Revealing hidden supercooled liquid states in Al-based metallic glasses by ultrafast scanning calorimetry: Approaching theoretical ceiling of liquid fragility

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Metallic glasses (MGs) are amorphous alloys with a number of unique properties that are attractive for the fundamental understanding of the nature and applications of disordered systems [1–17]. Generally, MGs might be grouped into two categories based on their glass forming ability (i.e., the ease of glass formation by cooling a liquid): in one case, large or bulk volumes may be slowly cooled to the glassy state from the melt. This category is usually called as bulk metallic glass formers [18–22]. In contrast, certain MGs, represented by aluminum (Al)-[23,24] and some iron (Fe)-[25,26] based MGs, can be synthesized mainly by rapid solidification processes such as melt spinning or vapor deposition. These MGs are often denoted as marginal MG-formers [23–25].

With the rapid developments of MGs, many previously identified marginal glass formers have been successfully made into bulk metallic glasses by composition strategies (such as Fe- and Ni-based MGs) [8,25,26,28]. However, one remarkable exception is the family of Al-based MGs [23,24]. Although there have been continuous efforts in optimizing compositions and improving processing techniques since its first discovery [29] several decades ago, the glass forming ability of Al-MGs is still limited nowadays [23,30,31]. Recently, Wu *et al.* [30] reported that the hitherto best glass forming ability for Al-MGs is from $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$ with a fully glassy rod of 1.5 mm in diameter. Although the glassy rod can reach 2.5 mm for the same composition after a refined flux-treatment of the liquid [31], this critical size is still much smaller than those of typical Zr-based MGs (~75 mm) [32], Mg-MGs (25 mm) [18] and Pd-MGs (80 mm) [33]. Moreover, the glass forming ability of Al-MGs is very

sensitive to compositions. Only a few percent change of the constituting elements would dramatically reduce this critical size [21,27,30,34,35]. Consequently, it is more difficult to develop Al-MGs than other MGs. Fundamentally, it remains to be a puzzling issue why the Al-MGs are so unique [27,30,36].

Among several factors, one clue for the distinction between bulk glasses and marginal glass formers is based upon their supercooled liquids [19,23,26,27]. The change of the relaxation dynamics (e.g., viscosity, diffusivity or relaxation time) with the temperature is highly material-specific. Angell introduced the concept of fragility (m) for the classification of glass-forming materials, which was defined as the apparent activation energy of relaxation time τ_α normalized to glass transition temperature T_g : $m = d\log(\tau_\alpha)/(dT_g/T)|_{T=T_g}$ [37]. A stronger deviation from Arrhenius behavior (with a larger m value) corresponds to a more fragile system; otherwise, the system is strong [37–40]. Wang *et al.* [41] theoretically pointed out that the fragility index for non-polymeric glasses should have a lower limit $m = 16.5$, and an upper limit $m \sim 175$.

Recently, Johnson *et al.* [42] conducted a critical assessment of the database of metallic glasses, and they proposed that the glass forming ability can be expressed by a two-variable empirical function based on m and T_{rg} (T_{rg} is the reduced T_g). The larger values of T_g/T_m and the smaller values of m are favored by stronger glass formation. Their findings highlight the important role of liquid dynamics on the glass formation.

However, until now, almost none of the melt-quenched Al-MGs exhibits recognizable glass transition or the supercooled liquid region when measured by the differential

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scanning calorimetry (DSC) [23,27,30,43]. Instead, they show an exothermic process due to the primary crystalline phase formation of aluminum [23,27,30]. Hence, properties of the supercooled liquid and especially the fragility of Al-MGs are still unknown. In a previous work, Hu *et al.* [44] inferred that the Al-MGs might have large values of m . However, as the glass transition of Al-MGs could not be probed by DSC, they used the crystallization process as an estimation of the glass transition.

In this work, utilizing the recently developed fast scanning calorimetry (FSC) [45–55] to bypass the primarily crystallization process, we present the direct characterization of the glass transition and supercooled liquid states of 20 different Al-based MGs with different compositions and glass forming ability. The results indicate that the Al-MGs feature remarkably high values of fragility, which are sensitive to minor compositional adjustment. Some of them almost reach the theoretical upper limit of fragility [41]. The lowest fragility in these studied Al-MGs is found in the $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$ MG which also has the best glass forming ability. Our findings suggest that the highly fragile nature of the su-

percooled liquids could be a common controlling factor for the marginal glass forming ability of Al-MGs. Thus, strategies for reducing fragility could be taken into considerations in enhancing glass forming ability of Al-MGs. Meanwhile, the Al-MGs provide a benchmark model for the understanding of the origin of fragility in glasses.

We investigated 20 different Al-MGs as listed in Table 1 by melt-spinning techniques. First, ingots of the Al-based alloy were prepared by melting high purity elements (purity ≥ 99.99 at.%) under a Ti-gettered argon atmosphere in an arc-melting furnace. The ingots were re-melted five times to ensure homogeneity. Then, amorphous ribbons of different thicknesses were achieved by varying the rotational speed ($10\text{--}60\text{ m s}^{-1}$) of the rollers. The glass forming ability was characterized by the critical thickness at which fully amorphous materials can be obtained. X-ray diffraction (XRD, Bruke D2 phaser) and DSC were used to check the amorphous nature of these ribbons.

The glass transition and crystallization of alloys at relatively high heating rates were obtained by continuous heating on a Flash DSC (Mettler Toledo FSC 2+) under

Table 1 Compositions of Al-MGs studied in this work and their T_g , T_x and ΔT_x (measured at 600 K s^{-1}), T_m , T_{g20} , h_c , and m (± 5 error bar). T_{g20} is the extrapolated T_g at a heating rate of 20 K min^{-1} (which is commonly used in glass physics). h_c ($\pm 5\text{ }\mu\text{m}$ error bar) is the critical thickness of glass ribbon which is fully amorphous.

	Composition	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_{g20} (K)	h_c (μm)	m
1	$\text{Al}_{84}\text{Ni}_{10}\text{Ce}_6$	564.5	629.7	65.2	892.3	529.6	60	107
2	$\text{Al}_{86}\text{Ni}_9\text{Ce}_5$	556.2	621.6	65.4	890.6	525.7	60	129
3	$\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Ce}_5$	556.2	611.8	55.6	889.4	526.8	50	164
4	$\text{Al}_{86}\text{Ni}_4\text{Co}_5\text{Ce}_5$	581.9	621.5	39.6	897.9	547.8	40	120
5	$\text{Al}_{86}\text{Co}_9\text{Ce}_5$	633.2	662.1	28.9	903.1	593.8	20	127
6	$\text{Al}_{86}\text{Ni}_9\text{La}_5$	595.7	658.0	62.3	890.5	561.3	40	119
7	$\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{La}_5$	551.7	609.5	57.8	893.7	526.3	40	164
8	$\text{Al}_{86}\text{Ni}_4\text{Co}_5\text{La}_5$	591.5	640.8	49.3	900.0	558.3	30	117
9	$\text{Al}_{85}\text{Ni}_{10}\text{Sm}_5$	539.6	607.8	68.2	897.9	510.4	50	146
10	$\text{Al}_{85}\text{Ni}_{10}\text{Ce}_{1.75}\text{Sm}_{3.25}$	541.4	607.6	66.2	895.8	514.8	140	122
11	$\text{Al}_{85}\text{Ni}_{10}\text{Ce}_{3.25}\text{Sm}_{1.75}$	547.0	608.4	61.4	889.4	512.0	110	104
12	$\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$	549.7	612.6	62.9	892.6	519.7	80	132
13	$\text{Al}_{84}\text{Ni}_{11}\text{Sm}_5$	580.1	646.8	66.7	897.9	540.2	70	102
14	$\text{Al}_{86}\text{Ni}_9\text{Sm}_5$	522.3	566.7	44.4	899.7	491.9	90	128
15	$\text{Al}_{87}\text{Ni}_8\text{Sm}_5$	532.8	584.6	51.8	895.8	498.6	50	107
16	$\text{Al}_{90}\text{Sm}_{10}$	531.6	563.1	31.5	906.4	505.2	20	162
17	$\text{Al}_{90}\text{Ce}_{10}$ ^a				909.6		10	
18	$\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Sm}_{3.25}\text{La}_{1.75}$	549.0	606.3	57.3	889.4	513.6	90	111
19	$\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Sm}_{3.25}\text{Ce}_{1.75}$	546.1	602.9	56.8	889.4	516.2	50	120
20	$\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$	543.2	598.5	55.3	896.8	503.7	170	96

a) The glass transition could not be probed by FSC even with the maximum heating rate of $15,000\text{ K s}^{-1}$.

80 mL min⁻¹ argon gas flow. The twin-type chip sensor based on MEMS technology was made with a sample and a reference side. Samples were placed on the sensitive area of a MultiSTAR UFS 1 MEMS chip sensor in a range of heating rates from 5 to 15,000 K s⁻¹. In order to ensure the reliability of the measurement, each crystallized sample was heated again to obtain a baseline. The crystal melting temperature and the liquid temperature were measured using a differential thermal analysis (TA SDT Q600) instrument at a heating rate of 20 K min⁻¹ under a 100 mL min⁻¹ argon gas flow. These samples were also measured at relatively low heating rates by a conventional DSC (Mettler Toledo DSC 3) under a 50 mL min⁻¹ nitrogen gas flow. The conventional DSC was calibrated by using pure In and Zn as standard references.

Fig. 1a compares two typical heat flow curves of an Al₈₅Ni₁₀Ce₅ MG measured by a conventional DSC (at a heating rate $Q = 0.333$ K s⁻¹ or 20 K min⁻¹) and a FSC ($Q = 600$ K s⁻¹), respectively. The DSC curve shows only an unobvious signature of glass transition onset which is truncated by a sharp exothermic peak of the primary crystallization. In contrast, the FSC curve exhibits a clear glass transition ($T_g = 549.7$ K at this heating rate). The first crystallization peak has been shifted to a higher temperature ($T_x = 612.6$ K, where T_x is the first crystallization temperature) by the rapid heating. The temperature difference between T_x and T_g defines the supercooled liquid region $\Delta T_x = 63$ K at this heating rate.

Thus, the FSC provides us a unique means to characterize the supercooled liquid states of Al-MGs.

Fig. 1b shows a set of typical FSC measurements over a wide range of heating rates, ranging from $Q = 10$ to 4500 K s⁻¹. We find that only for $Q \geq 30$ K s⁻¹, the glass transition can be fully resolved by our FSC measurements. This critical heating rate is much higher than the commonly used DSC (0.1–1 K s⁻¹). The inset of Fig. 1c summarizes the primary (first) crystallization peak temperature both from DSC and FSC at different heating rates, in terms of the so-called Kissinger plot [38]. It shows that the two sets of data (DSC and FSC) match with each other consistently. This suggests that the primary crystallization on the FSC might be the same process as DSC but delay to a higher temperature by the fast heating.

We determined the fragility index m based on the heating rate dependence of T_g , as shown in Fig. 1c. By fitting these data with the Vogel-Fulcher-Tammann (VFT) equation, we calculated $m = 132 \pm 3$ for the Al₈₅Ni₁₀Ce₅ MG, which implied a rather fragile behavior. In the Supplementary information, we validated our approach by comparing the fragility for a Pd₄₀Ni₃₀Cu₁₀P₁₀ MG between known fragility ($m = 52 \pm 2$) from previous viscosity measurement [56] and current method ($m = 55 \pm 3$, Fig. S1a). In a previous work, Evenson *et al.* [57] illustrated that by heating and cooling a glass to the supercooled liquid state at the same rate would result in a

Figure 1 Typical scanning calorimetry for Al₈₅Ni₁₀Ce₅ MG. (a) Comparative studies between low heating rate (conventional DSC) and high heating rate (FSC). (b) Heat flow curves measured by FSC using different heating rates. (c) The onset temperature of glass transition, T_g^{onset} , against the heating rates. The black solid line is a fit using the VFT equation. The inset is Kissinger plot for crystallization of the Al₈₅Ni₁₀Ce₅ MG.

more accurate determination of m based on DSC measurements. In Fig. S1c, we show that for the present $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ MG, this method ($m = 125 \pm 3$) and ours ($m = 132 \pm 3$) yield roughly the same values of fragility within the experimental uncertainty. As another check for the high fragility for the present Al-MG, we used the correlation between thermodynamic properties with fragility: $m \approx m_{\text{cal}} = 56T_g \Delta C_p(T_g)/\Delta H_m$, where $\Delta C_p(T_g)$ is the heat capacity jump at T_g , ΔH_m is the enthalpy of melting. The theory was firstly reported by Wang *et al.* [58] and subsequently rationalized within framework of the random first order transition. With these parameters measured by FSC (Fig. S1d), we estimate $m_{\text{cal}} = 138 \pm 5$ by the above relation, which is in good agreement with the FSC ($m = 132 \pm 3$). Together, these results suggest that our measurement of fragility by FSC is reliable, and the large m of the present Al-MG could be an inherent feature of the supercooled liquid.

Table 1 lists all the m values studied in this work for 20 typical Al-MGs with different compositions. They all have the similar composition as $\text{Al}_{(100-a-b)}\text{TM}_a\text{RE}_b$ where TM is the transition metal (Co, Ni), RE is the rare earth element (Y, La, Ce, Sm). We find that all of them have relatively large m values. Fig. 2 contrasts them with other glass formers with different bonding nature. Specifically, we present the data in an m - T_g plot, since T_g is more likely to be determined by the bonding mechanisms. The Al-MGs are standing out as they have lower T_g but larger m . It is noteworthy that several Al-MGs exhibit large fragility values (e.g., $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Ce}_5$, $m = 164 \pm 3$) that approach the theoretical upper limit value $m = 175 \pm 3$ [41]. For comparisons, the highest fragility in molecular and ionic liquids is $m = 145$ for decalin [41] and $m = 115$ of Li acetate [41,58], respectively. And the previously known highest fragility in MGs is $m = 136$ of $\text{Ni}_{59.5}\text{Nb}_{40.5}$ [59,60]. For polymers [61,62], there are a number of cases where $m > 175$, but Sokolov and co-workers [62] have shown there are polymer-specific factors in operation. Thus, we do not include polymers for comparisons. In short, the Al-MGs exhibit the highest m value in MGs and non-polymeric glasses. Meanwhile, Fig. 2 also suggests that although the values of T_g are concentrated for different types of glass formers, there is no universal correlation between T_g and m .

Another interesting feature about the fragilities of the Al-MGs is that they are sensitive to minor compositional adjustments (i.e., micro-alloying). To illustrate this point, Fig. 3 shows four typical systems of Al-MGs by systematically varying the compositions. For example, when replacing Ni with Co in the $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Ce}_5$ MGs, the

Figure 2 m - T_g plot. Glass formers with different bonding nature are compared, including molecular glasses, oxide glasses, the Al-MGs in this work and other MGs.

fragility increase sharply from $m = 132 \pm 3$ for $x = 0$ to $m = 164 \pm 3$ for $x = 2$, which means that only 2% composition variation would remarkably change about 20% of the magnitude of m values. However, with further increasing of x , the m values drop quickly, resulting in a maximum of m value at $x = 2$. A qualitatively similar trend is observed in another system with the composition formula $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{La}_5$. Fig. 3c, d illustrate the effects of substitution on fragility for Ce/Sm in the $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_x\text{Sm}_{5-x}$ MGs and for Al/Ni in the $\text{Al}_{95-x}\text{Ni}_x\text{Sm}_5$ MGs, respectively. Again, they indicate that minor composition changes introduce large variation of m .

We next studied the relation between glass forming ability of Al-MGs and the liquid properties. We characterized the glass forming ability of the Al-MGs by the h_c of the ribbons that can retain the fully amorphous phase. As summarized in Table 1, these values range from 10 μm ($\text{Al}_{90}\text{Ce}_{10}$) to 170 μm ($\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$). We find a modest correlation between h_c and m for Al-based MGs, as shown in Fig. 4a. Specifically, the glass forming ability are characterized by a parameter of $\log(d_{\text{max}}^2)$ as introduced by Johnson *et al.* [42], where d_{max} is the critical effective diameter for a rod-like MG. According to Ref. [42], we use $d_{\text{max}} = 4h_c$. A general trend can be observed that a large m value could weaken the glass forming ability.

Meanwhile, we include more data from literature [42] about the glass forming ability and plot them against m (Fig. 4a). Thus, it covers nearly the whole range of m . One can see that these data exhibit a consistent correlation and the Al-MGs are at the down-right corner: the highest m but the lowest glass forming ability. It is noteworthy that

for $m < 100$, $\log(d_{\max}^2)$ is nearly a linear function of m , but strong deviations (or nonlinear behavior) commences for $m > 100$. The data also imply that $m < 100$ could be critical for achieving Al-MGs with good glass forming ability. It is noted that the lowest fragility, $m = 96$ in our studied Al-MGs, coinciding with the best glass forming ability of the $\text{Al}_{86}\text{Ni}_{6.75}\text{Co}_{2.25}\text{Y}_{3.25}\text{La}_{1.75}$ MG [30].

Fig. 4b plots the $\log(d_{\max}^2)$ versus T_{rg} for different MGs. One can see that the relation between glass forming ability and T_{rg} for our Al-MGs is not consistent with other MGs. This means that, unlike other MGs, T_{rg} may be less effective for controlling the glass forming ability in Al-MGs. Therefore, the present data suggest that the unusual high fragility could be a controlling factor to the marginal glass forming ability of Al-MGs.

We reflect on why the fragilities of Al-MGs are so high and why they tend to correlate with the glass forming ability. At present, the origin of fragility is still not clearly established [40,63–68]. A useful proposal that might be relevant for the Al-MGs can be developed based on the work of Tanaka and coworkers [67,68]. They suggested

that both the glass formation and fragility were related to the frustration of medium-range crystalline order, which had similar structural features with the crystalline ground state. By simulations of several two-dimensional models, they demonstrated that systems suffering from weaker frustration effects against crystallization were more fragile [67,68]. This argument seems to be consistent with our experimental findings on the correlation between fragility and glass forming ability. In general, for MGs the dominant structural features might not be the medium-range crystalline order, but the icosahedral or five-fold orders, instead [63,69]. However, recently Sun *et al.* [70] revealed that in an $\text{Al}_{90}\text{Sm}_{10}$ MG, the structural order was indeed similar with the crystalline, suggesting the basic promise (i.e., medium-range crystalline order) of Tanaka's proposal was satisfied in the Al-MGs. Meanwhile, the XRD pattern of the Al-MGs (Figs S10–S12) show low angle diffraction humps indicating the medium range orders (1–2 nm, depending on compositions). In this way, the very high fragility might be the result of weaker structural frustration in Al-MGs, since the Al

Figure 3 Micro-alloying effects on fragility in different Al-MGs. (a) $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{Ce}_5$ ($x=0, 2.25, 5, 9$ at.%); (b) $\text{Al}_{86}\text{Ni}_{9-x}\text{Co}_x\text{La}_5$ ($x=0, 2.25, 5$ at.%); (c) $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_x\text{Sm}_{5-x}$ ($x=0, 1.75, 3.25, 5$ at.%); (d) $\text{Al}_{96-x}\text{Ni}_x\text{Sm}_5$ ($x=8, 9, 10, 11$ at.%).

Figure 4 Relationship between glass forming ability and fragility (a), the ratio of the T_g (b) for Al-MGs. To be consistent with previous works, the T_g are used values at a DSC heating rate of 20 K min^{-1} , which is extrapolated from the FSC data. Using T_g based on other heating rate gives the similar results.

element takes up more than 80%.

Another framework to rationalize the fragility is based on the interatomic potentials [65,66]. Krausser *et al.* [65] proposed that MGs with a steeper (or harder) repulsive part of the interatomic interaction were more fragile. On the other hand, Pueblo *et al.* [66] suggested reversely: MGs with softer repulsive interaction would be more fragile. As the Al-MGs having exceptional high fragility, they would offer a model system to judge the different views. Accurate deterioration of the inter-atomic potential [69] (e.g., based on density functional theory) would be helpful.

In summary, we have shown that by FSC to suppress the early crystallization, the supercooled liquid state of the Al-MGs can be directly characterized. The results indicate that the Al-MGs are unique as they have very large liquid fragility, with some of them approaching the theoretical upper-limit value. They provide a benchmark model for understanding the origin of fragility and the fragility-property correlation in glasses. We reveal a non-linear correlation between fragility and the glass forming ability, which provides a useful guide for designing Al-MGs and other MGs.

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Supplementary information Supporting materials are available in the online version of the paper.

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超快扫描量热揭示铝基金属玻璃过冷液态：接近液体脆度的理论极限

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摘要 铝基非晶合金具有密度低、强度高、耐腐蚀等诸多优异性能；然而，铝基非晶合金形成能力差，一般需要非常高的冷却速率，这限制了铝基非晶合金的应用。玻璃形成理论认为形成能力与过冷液体密切相关。但在一般升温测量时，铝基非晶合金不显示玻璃转变或过冷液体，而是直接变成晶态。目前为止，关于铝基非晶合金的玻璃转变和过冷液体属性仍然是未知的。本文采用超快速差热分析方法(Flash DSC)使得升温速度达到 10000 K s^{-1} ，测量了20余种常见铝基非晶合金的玻璃转变行为和过冷液体特征。发现铝基非晶合金普遍具有很高的液体脆度系数(m)，其中某些成分 $m > 160$ ，已经接近理论上预测的脆度系数上限 $m \sim 175$ 。通过系统研究这些成分的形成能力，发现铝基非晶合金的玻璃形成能力与脆度系数成反相关，而且这种相关不是线性的。只有 $m < 100$ 时，降低 m 才会对玻璃形成能力有明显影响；相反， $m > 100$ 的玻璃形成能力普遍较弱，而且随 m 变化不显著。因此，过高的液体脆度系数可能是铝基非晶合金形成能力差的一个重要原因。