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# Critical Crystallization for Embrittlement in Metallic Glasses

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**Abstract:** We studied the effect of crystallization on the embrittlement of bulk metallic glasses. Specifically, we measured fracture toughness for  $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$  and  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  after annealing at various times to introduce controlled volume fraction of crystallization. We found that crystallization of up to ~6% by volume does not measurably affect fracture toughness. When exceeding ~6%, a dramatic drop in fracture toughness occurs; An additional 1% of crystallization reduces fracture toughness by 50%. Such a dramatic transition can be explained by the interaction among the crystals' stress fields in the amorphous matrix which becomes effective at ~7% crystallinity. Our findings of a critical crystallization for embrittlement of metallic glasses help in designing tough metallic glasses and their composites, as well as defining processing protocols for the unique thermoplastic forming of metallic glasses to avoid embrittlement.

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Within the material class of bulk metallic glasses (BMGs), fracture toughness varies from ideally brittle behavior such as that observed in magnesium-based BMG [1] to exceptionally tough as observed in zirconium-based and precious metal BMGs [2-5]. Generally, measuring fracture toughness has been difficult for BMGs, reflected by the wide scatter in the fracture toughness values that have been reported for the same BMG [6]. Uncontrolled partial crystallization has been suggested as one origin for the observed wide scattering [6,7]. Due to the metastable nature of BMGs, crystallization can occur during liquid cooling or thermoplastic forming (TPF), and complete avoidance has been proven difficult [8-11]. For the majority of BMG forming alloys, partial crystallization has been shown to degrade properties [12-17]. However, it has also been reported that in some cases, partial crystallization enhances fracture toughness [3,14,18,19]. To date, a quantitative understanding of the effect of partial crystallization of metallic glass forming alloys on their fracture toughness and hence, a mechanistic understanding, is lacking.

Here, we study the effect of the crystallized volume fraction (crystallinity) formed during devitrification on the fracture toughness and offer a mechanistic model that can describe our and previous findings. For representative BMGs we consider  $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$  (Zr-BMG) and  $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$  (Pd-BMG) as BMGs with a low (Zr-BMG) and high (Pd-BMG) critical fictive temperature [20]. Crystallization is introduced through isothermal annealing. We found that up to 6% crystallinity does not measurably affect the BMG's fracture toughness. However, when the volume fraction reaches  $\sim 7\%$ , a dramatic drop in fracture toughness  $K_Q$ , occurs. We explain this dramatic behavior of  $K_Q$  utilizing finite element modeling by a rapid intensification of stresses in

the amorphous matrix between two adjacent nanocrystal particles when a volume fraction of ~7% is approached.

Thermoplastic forming (TPF)-based molding of BMG into silicon molds was utilized to fabricate the single-edge notched tensile (SENT) specimen samples (Fig.1). Silicon molds were fabricated through photolithography and deep reactive ion etching (DRIE). Subsequently, these silicon molds were replicated with BMGs through TPF-based compression molding (Fig 1(a)-(b)). To precisely control crystallized volume fraction, as-fabricated samples were partially crystallized under isothermal annealing for various times in the supercooled liquid region in a heated liquid salt bath. In order to rule out thermal effects that can cause embrittlement of the glass phase, as it has been reported previously [21-24], all samples were heated to  $T_g + 10^\circ\text{C}$  for 1 minute to ensure the same thermal history for the glass phase in all samples. Crystallized volume fractions were quantified through thermal analysis upon subsequent heating with 20 K/min quantified in the heat of crystallization [25]. In addition, transmission electron microscopy (TEM) was employed to alternatively determine size and crystallized volume fraction of crystals (Fig. 2 (a)-(c)). Annealing times were chosen so as to result in crystallization of 0%, 2.5%, 4%, 5%, 6%, 7%, 18%, 55%, and 100% for Zr-BMG and 0%, 2%, 4%, 6%, 7%, and 55% for Pd-BMG. TEM reveals crystallized volume fractions (Fig.2) with some discrepancy as compared to the volume fraction determined from DSC. This discrepancy is represented in the horizontal errors in Fig. 3(a).

Uniaxial tensile testing with quasi-static displacement control (initial strain rate of  $10^{-4} \text{ s}^{-1}$ ) was conducted to characterize the fracture toughness of the as-fabricated BMG SENT samples. The development of a plastic zone through shear band formation and

propagation was captured by in-situ microscopy during the deformation (Fig. 1(d)). Due to the metastable nature of BMGs, which limits their size, it is generally difficult to obey standards to determine intrinsic plain strain toughness  $K_{IC}$ . Particularly for tough BMGs,  $K_Q$  is typically determined instead of  $K_{IC}$ . Following this strategy, the effect of crystallinity on fracture toughness of BMGs is quantified through the stress intensity factor  $K_Q = \sigma\sqrt{\pi a}F\left(\frac{a}{W}\right)$ , with a notch crack length (notch root radius  $\rho=10\text{ }\mu\text{m}$ , notch length  $a=2.5\text{ mm}$ , sample width  $W=5\text{ mm}$ , applied far-field stress  $\sigma$ , and sample configuration correction  $F\left(\frac{a}{W}\right)$  [26], shown as

$$F\left(\frac{a}{W}\right) = \sqrt{\frac{2W}{\pi a} \tan \frac{\pi a}{2W}} \cdot \frac{0.752 + 2.02\left(\frac{a}{W}\right) + 0.37\left(1 - \sin \frac{\pi a}{2W}\right)^3}{\cos \frac{\pi a}{2W}}.$$

We measured the average  $K_Q$  of as-fabricated Zr-BMG sample to be  $\sim 103\text{ MPa}\cdot\text{m}^{1/2}$ . This number is comparable to the reported toughness of  $\sim 100\text{ MPa}\cdot\text{m}^{1/2}$  for 7 mm thick  $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$  [27]. Most important for the presented study is the precise identification of relative changes; absolute values may have similar limitations as previous measurements on fracture toughness of BMGs.

The effect of crystallinity of Zr-BMG on the fracture toughness is presented in Fig. 3(a). For a crystallinity of up to  $\sim 6\%$ , no measurable effect was observed on  $K_Q$ . However, when crystallinity increases to  $\sim 7\%$ , fracture toughness drops dramatically by  $\sim 50\%$ . We observed a similar trend with a dramatic drop in  $K_Q$   $\sim 7\%$  crystallinity for Pd-BMG (Fig. 3(a)-black). A further increase in crystallinity lowers the fracture toughness of both BMGs. For high crystallinity,  $K_Q$  approaches  $1\text{ MPa}\sqrt{\text{m}}$ , which is close to the ideal brittle behavior for BMGs assuming a surface energy of  $0.01\text{ J/m}^2$  [28]. The observed decrease in the critical plastic zone,  $R_p$ , shows a parallel trend to the fracture toughness

dependence on crystallization (Fig. 3(c)). Fig. 3(b) and Fig. 3(d).

Fracture toughness of BMGs has been associated with fracture surface roughness and fracture morphology [29-31]. To investigate a correlation between  $K_Q$  and surface roughness and morphology, we performed differential interface contrast (DIC) experiments to observe the overall surface roughness. We found that roughness on the fracture surface decreases as the crystal volume fraction increases (Fig. 4). (See supplemental material for DIC analysis). Fully amorphous samples contain characteristic river-like patterns, large vein-like patterns, and radiative-like patterns developed over the fracture surface. These features contribute to higher global surface roughness [30]. At ~6% crystallinity, the fracture morphology contains regions of river and radiative-like patterns with shallow and deep vein-pattern coexisting. Such morphology has been previously associated with ductile behavior [32,33]. At 7% crystallinity, high density of smaller vein patterns are present over the surface. The pattern suggests that the majority of the material remains amorphous, but fracture surface appears more brittle-like, for example as observed in the brittle Mg-based BMGs [1,31,34]. The observed trend of surface roughness and microstructures in the fractured surfaces agrees qualitatively with the correlation of fracture toughness and crystallinity.

In general, the mechanical properties of a composite such as a partially crystallized BMG forming alloy are determined by the properties of both the matrix and the secondary phase material (e.g. crystal), as well as their interface [35,36]. For example, the secondary phase can either increase or decrease the fracture toughness of a composite, which depends on the mechanical properties, volume fraction, size of the secondary phase, and interfacial strength between the matrix and the secondary phase [14,16,18,37-

39]. In order to develop a mechanistic understanding of the effect of crystallinity on the fracture toughness of BMGs, we calculated the crystals' contribution to the strength of the composite. Previous studies revealed that strength directly scales with fracture toughness in Zr-based and Ni-based partially crystallized BMGs [40,41].

The strength of a particle-enhanced metal composite ( $\sigma_{CM}$ ) can be quantified by the continuum shear lag model [42]

$$\sigma_{CM} = \frac{1}{4} V_p \sigma_m s + V_m \sigma_m \quad (1)$$

where  $\sigma_m$  is the yield stress of the matrix,  $V_p$  and  $V_m$  are the volume fraction of particles and matrix, respectively, and  $s$  is the particle size aspect ratio. Assuming a sphere-like shaped crystalline phase,  $s = 1$ , and substituting  $V_m = 1 - V_p$ , Eq.(1) becomes

$$\frac{\sigma_{CM}}{\sigma_m} = \left( \frac{3}{4} - \frac{1}{2} V_p \right) \quad (2)$$

which suggests that the strength of composites linearly decreases as the crystals volume fraction increases. This relationship cannot rationalize the observed dramatic drop in  $K_Q$  at 7% crystallinity and considers neither the stress concentration nor interactions between the adjacent particles in the matrix.

We propose that such a sharp drop originates from the stress field interaction between particles. Even though crystals nucleate randomly during the very early stages of devitrification, due to the difference in composition between the liquid and the forming crystal, so called primary crystallization, which is typically present in metallic glass forming liquids, the distribution of following crystals is controlled by the presence and location of previous crystals. Hence, the overall distribution of crystals during primary crystallization is more homogenous than a random distribution [43]. We simulate this

scenario by a stress field interaction of two adjacent particles and observe the stresses at their center point, point B as shown in Fig. 5 (a)-inset (see Supplemental Material for simulation specifics [44]).

The tensile stresses at point B ( $\sigma_{yy, B}$ ) for different crystal fractions with the same far-field loading stress (1GPa) and perfect interface are compared (dotted-red line in Fig. 5(a)). An abrupt change in stress concentration is observed once the sample reaches  $\sim 7\%$  crystallized volume fraction when we assume  $G_{MG} < G_c$ ,  $\sigma_{MG}^f > \sigma_c^f$ , where  $G$  is the shear modulus and  $\sigma^f$  is the fracture strength,  $MG$  and  $c$  denotes that properties of the metallic glass and the crystals, respectively. In general, the shear modulus of the metallic glass is lower than the shear modulus of its competing crystal [47-51]. However, no clear trend has been observed for the fracture strength. In some cases the competing crystal's fracture strength has been found to be higher [3,14,52-54] and in others lower [40,47,48,51,55-58] than the fracture strength of the metallic glass. Therefore, we consider two cases here: (i)  $G_{MG} < G_c$ ,  $\sigma_{MG}^f > \sigma_c^f$  and (ii)  $G_{MG} < G_c$ ,  $\sigma_{MG}^f < \sigma_c^f$ . For case (i) (Fig 5(b-i)), upon elastic loading, the stresses in the crystals are higher than in the matrix due to the larger shear modulus of the crystals. This causes fracture to first occur in the crystal phase. Such fracture creates sharp rises in stress, which can drastically increase stresses in the matrix. This enhancement of stresses in the matrix becomes effective once crystallization volume fraction exceeds  $\sim 7\%$  (Fig 5 (a)). As a result, metallic glasses including more than  $\sim 7\%$  crystallinity with  $G_{MG} < G_c$ ,  $\sigma_{MG}^f > \sigma_c^f$  embrittles. Such a behavior is most typical for partially crystallized BMGs. In case (ii),  $\sigma_{MG}^f < \sigma_c^f$ ,  $G_{MG} < G_c$ , the secondary phase carries higher load than the matrix, and stresses are therefore reduced in the matrix for the same far-field stress (Fig 5(a-black



line) and Fig 5(b-ii)). This cause delayed shear band formation before eventual fracture and hence increased toughness. Such a behavior, even less common, may have been observed in some previous studies [3,53].

So far, discussed cases assumed a perfect interface. However, if  $\sigma_i$  has a final strength comparable to the strength of  $\sigma_{MG}$  or  $\sigma_c$ , embrittlement can also occur even if  $\sigma_{MG}^f < \sigma_c^f$  and  $G_{MG} < G_c$  (Fig. 5(c)). The reason for this is that a damaged interface generates stress concentrations in the amorphous matrix similar to a fractured crystal and, as a result, embrittles the material. Therefore, in order to observe a toughening behavior in a partially crystallized BMG,  $\sigma_{MG}^f < \sigma_c^f$  and  $G_{MG} < G_c$  must hold true, and the interface between the two phases must be strong such that fracture does not originate from the interface. Figure 5(c) compares simulation results for variations of  $\sigma_i$  of  $0.5\sigma_{MG}$  and  $\sigma_i$  of  $1.2\sigma_{MG}$  for the case of  $\sigma_{MG}^f < \sigma_c^f$  and  $G_{MG} < G_c$ . At  $\varepsilon \sim 0.2\%$ , stress is higher in the crystal phase. At  $\varepsilon \sim 0.8\%$  of the system with  $\sigma_i = 0.5\sigma_{MG}$ , stresses migrate from the crystal to the interface and induce high stress concentration on the amorphous matrix ( $\varepsilon \sim 1.7\%$ ), while this behavior is not observed in system with  $\sigma_i = 1.2\sigma_{MG}$  due to the fracturing of the interface for  $\sigma_i = 0.5\sigma_{MG}$  compared to the still intact interface for  $\sigma_i = 1.2\sigma_{MG}$ .

It is important to mention that the above cases do not represent previously observed toughening in BMG composites where the secondary phases are large in size and spacing [37,59,60]. For these composites, the secondary phase is spaced such that it coincides with the plastic zone size of the matrix. The softer secondary crystalline phases reduce stress through absorbing strain, and hence shear band formation without fracture.

These plastic zone sizes are on the order of  $\sim 100$  microns, which is about 10,000 times larger than the spacing of the secondary phase in our present case.

The complete mechanical behavior of composites is more complicated than as discussed here, but we propose that their behavior and interactions can be categorized into two scenarios, one of which reflects our experimental findings. For  $\sigma_{MG}^f < \sigma_c^f$  and  $G_{MG} < G_c$ , crystallization can enhance toughness. Typically, and experimentally observed here,  $\sigma_{MG}^f > \sigma_c^f$  and  $G_{MG} < G_c$  and the deformation of the nanocrystals induces a high stress concentration in the BMG. Therefore, failure occurs at low deformation, which is indicative of embrittlement. For both cases, the transition region was observed around 7% crystallization by volume.

In conclusion, we have observed a highly non-linear dependence of crystallinity of BMG forming alloys on their fracture toughness. Below  $\sim 6\%$ , crystallinity does not appear to affect their fracture toughness. This finding is very encouraging for thermoplastic forming processing of BMGs where, even though highly predictable, small amounts of crystallinity are unavoidable. A dramatic drop occurs above  $\sim 7\%$  where minute additional crystallinity drastically degrades fracture resistance. This behavior can be explained by the stress field interaction of the typically stiffer but lower fracture strength crystalline inclusion.

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Fig.1

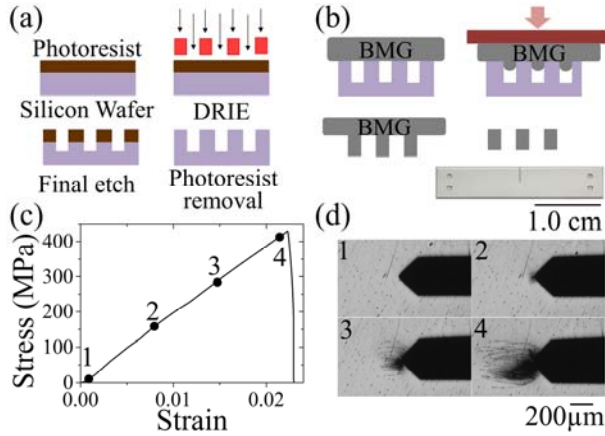


FIG.1 BMG single edge notched tensile (SENT) fracture toughness fabrication technique comprises of (a) mold fabrication and (b) mold replication. (a) As-designed silicon mold fabricated by photolithography technique and deep reactive ion etching (DRIE) to accommodate SENT samples of  $25 \times 5 \times 0.25 \text{ mm}^3$  with a notch depth of 2.5 mm,  $a/w=0.5$ , thickness of  $250 \pm 5 \text{ μm}$  and a notch root radius of 10  $\text{μm}$ . (b) Mold replication is achieved through thermoplastic forming based molding of the BMG into silicon mold at temperatures above  $T_g$  with application of pressure (c) a typical stress-strain plot of Zr-BMG SENT, and (d) in-situ observation of the development of corresponding plastic zone.

Fig.2:

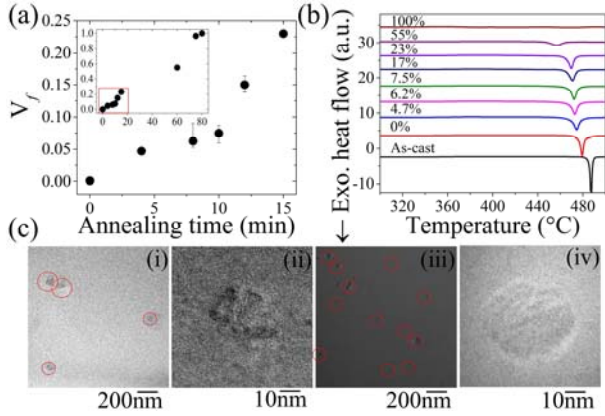


FIG 2 Determination of the crystallized volume fraction through a combination of thermal analysis using differential scanning calorimetry (DSC) under a heating rate of 20 K/min (a, b) and transmission electron microscope (TEM) (c). TEM bright field images of crystals embedded in amorphous matrix of sample with volume fraction of ~4% (i)-(ii), and ~7% (iii)-(iv).

Fig.3

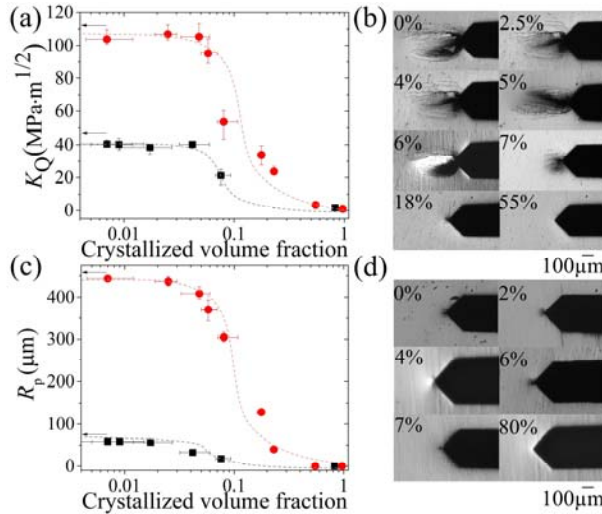


FIG. 3 (a) Measured  $K_Q$  as a function of crystallized volume fraction for  $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$  (●) and  $Pd_{43}Cu_{27}Ni_{10}P_{20}$  (■). Errors originate from standard deviation from five samples per data point (vertical) and the evaluation of the crystallized volume fraction through thermal analysis and TEM (horizontal). The dashed lines help guide the eye. (b) In-situ images of the critical plastic zone  $R_p$  of Zr-BMG prior to fracture. (c) Measured  $R_p$  for various degrees of crystallinity corresponding to each data points in Fig. 3(a). (d) In-situ images of critical plastic zone of Pd-BMG prior to fracture corresponding to Fig. 3(c).

Fig.4:

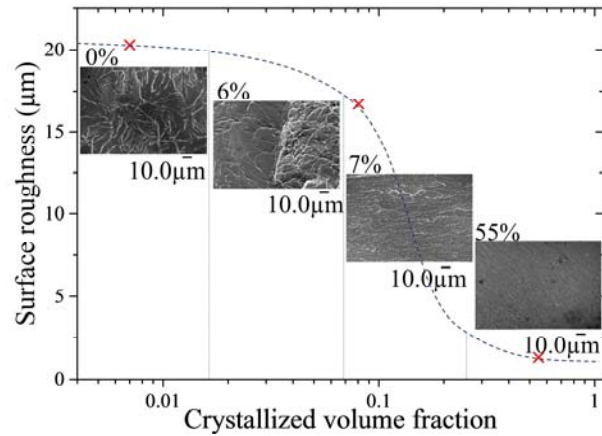


FIG. 4 Summary of the surface roughness on the fractured surface of Zr-BMG with different crystallized volume fraction. Superimposed are scanning electron microscopy images of the fracture surfaces for amorphous, 6%, 7%, and 55% crystallinity. Roughness is measured from differential interface contrast (DIC) measurement, revealing a decrease in surface roughness with increasing crystallinity. Measured data are marked in red. The dashed line helps guide the eye.

Fig.5:

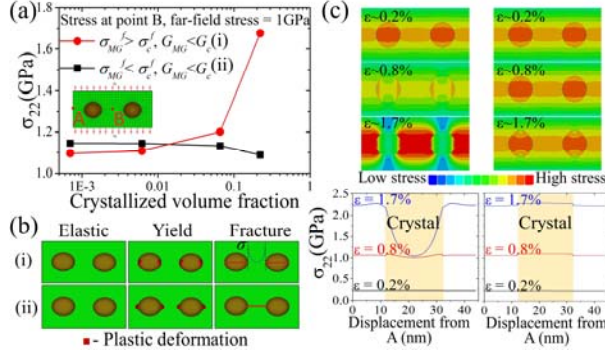


FIG. 5 Finite element analysis of the stress field interaction of crystals of various properties embedded in an amorphous matrix quantifying (a) stress in the matrix at the midpoint between two crystals (point B), reflecting the interaction between the crystals for  $\sigma_{MG}^f < \sigma_c^f$ ,  $G_{MG} < G_c$  (■) and  $\sigma_{MG}^f > \sigma_c^f$ ,  $G_{MG} < G_c$  (●) for various crystallized volume fraction (subscript  $MG$  denotes properties of the matrix, and  $c$  that of the crystals). The inset shows a unit cell containing two crystals under uniform tensile stress ( $\sigma_0$ ) along the y-direction used in the model set-up. (b) The two possible cases for amorphous-nanocrystalline composites as a consequence of various properties of crystals and amorphous matrix. Case (i) shows the progression of the system under tensile stress in Fig. 5 (a-●). During elastic loading, the crystal carries larger stress than the amorphous matrix because  $G_{MG} < G_c$ . Further loading causes crystal to fracture prior to the matrix as present in our experiments. It is also possible that  $\sigma_{MG}^f < \sigma_c^f$ ,  $G_{MG} < G_c$  as in Fig. 5(a-■) and is reflected in case (ii). Nanocrystal-BMG interfaces were considered in (c). The interfacial strength  $\sigma_i$ , between the metallic glass and the nanocrystals were varied in the simulation with its strength of  $0.5\sigma_{MG}^f$  (Fig. 5(c) left) and  $1.2\sigma_{MG}^f$  (Fig 5(c) right). For both cases in their elastic region,  $\varepsilon \sim 0.2\%$ , the stress is higher in the crystal. With increasing far field stress resulting in a strain of  $\varepsilon \sim 1.7\%$ , for weaker interface,  $\sigma_i = 0.5\sigma_{MG}^f$  stress is highly concentrated in the amorphous matrix, whereas relatively uniform distributed throughout crystal, matrix, and interface for  $\sigma_i = 1.2\sigma_{MG}^f$ .

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