THERMODYNAMICS OF GLASS-FORMATION IN CU-BASED ALLOYS

Marcello Baricco[1], Mauro Palumbo[1], Marta Satta[1] and Gabriele Cacciamani[2]

[1]Dipartimento di Chimica IFM and NIS/INSTM/CNISM, Università di Torino, v. Giuria 9, I-10125 Torino, Italy
[2]Dipartimento di Chimica e Chimica Industriale and INSTM, Università di Genova, v. Dodecaneso 31, I-16146 Genova, Italy

Abstract. A thermodynamic analysis of glass-formation in binary Cu-Mg and Cu-Zr alloys has been carried out. To this purpose, the thermodynamic assessment of binary systems has been reviewed and suitable thermodynamic models for undercooled liquid alloys and for glass transition have been selected. Various binary Cu-Mg compositions have been prepared and amorphous samples have been obtained by rapid solidification. Experimental results both on equilibrium and non-equilibrium phases have been used in the assessment procedure. New parameters have been introduced in order to describe the liquid/amorphous phase. The agreement between calculated thermodynamic quantities and corresponding experimental data has been significantly improved. From calculated thermodynamic functions of Cu-Mg and Cu-Zr systems, driving forces for nucleation of various intermetallic phases have been estimated as a function of temperature and composition.

1. INTRODUCTION

Glass formation is essentially the result of the competition between undercooled melt and crystalline phases [1]. In fact, if the nucleation and growth of crystals is avoided for kinetic reasons, the undercooled liquid can reach, during quenching, the glass transition temperature and then it collapses into a glass. When dealing with the nucleation frequency, either a thermodynamic and a kinetic aspect must be considered, according to:

$$I_v = \frac{DN_v}{a^2} \exp\left(-\frac{16\pi\gamma^3}{3\Delta G_v^2} \times \frac{1}{RT} \right),$$

where N_v is the number of nucleating sites available per unit volume, R is the gas constant and T is the temperature. Thermodynamics is mainly related to the driving force for nucleation (ΔG_v), which represents the tendency of the liquid to transform into a crystalline phase. The interfacial energy (γ) has been often related to other thermodynamic quantities of the alloy [2]. The diffusion coefficient (D) contains the kinetic aspect of nucleation and it is related to the possibility of atoms from the liquid to move for a distance (a) across the interface, allowing the formation of the nucleus. All quantities involved in the nucleation frequency are difficult to be measured and they are often estimated by suitable models [3].

The driving force for nucleation might be estimated if the free energy of the undercooled liquid and crystalline phases is known as a function of composition and temperature. In fact, when dealing with a nucleating crystal with a composition different from the parent liquid, the driving force can be obtained from the parallel tangent construction [4], which is based on the description of the maximum difference in the chemical potential between

Corresponding author: Marcello Baricco, e-mail: marcello.baricco@unito.it

the liquid and the crystalline phases. This goal might be reached if a fully thermodynamic assessment is carried out by the CALPHAD method [5], so that the chemical potential of various phases can be calculated as a function of temperature and composition. Because nucleation is a process that intrinsically happens in metastable conditions (i.e. when the liquid is in the undercooling regime), special care must be taken in the thermodynamic description of the undercooled liquid. In addition, the glass transition has to be described from a thermodynamic point of view, in order to consider this transformation during the calculation. A general characteristic of glass-forming melts is the occurrence of a short-range ordering in the undercooling liquid, which has the double effect to stabilise the liquid with respect to the crystals and to increase the viscosity, i.e. reducing the diffusivity. This short-range ordering effect is evidenced by the presence of an excess specific heat in the liquid [6], which disappears when the glass transition is reached on undercooling. The existence of an excess specific heat leads to a temperature dependence of the enthalpy and entropy of mixing in the undercooled liquid, which become more and more negative as long as the liquid is cooled.

The CALPHAD method is based on a least squares fitting of experimental data, which leads to a parametric description of the free energy. When the equilibrium phase diagram is assessed, only equilibrium experimental data are usually considered and the thermodynamic description of the various phases is reliable only in the temperature range of existence of that phase. In order to describe the glass formation by using the CALPHAD method, experimental information on the glassy phase must be included and a suitable model for the undercooled liquid and amorphous phases must be defined [7-9]. In this paper, the glass formation in two Cu-containing binary systems is considered from a thermodynamic point of view. In fact, Cu-based bulk metallic glasses have recently gained strong interest, because of their peculiar mechanical properties [10]. Even if big sized bulk metallic glasses are usually obtained for multicomponent systems, the knowledge of the fundamental thermodynamic properties of the parent binary systems may drive the discovery of new compositions. The thermodynamic assessments of Cu-Mg and Cu-Zr binary systems will be described and the driving forces for nucleation of various crystalline phases will be discussed.

2. THERMODYNAMIC MODELLING

In the frame of the CALPHAD approach, the free energy is described as:

$$G = {}^{ref}G + {}^{id}G + {}^{ex}G, \qquad (2)$$

where ${}^{ref}G$ represents the lattice stabilities and $\mathbf{{}^{id}G}$ is ideal free energy. Lattice stabilities are usually taken from the SGTE database [11]. The excess term (${}^{ex}G$) is expressed in terms of suitable models and, for solution phases, Redlich-Kister polinomia are often used:

$$^{ex}G = x_A x_B \sum_{\nu=0}^{n} {}^{\nu}L\left(x_A - x_B\right)^{\nu}, \qquad (3)$$

where ${}^{\nu}L$ is the interaction parameter of the solution phase, which can be temperature dependent, and x_A and x_B are the molar fraction of the components. In some cases, the liquid phase has been described on the basis of the associated solution model [12]. Line compounds are simply described considering a single value for enthalpy and entropy of formation, but they may also be modelled on the basis of suitable sub-lattices, which allows to describe the composition dependence of the free energy [5].

A thermodynamic model for the glass transition has recently been proposed by Shao [9] and it has been applied to several binary systems. This approach stems from the recognition of a similarity, in the variation of thermodynamic quantities as a function of temperature, between glass transition and paramagnetic-ferromagnetic (Curie) transition. Despite the successful application of the Shao's approach to several binary systems, this model is not completely suitable to describe the behaviour of the specific heat of a liquid phase on undercooling. Kubaschewski [13] has suggested the following expression for the specific heat (Cp) of a liquid phase:

$$C_p = 3R + aT + bT^{-2}, \qquad (4)$$

where a and b are fitting parameters. This expression provides a good description for the Cp on undercooling but does not account for glass transition. So, a modification of Shao's model may be applied to describe the glass transition, so that in the polynomial expression of the free energy of the liquid phase above the glass transition temperature (T_g), a T^{-1} term has been added, according to Eq. (4).
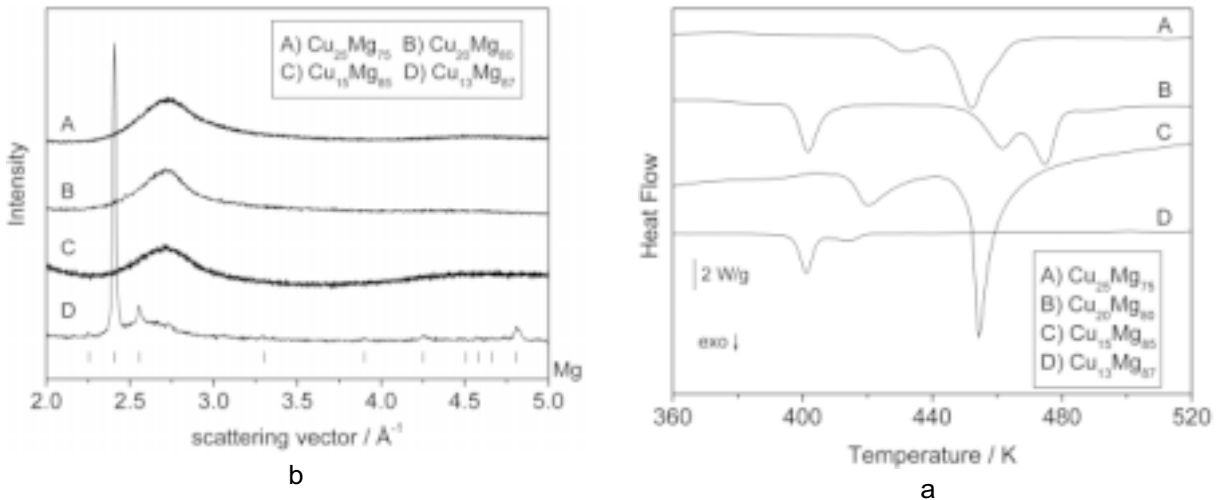
Fig. 1. (a) X-ray diffraction patterns of as-quenched Mg-Cu ribbons. The scattering vector is $s = 4\pi\sin\theta/\lambda$, where θ is the scattering angle and λ is the X-ray wavelength. (b) DSC traces of as-quenched Mg-Cu ribbons, obtained with an heating rate of 40K min^{-1}.
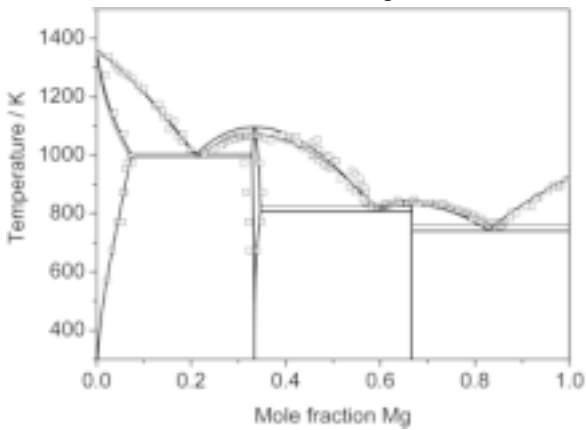

Fig. 2. Calculated Cu-Mg phase diagram according to the present work (thick lines) and to Ref. [14] (thin lines). Points represent experimental values of temperatures of transformation as detailed in Ref. [14].
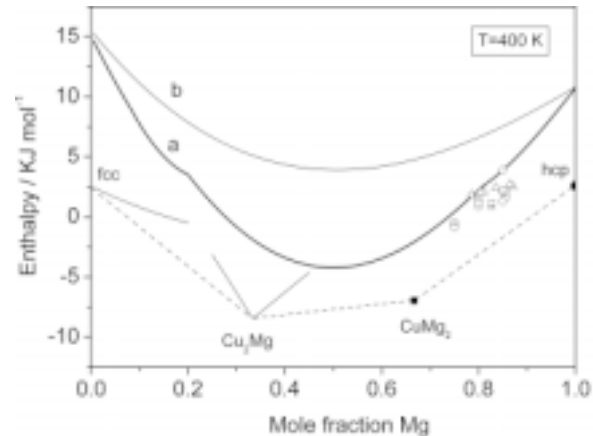
Fig. 3. Calculated enthalpy at 400K for liquid (a) and crystalline phases in the Cu-Mg system. Point represent experimental values of heat of crystallisation of amorphous alloys, taken from this work (circles) and from Refs. [16] (triangles) and [17] (squares). Enthalpy of mixing of the liquid phase according to ref. [14] is shown for comparison (b).

2.1. Cu-Mg

The Cu-Mg equilibrium phase diagram has been assessed by several authors and the most recent thermodynamic description, carried out by Liang *et al.* [14] as part of the modelling of the ternary Cu-Mg-Zn system, has been taken as a starting point. All solid phases have been described according to Ref. [14], but the liquid phase has been modified as described above, in order to consider the glass formation. The optimised parameters have been obtained through a fitting procedure carried out with the Parrot module in ThermoCalc software [15].

In order to determine experimental values of thermodynamic properties related to the amorphous phase, glassy ribbons have been prepared. Glass formation in the Cu-Mg system has been extensively studied in the past [16,17] and it appears a glass forming range (GFR) around the eutectic between hcp-Mg and $CuMg_2$ phases. The synthesis of master alloys with composition $Cu_{25}Mg_{75}$, $Cu_{20}Mg_{80}$, $Cu_{15}Mg_{85}$ and $Cu_{13}Mg_{87}$ has been carried out by induction melting of the pure

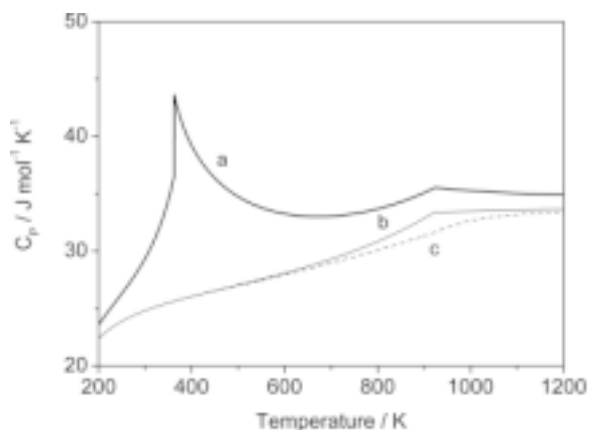**Fig. 4.** Heat capacity of the liquid (amorphous) phase as a function of temperature for $Cu_{15}Mg_{85}$ (a). Values calculated form Ref. [14] for liquid (b) and crystalline (c) phases are reported for comparison.

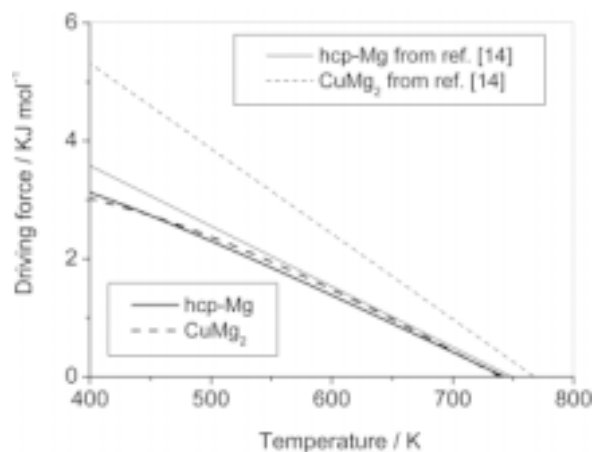**Fig. 5.** Driving force for nucleation of hcp-Mg (continuous lines) and $CuMg_2$ (dashed lines) from $Cu_{13}Mg_{87}$ liquid as a function of temperature, according to present work (thick lines) and to Ref. [14] (thin lines).

parent elements. Amorphous ribbons have been prepared by melt spinning in controlled Ar atmosphere. The results of the X-ray diffraction analysis are shown in Fig. 1a and they confirm the occurrence of a fully amorphous phase up to 85% Mg. For higher Mg content, crystals of Mg have been obtained embedded in an amorphous matrix. The crystallisation of the amorphous phase has been studied by DSC and the results are reported in Fig. 1b. The crystallisation behaviour is strongly dependent on composition, as already evidenced for samples with similar compositions [17], but in all cases the crystallisation products appear as Mg and $CuMg_2$. An experimental evidence of the glass transition at 401K was possible only with the $Cu_{15}Mg_{85}$ alloy, when analysed with a DSC scanning rate higher than 40 K/min. In fact, values of T_g in Cu-Mg amorphous alloys have only been estimated, either by a thermodynamic cycle [16] or by molecular dynamics [18] and they appear in good agreement with the obtained experimental value. Data on the glass transition temperature and on crystallisation enthalpy have been collected and they have been added to the equilibrium data for the fitting procedure. The details on the assessed parameters will be reported elsewhere [19].

The calculated equilibrium phase diagram is in good agreement with experimental values of transformation temperatures, as shown in Fig. 2, where

the phase diagram calculated according to Ref. [14] is also reported for comparison. The results are well comparable, in the frame of the experimental uncertainty, with a maximum deviation of the eutectic temperatures of 15K. The calculated enthalpy of the various phases at 400K is reported in Fig. 3 as a function of the composition. The temperature for the calculation has been selected as an average of the crystallisation temperature of the fully amorphous alloys. Experimental values of the enthalpy of crystallisation are reported in Fig. 3, starting from the equilibrium of the crystallisation products, and they appear in good agreement with the calculated enthalpy of the amorphous phase. The extrapolation at 400K of the enthalpy of mixing of the liquid phase calculated according to Ref. [14], clearly underestimate the enthalpy of the amorphous phase, strongly supporting the needs of a re-assessment of the Cu-Mg system for the description of the glassy phase.

As already stated above, the occurrence of a short range ordering in the undercooled liquid is evidenced by the presence of an excess heat capacity. The calculated heat capacity for the liquid (amorphous) and solid phases $Cu_{15}Mg_{85}$ is reported in Fig. 4, together with the trend calculated for the liquid phase according to ref. [14]. The C_p of the liquid progressively increases on undercooling and rapidly drops to that of the crystalline phases be-
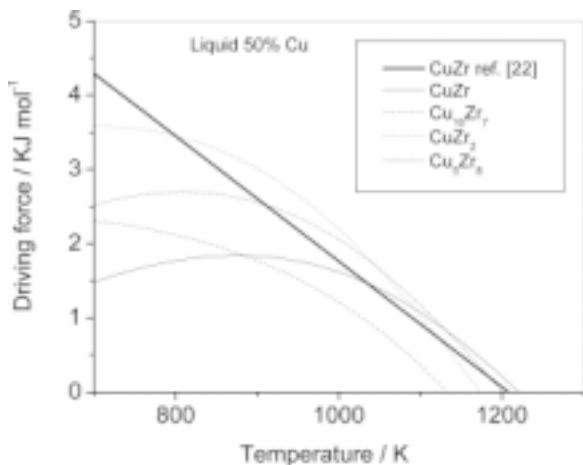
Fig. 6. Driving force for nucleation of crystalline phases from $Cu_{50}Zr_{50}$ liquid as a function of temperature, according to Ref. [23]. The same quantity calculated for the CuZr phase according to Ref. [22] is reported as a thick line.
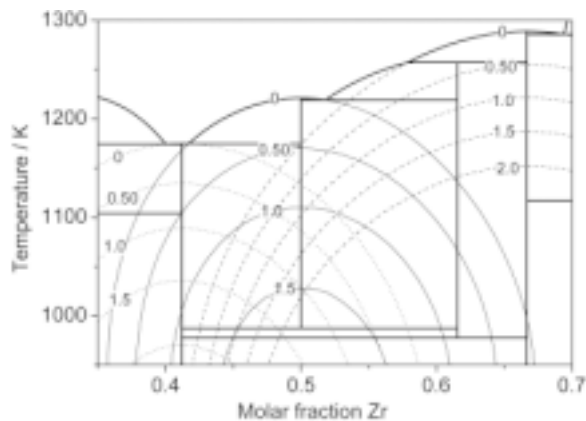

Fig. 7. Driving force for nucleation of crystalline phases from liquid Cu-Zr alloys, as a function of composition and temperature. Continuous lines: CuZr; dashed lines: $CuZr_2$; dotted lines: $Cu_{10}Zr_7$. Numbers represents the driving force for nucleation in KJ mol^{-1}.

low T_g. It is clear that the modelling of the glass transition according to the approach described above allows a more realistic description of C_p of the undercooled liquid, with respect to that suggested by the assessment of the equilibrium system [14]. Even if the lack of C_p data on amorphous Cu-Mg alloys does not allow a direct comparison with experimental values, the suggested approach has been proved to be valid for the Mg-Cu-Y system [20], where several experimental values of the glass transition temperature and of the C_p difference between the undercooled liquid and crystalline phases are available.

From the calculated free energy of all phases, the driving force for nucleation can be calculated as a function of composition and temperature. As an example, the results obtained for the eutectic composition, $Cu_{17}Mg_{83}$, is shown in Fig. 5, where the results obtained considering the assessment reported in ref. [14] are also shown for comparison. The present assessment leads to a reduction of the calculated driving forces for nucleation, because of the presence of an excess specific heat. This effect is much higher for the $CuMg_2$ compound, with respect to hcp-Mg, so that the tendency to nucleation of the crystalline phases becomes similar, promoting the glass formation by rapid solidification. An higher Mg content in the alloy brings

rapidly to the nucleation of hcp-Mg, as observed in $Cu_{13}Mg_{87}$ alloy.

2.2. Cu-Zr

Glass formation in Cu-Zr alloys has been widely studied in the past, either by rapid solidification and by ball milling. The system became recently of interest because bulk metallic glasses have been obtained by copper mould casting for compositions close to the central part of the phase diagram [21]. Several assessments of the equilibrium phase diagram has been proposed and the most recent has been considered in the present paper [22]. In this case, the liquid phase is described as a Redlich-Kister polynomial (Eq. (3)), without any temperature dependence of the enthalpy of mixing. In addition, a thermodynamic assessment of the Cu-Zr binary system has been recently published by Abe *et al.* [23], including experimental data involving the amorphous phase. In this case, the liquid phase has been described by the associate solution model, considering a single Cu_2Zr_1 associate. The glass transition has been described on the basis of the Shao model [9], without any further contribution to the heat capacity of the undercooled liquid. All solid phases has been treated as a line compound and the corresponding thermodynamic

data have been taken from Ref. [24]. It is worth noting that the existence of a Cu_5Zr_8 phase is considered in Ref. [23], but it is not generally accepted and it was not considered in Ref. [22]. The calculated phase diagrams are rather similar and both agree reasonably with equilibrium experimental data. On the contrary, when an extrapolation of the liquid in the undercooling regime is carried out, the two approaches differ significantly. As an example, the driving force for nucleation of the CuZr cubic phase from a $Cu_{50}Zr_{50}$ liquid alloy is reported in Fig. 6 as a function of temperature. It is clear that, because of the model used for the undercooled liquid and for the glass transition, the driving force calculated on the basis of Ref. [23] is much lower than that obtained on the basis of the assessment reported in Ref. [22]. As a consequence, a reduced driving force for nucleation increases the glass forming tendency of the alloy, thus explaining the amorphous phase formation obtained by moderate quenching rates, i.e. by copper mould casting. The calculated driving forces for nucleation of various crystalline phases are also reported in Fig. 6. It can be observed that the degree of liquid undercooling reached on nucleation has a strong effect on the phase selection. From the present analysis, the $Cu_{50}Zr_{50}$ liquid alloy does not show any driving force for nucleation of the $Cu_{51}Zr_{14}$ phase, even at very high undercoolings.

In order to understand the role of the alloy composition on glass formation, the driving force for nucleation of the crystalline phases has been estimated as a function of composition and temperature. The calculation has been performed on the basis of the assessment reported in Ref. [23] and the results are reported in Fig. 7, where the calculated phase diagram is also reported for comparison. For clarity, the Cu_5Zr_8 phase has not been considered in the calculation. It is clear that highest values of the driving force occur for compositions corresponding to the crystalline phases and it increases on undercooling. The $CuZr_2$ phase shows the fastest increase of the driving force, which reaches a value close to 2 KJ mol^{-1} for an undercooling of about 150K. The value of the driving force for nucleation of the various crystalline phases is very sensitive on composition, suggesting a significant change in the glass forming tendency of the alloys even for small changes in composition. As a consequence, the best glass forming alloy can be found as off-eutectic, as actually shown in the Cu-Zr system [25]. As an example, for the composition range shown in Fig. 7, a local

minimum in driving forces is observed for the composition with 48 at.% Zr, where only a low driving force for nucleation of the CuZr phase is acting for more than 120K of undercooling.

The proposed analysis of the glass formation in the Cu-Zr system, based on the values of the driving forces for nucleation as a function of temperature and composition, might be partially overcome by the effect of the interfacial energy on the nucleation frequency (Eq. (1)). Even if some modelling of the interfacial energy has been suggested [2], this parameter cannot be easily estimated. In addition, its temperature dependence on undercooling might change significantly the phase selection scenario. Furthermore, it has been suggested that a spinodal decomposition might act in the amorphous $Cu_{50}Zr_{50}$ amorphous alloys after annealing below the glass transition [26]. From a careful analysis of the radial distribution function of the annealed sample, the composition of the separated amorphous phases has been estimated close to $Cu_{10}Zr_7$ and $CuZr_2$ [26]. If this spinodal decomposition was already active in the undercooled liquid, the calculation of the driving forces would give significantly different results. In fact, in the case of a decomposition in the liquid (amorphous) phase, Cu-rich and Zr-rich phases would bring to the nucleation of different crystalline structures. The occurrence of a liquid phase decomposition for high undercooling might explain the presence of the $Cu_{51}Zr_{14}$ crystals embedded in an amorphous matrix as a result of copper mould casting of $Cu_{50}Zr_{50}$ alloy [27], which cannot be justified from the description of the free energy of the liquid phase obtained in Ref. [23].

3. CONCLUSIONS

Glass formation in Cu-Mg and Cu-Zr system has been analysed from a thermodynamic point of view by means of the CALPHAD method. The driving force for nucleation of crystalline phases has been calculated as a function of composition and temperature in the undercooling regime.

A new thermodynamic assessment has been obtained for the Cu-Mg, taking into account the occurrence of an excess specific heat in the liquid phase. Experimental values of the enthalpy of crystallisation of amorphous phases with different compositions have been introduced in the fitting procedure. The glass transition has been described according to the Shao's and Kubaschewski's models. From a comparison between experimental and calculated thermodynamic quantities it has been

evidenced the crucial role of a proper description of the free energy of undercooled melt.

The Cu-Zr system has been analysed on the basis of available thermodynamic assessments. When the experimental data of amorphous alloy are used for the fitting process, a more reliable description of the thermodynamics of the system is obtained. The driving forces for nucleation of various crystalline phases have been calculated, showing a crucial effect of small changes in the composition of the alloy for obtaining an amorphous alloy. Possible spinodal decomposition in the undercooled liquid has been discussed for explaining reported experimental evidences.

ACKNOWLEDGEMENTS

REFERENCES

[1] K.J.Rao, *Structural Chemistry of Glasses* (Elsevier, Amsterdam, 2002).

[2] L.Battezzati // *Mater. Sci. Eng. A* **304-306** (2001) 103.

[3] K.Kelton // *Sol. State Phys. Adv. Res,* **App. 45** (1991) 75.

[4] J.W.Christian, *The Theory of Transformations in Metals and Alloys* (Pergamont, Oxford, 1975).

[5] N. Saunders and A. P. Miodownik, *CALPHAD, Calculation of phase diagrams*, ed. by R. W. Cahn (Pergamon Materials Series, New York, 1998).

[6] H.J.Fecht and R.K. Wunderlich // *Mater. Sci. Eng. A* **178** (1994) 61.

[7] R. Bormann // *Mater. Sci. Eng. A* **178** (1994) 55.

[8] M. Palumbo, G. Cacciamani, E. Bosco and M. Baricco // *Calphad* **25** (2001) 625.

[9] G. Shao // *J. Appl. Phys.* **88** (2000) 4443.

[10] D.Xu, B.Lohwongwatana, G.Duan, W.L.Johnson and C.Garland // *Acta Mater.* **52** (2004) 2621.

[11] *SGTE Pure Elements database ver.3.00*, updated from: A. T. Dinsdale // *Calphad* **15** (1991) 317.

[12] F. Sommer // *Calphad* **2** (1977) 319.

[13] O. Kubaschewski, C. B. Alcock and P. J. Spencer, *Materials Thermochemistry* (Pergamon, New York, 1993).

[14] P.Liang, H.J.Seifert, H.L.Lukas, G.Gosh, G.Effemberg and F.Aldinger // *Calphad* **22** (1998) 527.

[15] www.thermocalc.com.

[16] F. Sommer, G.Bucher and B.Predel // *J. de Phys. Colloque C8, suppl. 8* **41** (1980) C8-563

[17] A.T.W.Kempen, H.Nitsche, F. Sommer and E.J.Mittemeijer // *Metall. Mater. Trans. A* **33A** (2002) 1041.

[18] N.Bailey, J.Sciřtz and K.W.Jacobsen // *Phys. Rev. B* **69** (2004) 144205.

[19] M. Palumbo, M. Satta, G.Cacciamani and M.Baricco, to be published.

[20] M. Palumbo, M. Satta, G.Cacciamani and M.Baricco // to appear in *Mater. Trans.*

[21] A.Inoue and W.Zheng // *Mater. Trans.* **47** (2006) 2950.

[22] K.J.Zeng, M.Hämäläinen and H.L.Lukas // *J. Phase Equil.* **15** (1994) 577.

[23] T. Abe, M. Shimono, M. Ode and H. Onodera // *Acta Mater.* **54** (2006) 909.

[24] A.I.Zaitsev and N.E.Zaitseva // *High Temp.* **41** (2003) 42.

[25] D.Wang, Y.Li, B.B.Sun, M.L.Sui, K.Lu and E.Ma // *Appl. Phys. Lett.* **84** (2004) 4029.

[26] R.Schultz, K.Samwer and W.L.Johnson // *J. Non-Cryst. Sol.* **61 & 62** (1984) 997.

[27] W.H.Wang, J.J.Lewandowsky and A.L.Greer // *J. Mater. Res.* **20** (2005) 2307.