delta G_a(T, c)$ on these parameters (see SI Materials and Methods for a more detailed discussion). Below we argue that the observed compositional dependence of GFA in the present work is attributable almost entirely to the combined effects of varying $\tau_g$ and $m$ with composition.

To clarify the origin of the composition dependence of GFA, we performed detailed calorimetric and rheometric measurements to evaluate both $\tau_g$ and $m$ as functions of composition along the representative alloy series III (Fig. 4C), Ni$_{69}$Cr$_{11.5}$Nb$_3$P$_{19.5}$B$_3$ (see Materials and Methods for details on measurements of $m$ and $\tau_g$, and SI Materials and Methods for calorimetry and viscosity plots). A similar analysis can be applied to the other composition series. The GFA composition data along this series are plotted in terms of $d_{cr}$ vs. $z$ in Fig. 5A; the data were fitted by two exponential functions of composition for the two branches of the GFA curve. For a local GFA maximum at composition $c_p$, like the one at 3 atomic percent B (i.e., at $z_p = 3$), the $\tau_g$ values for two different competing crystallization pathways cross over and are mutually equal at $z_p$. We arbitrarily refer to the two crystal branches (low and high $z$) of the GFA curve using crystal labels “α” and “β”.

Firstly, within the error of our calorimetry data, we observe that $c_p$ is located quite precisely at a eutectic composition for which the alloy liquidus is minimum (see SI Materials and Methods for melting data). This is actually true for all of the alloy series I–IV (Fig. 4). GFA is therefore optimized very close to a quinary eutectic composition. The $d_{cr}$ data for series I–IV, therefore, describe GFA along lines in composition space that all pass through this eutectic composition. From the calorimetric liquidus measurements along series III, the $\alpha$ region $z < z_p$ is a hypoeutectic (with a falling liquidus curve as $z$ increases) whereas the $\beta$ region $z_p > z_p$ is hypereutectic (with a rising liquidus curve as $z$ increases). Because $\tau_g$ depends inversely on the liquidus temperature, its composition dependence demonstrates a cusp-like maximum with discontinuous slope at $z_p$. The plot of $\tau_g$ along series III shown in Fig. 5B reveals this sharp discontinuity. Specifically, $\tau_g$ is highest at the eutectic composition and drops precipitously for $z > z_p$. In contrast, $\tau_g$ increases very slightly as $z$ approaches $z_p$ in the hypoeutectic region. On the other hand, the experimental liquid fragility, $m$, being a property of the liquid phase alone and independent of the crystal/liquid phase equilibria, is shown in Fig. 5C to be a continuous and monotonically decreasing function of $c$. Specifically, $m$ drops steeply as $z$ increases with an approximately exponentially decaying trend. A decreasing $m$ corresponds to a higher
steep and should lead to rapid exponential decay of GFA. This hypo- and hypereutectic branches of the GFA map are apparently the result of an interplay of the $t_o$ and $m$ variations with composition.

To quantify the analysis above, consider Eq. 2 and the exponential decay parameters $\lambda_\alpha$ and $\lambda_\beta$ obtained from the exponential fits to the GFA data for the respective hypo- and hypereutectic branches of the GFA curve. According to Eq. 2, the discontinuity in the slope of $\ln d_z$ vs. $z$ at the GFA cup is simply given by the difference $\lambda_\beta - \lambda_\alpha$. Without loss of generality, one can show that $\lambda_\alpha$ and $\lambda_\beta$ can be separated into contributions arising from variations in $t_o$ and $m$, and potentially any other relevant material parameters that enter the expression for $\ln d_z(e)$ (the mathematical details of this separation are presented in SI Materials and Methods). Using the chain rule to evaluate $\lambda_\alpha = \partial (\ln d_z) / \partial (\ln m)$, one obtains

$$\lambda_\alpha = \Delta \lambda = \Delta \lambda_{	ext{intrinsic}}$$

$$\lambda_\beta = \Delta \lambda = \Delta \lambda_{	ext{intrinsic}}$$

Here $\lambda_\alpha$ being a property of the liquid phase only, is identical for both branches; its composition dependence given by $\Delta \lambda = \{d(\ln d_z) / dm\}$. The $\Delta \lambda$ parameters depend on the nucleating crystal and are different for $\alpha$ and $\beta$; they are given by $\Delta \lambda = \{d(\ln d_z) / dt_o\}$. The $\Delta \lambda$ jumps discontinuously with varying $e$ on going from the $\alpha$- to the $\beta$-branch of the curve due to the change in the slope $dt_o / dG$ (as seen in Fig. 5B). It was already pointed out that the composition $e_\alpha$ of the GFA cup coincides precisely with the eutectic composition (at which the $\alpha$- and $\beta$-eutectic curves cross). From this, one can conclude that any other parameter that influences GFA (e.g., the melt–crystalline interfacial energy for the $\alpha$- and $\beta$-eutectic phases) must be nearly equal for both branches of the GFA curve. Were this not the case, the GFA cup would be shifted off the eutectic composition, $e_\alpha$. The above facts suggest that $\Delta \lambda$ and $\Delta \lambda$ in Eqs. 3a and 3b are determined mainly by the measured composition dependences of $t_o$ and $m$. In this case, Eqs. 3a and 3b become a pair of linear equations with two unknowns, $\Delta \lambda_{\alpha}$ and $\Delta \lambda_{\beta}$: $\partial (\ln d_z) / \partial t_o$. At the cup composition, experimental fitting yields $\Delta \lambda_{\alpha} = 1.43$, $\Delta \lambda_{\beta} = -0.693$, $dt_o / dG = 0.00211$, and $dt_o / dG = -0.0213$ (where $e$ is in units of $z$, i.e., in atomic percentages of B, and $d_z$ is in millimeters; Fig. 5A and B and SI Materials and Methods). Solving for the two unknowns one obtains $\Delta \lambda_{\alpha} = 1.24$ and $\Delta \lambda_{\beta} = 90.6$, which give $\Delta \lambda_{\alpha} = 0.191$ and $\Delta \lambda_{\beta} = -1.93$. One finds that $\Delta \lambda_{\alpha}$ consists of a fragment contribution $\Delta \lambda_{\alpha}/\lambda_{\alpha} = 87\%$, and a contribution from Turnbull’s parameter $\Delta \lambda_{\alpha}/\lambda_{\alpha} = 13\%$. In the hypoeutectic $\alpha$-region, therefore, the decreasing liquid fragility parameter (i.e., the increasing liquid viscosity at the nucleation nose) dominates the exponential rise in GFA. By contrast, the negative $\lambda_\beta$ consists of an overwhelming negative contribution from Turnbull’s parameter $\Delta \lambda_{\beta}/\lambda_{\beta} = 278\%$, and a positive contribution from fragility $\Delta \lambda_{\alpha}/\lambda_{\alpha} = -178\%$. Hence, the exponential GFA decay in the hypereutectic $\beta$-region would have been significantly greater (by a factor of 2.78) had the fragility of the liquid not been decreasing with increasing $e$.

As follows from the analysis above, the Turnbull parameter and fragility alone give a plausible and self-consistent account of the composition variations of GFA. Specifically, the large variation in fragility over a fairly narrow compositional change has a dramatic effect on the compositional dependence of GFA; it steepens the GFA rise in the hypoeutectic region and offsets the GFA drop in the hypereutectic region. Finally, we note that from our fit for $m(e)$ in Fig. 5C, we have $dm / d_e = -5.4$ as evaluated at $z_o$. Using our value of $\lambda_{\alpha}$, one obtains the intrinsic dependence of

![Diagrams](attachment:diagram.png)

**Fig. 5.** (A) Compositional dependence of GFA plotted in terms of $d_z^2$ against the B atomic concentration as a substitute for P according to Ni50Cr8.5Nb3.5B19.5. Solid lines are exponential fits to the experimental data (open circles) on each side of the peak (at 3 at. % B). (B) Reduced glass transition temperature $T_g$ plotted against the B atomic concentration as a substitute for P according to Ni50Cr8.5Nb3.5B19.5. Solid lines are polynomial fits to the experimental data (open circles) on each side of the cup (at 3 at.% B). (C) Liquid fragility $m$ plotted against the B atomic concentration as a substitute for P according to Ni50Cr8.5Nb3.5B19.5. The solid line is an exponential fit to the experimental data (open circles).
GFA on \( m \), i.e., \( d(\ln d_{trg}^m)/dm = -0.23 \). For a fixed \( \tau_{trg} \), this value implies that a decrease in the fragility parameter \( m \) of about 4.5 is associated with a remarkable 65% increase in \( d_{trg} \). Clearly, the liquid fragility \( m \) plays a very important role in determining glass formation. Mukherjee et al. (21) directly measured the TTT diagrams for a series of compositionally distinct Zr-based glasses all having nearly the same \( \tau_{trg} \) but varying liquid fragility. The measured \( \tau_{trg} \), which was found to vary by more than 1 order of magnitude among these alloys, was shown to be directly proportional to the liquid viscosity at the nose temperature \( T_{trg}^m \). It was argued that the GFA variation among these Zr-based glasses arises mainly from the variation in fragility \( m \). In a separate work, Na et al. (22) studied the fragility of compositionally distinct Fe-based metallic glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude.

Na et al. (22) studied the fragility of compositionally distinct Fe-based metallic glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these Fe-based glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these glasses. It was argued that the GFA variation among these Zr-based glasses arises mainly from the variation in fragility \( m \). In a separate work, Na et al. (22) studied the fragility of compositionally distinct Fe-based metallic glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these Fe-based glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these glasses. It was argued that the GFA variation among these Zr-based glasses arises mainly from the variation in fragility \( m \). In a separate work, Na et al. (22) studied the fragility of compositionally distinct Fe-based metallic glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these Fe-based glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these glasses. It was argued that the GFA variation among these Zr-based glasses arises mainly from the variation in fragility \( m \). In a separate work, Na et al. (22) studied the fragility of compositionally distinct Fe-based metallic glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these Fe-based glasses, and showed that their GFA and fragility obey a fairly tight correlation that extended over nearly 2 orders of magnitude among these glasses. It was argued that the GFA variation among these Zr-based glasses arises mainly from the variation in fragility \( m \).

Based on the present work, it is clear that the successful prediction of GFA requires, at a minimum, properly describing the roles of Turnbull’s parameter and liquid fragility.

**Materials and Methods**

Alloy ingots were prepared by inductively melting pure elements in silica tubes under high-purity argon. The purity levels of the constituent elements were as follows: Ni 99.995%, Cr 99.966%, Nb 99.95%, P 99.9999%, B 99.5%, and Si 99.9999%. Amorphous rods were produced by remelting the alloy ingots in silica tubes having 0.5-mm-thick walls in a furnace at 1250 °C under high-purity argon, and after achieving a uniform-temperature melt state, rapidly quenching in a stirred room temperature water bath. The 17-mm amorphous rod of Nia,Cr40,MnbP20,B12,Si5 was produced by remelting the alloy ingot together with dehydrated boron oxide flux in a silica tube having a 1-mm-thick wall in a furnace at 1350 °C under high-purity argon, and after allowing the melt to interact with the molten flux for ~2 h at 1350 °C, then rapidly quenching in a stirred room temperature water bath. To determine the GFA of each composition, two to four separate sample rods were produced with diameters varying in 1-mm increments. The reported values of \( d_{trg} \) therefore, have an experimental uncertainty of ±0.5 mm. The amorphous structure of the rod was verified by X-ray diffraction using CuK\( \alpha \) radiation.

The reduced glass transition \( \tau_{trg} \) was evaluated by measuring the glass transition temperature, \( T_g \) and the alloy liquidus temperature, \( T_L \), and using differential scanning calorimetry. \( T_g \) was evaluated as the onset of the glass transition at a scan rate of 20 K/min. \( T_L \) was evaluated at a scan rate of 5 K/min to reduce scan rate effects and instrumental broadening of the melting transition. The liquid fragility \( m \) was evaluated by measuring the temperature dependence of the equilibrium viscosity around the glass transition temperature. The equilibrium viscosity was measured by performing three-point beam bending of amorphous rods 2 mm in diameter and 10 mm in length using a thermostatically controlled analyzer, as described by Hagy (23) (SI Materials and Methods).

Supporting Information

Na et al. 10.1073/pnas.1407780111

SI Materials and Methods

Series I

\[ \tau = \frac{L^3}{144 t_L v} \left( M + \frac{5 \rho A L}{8} \right) \]  

where \( \eta \) is the apparent viscosity (Pa·s), \( g \) the gravitational constant (meters per second squared), \( L \) the support span length (meters), \( t_L \) the cross-sectional moment of inertia (meters to the fourth power), \( \nu \) the midpoint deflection velocity (meters per second), \( M \) the applied load (kilograms), \( \rho \) the density (kilograms per meter cubed), and \( A \) is the cross-sectional area (meters squared). Loads ranging from 20 to 1,000 mN were applied. Measured data for Ni$_{60}$Cr$_{8.5}$Nb$_{1.5}$P$_{16.5}$B$_{3}$, Ni$_{60}$Cr$_{8.5}$Nb$_{3.5}$P$_{16.5}$B$_{3}$, and Ni$_{60}$Cr$_{8.5}$Nb$_{3}P_{14.5}B_{3}$ were presented in Fig. S3.

To describe the temperature dependence of viscosity \( \eta(T) \), the cooperative shear model is used (2, 3):

\[ \eta(T) = \eta_\infty \exp \left\{ \frac{W_g}{kT} \exp \left[ 2n \left( 1 - \frac{T}{T_g} \right) \right] \right\} \]  

where \( \eta_\infty \) is the high-temperature limit of viscosity, which is assumed to be 10$^{-2}$ Pa·s for all alloys, \( W_g \) is the activation energy barrier at the glass transition, approximated by \( W_g \approx kT_g \log(\eta_\infty / \eta_\infty) \), where \( \eta_\infty \approx 1 \times 10^{22} \) Pa·s, \( n \) is the effective fragility parameter, \( k \) the Boltzmann constant, \( T \) temperature, and \( T_g \) the glass transition temperature associated with a viscosity value of 10$^{12}$ Pa·s. The fragility parameter \( m \) is related to \( n \) via

\[ m = (1 + 2n) \log(\eta_\infty / \eta_\infty). \]  

The fitting curves for Ni$_{60}$Cr$_{8.5}$Nb$_{3}P_{16.5}$B$_{3}$, Ni$_{60}$Cr$_{8.5}$Nb$_{1.5}$P$_{16.5}$B$_{3}$, and Ni$_{60}$Cr$_{8.5}$Nb$_{3.5}$P$_{16.5}$B$_{3}$ are presented in Fig. S3, whereas the fit parameters \( T_g \) and \( n \) and the calculated fragility \( m \) are given in Table S3.

Mathematical Analysis

The actual dependence of \( \ln r_C^z(e) \) on \( W \) and \( \Delta G_s \) depends on the theoretical model used to describe these barriers. In this analysis, we assume only that \( \ln r_C^z(e) \) is a well-behaved function of composition that depends on the dimensionless parameters \( r_{\text{ic}} m \) and any other potentially relevant material parameters (e.g., the interfacial free energy, \( \sigma_{\text{ic}} \), of the liquid-crystal interface). In other words we take \( \ln r_C^z(e) = \ln f(e, r_{\text{ic}}, m, \sigma_{\text{ic}}, \ldots) \), where \( f \) is an unknown function of the parameters \( r_{\text{ic}}(e), m(e), \sigma_{\text{ic}} \), etc. that are themselves functions of composition.

For a 1D composition variation \( z \) as in our alloy series, the compositional derivative of \( \ln f \) with respect to \( z \) becomes

\[ \frac{d \ln f}{dz} = \frac{1}{f} \frac{df}{dz} + \frac{1}{f} \frac{df}{dg} \frac{dg}{dz} + \frac{df}{dm} \frac{dm}{dz} + \frac{df}{d\sigma_{\text{ic}}} \frac{d\sigma_{\text{ic}}}{dz} + \cdots \]  

The first term on the right includes any explicit dependence of \( f \) on composition not described by our parameters. For a model of crystal nucleation, this term can be assumed to vanish because the independent parameters taken together with their dependence on \( z \) and \( T \) are assumed to give a full description of the nucleation rate. The series expansion of Eq. S5 along the \( z \) direction then becomes to first order:

\[ \ln(f(z)) = \ln(f(z_0)) + \frac{1}{f(z_0)} \frac{df}{dz} |_{z_0} dz + \frac{1}{f(z_0)} \frac{df}{dm} \frac{dm}{dz} |_{z_0} dz + \frac{1}{f(z_0)} \frac{df}{d\sigma_{\text{ic}}} \frac{d\sigma_{\text{ic}}}{dz} |_{z_0} dz + \cdots \]  

Referring to Eq. S6, one sees that the term in the square bracket can be identified as the \( z \) component of the \( \lambda_{\beta} \) vector, where \( z = \lambda_{\alpha} \cdot (e - e_0) \). Further, one observes that the \( \lambda_{\beta} \) for the alloy series naturally separates into contributions arising from each independent variable \( t_{\beta}(e), m(e), \) etc. We write:

\[ \lambda_{\beta} = \lambda_{\beta_a} + \lambda_{m,a} + \ldots \]  

where \( \lambda_{\beta_a} = (d f / d t_{\beta_a}) |_{t_{\beta_a}} \), \( \lambda_{m,a} = (d f / dm) |_{m} \), etc. for each independent parameter. Eq. S7 is essentially Eq. 3a for analyzing the glass-forming ability (GFA) cusp.
One may separate the exponential dependence of GFA on composition into contributions associated with each independent parameter in a nucleation model. We may use this property to analyze experimental GFA data for our alloy series. Because $t_{rg}$, $m$, etc. are experimentally accessible material properties that are composition dependent, one can measure the derivatives, $dt_{rg}/dz$, $dm/dz$, etc. Our GFA composition data provide experimental values of the total $\lambda_\alpha$. For a cusp composition (i.e., the eutectic composition), we have two separate equations associated with hypo- and hypereutectic crystallization pathways thereby obtaining two sets of these equations at the same value of $z_o$. These coupled equations may be solved to obtain the derivatives, $df/dt_{rg}$, $df/dm$, etc. These are theoretical quantities that depend on the model used to describe crystal nucleation. Using this analysis along with relevant experimental data, we show that the composition dependence of GFA in the present Ni-based alloys arises mainly from the composition dependence of the two parameters $t_{rg}$ and $m$.


![Fig. S1. Calorimetry scans around the glass transition for Ni$_{69}$Cr$_{8.5}$Nb$_{3}$P$_{19.5}$−$z$B$_{z}$ (series III) metallic glass alloys with $z$ between 1.5 and 6. Arrows designate the glass transition temperature (left arrow) and crystallization temperature (right arrow). The enthalpies of crystallization are also noted in the plot.](image-url)
Fig. S2. Calorimetry scans around the melting transition for Ni$_{69}$Cr$_{8.5}$Nb$_3$P$_{19.5}$−$z$B$_z$ (series III) metallic glass alloys with $z$ between 1.5 and 6. Arrows designate the solidus temperature (left arrow) and liquidus temperature (right arrow). The enthalpies of melting are also noted in the plot.

Fig. S3. Data and fitting curves for the equilibrium viscosity of Ni$_{69}$Cr$_{8.5}$Nb$_3$P$_{19.5}$−$z$B$_z$ (series III) metallic glass alloys with $z = 1.5$, 3, and 5.
Table S1. Fitting coefficients to GFA vs. composition data according to Eq. S1 for series I–IV alloys

<table>
<thead>
<tr>
<th>Alloy series</th>
<th>Hypoeutectic</th>
<th>Hypereutectic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Series I</td>
<td>0.0724</td>
<td>0.511</td>
</tr>
<tr>
<td>Series II</td>
<td>2.25</td>
<td>0.566</td>
</tr>
<tr>
<td>Series III</td>
<td>0.212</td>
<td>1.17</td>
</tr>
<tr>
<td>Series IV</td>
<td>2.73 × 10⁻⁵</td>
<td>0.654</td>
</tr>
</tbody>
</table>

Table S2. Glass transition temperature $T_{go}$, crystallization temperature $T_x$, solidus temperature $T_S$, liquidus temperature $T_L$, and Turnbull parameter $t_{rg}$ for series III alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_{go}$, K</th>
<th>$T_x$, K</th>
<th>$T_S$, K</th>
<th>$T_L$, K</th>
<th>$t_{rg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{18}$B$_{1.5}$</td>
<td>664</td>
<td>705</td>
<td>1114</td>
<td>1134</td>
<td>0.5856</td>
</tr>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{17.5}$B$_2$</td>
<td>667</td>
<td>711</td>
<td>1114</td>
<td>1134</td>
<td>0.5882</td>
</tr>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{16.5}$B$_3$</td>
<td>668</td>
<td>713</td>
<td>1114</td>
<td>1134</td>
<td>0.5891</td>
</tr>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{15.5}$B$_4$</td>
<td>668</td>
<td>720</td>
<td>1113</td>
<td>1187</td>
<td>0.5628</td>
</tr>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{14.5}$B$_5$</td>
<td>668</td>
<td>721</td>
<td>1114</td>
<td>1214</td>
<td>0.5505</td>
</tr>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{13.5}$B$_6$</td>
<td>671</td>
<td>720</td>
<td>1112</td>
<td>1285</td>
<td>0.5222</td>
</tr>
</tbody>
</table>

Table S3. Fit parameters $T_{go}$ and $n$ and calculated fragility $m$ for series III alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_{go}$, K</th>
<th>n</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{18}$B$_{1.5}$</td>
<td>661.2</td>
<td>2.05</td>
<td>76.5</td>
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<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{16.5}$B$_3$</td>
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<td>1.46</td>
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<tr>
<td>Ni$<em>{69}$Cr$</em>{8.5}$Nb$<em>3$P$</em>{14.5}$B$_5$</td>
<td>667.8</td>
<td>1.30</td>
<td>54.0</td>
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