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Microstructure evolution and plasticity in Zr-based glass-forming alloys

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The microstructure characteristic scale, in partially devitrified Zr-based glass-forming alloys, is examined in the light of classical nucleation and growth theory. It is then related to the high-ductility properties of these materials. Stabilization of the icosahedral phase under addition of isoelectronic elements, as evidenced in recent experiments, is discussed on a qualitative basis.

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Zr(Cu,Ni)-based multicomponent alloys are characterized by both high glass-forming ability and broad supercooled-liquid range. When doped with Ti, or Ag, or Pd (isoelectronic to, respectively, Zr, Cu, and Ni), they can be brought to a partially devitrified, generally metastable, state consisting of spherulitic, icosahedral quasicrystalline grains embedded in the amorphous matrix. The characteristic size of these depends on composition and thermal treatment. (It has been known for some time that oxygen impurities also favor precipitation of the icosahedral phase.) Recently published examples include: $Zr_{62-x}Ti_xCu_{20}Ni_8Al_{10}$ [1], $Zr_{57}Ti_8Nb_{2.5}Cu_{14}Ni_{11}Al_{7.5}$ [2], $Zr_{65}Cu_{7.5}Ni_{10}Al_{7.5}Ag_{10}$ [3,4], $Zr_{65}Cu_{12.5}Ni_{10}AL_{7.5}Ag_5$ [5], $Zr_{70}Ni_{10}M_{20}$ ($M=$Pd, Au, Pt) [6], and even $Zr_{70}Pd_{30}$ [7].

Such a microstructure in partially devitrified metallic glasses leads to interesting mechanical properties—specifically, to substantially enhanced ductility [8] (in addition to the high strengths that are due to absence of crystal slip in the homogeneous, finely divided, material structure).

We shall examine and discuss, in turn: nucleation and growth of quasicrystalline grains, ductility optimization as a function of precipitated volume fraction, and stabilization of icosahedral clusters upon addition of isoelectronic elements.

I. NUCLEATION AND GROWTH

The grain size scales generally in nanometers, or tens of nanometers, on heating above glass temperature and annealing. This has been interpreted as indicative of phase decomposition in the supercooled liquid [9] or, in the case of very fine grains, of transient nucleation [10]. In classical nucleation and growth theory [11], the volume fraction transformed z is given by the Avrami relation:

$$z=1-\exp(-kt^n).$$

In Ref. [3], for example, n is about 3.5–3.7, pointing to homogeneous nucleation with a solid-liquid interface-controlled growth mechanism.

In a multicomponent system, diffusion and growth is, of course, a complex kinetic process. We shall, however, assume that it is dominated by a single, effective, thermally activated diffusion coefficient D corresponding to interfacial attachment-limited growth. Such may be the case, in particular, when a relatively small atom is substituted for a heavier one—as, e.g., Ti for Zr in Refs. [1,2].

With a free-energy barrier (per unit volume) between stable and metastable phases, of height g_0, and a supersaturation Δg, the critical nucleus size R_c and nucleation barrier E_c are given (in order of magnitude and for weak supersaturations $\Delta g \ll g_0$) by

$$R_c=\xi\left(\frac{g_0}{\Delta g}\right),\quad E_c=\epsilon_0\left(\frac{g_0}{\Delta g}\right)^2,\quad \left[E_c=\frac{16\pi}{3}\frac{\gamma^3}{(\Delta g)^2}\right], \tag{1}$$

with ξ a molecular length, $\epsilon_0 \simeq g_0\xi^3$, and γ the solid-liquid interfacial tension. The growth rate, in the early stages, is essentially constant (this is consistent with experiment, see e.g., Ref. [4]):

$$u=\frac{dR}{dt}=(\text{const})\times D\Delta c=(\text{const})\times\Delta c\,\exp-\frac{Q}{k_BT}, \tag{2}$$

where Δc ($\sim\Delta g$) is a characteristic difference in composition, related to the chemical potential control parameter in the supersaturated mixture; Q is an Arrhenius activation energy for attachment fluxes and growth. In the compact metallic alloys we are considering, the kinetics are sluggish and Q is large (the high compacity arises, in large part, from the variety of different atomic sizes). For example, in $Zr_{65}Cu_{7.5}Ni_{10}Al_{7.5}Ag_{10}$ [3,4]: $Q\simeq 400\ \text{kJ mol}^{-1}$.

The nucleation rate I_n is the current of viable nuclei in size space. As such, it obeys a Fokker-Planck equation

$$I_n=f\dot{R}-B\frac{\partial f}{\partial R},$$

where $f(R)$ is the equilibrium distribution of nuclei and B a diffusion coefficient in size space. And I_n goes as

$$I_n\sim Df_c,\qquad f_c=(\text{const})\times\exp-\frac{E_c}{k_BT}, \tag{3}$$

giving the familiar time-temperature-transformation relation:

$$I_n=(\text{const})\times\exp-\frac{E_c+Q}{k_BT}. \tag{4}$$

E_c is large near liquidus, and usually smaller than Q at substantial supercoolings.

Coming back to the volume fraction z of the primary crystallization, icosahedral phase, we may write,

$$z(t)=\int_0^t (I_n dt')\frac{4\pi}{3}[u(t-t')]^3, \tag{5}$$

or, in order of magnitude: $z(t)\sim I_n u^3 t^4$. In principle the transformation ends at $t=t_*$, when $z\simeq 1$. Recall however that the primary, quasicrystalline phase is usually metastable, and its growth may be blocked by intergrain elastic interactions (experimentally, after sufficient annealing, z may saturate to values between, typically, 10 and 80%). A clear tendency to growth deceleration and grain-size leveling is usually observed (see e.g. Ref. [4]. In small nanometric grains, this probably signals particular stability of icosahedral clusters with such sizes (see Sec. III below). From Eq. (5), the microstructure scale is given, again in order of magnitude, by

$$R_{\max}\equiv R_*\sim ut_*\sim\left(\frac{u}{I_n}\right)^{1/4}; \quad t_*\sim(u^3 I_n)^{-1/4} \tag{6}$$

(and, due to the weak exponent $\frac{1}{4}$, the exact value of $z_{\max}$ does not matter much).

One simple test would provide much insight: measure, simultaneously, I_n, u and R_* over the Zr-based family; whenever R_* scales with u and u with $I_n^{-1/3}$ as composition is varied, the classical model should provide a reasonable first approximation for nucleation and growth. In $Zr_{65}Cu_{7.5}Ni_{10}Al_{7.5}M_{10}$ ($M=$Ag, Pd) for example, substitution of 10% Ag or Pd boosts the nucleation rate I_n from 10^{16} to 10^{20} $m^{-3}\,s^{-1}$, while the initial grain-growth rate u decreases from about 10^{-8} to 10^{-9} $m\,s^{-1}$ [4]. R_*, then, should scale essentially as u.

Given the large value of Q, changes in u due to changes in composition are likely to be driven by small changes in activation energy Q. At a given characteristic annealing temperature ($T=700$ K [4]), a one order-of-magnitude decrease in u upon substituting 10% Ag or Pd, requires only about 12 $kJ\,mol^{-1}$ increase in Q: $\Delta Q\simeq 3\% Q$. Conversely, the four order-of-magnitude increase in nucleation rate clearly calls for a substantial reduction in nucleation barrier E_c. This makes sense: adding Ag or Pd stabilizes the icosahedral ''i'' phase; that is, at a given supersaturation level Δg, free-energy barrier g_0 and interfacial tension γ are reduced, leading through Eq. (1) to a smaller E_c.

Similar considerations should probably apply to stabilization of the *i* phase upon substitution of Zr by small amounts of Ti in $Zr_xCu_{1-x}Ni_yAl$ alloys [1] (see Sec. III). Primary quasicrystallization occurs at progressively lower temperatures, with a progressively finer microstructure, as the titanium concentration increases. Why, in the present simplified picture for nucleation and growth—where $R_*\sim u\sim\exp-(Q/T)$—should the activation energy Q become larger upon adding more of the smaller Ti atoms? In fact, the latter find their way, relatively rapidly compared to Zr atoms, to stable sites in icosahedral clusters, thereby stabilizing the *i* phase itself (which indeed is absent when titanium is absent [1]). But then, above some small Ti concentration (smaller than 3% [1]), collective rearrangements become somewhat more difficult and attachment kinetics slows down upon adding more titanium: Q increases and the microstructure size decreases.

To sum up, we have argued that the microstructures observed in Zr-based multicomponent alloys might be qualitatively understood along the lines of classical nucleation and growth. It is natural that the *i* phase, albeit metastable, tends to show up in primary crystallization since icosahedral short-range order is present in the densely-packed undercooled molten, and quenched-amorphous, phases. In large grains, formed upon heating and annealing, the resulting quasicrystalline phase is chemically disordered and, therefore, crystallographically distorted; it can accommodate significant local-composition variations [2]. Selected isoelectronic atomic species such as Ti, Pd, or Ag substituted in the alloy, may stabilize icosahedral short-range order in the liquid and, therefore, lower the energy minima of corresponding configurations in the potential-energy landscape of the disordered system—the so-called inherent structures [12]. As we shall argue in Sec. III, this will tend to stabilize the primary-precipitation icosahedral phase and lead, progressively, to smaller, better-ordered *i* grains. Quantitatively, the problem is immensely more complex than whatever picture of it the classical nucleation model might provide us with. Nonetheless, such a picture seems to be compatible with what experiment tells us about microstructural sizes or nucleation and growth rates in these systems.

II. DUCTILITY OPTIMIZATION

Let us turn our attention now to the connection between microstructure and plasticity. Very fine *i* cluster sizes have been observed in $Zr_{60}Cu_{20}Al_{10}Pd_{10}$: $R_*\sim 1-2$ nm (at intermediate volume fraction z), by Fan and Inoue [8]. The authors have demonstrated, at nanocrystalline volume fraction $z=z^*=25\%$, a plastic-strain peak under compression: $\epsilon_p^{\max}=4-4.5\%$ (ϵ_p is 2% at $z=7\%$ and vanishes at $z=70\%$). For such small clusters, the Kelton model [10] for transient nucleation may be relevant. It predicts, around each precipitated nanocrystal (here, icosahedral cluster), a sort of halo that—due to redissolution—is richer than the parent amorphous phase in crystal-forming elements. These ''halo'' zones are densely populated (same volume fraction, and approximate size, as the clusters themselves). Each one of them however should be, for compositional reasons, somewhat *less compact* than the randomly close-packed parent phase.

The halo zones, then, bring local *free volume* to the system and—since they are structurally less stable than the *i* clusters—they therefore enhance its potential for plastic deformation. It is reasonable to expect that: (i) under mechanical stress, shear bands will be nucleated, and pinned, at these zone sites—thus preventing brittle fracture, even under tensile stress; (ii) at a given annealing temperature, there will be an optimum nanocrystallite volume fraction z^* that will lead, after quenching to room temperature, to maximum ductility: below z^* the halo zones surrounding every cluster are not large enough to provide maximum inelastic shear strain, ϵ_d^{in}; above z^* they are large but less efficient as their composition goes closer [10] to the parent-phase average composition (thereby increasing their compacity), and this loss in efficiency is aggravated by the fact that the zones start to overlap or interfere with one another. Within this picture, the experimental finding $z^* \simeq 25\%$ [8] seems quite realistic.

It is possible, however, to go a little farther by *identifying* the halo zones in partially devitrified metallic glasses with the so-called shear transformation zones recently introduced and discussed by Falk and Langer [13], in the context of dynamic fracture. These objects are *bistable*, microscopic, disordered regions within an amorphous matrix, with characteristic volume V_z and equilibrium number density n_∞, that can switch under external *shear* stress σ_s back and forth between two structural arrangements $(\pm)$ differing by an increment in plastic local shear strain: $\Delta\epsilon$. (Note that, in this model, they can also be created or annihilated under stress, contrary to the halo zones that are attached to nanocrystal clusters; this allows proper assignment of yield stress and plastic flow.) The required excess free volume for a $+\rightarrow-$ transition is of the form,

$$\Delta V^*(\sigma_s)=V_0^*\exp-\frac{\sigma_s}{\bar{\mu}},$$

where V_0^* is a molecular volume and $\bar{\mu}$ an internal shear modulus somewhat smaller than a typical plastic-yield stress $\sigma_y \equiv \bar{\sigma}$. With these ingredients, the authors were able to write down rate equations for $n_\pm$, the number densities of shear transformation zones (STZ) in the $\pm$ states. (These rates are governed by the rate $\sigma_s \dot{\epsilon}_s^{\mathrm{in}}$ at which irreversible work is done on the system). In typical situations for simple amorphous solids, described and simulated within a Lennard-Jones model, they found:

$$n_\infty V_z \Delta\epsilon \sim 6\%,$$

which is realistic as this dimensionless quantity represents the total strain one gets if all STZ switch together in the same direction ($n_\infty V_z$ is the STZ volume fraction in the system).

It is interesting to note that $n_\infty V_z \Delta\epsilon$ also provides a measure for maximum plastic shear strain before failure, that is, for ductility: the yield stress $\bar{\sigma}$ marks the crossover between static deformation and plastic flow (which of course eventually leads to failure); close to yield, the final inelastic shear strain is given approximately by (see Ref. [13]):

$$\epsilon_s^{\mathrm{in}}=\frac{1}{2}(n_\infty V_z \Delta\epsilon)\ln\frac{2}{1-(\sigma_s/\bar{\sigma})}. \tag{7}$$

For $\sigma_s = 0.9\bar{\sigma}$, this amounts to: $\epsilon_s^{\mathrm{in}} \simeq \frac{3}{2}(n_\infty V_z \Delta\epsilon)$. With the parameter values chosen in the model system of Ref. [13], this gives: $\epsilon_s^{\mathrm{in}} = 9\%$, twice the value $\epsilon_s^{\mathrm{max}} = 4$–$4.5\%$ as measured under compressive stress in $\mathrm{Zr_{60}Cu_{20}Al_{10}Pd_{10}}$ [8] (recall that, under uniaxial stress, uniaxial strain is significantly smaller than the corresponding, $(\pi/4)$-deviatoric, shear strain). As mentioned above, an optimal nanocrystal volume fraction z^* will maximize $(n_\infty V_z \Delta\epsilon)$ which is the product of volume fraction $(n_\infty V_z)$ and efficiency $(\Delta\epsilon)$ of plastically active zones. Within the present picture one gets: $(n_\infty V_z)^{\mathrm{opt}} = z^* \simeq 25\%$, corresponding (since $z^* \Delta\epsilon \sim 6\%$) to an average increment in local shear strain, in each bistable plastic zone, of typically: $\Delta\epsilon \simeq 0.25$—which seems to make sense.

Thus, the high-ductility levels, characteristic of partially devitrified multicomponent alloys, can be understood on a semiquantitative basis, inasmuch as the "halo" nanoregions that surround individual quasicrystalline clusters, and endow the disordered system with extra free volume, may be considered as shear transformation zones.

III. STABILIZATION OF ICOSAHEDRAL CLUSTERS

Short-range icosahedral order in the undercooled liquid, and quenched amorphous solid, is favored in the compact systems we are considering, as this cluster symmetry minimizes the area over volume ratio. In this section we address the following question: given that short-range ordering (SRO) in the liquid provides a template [14] for the nucleation of precipitated grains in the annealed solid, in what measure can we expect small amounts of substituted, selected isoelectronic species to control the appearance, size and stability of quasicrystalline grains formed within the amorphous matrix under subsequent heating [e.g., in a differential scanning calorimetry run (DSC)]? We shall concentrate on the well-documented system $\mathrm{Zr}_{62-x}\mathrm{Ti}_x\mathrm{Cu}_{20}\mathrm{Ni}_8\mathrm{Al}_{10}$ (see Ref. [1]).

In this particular system, the i phase is absent for $x=0$ and the only precipitated phases are cubic $\mathrm{NiZr_2}$ and tetragonal $\mathrm{CuZr_2}$. For 1–$2\% < x < 5$–7%, primary precipitation is icosahedral, with better stability and smaller grains as x increases. This indicates that titanium enhances SRO and that clusters are Ti *rich* in the liquid as well as solid phases. Already at $x=5\%$, the higher DSC exothermic peak seems to be eliminated, at least for rapid quenches. Finally, there is a remarkably *fast* decrease in grain size, from 50–100 nm at $x=3\%$ to 5 nm at $x=5\%$, and $\lesssim 3$ nm at $x=7.5\%$ [1].

Let us call N the number of atoms in the icosahedral building-block clusters that are nucleated from the melt, v their average valence, and X the fraction of Ti atoms substituted for Zr within these clusters. Icosahedral symmetry is compatible with different sizes, internal structures, and chemical decorations of these i clusters. X is large, as we have seen, and this may be understood from the relative smallness of Ti atoms, which helps overcome excluded-volume effects and is likely to lead to an increase in N. At small overall compositions x, X is an increasing function of x—at least up to some value x_0. For every type of elementary i building block, there is a "magic" number M such that when $Nv=M$, then the i cluster shows particular stability due to its *inertness* (cf. rare gases, or saturated molecules). For alkali-atom clusters such as Na_n, and in a jellium-cluster model, the magic series is: $M=2, 8, 18, 20, 34, 40, 58, 92, \ldots$ [15]. For instance, $\mathrm{Al_{12}C}$ (or Al_{13}^-) that has 40 valence electrons, forms a stable, closed-shell configuration:

$1s^2\,1p^6\,1d^{10}\,2s^2\,1f^{14}\,2p^6$. Al_{13} clusters, in contrast, with 39 electrons each, are strongly reactive (with, e.g., oxygen): see Ref. [15]. Similar considerations hold for larger blocks such as, for example, the Mackay pseudo-icosahedron (MPI) which is a compact, almost spherical cluster of 51 atoms ($N=51$) and, in the case of the stable Al_xPd_zMn quasicrystal, its inert configuration corresponds to $M=92$ (i.e. average valence $v\simeq 1.8$). In this case it has been shown (see, e.g., [16] and references therein) that, for some small deviation δ from the latter value, the stable *i* phase grows from the elementary MPI's according to an *expansion* symmetry (with expansion factors that are irrational, Fibonacci-like numbers). The elementary MPI is about 1 nm in size, the second "generation" about 4 nm, the third 18 nm, etc. Note that such a sequence is, away from strict stoichiometric conditions, likely to be interrupted rather early in view of kinetic limitations due to the size of elementary units.

Let us now come back to our Zr(Ti)-based system. There, both N and, hence, M depend on X (and on the electronic structure of the embedding amorphous matrix). The balance equation, for total valence, writes:

$$N(X)v=M(N(X))+\delta, \tag{8}$$

where δ, the shift relative to the relevant magic number $M(X)$, accounts for cluster reactivity and *i* grain growth.

We argue that, at small x and X, the elementary clusters are poorly stable and strongly reactive, leading to relatively large grains (with many defects, in all likelihood). Upon increase in x and X, cluster stability increases and cluster reactivity (as measured by δ) decreases. If we assume that δ goes to zero at $x=x_0$ ($\sim 5-7\%$, as we have seen), then the grain size should reduce to the "magic-cluster" size (~ 2 nm), with $X=X_{\max}=X(x_0)$, for $x>x_0$. Such a picture is comforted by the experimental results of Xing *et al.* [1]. The almost abrupt decrease in grain size between $x=3\%$ (50–100 nm) and $x=5\%$ ($\simeq 5$ nm), suggests that, in this composition range, it is energetically favorable for the elementary icosahedral units to switch to a finer size; so that N, M, and δ all jump to lower values there, analogous to, say, a $M=92\rightarrow M=58$ jump in the jellium model.

Clearly, many more experimental data (especially as to small-grain chemical composition) will be necessary before strong support can be brought to this line of reasoning. The latter, however, is sufficiently flexible to be adaptable to other systems than just $Zr(Ti)Cu_xNi_{1-x}Al$.

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