On the Effect of the Number of Components on Glass-Forming Ability of Alloys from the Liquid State: Application to the New Generation of Multicomponent Bulk Glasses

P. J. Desré

*Laboratoire de Thermodynamique et Physicochimie Métallurgiques, CNRS UMR 5614,
Institut National Polytechnique de Grenoble, University Joseph Fourier, BP 75, 38402
Saint Martin d'Heres, France*

The aim of this work is to demonstrate that an increase of the number of components in a liquid glass forming alloy may contribute to inhibit intermetallic nucleation thus enhancing glass-forming ability. The approach is based on an analysis of the distribution of concentration fluctuations in undercooled multicomponent liquid alloys. It is demonstrated that fluctuations in the undercooled liquid can help intermetallic nucleation in a certain range of temperature and concentration. Addition of one component lowers the probability of creating a nucleant fluctuation by a factor of ten. Furthermore such a stochastic approach shows that, provided the wettability of the embryo on heterophase nucleants remains moderate, heterogeneous nucleation can even be suppressed in the highly undercooled domain of the multicomponent liquid. The possibility of obtaining multicomponent bulk metallic glasses with low cooling rates from high purity liquid alloys, which however contain a significant amount of heterophase nucleants, can be explained by the proposed approach.

(Received October 9, 1996)

Keywords: statistical thermodynamic, nucleation, metallic glasses, undercooled liquids, phase diagrams

I. Introduction

Recently, metallic glasses including more than 3 components⁽¹⁾⁻⁽³⁾ have been obtained from the liquid state with cooling rates of 10 K/s or less. Such cooling rates are considerably smaller than the 10⁵ K/s which have been necessary to produce the classical metallic glasses. This new generation of metallic glasses is characterized by a significant temperature difference between the glass transition temperature (on heating) and the onset temperature of crystallisation; property which demonstrates a high resistance of these undercooled liquids to crystalline nucleation.

The increase in the random atomic packing of the liquid due to the difference between the atomic size of the components (in their pure state)⁽⁴⁾ has been invoked in order to explain such an easy glass forming ability. Independently of the previous argument, the effect of the number of components on glass-forming ability (GFA) has already been discussed on a qualitative way⁽⁵⁾. The present work is an attempt to give a quantitative approach to such an effect from an analysis of the concentration fluctuations (designated in the following by c.f.) in the undercooled range of multicomponent liquids exhibiting strong heteroatomic bonding.

This paper is structured in two parts. The first one concerns the role which can be played by the c.f. within the liquid prior crystalline nucleation. In a second part, the effect of the number of components on GFA is studied.

II. Concentration Fluctuations in the Liquid and Nucleation of Intermetallics

When dealing with multicomponents glass-forming liquid alloys, the amount of undercooling is mainly limited by nucleation of intermetallics.

Concentration fluctuations leading to the composition of a critical intermetallic nucleus can be considered as developing either within the undercooled liquid prior to crystalline nucleation or simultaneously during the crystalline embryo construction. In fact, the classical theory of nucleation stipulates that fluctuations of composition and structure are simultaneous events. However, thermal c.f. in the liquid generating the composition which matches the nominal composition of the compound, at the scale of the critical embryo size, will favour intermetallic nucleation.

Such fluctuations will be designated as "nucleant fluctuations" (noted n.f. in the following). A quantitative aspect justifying the role of the n.f. on nucleation can be found from the comparison between the minimum work required to create a n.f. in the liquid state, and the classical Gibbs energy barrier corresponding to simultaneous fluctuations of composition and structure for the construction of a critical intermetallic embryo.

The probability of a concentration fluctuation in a multicomponent liquid including v components from an average composition defined by the set of $(v-1)$ molar fractions: $c_{1,0}, c_{2,0}, \dots, c_{v-1,0}$, represented by a vector C_0 , to the set of the "instantaneous concentrations" c_1 ,

$c_2, \dots, c_{v-1}$ represented by a vector C , is given by the following relation:

$$\omega = \frac{1}{Q_f^{(v)}(n)} \exp -\frac{n}{RT} \Delta G_f(C, C_0) \quad (1)$$

where $Q_f^{(v)}(n)$ is the partition function associated with the concentration fluctuations ensemble. n is the number of atoms constituting the fluctuations. $\Delta G_f(C, C_0)$ is the isothermal Gibbs energy of formation of one mole of c.f., of composition C , from a great quantity of liquid such that the average concentration C_0 would remain unchanged when a fluctuation occurs. The minimum work W_f required to form a concentration fluctuation of concentration containing n atoms is:

$$W_f = \frac{n}{N_A} \Delta G_f(C, C_0) \quad (2)$$

where N_A is the Avogadro number. The absence of an interfacial liquid-liquid free energy in relation (2) is justified when the number of atoms at the edge of the fluctuation remains small compared to the number of atoms constituting the fluctuation. But in the present application the considered liquid alloys exhibit strong heteroatomic bonds, consequently the main part of the work required to form a c.f. comes from a bulk contribution. In fact, an heterogeneity of composition in the liquid generates a negative chemical contribution to the interface energy which is merely due to the excess of heteroatomic bonds at the interface (the application of the Becker's model with the regular solution approximation yields a rough evaluation of this negative contribution). The unknown positive structural contribution to the interface energy is expected to compensate the chemical contribution in order to give finally a small positive resultant interface energy. This is why the work required to form a concentration fluctuation will be taken equal to the bulk term and this with a good approximation even for fluctuations of very small size.

Furthermore, from the application of the classical theory of nucleation the Gibbs energy barrier for the formation of a spherical critical nucleus of an intermetallic of concentration C from a liquid of concentration C_0 and containing n_c atoms is given by:

$$\Delta G^*(C, C_0) = -\frac{1}{2} \frac{n_c(T)}{N_A} \Delta G_v(C, C_0) \quad (3)$$

where n_c is the number of atoms in the critical nucleus. $\Delta G_v(C, C_0)$ is the molar Gibbs energy change when forming a mole of compound of composition C in a great quantity of liquid of composition C_0 . For a binary system $\Delta G_v(C, C_0)$ is deduced from the application of the classical tangent rule as represented in Fig. 1.

It must be emphasized that relation (3) remains valid when applied to homogeneous or heterogeneous nucleation.

The ratio ρ between the Gibbs energy barrier $\Delta G^*(C, C_0)$ and the minimum work required to form a fluctuation of concentration from C_0 to C and containing n_c atoms (n_c representing $n_c^{\text{hom}}(T)$ in homogeneous

Fig. 1 Typical molar Gibbs energy of formation versus mole fraction for a binary liquid: ----, and for a compound: —.

nucleation and $n_c^{\text{het}}(T)$ in heterogeneous nucleation) is given by:

$$\rho = \frac{\Delta G^*(C, C_0)}{W_f} = -\frac{1}{2} \frac{\Delta G_v(C, C_0)}{\Delta G_f(C, C_0)} \quad (4)$$

Let us introduce the polymorphous Gibbs energy of crystallisation $\Delta G_{pc}(C)$ which is the Gibbs energy variation associated with the establishment of long range ordering from an undercooled liquid having an identical concentration.

At first, let us treat the case of a binary system. Developing the Gibbs energy of formation of the liquid $\Delta G(c)$ to the second order in $(c - c_0)$ it is shown that:

$$\Delta G_f(c, c_0) = \frac{1}{2} \left(\frac{\partial^2 \Delta G}{\partial c^2} \right)_{c=c_0} (c - c_0)^2$$

which is represented in the Gibbs energy diagram of Fig. 1 by the segment JK where J is at the intersection of the tangent to the Gibbs energy curve at c_0 with the vertical line at c . ΔG_{pc} is represented by the segment KI . As: $\Delta G_v(c, c_0) = \Delta G_{pc}(c) + \Delta G_f(c, c_0)$ the expression of ρ becomes merely:

$$\rho = \frac{1}{2} \left[\frac{-\Delta G_{pc}(c)}{\Delta G_f(c, c_0)} - 1 \right] \quad (5)$$

Note in Fig. 1 that c'_0 is the conjugated concentration to c_0 which gives the same value of ΔG_f .

The minimum work required to form the fluctuation in the binary liquid is smaller than the classical Gibbs energy barrier of nucleation when $\rho > 1$, which means $-\Delta G_{pc}(c) > 3\Delta G_f(c, c_0)$. The point J_f located at one third of the way along IK starting from K , represented in Fig. 1, defines the segment $J_f K = (1/3)IK = (1/3)(-\Delta G_{pc}(c)) = \Delta G_f(c, c_0) = \Delta G_f(c, c'_0)$ which corresponds to $\rho = 1$.

As the frequency of nucleation and the frequency of

appearance of n.f. are given by exponential laws, a drastic variation of the ratio between the population of classical critical nuclei and the n.f. in the liquid is expected around the condition $\Delta G^* = W_f$ (relation which from relation (4) is equivalent to $\Delta G_v = -2\Delta G_f$). In such a way, $\rho = 1$ appears to be a critical condition for the frequency of formation of the n.f.

It is now of interest to determine, for a given temperature, the composition range in which the n.f. are expected to be predominant when compared to intermetallic critical nucleus. For this purpose, the locus curve described by points J_f in the concentration range where the Gibbs energy of the intermetallic is below the Gibbs energy of the liquid is drawn in Fig. 1. Drawing the common tangent to this locus curve and the Gibbs energy of the liquid on each side of the concentration c_m , where the Gibbs free energy of the compound is minimum, the concentrations $c_0^{(f)}$ and $c_0'^{(f)}$ are obtained.

Any tangent drawn from a concentration c_0 such that $c_0^{(f)} < c_0 < c_0'^{(f)}$ will cut the area limited on one side by the Gibbs energy of the liquid and the J_f locus curve on the other side. This means that, in this range of concentration, it exists a concentration fluctuation domain where n.f. can be predominant. The extent of the concentration range $c_0'^{(f)} - c_0^{(f)}$ depends on temperature and is lowered when the temperature increases. The locus of $c_0^{(f)}$ and $c_0'^{(f)}$ when the temperature is varied leads to a unique curve which is designated "Intermetallic T_f line". Consequently, in the temperature-concentration coordinates, the n.f. are expected to be predominant in the region located below the T_f line. Such T_f concept has formerly been proposed by the author in an application to homogeneous nucleation of supersaturated binary solid solutions⁽⁶⁾.

It is noteworthy that the more the Gibbs stability of the intermetallic is small (small value of the second derivative of the Gibbs energy of the intermetallic in function of concentration) the larger is the domain where the n.f. are predominant. When a binary system exhibits several intermetallic compounds of low Gibbs energy stability (which means generally a significant deviation from stoichiometry), the overlap of T_f lines can enhance the n.f. in a temperature range where the kinetics of nucleation are high. It has been observed that systems presenting intermetallics with large deviations from stoichiometry are not good glass formers.

As an example, the T_f line has been calculated from available thermodynamic data of the liquid binary alloy Al-Zr⁽⁶⁾ and the intermetallic Al_3Zr which has been taken as a line compound. The T_f line is obtained by calculating, for different temperatures, the concentrations $c_0^{(f)}$ and $c_0'^{(f)}$ previously defined and which are represented in the schematic Gibbs energy diagram given in Fig. 1. The loci of $c_0^{(f)}$ and $c_0'^{(f)}$ when the temperature varies lead to the T_f line given in Fig. 2.

The n.f. are expected to be predominant in the region extending below the T_f line around the nominal concentration of the compound. The metastability of the undercooled liquid is expected to be menaced inside such

Fig. 2 Calculated T_f lines for the intermetallic Al_3Zr considered as a line compound.

domains and particularly in a temperature range where the frequency of nucleation is high. As a consequence of relation (3), it is emphasized that the definition of the T_f lines does not depend upon the nucleation process chosen as reference which can be either of homogeneous or heterogeneous nature.

Note that if n.f. are predominant for highly undercooled liquid alloys, ($T < T_f$) this is not the case for small amount of undercooling. This latter case is classically obtained due to the presence of heterophases within the liquid yielding heterogeneous nucleation. Consequently, the previous analysis demonstrates that when nucleation occurs for small amount of undercooling the fluctuations of concentration are not expected to intervene in the nucleation process. The previous approach can be extended, through straight forward algebra, to liquids including more than 2 components. In this case, the previous ratio ρ takes the following form:

$$\rho = \frac{1}{2} \left[\frac{-\Delta G_{pc}(C)}{\Delta G_f(C, C_0)} - 1 \right]$$

where C and C_0 are the previously defined concentration vectors. A development of the Gibbs energy of formation of the liquid $\Delta G(C)$ versus $C - C_0$ to the second order in $C - C_0$ yields the following expression of $\Delta G_f(C, C_0)$:

$$\Delta G_f(C, C_0) = \frac{1}{2} \Delta C_t \cdot G_{v-1} \cdot \Delta C \quad (6)$$

where ΔC_t and ΔC are the row and column vectors whose elements are Δc_i . G_{v-1} is a symmetric matrix whose elements are:

$$G_{ij} = \partial^2 \Delta G(C) / \partial c_i \partial c_j.$$

Again here the condition

$$\rho = \frac{1}{2} \left[\frac{-\Delta G_{pc}(C)}{\Delta G_f(C, C_0)} - 1 \right] = 1$$

allows to define a T_f surface for a ternary liquid and $T_f(C_0^{(f)})$ hyper surfaces for liquids with more than 3 components. In the latter cases, nucleant fluctuations in the

liquid are expected to dominate in the domain limited by hyper surfaces, towards low temperature region, or for a given temperature in the concentration range where

$$\Delta G_f(C, C_0) < \frac{1}{3} |\Delta G_{pc}(C)|. \quad (7)$$

The preceding analysis suggests that, in a certain range of composition, the occurrence of concentration fluctuations in the liquid would act as an a priori local chemical requirement in order to generate long distance chemical ordering which is specific to the intermetallic crystalline structure. In other terms, the first stage of the formation of an intermetallic embryo would occur through the setting up of a specific local chemistry, produced by concentration fluctuations in the liquid extending over the critical nucleus size and the effect would be the genesis of the fitting crystalline symmetry where the metallic ions are driven towards their crystalline sites through indirect ion-ion interactions via bonding electrons, the resulting crystalline embryo being partially or completely ordered.

III. Effect of the Number of Components on Intermetallic Nucleation

Returning to the distribution of the c.f. given by relation (1), the normalisation of the probability yields, after integration, to the following expression for the c.f. partition function⁽⁷⁾:

$$Q_f^{(v)}(n) = \frac{(2\pi nRT)^{(v-1)/2}}{|G_{v-1}|^{1/2}} \quad (8)$$

$|G_{v-1}|$ is the determinant of order $v-1$ associated to the matrix G_{v-1} . $|G_{v-1}|$ is a positive quantity for a stable or metastable liquid. Thus, the probability of a c.f. containing n atoms is such:

$$\omega(n) = \frac{|G_{v-1}|^{1/2}}{(2\pi nRT)^{(v-1)/2}} \exp \left[-\frac{n}{RT} \Delta G_f(C, C_0) \right] \quad (9)$$

In order to focus the study on the effect of the number of components on GFA, it is proposed to scale the probability of the c.f. on the basis of the maximum value of the distribution $\omega_{\max}$ which is equal to the pre-exponential factor of relation (9). Though generally a c.f. is characterized by a significant concentration difference $C - C_0$, whose probability remains much smaller than the maximum value of the distribution, the proposed scaling is the simplest way to quantify the effect of the number of components.

The expression giving the maximum of the distribution for a fluctuation size n and a liquid containing v components is of the form:

$$\omega_{\max}^{(v)}(n) = \frac{\Phi}{n^{(v-1)/2}} \quad (10)$$

with

$$\Phi = \frac{|G_{v-1}|^{1/2}}{(2\pi RT)^{(v-1)/2}} \quad (11)$$

$\omega_{\max}^{(v)}(n)$ depends upon the number of components v through an explicit function of the number of atoms n in the fluctuation. $\omega_{\max}$ is lowered by an increase of the number of components. The greater fluctuation size the higher is the effect of this increase.

The size independant dimensionless function Φ , which is governed by the atomic interactions in the multicomponent liquid, can be decomposed as follows:

$$\Phi = \Phi^{\text{id}} + \Phi^{\text{xs}} \quad (12)$$

where Φ^{id} is the interaction function of an ideal solution:

$$\Phi^{\text{id}} = \{(2\pi)^{(v-1)} c_1 \cdots c_i \cdots c_v\}^{-1/2} \quad (13)$$

Φ^{xs} measures the deviation from the ideality of the liquid solution and is not a simple function of concentration and temperature.

For simplicity and accounting for the fact that the bulk metallic glasses are concentrated alloys, the concentrations are chosen such that:

$$c_1 = c_2 = \cdots = c_i = \cdots = c_v = \frac{1}{v} \quad (14)$$

From relations (10), (11), (13) and (14), the logarithm of the probability $\omega_{\max}$ can be expressed as follows:

$$\ln \omega_{\max} = -\frac{(v-1)}{2} \ln 2\pi n + \ln [v^{v/2} + (2\pi)^{(v-1)/2} \Phi^{\text{xs}}] \quad (15)$$

which for an ideal solution reduces to:

$$\ln \omega_{\max} = -\frac{(v-1)}{2} \ln 2\pi n + \frac{v}{2} \ln v \quad (16)$$

As the number of components v is obviously much smaller than the number of atoms n constituting the c.f., the first term of the RHS of relation (15) is preponderant unless Φ^{xs} approaches a critical value corresponding to a phase separation which would yield an infinite value for the second term of relation (15). It is obvious that, in such a case, the proposed scaling for the c.f. probabilities becomes irrelevant. In fact, the risk encountered by an undercooled multicomponent liquid, exhibiting strong heteroatomic bonding, to undergo phase separation in the liquid state must be considered when studying glass forming ability of multicomponents liquid alloys. Generally, for glass-forming liquid alloys, which exhibit strong heteroatomic bonding, Φ^{xs} remains a positive quantity. Thus, provided the liquid is far from critical conditions equation (16) gives a lower limit of $\omega_{\max}$.

In order to measure the effect of the number of components, the probability $\omega_{\max}(v)$ is referred to $\omega_{\max}(v=2)$ which is obtained for a binary liquid:

$$\Omega = \omega_{\max}(v) / \omega_{\max}(v=2) = \frac{v^{(v/2)}}{2(2\pi n)^{[(v/2)-1]}} \quad (17)$$

Application to homogeneous nucleation

When the undercooled liquid is close to homogeneous nucleation conditions the number of atoms n of the nucleant fluctuation is taken equal to the number of atoms constituting a critical nucleus n_c^{homo} . For a spheri-

cal embryo with a typical critical radius of 1 nm and a molar volume of 10^{-5} m^3 , $n_c^{\text{homo}} = 250$ atoms. When applying relation (17) to a 5 components liquid: $\Omega = 4.5 \times 10^{-4}$ which means that the probabilities of the fluctuations are of the order of 10^{-4} lower than the corresponding probabilities in a binary liquid. More generally, it is found that one component added reduces the probability ratio by a factor of ten. In fact such a significant decrease in the probability is due to an increase of the number of fluctuation states whereas the chemical constraint for the intermetallic embryo construction remains.

Application to heterogeneous nucleation

It is well known that insoluble particles dispersed through an undercooled liquid may act as heterophase nucleants. The critical radius r_c^{het} of a spherical cap nucleus, on a crystalline nucleant substrate is classically expressed versus the liquid-embryo interfacial free energy σ and the molar crystallization driving force ΔG_v as:

$$r_c = -2\sigma V_m / \Delta G_v \quad (18)$$

For a multicomponent undercooled liquid, at a temperature T , the application of relations (5) and (6) leads to the following more general expression of the critical radius:

$$r_c = \frac{2\sigma V_m}{|\Delta G_{pc}| - \frac{1}{2} \Delta C_i \cdot G_{v-1} \cdot \Delta C} \quad (19)$$

with

$$|\Delta G_{pc}| = |\Delta H_{pc}| \frac{T_m - T}{T_m} \quad (20)$$

ΔH_{pc} and T_m are the enthalpy of polymorphous crystallization and the congruent melting temperature of the compound respectively.

The application of relations (10) and (11) yields the following expression of the logarithm of the ratio of the probability obtained for an heterogeneous process to the probability for an homogeneous nucleation versus the number of atoms constituting a critical nucleus in the heterogeneous and homogeneous processes:

$$\ln \frac{\omega_{\max}^{(\text{het})}}{\omega_{\max}^{(\text{homo})}} = -\frac{(v-1)}{2} \ln \frac{n_c^{\text{het}}(T)}{n_c^{\text{homo}}(T)} \quad (21)$$

Applying the classical theory of nucleation at a given temperature, equation (21) becomes:

$$\ln \frac{\omega_{\max}^{(\text{het})}}{\omega_{\max}^{(\text{homo})}} = -\frac{(v-1)}{2} \ln f(\theta) \quad (22)$$

θ is the contact angle formed between the nucleus and the heterophase and

$$f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4$$

As $f(\theta) < 1$ and $v > 1$, it follows from relation (22), that in the case where homogeneous and heterogeneous nucleation would develop at the same temperature, the probability of the c.f. and consequently of the nucleant fluctuations n.f. would always be greater through the heterogeneous nucleation process.

The temperatures at which heterogeneous and homogeneous nucleation occur upon cooling of bulk glass forming liquid alloys, are obviously unknown since crystal nucleation is suppressed. Note that for such liquid alloys it is observed that classical heterogeneous nucleation occurring at small amount of undercooling is avoided. It is of interest to examine the case where the intermetallic nuclei would be expected to form through a heterogeneous process in the undercooled region where the c.f. becomes predominant ($T < T_f$) but at a temperature which remains greater than the temperature of homogeneous nucleation. Such a last situation must not be considered as exceptional because the temperature of homogeneous nucleation T_{homo} is classically considered as an unattainable lower limit of nucleation temperature.

T_{het} designates a temperature at which heterogeneous nucleation would occur at $T_{\text{het}} > T_{\text{homo}}$ provided that at T_{het} the following condition is satisfied: $|\Delta G_{pc}(C)| > \Delta G_f(C, C_0)$ in order for a crystallization driving force to remain available. It follows from relations (5), (6), (19) and (20) that:

$$\frac{n_c^{\text{het}}}{n_c^{\text{homo}}} = \left[1 + \frac{\Delta T}{(T_m - T_{\text{homo}}) - \Delta T - \Delta G_f(C, C_0) T_m / |\Delta H_{pc}|} \right]^3 f(\theta) \quad (23)$$

where $\Delta T = T_{\text{het}} - T_{\text{homo}}$. The variation of $\Delta G_f(C, C_0) = (1/2) \Delta C_i \cdot G_{v-1} \cdot \Delta C$ with temperature between T_{het} and T_{homo} has been neglected in the establishment of relation (23). For a given value of $\Delta T > 0$, a critical contact angle θ^* for which $n_c^{\text{het}} = n_c^{\text{homo}}$ can be defined. θ^* is such that:

$$f(\theta^*) = \left[1 + \frac{\Delta T}{(T_m - T_{\text{homo}}) - \Delta T - \Delta G_f(C, C_0) T_m / |\Delta H_{pc}|} \right]^{-3} \quad (24)$$

From equations (21) and (23) it follows that when $\theta > \theta^*$, the occurrence of a nucleant fluctuation through a heterogeneous nucleation process would become less probable than for a homogeneous nucleation process. This is due to the fact that, under such a condition, the number of atoms involved in the heterogeneous process becomes greater than for the homogeneous process. An evaluation of θ^* versus $\Delta T / T_m$ has been done on the basis of the following set of data:

(i) The temperature of homogeneous nucleation is taken as: $T_{\text{homo}} = 0.6 T_m$

(ii) As the nucleant fluctuations are expected to occur in a temperature-concentration region where they are predominant, $\Delta G_f(C, C_0)$ must be taken such that: $\Delta G_f(C, C_0) < (1/3) |\Delta G_{pc}|$ which means, with $T_{\text{homo}} = 0.6 T_m$ and from (23): $\Delta G_f(C, C_0) / |\Delta H_{pc}| < 0.133$. The following value for $\Delta G_f(C, C_0) / |\Delta H_{pc}| = 0.100$ has been chosen for the application. Under these conditions relation (24) reduces to: $f(\theta^*) = [1 - (1/0.3)(\Delta T / T_m)]^3$.

The curve representing θ^* versus $\Delta T / T_m$ is displayed in Fig. 3. In the region located above the curve $\theta^*(\Delta T / T_m)$, the probability of a nucleant fluctuation through a heterogeneous process is expected to be lower than for a homogeneous nucleation process. Note that a rapid drop of the curve θ^* is observed for small values

Fig. 3 Contact angle θ^* versus $\Delta T/T_m$. ΔT is the temperature difference between the occurrence of heterogeneous and homogeneous nucleation.

of $\Delta T/T_m$ yielding a significant range in θ where $\omega_{\max}^{(\text{het})} < \omega_{\max}^{(\text{homo})}$. It is noteworthy from relation (21) that in the previous region the lowering effect of $\omega_{\max}^{(\text{het})}$ in comparison with $\omega_{\max}^{(\text{homo})}$ increases with an increase of the number of components. As an example illustrating this effect, for a contact angle $\theta=90^\circ$ and for $\Delta T/T_m=0.1$, the corresponding point in Fig. 3 is located in the region where $\omega_{\max}^{(\text{het})} < \omega_{\max}^{(\text{homo})}$. For $\Delta T/T_m=0.1$, when the number of components increases from 3 to 5, the ratio $\omega_{\max}^{(\text{het})}/\omega_{\max}^{(\text{homo})}$ changes from 0.18 to 0.03 and for $\Delta T/T_m=0.2$, it drops from 1.4×10^{-6} to 1.9×10^{-12} .

Due to the exponential dependence of the ratio $\omega_{\max}^{(\text{het})}/\omega_{\max}^{(\text{homo})}$ on the number of components, an increase of this number results in an important lowering of the nucleation probability through a heterogeneous process and the effect is further enhanced for a greater difference between the expected temperature of heterogeneous and homogeneous nucleation in the highly undercooled region of the liquid alloy.

It results from this stochastic approach and the previ-

ous example, that the wetting condition which has to be satisfied in order that $\omega_{\max}^{(\text{het})} < \omega_{\max}^{(\text{homo})}$ is not highly restrictive.

IV. Conclusion

The proposed stochastic approach has shown that a significant enhancement of glass-forming ability is expected with an increase of the number of components.

In the case of homogeneous nucleation, it is found that one component added lowers the probability of the formation of any concentration fluctuations by a factor of the order of ten. The extension to heterogeneous nucleation shows that the probability of nucleation can become even smaller than for homogeneous nucleation provided that the wetting by the embryo of the crystalline inclusions within the liquid or on the container walls, remains moderate. The important point is that the effect is strongly enhanced by an increase of the number of components provided that phase separation in the liquid does not occur.

It is well known that, even for high purity liquid alloys, the population of heterophase nucleants remains significant and of the order of 10^{12} particles/m³(8). This last remark and the fact that bulk glass-forming ability has been observed experimentally in multicomponent liquid alloys together constitute a major argument in favour of the proposed stochastic approach.

Acknowledgements

The author thanks Dr. I. Ansara for his contribution on the phase diagram calculations and Dr. L. Greer for the fruitful discussions about the "confusion principle".

REFERENCES

- (1) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans., JIM*, **31** (1990), 425.
- (2) A. Peker and W. L. Johnson: *Appl. Phys. Lett.*, **63** (1993), 2342.
- (3) K. Busch, Y. J. Kim and W. J. Johnson: *J. Appl. Phys.*, **77** (1995), 4039.
- (4) A. Inoue, A. Makino and T. Masumoto: *Mat. Sci. Forum*, **179-181** (1995), 497.
- (5) L. Greer: *Nature*, **366** (1993), 127.
- (6) P. J. Desr: *J. of Mat. Sci.*, **22** (1987), 57.
- (7) P. J. Desr, T. Itami and I. Ansara: *Z. Metallkd.*, **3** (1993), 84.
- (8) H. Perepezko: *Mat. Sci. Eng.*, **65** (1984), 125.