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EFFICIENT LOCAL PACKING IN METALLIC GLASSES

D.B. Miracle

Metals Branch, Metals Development (AFRL/MLLMD)
Metals, Ceramics, and Nondestructive Evaluation Division
Materials and Manufacturing Directorate
Air Force Research Laboratory, Air Force Materiel Command
Wright-Patterson AFB, OH 45433-7750

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Pamela M. Schaefer
Principal Materials Engineer
Technical & Strategic Planning Office
Materials and Manufacturing Directorate

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A simple topological model in an earlier manuscript has shown that efficient atomic packing is a fundamental principle in the formation of metallic glasses. An approach for defining and quantifying the local packing efficiency, P, was developed for solute-centered clusters that contained only solvent atoms in the first coordination shell. In the present research, this methodology is extended to allow quantification of P when more than one atomic species is present in the first coordination shell. This analysis is applied to several metallic glasses using published data of atom radii and partial coordination numbers. It is shown that packing is generally very efficient, and that the values of P obtained for the metallic classes are essentially identical to the values obtained from a similar analysis of the competing crystalline structures. These results are consistent with frequent reports of topological short range ordering in metallic glasses, and are inconsistent with a structural model on dense random packing of atoms.

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Efficient local packing in metallic glasses

D.B. Miracle *

*Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB,
2230 Tenth Street, Dayton, OH 45433-7817, USA*

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Abstract

A simple topological model in an earlier manuscript has provided additional support for the concept that efficient atomic packing is a fundamental principle in the formation of metallic glasses. In that work, an approach for defining and quantifying the local packing efficiency, P, was developed for solute-centered clusters that contained only solvent atoms in the first coordination shell. In the present work, this methodology is extended to allow quantification of P when more than one atomic species is present in the first coordination shell. This analysis is applied to several metallic glasses using published experimental data of partial coordination numbers. It is shown that packing in the first coordination shell is generally very efficient, even though the systems studied have significant differences in atomic species, compositions and relative atomic sizes. It is shown that packing is generally efficient around both solute and solvent atom species. Local packing efficiencies much less than unity are expected to be uncommon, since the global average packing efficiency is near unity and local packing efficiencies greater than unity are physically improbable. Deviations from efficiently packed configurations are discussed with respect to the local packing efficiencies in competing crystalline structures and with poorer glass forming ability. The values of P obtained for metallic glasses are essentially identical to the values obtained from a similar analysis of the competing crystalline structures. These results are consistent with frequent earlier reports of topological short range ordering in metallic glasses and with developments that have established the relationship between dense atomic packing and glass formation.
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1. Introduction

The exceptionally small decrease in density of bulk metallic glasses relative to the crystalline state of the same alloys [1,2], the development of volume effects during melting and solidification [2–5] and consideration of the relationship between molar volume and glass stability [6,7] all suggest that efficiently packed atomic configurations are common in the structures of these systems. A recent further development of this concept predicts

that solute atoms with specific radius ratios relative to the solvent, R^*, are capable of producing efficient atomic packing in the first coordination shell [8]. A clear preference for these predicted radius ratios was demonstrated by analyzing a large number of binary and complex metallic glasses. In this recent work, atomic clusters comprised of a central solute atom surrounded in the first coordination shell by solvent atoms were considered. All atoms were idealized as hard spheres. A derivation of the theoretical coordination number, N^T, was obtained by considering the area associated with a solvent atom of radius, r_w, on the curved surface of a central solute atom of radius, r_u. The result was given as [8]

* Tel.: +1 937 255 9833; fax: +1 937 255 3007.
E-mail address: daniel.miracle@wpafb.af.mil

$$N^T = \frac{4\pi}{\pi(2-q) + 2q \arccos\{(\sin(\pi/q))[1 - 1/(R+1)^2]^{1/2}\}}. \tag{1}$$

N^T is a real number, where the integer portion represents the number of solvent atoms in the first shell and the fractional part represents the gaps between solvent atoms in the first coordination shell. N^T is only a function of the radius ratio between the solute and solvent atoms, $R = r_u/r_w$, and the maximum surface symmetry, q (described in [8]). The maximum surface symmetry is also a function of R, where

$$q = 3 \quad \text{for } 0.225 \leqslant R < 0.414, \tag{2a}$$

$$q = 4 \quad \text{for } 0.414 \leqslant R < 0.902, \tag{2b}$$

$$q = 5 \quad \text{for } 0.902 \leqslant R < \infty. \tag{2c}$$

This representation of N^T provides a more accurate description than an earlier equation [9]. Details regarding the derivation of Eq. (1) are provided elsewhere [8].

A simple definition of local atomic packing efficiency, P, is given as the ratio of the actual coordination number, N, normalized by the theoretical maximum coordination number, N^T. N may be determined analytically from Eq. (1) by truncating N^T, or may be determined experimentally from high quality diffraction data.

The earlier analysis of efficient atomic packing provides a theoretical treatment of atomic clusters with solvent atoms only in the first coordination shell [8]. Although this idealization is satisfied in many important systems, including the local environment of metalloid solutes in metal–metalloid glasses, in many cases the first coordination shell around a given solute atom has multiple atomic species. Further, the first coordination shell around solvent atoms will generally contain both solvent and solute atom species. The objective of the present paper is to provide an approach for quantifying the local packing efficiency when multiple atomic species occupy the first coordination shell. Concepts of efficient packing have been developed in the past based on bulk observations such as density, volume changes upon solidification and molar volume [1–7]. However, this general view is not sufficiently specific to establish if efficient atomic packing is a characteristic feature for all atomic species in metallic glasses, or if packing is efficient only around selected atomic species. Thus, the present analysis can provide new insights into metallic glasses, and will enable correlation with characteristics such as atomic structure, glass formability and deformation. This concept is applied via an analysis of diffraction data reported in the literature for several metallic glasses.

2. Packing efficiency of multiple atomic species in the first coordination shell: the model

Eq. (1) allows the maximum theoretical coordination number and packing efficiency to be determined from R and from diffraction data for a binary system. Although this approach was developed for occupancy of only one atomic species (i.e., the solvent) in the first coordination shell, it can be extended to determine the local packing efficiency when multiple atomic species occupy the first coordination shell. In this analysis, 'interstitial' occupancy of much smaller solutes between much larger atoms in the 1st coordination shell is not considered. This is supported by the observation that solutes small enough to fit in the interstices formed by a nearly planar configuration of efficiently packed larger atoms do not occur in practice in metallic glasses, as described in more detail in Section 4.

Consider a ternary alloy with solute atoms u and v, and solvent atoms, w. There are three partial coordination numbers that describe the first coordination shell about any given atom. For example, about a solute atom, u, these partial coordination numbers are N_{uu}, N_{uv}, and N_{uw}. Three partial local packing efficiencies are obtained, P_{uu}, P_{uv}, and P_{uw}, where

$$P_{u\phi} = N_{u\phi}/N_{u\phi}^T, \tag{3}$$

$N_{u\phi}$ is the partial coordination number of $\phi(= u, v, \text{ or } w)$ atoms that are first nearest neighbors with u atoms, and $N_{u\phi}^T$ are the values of N^T determined from Eq. (1) using $R = r_u/r_\phi$ of the specific $u-\phi$ pair being considered. Summing the partial local packing efficiencies for all species in the first coordination shell allows a determination of the total local packing efficiency. As an independent constraint, this sum of local partial packing efficiencies should not exceed unity (see Section 4 for further details).

$$\sum_\phi (N_{u\phi}/N_{u\phi}^T) \leqslant 1. \tag{4}$$

Thus, closer is the total local packing efficiency to unity, the higher is the local packing efficiency.

High quality diffraction experiments provide an approach for measuring partial coordination numbers in metallic glasses. The most accurate values are obtained when special care is exercised in the experiments and analysis, so that partial radial distribution functions ($p-rdfs$) are obtained. However, the number of $p-rdfs$ required to define the local chemical environment around each of the atoms in the system increases with alloy complexity – a binary alloy requires three unique diffraction experiments for all combinations of atomic pairs, while a ternary alloy requires six. As a result, a full set of $p-rdfs$ is rarely available for alloys with three or more elements. The widest set of complete diffraction data exists for binary metal–metalloid glasses, and data

are also available for a number of other systems. In the following section, the analysis described above will be used to determine the local packing efficiency around each atom type in selected metallic glass alloys.

3. Packing efficiency of multiple atomic species in the first coordination shell: analysis

The partial and total local packing efficiencies were determined from published diffraction data for Fe–B [10], Ni–B [11,12], Co–P [13], Ni–Nb [14] and for Al–Y and Al–Y–Ni [15]. The atomic radii used in the present analysis were those determined in the respective publications, with the exception of the Al-based glasses, where the atomic radii were assumed in that work to be equal to metallic radii published in handbooks. Assessed values of atomic radii that have attempted to account for changes in bond length with alloying [9,16] were used for the Al-based glasses in the present analysis.

The partial and total local packing efficiencies for these alloys are shown in Table 1. In general, the total local packing efficiencies are within an assessed accuracy of ±10% of unity (see Section 4 for a description of the origin and magnitude of the assessed accuracy of P), showing that local packing is typically very efficient in metallic glasses. Packing is efficient not only around solute atom centers, but also around solvent atoms. The exceptions are both P and Co atom centers in $Co_{80}P_{20}$, where the packing efficiencies are 87–88%, and Al atom centers in $Al_{87}Y_8Ni_5$, where the total packing efficiency is less than 70%.

Insufficient diffraction data are available to fully determine the packing around Ni atoms in Al–Y–Ni. However, $P_{Ni–Al} + P_{Ni–Y} \cong 1$, so that $P_{Ni–Ni} \cong 0$ and therefore no Ni–Ni nearest neighbor bonds are expected to form [17]. This is consistent with the discussion in [15]. Nevertheless, a small fraction of Ni occupancy in the first coordination shell cannot be ruled out given the accuracy of the data obtained from total radial distribution functions in that work.

4. Discussion

Analysis of the local atomic packing efficiency shows that a total packing efficiency near unity, within an assessed error of ±10% (see discussion below), is common in metallic glasses (Table 1). The systems selected for analysis represent a range of glasses that are topologically distinct, since the solute-to-solvent atom radius ratios range from 0.6654 to 1.258. Efficient atomic packing is maintained in binary systems even when the concentrations of the elements present are changed, as shown for Ni–B and Nb–Ni glasses (Table 1). In fact, the Nb–Ni glasses cover a range of compositions such that

the solute species becomes the solvent species, and an atomic packing efficiency near unity is maintained for both species in the full range of compositions. In contrast to these trends, the addition of Ni to Al–Y glasses produces important changes in the local packing efficiency around Al atoms.

These high values support the conclusion that local atomic packing is generally very efficient in metallic glasses. The diffraction data used in this analysis represent globally averaged signals, so that efficient local packing must be considered as a global average state of the system. The variations in local atomic packing efficiency around a given atom type are likely to be relatively small throughout the structure, since local packing efficiencies significantly less than unity around some atoms will require the improbable result of local packing efficiencies significantly greater than unity around others to obtain a global average near unity.

The present results are inconsistent with a random arrangement of atoms in the first coordination shell. For a dense random packed array of monosized spheres, the mean coordination number ranges from about 7.5 to 11 [18,19] so that the total local packing efficiency ranges from 0.56 to 0.83. Systems containing both larger and smaller spheres can provide more efficient packing than a unimodal size distribution [20,21], and specific radius ratios, R^*, have been shown to enable especially efficiently packed configurations [8]. Further, short range ordering is commonly observed in metallic glasses [11,22–32]. It is suggested here that the introduction of solutes of special radius ratios, R^*, relative to the solvent atoms enable efficient atomic packing by replacing randomness with topological ordering. The current quantitative analysis provides additional support to the earlier observations that efficiently packed local atomic configurations associated with short range ordering is a governing paradigm for the structure of metallic glasses.

For comparison, local packing efficiencies were calculated for the crystalline phases nearest the compositions of the metallic glasses in Table 1. Intermetallic compounds nearest the metallic glass compositions were identified from [33] and the local crystal configurations and partial coordination numbers were obtained from [34]. The crystal structure prototype(s) and Pearson symbol(s) considered for the intermetallic crystalline compounds closest to the glasses studied here are given in Table 2. The partial coordination numbers for the crystalline phases were determined for each of the polyhedra listed in [34]. To allow direct comparison between local packing efficiencies for the amorphous and crystalline forms, this analysis included only atoms whose centers were within a spherical shell defined by the integration limits used in the determination of the experimental partial coordination numbers (Table 1). Where limits were not provided, an estimated limit of ±25% of the sum of the atomic radii was used. The local

Table 1
Local and total packing efficiencies obtained from published diffraction data

Alloy	$R_{u\phi}$[a]	$N_{u\phi}$[b]	$N_{u\phi}^{\mathrm{T}}$ at $R_{u\phi}$	$P_{u\phi}$	Integration limits (pm)
$Fe_{80}B_{20}$ [10]	$r_B = 85.5$ pm				
	$r_{Fe} = 128.5$ pm				
B–B	1	0	13.33	0	–
B–Fe	0.6654	8.64	8.52	1.01	$190 \leqslant r \leqslant 255$
B total		8.64		1.01	
Fe–B	1.503	2.16	21.2	0.102	$190 \leqslant r \leqslant 255$
Fe–Fe	1	12.4	13.33	0.930	$225 \leqslant r \leqslant 345$
Fe total		14.56		1.03	
$Ni_{81}B_{19}$ [11]	$r_B = 85$ pm				
	$r_{Ni} = 126$ pm				
B–B	1	0	13.33	0	–
B–Ni	0.6746	9.3	8.62	1.08	$180 \leqslant r \leqslant 255$
B total		9.3		10.8	
Ni–B	1.482	2.2	20.85	0.106	$180 \leqslant r \leqslant 255$
Ni–Ni	1	10.8	13.33	0.810	$215 \leqslant r \leqslant 300$
Ni total		13.0		0.916	
$Ni_{64}B_{36}$ [12]	$r_B = 86$ pm				
	$r_{Ni} = 127.5$ pm				
B–B	1	1.1	13.33	0.083	Not reported
B–Ni	0.6745	8.7	8.61	1.01	Not reported
B total		9.8		1.09	
Ni–B	1.483	4.9	20.86	0.235	Not reported
Ni–Ni	1	9.2	13.33	0.690	Not reported
Ni total		14.1		0.925	
$Co_{80}P_{20}$ [13]	$r_P = 104.5$ pm				
	$r_{Co} = 127.5$ pm				
P–P	1	0	13.33	0	–
P–Co	0.8196	8.9	10.24	0.869	$180 \leqslant r \leqslant 320$
P total		8.9		0.869	
Co–P	1.220	2.09	16.56	0.126	$180 \leqslant r \leqslant 320$
Co–Co	1	10.1	13.33	0.758	$180 \leqslant r \leqslant 340$
Co total		12.19		0.884	
$Nb_{60}Ni_{40}$ [14]	$r_{Ni} = 125$ pm				
	$r_{Nb} = 149$ pm				
Ni–Ni	1	3.8	13.33	0.285	Not reported
Ni–Nb	0.8389	8.2	10.46	0.784	Not reported
Ni total		12.0		1.07	
Nb–Ni	1.192	5.5	16.13	0.341	Not reported
Nb–Nb	1	9.0	13.33	0.675	Not reported
Nb total		14.5		1.02	
$Nb_{50}Ni_{50}$ [14]	$r_{Ni} = 125$ pm				
	$r_{Nb} = 151$ pm				
Ni–Ni	1	5.0	13.33	0.375	Not reported
Ni–Nb	0.8278	7.4	10.33	0.716	Not reported
Ni total		12.4		1.09	
Nb–Ni	1.208	7.4	16.38	0.452	Not reported
Nb–Nb	1	7.5	13.33	0.563	Not reported
Nb total		14.9		1.01	
$Nb_{44}Ni_{56}$ [14]	$r_{Ni} = 124$ pm				
	$r_{Nb} = 151$ pm				
Ni–Ni	1	5.5	13.33	0.413	Not reported

Table 1 (*continued*)

Alloy	$R_{u\phi}$[a]	$N_{u\phi}$[b]	$N_{u\phi}^{\mathrm{T}}$ at $R_{u\phi}$	$P_{u\phi}$	Integration limits (pm)
Ni–Nb	0.8212	6.6	10.26	0.643	Not reported
Ni total		12.1		1.06	
Nb–Ni	1.218	8.4	16.53	0.508	Not reported
Nb–Nb	1	6.5	13.33	0.488	Not reported
Nb total		14.9		0.996	
Nb$_{37}$Ni$_{63}$ [14]	$r_{\mathrm{Ni}} = 125$ pm				
	$r_{\mathrm{Nb}} = 153$ pm				
Ni–Ni	1	6.6	13.33	0.495	Not reported
Ni–Nb	0.817	5.9	10.21	0.578	Not reported
Ni total		12.5		1.07	
Nb–Ni	1.224	10.0	16.63	0.602	Not reported
Nb–Nb	1	5.6	13.33	0.420	Not reported
Nb total		15.6		1.02	
Al$_{90}$Y$_{10}$ [15]	$r_{\mathrm{Y}} = 180.15$ pm				
	$r_{\mathrm{Al}} = 143.174$ pm				
Y–Y	1	1.1 ± 0.4	13.33	0.09	$270 \leqslant r \leqslant 450$
Y–Al	1.258	14.1 ± 1.5	17.16	0.828	$243 \leqslant r \leqslant 404$
Y total		15.2		0.918	
Al–Y[c]	0.7947	1.6 ± 0.2	9.95	0.161	$243 \leqslant r \leqslant 404$
Al–Al[c]	1	10.7 ± 0.8	13.33	0.803	$215 \leqslant r \leqslant 358$
Al total		12.3		0.964	
Al$_{87}$Y$_8$Ni$_5$ [15]	$r_{\mathrm{Y}} = 180.15$ pm				
	$r_{\mathrm{Ni}} = 128$ pm				
	$r_{\mathrm{Al}} = 143$ pm				
Y–Y	1	0.4 ± 0.4	13.33	0.030	$270 \leqslant r \leqslant 450$
Y–Ni	1.407	2.7 ± 0.7	19.57	0.138	$231 \leqslant r \leqslant 385$
Y–Al	1.260	14.3 ± 1.9	17.19	0.832	$243 \leqslant r \leqslant 404$
Y total		17.4		1.00	
Ni–Y[c]	0.7105	3.5 ± 2.6	9.01	0.389	$231 \leqslant r \leqslant 385$
Ni–Ni[c]	1	∼0 (estimated)	13.33	∼0	$192 \leqslant r \leqslant 320$
Ni–Al[c]	0.8951	6.5 ± 0.2	11.13	0.584	$203 \leqslant r \leqslant 339$
Ni total		∼10.0		0.973	
Al–Y[c]	0.7938	1.2 ± 0.2	9.94	0.121	$243 \leqslant r \leqslant 404$
Al–Ni[c]	1.117	0.4 ± 0.1	15.01	0.027	$203 \leqslant r \leqslant 339$
Al–Al[c]	1	7.2 ± 0.8	13.33	0.540	$215 \leqslant r \leqslant 358$
Al total		8.8		0.688	

[a] The sources of the metallic radii are discussed in the text.
[b] The values of $N_{u\phi}$ are taken from the citations indicated in the table.
[c] Data obtained from total radial distribution functions.

packing efficiencies were determined for each of the polyhedra in the intermetallic phases as described above in Eqs. (1)–(4).

The results of this analysis are shown in Table 2. In some cases, analysis of more than one polyhedron in one or more intermetallic phases yielded a range in packing efficiencies. In general, the local packing efficiencies in the crystalline intermetallic compounds are close to unity. Notable deviations include the packing efficiency around Y in Al–Y and Al in Al–Y–Ni, which are significantly below unity, and the packing efficiency around Ni in Ni–Nb, which is significantly above unity.

This comparison supports the earlier concept that the local structure in metallic glasses is likely to be similar to local packing in competing crystalline phases [23].

Of the three metal–metalloid glasses considered here, packing is least efficient in the Co–P system, which is consistent with the poorer glass forming ability of this alloy relative to Fe–B and Ni–B. The origin of the relatively lower packing efficiencies around Co and P in the Co–P glass is not known. Of course, packing is still rather efficient, and is on par with the packing efficiency in the Co$_2$P structure. Two possible explanations for the

Table 2
Total local packing efficiencies in competing crystalline intermetallic compounds

Glass system	Nearest crystalline compound(s)	Prototype (Pearson symbol)	Total local packing efficiency around specified atom type		
Fe–B	Fe₃B	Ni₃P (*tI32*)	0.89–0.99 (Fe)	0.94–1.06 (B)	
	Fe₃B	CFe₃ (*oP16*)			
Ni–B	Ni₃B	CFe₃ (*oP16*)	0.97–1.00 (Ni)	0.93 (B)	
Co–P	Co₂P	Co₂Si (*oP12*)	0.90 (Co)	0.98 (P)	
Al–Y	Al₃Y	AuCu₃ (*cP4*)	1.00 (Al)	0.70 (Y)	
	Al₃Y	BaPb₃ (*hR12*)			
	Al₃Y	Ni₃Si (*hP8*)			
Al–Y–Ni	Al₄YNi	Al₄YNi (*oC24*)	0.77–1.00 (Al)	0.86 (Y)	0.85 (Ni)
Ni–Nb	NbNi₃	Cu₃Ti (*oP8*)	0.78–0.84 (Nb)	0.89–1.40 (Ni)	
	NbNi₃	Al₃Ti (*tI8*)			
	Nb₇Ni₆	Fe₇W₆ (*hR13*)			

low packing efficiency around Al in Al–Y–Ni have previously been discussed in detail [17]. The coordination numbers from Al–Y–Ni were obtained from less accurate total radial distribution functions. Further, the interatomic bond distances were assumed in [15] to be equal to the sum of metallic radii, even though significant bond shortening is known to occur, leading to an additional possible error in coordination numbers. An internal check [17] of the data of [15] show an Al deficiency, which further points to the possibility of errors in reported coordination numbers. Finally, it is added here that the packing efficiency around Al in crystalline Al₄YNi is as low as 0.77 (Table 2), so that poor packing efficiency around Al may be an intrinsic feature of this alloy.

The primary sources of error in the local packing efficiency result from uncertainty in the atomic radii and from inaccuracies in the experimentally determined partial coordination numbers, $N_{u\phi}$. The actual sizes of atoms in a material depend upon the local chemistry and structure. With the exception of the Al-based glasses, the atomic radii used here were determined in the material of interest, so that corrections for the influence of local chemistry and structure are included in this analysis. Atomic radii in the Al-based glasses were taken from assessments that have attempted to make some account of these effects [9,16]. In a more general sense, some degree of covalent bonding and an associated bond shortening is often present in metallic glasses. While this may produce an uncertainty in the absolute values of the constituent atomic radii, the radius ratios are less strongly affected, since shortening of both the solute and solvent atoms may occur. In the end, the present analysis was found to be relatively insensitive to the actual values used for atomic radii as long as the values are obtained in a consistent

manner. As a result, the conclusions above are not substantially different when elemental metallic radii obtained from handbooks are used in the present analysis.

An inherent error exists in the experimental determination of $N_{u\phi}$. Sources of this error include low information content in a highly averaged signal, which require deconvolution from adjacent signals. The information content can be improved by conducting carefully controlled experiments which produce partial radial distribution functions rather than total radial distribution functions. The data used for the analysis here were obtained as much as two decades ago. Studies using brighter light sources and more modern spectrometers should be able to provide improved signals and higher precision. An assessment of the errors associated with diffraction analysis at the time that these data were collected provides a probable error of ±10% in $N_{u\phi}$ [14], so that a similar error is expected in the present work for $P_{u\phi}$.

Eq. (1) provides the non-intuitive result that a theoretical coordination number of 13.33 is produced for a value of $R = 1$. The intuitive conclusion that a coordination number of 12 is the maximum possible for a cluster of equal-sized spheres seems to follow from the practical observation that a coordination number greater than 12 cannot be achieved in reality for hard spheres. Nevertheless, it can be shown qualitatively that two well-known clusters with a coordination number of 12 – the icosahedron and the 1st coordination shell of an *fcc* array – each possess extra space in the 1st shell. In the former case, an ideal, unstrained icosahedron is produced when the central (solute) sphere has a radius ratio of $R = 0.902$ relative to the (solvent) spheres in the 1st shell. Each sphere in the 1st shell contacts five others in the 1st shell, so that the surface symmetry,

q, is the maximum possible value for packing on a curved surface. This is the analog on a curved surface of efficient hexagonal packing of equal-sized spheres on a flat surface, so that a net of equilateral triangles is produced that perfectly tiles the surface of the central solute sphere of this icosahedron. A strain is produced in the first coordination shell as R is increased to unity, so that the equilateral triangles that tile the surface of the icosahedron expand uniformly and nearest neighbor spheres in the 1st shell no longer contact one another. The extra space thus produced is distributed uniformly between spheres in the first coordination shell. However, this strain is modest, and no single vacant site is produced within which a full extra sphere can be placed. Further, relaxation to reestablish contact of spheres in the 1st shell will not produce sufficient space in a single location for an additional sphere due to geometric constraints (see Fig. 4 in [35]). Rigorous contact is provided between equal-sized spheres in the 1st shell of in an *fcc* array. However, each sphere in this shell contacts only four other spheres in the 1st shell, so that packing is intrinsically less efficient. This is the analog on a curved surface of square packing of equal-sized spheres on a flat surface. The extra space produced by this less efficient packing is distributed in the interstices between the square arrays of spheres in the 1st shell, so that an additional solvent sphere cannot be placed on the surface. Since the spheres in the 1st shell are in physical contact with each other, a relaxation of this configuration cannot be accomplished. Thus, the practical result that a coordination number greater than 12 cannot be produced for a cluster of equal-sized spheres results from geometrical constraints of packing on a curved surface, and not from the unavailability of space for extra spheres. Eq. (1) quantifies the extra space that is distributed across the surface of these two clusters with the result that $N^T = 13.33$ for a value of $R = 1$.

The present analysis is developed broadly for metallic glasses, where R is observed to range from ~ 0.6 to ~ 1.4. Thus, it is not expected that smaller solutes will occupy the interstices between solvent atoms on the curved surface of the 1st coordination shell. Atoms in the 1st shell typically exist in an efficiently packed triangular array, or in the somewhat less efficiently packed square or rectangular arrays as described above. To fit within the interstices formed by these nearly planar configurations, a solute would require a radius less than 0.155 that of the larger atoms to fit in an equilateral triangular array, and less than 0.414 for a square array of larger atoms. Since atoms of such small relative size do not occur in metallic glasses, this interstitial occupancy is not expected to occur. However, such small solutes do exist in oxide glasses, so the analysis developed here for local packing efficiency may not be generally applicable to oxide glasses.

5. Summary

The main contribution of this work is to present a quantifiable analysis for the local packing efficiency in the structures of metallic glasses when more than one atomic species is present in the first coordination shell. This analysis has been applied to several metallic glasses using published diffraction data for atomic radii and partial coordination numbers. Application of this analysis has shown that local packing is quantitatively within experimental error of the maximum possible packing efficiency. This result is obtained for a number of topologically distinct glasses, including systems where the solutes are smaller than the solvent (Fe–B, Ni–B, Co–P and Nb–Ni) and systems where solutes are larger than the solvent (Ni–Nb, Al–Y and Al–Y–Ni). Packing is generally efficient not only around solute atoms, but also around solvent atoms. Finally, local packing efficiency is unaffected by significant changes in composition, as shown in the Ni–B and Nb–Ni systems. Efficient local packing is concluded to be a global state of the system, since the data upon which the analysis is based are global averages, and significantly lower packing efficiency around some atoms would require the physically improbable result that the packing efficiency is higher than unity around others to maintain the observed global average near unity. The local packing efficiencies are essentially equal to the local packing efficiencies in the competing crystalline phases. The analysis developed here is consistent with frequent earlier reports of short range ordering in metallic glasses. Local packing around Co and P atoms in Co–P, and around Al atoms in Al–Y–Ni are significantly less than the theoretical maximum. These exceptions have been discussed with respect to relative glass forming ability, errors in the available diffraction data and the local packing efficiency of competing crystalline structures.

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