

Thermodynamics of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ bulk metallic glass forming alloy

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Abstract Recently, multicomponent glass forming alloys have been found which exhibit extraordinary glass forming ability and cooling rates of less than 100 K/s are sufficient to suppress nucleation of crystalline phases and consequently bulk metallic glass (BMG) is formed. The undercooled melts of BMG systems have high thermal stability in the undercooled region. Therefore, it is interesting to study the thermodynamics of such materials. This article investigates the thermodynamic behavior of a BMG system namely $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ by estimating the Gibbs free energy difference ΔG , entropy difference ΔS , enthalpy difference ΔH between the undercooled liquid and corresponding equilibrium crystalline solid phase, in the entire temperature range from T_m to T_K . Glass forming ability (GFA) of this system has been investigated through various GFA parameters indicating the degree of ease of glass formation.

Keywords Bulk metallic glass ·
Thermodynamic properties · Undercooling ·
Glass forming ability

Introduction

In this modern era of new technology, a number of new bulk metallic glass (BMG) forming alloys have been developed. These alloys may solidify as a glass when cooled at sufficient rates, known as critical cooling rates. They possess excellent corrosion resistance, extremely high mechanical strength and have fairly good thermal stability. The thermodynamic functions of metallic glass forming alloys in the undercooled liquid phase provide information about their glass forming ability. It is normally accepted that the stability of the undercooled melt exponentially depends on nucleation rate of a crystalline phase, which is a good indicator of the glass forming ability (GFA) [1–3]. The classical nucleation theory suggests that the nucleation rate is known by thermodynamic and kinetic factors. The thermodynamic contribution is mainly given by the Gibbs free energy difference, ΔG , between the undercooled liquid and corresponding crystalline phase, entropy difference, ΔS and enthalpy difference, ΔH . Gibbs free energy difference, ΔG between undercooled melt and corresponding crystalline solid acts as the driving force of crystallization. In an amorphous alloy system, lower value of ΔG indicates less driving force of crystallization, which enhances stability of metallic supercooled liquid and leads to better glass forming ability. In fact, ΔG is the best glass forming ability indicator compared to other glass forming ability criteria. The Gibbs free energy difference, ΔG gives a qualitative measure of the stability of the glass compared to the crystalline state.

In this article, we investigate the thermodynamic behavior of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ by calculating ΔG in the entire temperature range from T_m to T_K . This amorphous multicomponent alloy is one of the best nonberyllium containing glasses, making it easier to process and

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manage [4]. In order to find out the thermodynamic properties of BMG, knowledge of specific heat difference, ΔC_p is required. However, in most of the cases, the specific heat capacity data of undercooled liquid is not available because of its metastable nature. Due to the nonavailability of specific heat data in the undercooled region, the temperature dependence of ΔG , ΔS , and ΔH must be estimated with the help of theoretical formulation.

Formulation of theoretical expressions

In this article, the expression for ΔG is based on linear and hyperbolic variations of ΔC_p with temperature and does not consider limited undercooling region to take care of large undercooled region of this alloy. The results obtained show excellent agreement with ΔG obtained using experimental data [4]. There are number of expressions available for calculations of ΔG in the literature [5–11], in which the assumption of $\Delta C_p = \text{constant}$ has been taken. Values of ΔG are obtained using these equations and compared with the present calculations.

Now, the Gibbs free energy difference between undercooled melt and corresponding crystalline phase is given by

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \quad (2)$$

and

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \quad (3)$$

where T_m is the melting temperature, ΔS_m is the entropy of fusion, and ΔH_m is the enthalpy of fusion. They are related to each other by the following relation:

$$\Delta S_m = \frac{\Delta H_m}{T_m} \quad (4)$$

ΔC_p , defined as $C_p^l - C_p^x$, is the difference in specific heats of the liquid and corresponding crystalline phases of metallic alloy. Therefore, experimental ΔG can be calculated using Eqs. 1–3, if the experimental specific heat data is available for the undercooled and the crystal phases of a material. However, metallic liquids are generally not stable over an extended temperature range in the supercooled liquid, making it difficult to determine the specific heat capacity; one has to switch to suitable expression of ΔC_p that effectively represents the temperature dependence of ΔC_p .

In this study, the difference in specific heat capacity is determined using linear and hyperbolic variations with temperature, which involves coefficients A & B for linear trend and C & D for hyperbolic trend. These four coefficients are easily evaluated with the help of ΔC_p^m and T_K , where ΔC_p^m is specific heat difference at melting temperature and T_K is Kauzmann temperature also known as isentropic temperature because at T_K the entropy difference, ΔS becomes zero.

Considering the most common linear expression which is given by

$$\Delta C_p = AT + B \quad (5)$$

Inserting Eq. 5, in Eqs. 2 and 3, Eq. 1 can be simplified to

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{1}{2} A (\Delta T)^2 + B \left(T \ln \frac{T_m}{T} - \Delta T \right) \quad (6)$$

where the undercooling $\Delta T = T_m - T$.

Now, taking the hyperbolic variation of ΔC_p , which is given by

$$\Delta C_p = \frac{C}{T} + D \quad (7)$$

Substituting ΔC_p from the above equation in Eqs. 2 and 3 and simplifying Eq. 1, one can get the following expression

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} + \ln \frac{T_m}{T} (DT - C) - \Delta T \left(D - \frac{C}{T_m} \right) \quad (8)$$

There are four unknown constants A & B and C & D in the ΔG expressions (6) and (8), respectively. Since there are two unknowns in both linear and hyperbolic case, one needs another expression for evaluation of the constants. By deriving an expression for ΔS from that of ΔG given by Eqs. 6 and 8 using the following relation

$$\Delta S = -\frac{\partial \Delta G}{\partial T} \quad (9)$$

one can easily find out the required constants.

In the case of linear dependence of ΔC_p on T , one gets the following expression for ΔS through Eq. 9

$$\Delta S = \frac{\Delta H_m}{T_m} - A\Delta T - B \ln \frac{T_m}{T} \quad (10)$$

Utilizing the condition that ΔS becomes zero at isentropic temperatures, T_K also known as Kauzmann temperature one easily gets the unknown constants A and B in terms of known experimental parameters

$$A = \frac{\frac{\Delta H_m}{T_m} - \Delta C_p^m \ln \frac{T_m}{T_K}}{T_m - T_K - T_m \ln \frac{T_m}{T_K}} \quad (11)$$

and

$$B = \Delta C_p^m - AT_m \quad (12)$$

Similarly, the expression for ΔS in case of hyperbolic dependence of ΔC_p on T obtained from Eq. 9 by partial differentiation of Eq. 8 provides

$$\Delta S = \frac{\Delta H_m}{T_m} - D \ln \frac{T_m}{T} - C \left(\frac{T_m - T}{T_m T} \right) \quad (13)$$

One gets the expressions for constants C and D from Eq. 13 after solving it for $\Delta S = 0$ at Kauzmann temperature, $T = T_K$

$$C = \frac{\Delta H_m - T_m \Delta C_p^m \ln \frac{T_m}{T_K}}{\frac{T_m - T_K}{T_K} - \ln \frac{T_m}{T_K}} \quad (14)$$

and

$$D = \Delta C_p^m - \frac{C}{T_m} \quad (15)$$

Either of the Eqs. 6 and 8 can be used to evaluate ΔG in the entire undercooled region, when the constants A & B for linear nature and C & D for hyperbolic trend are known through Eqs. 11 & 12 and 14 & 15, respectively.

Results and discussion

Figure 1 shows the Gibbs free energy difference between undercooled liquid and corresponding crystalline solid for

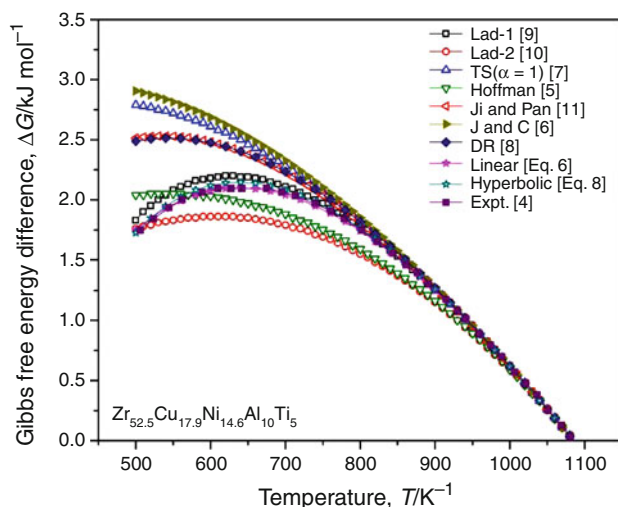


Fig. 1 Gibbs free energy difference, ΔG as a function of temperature, T for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$

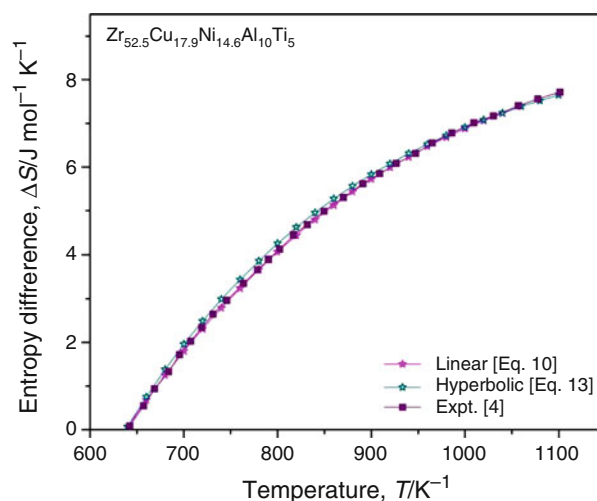


Fig. 2 Entropy difference, ΔS as a function of temperature, T for $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$

$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$. It is obvious from the figure that plots of ΔG estimated using linear and hyperbolic variation of ΔC_p almost coincide with the experimental points in the entire undercooled region and hence are in excellent agreement with the experiment. The parameters used [4] for calculations of ΔG are given in Table 1. Surprisingly, expression given by Lad et al. [9] abbreviated as Lad-1 provides results somewhat closer to the experimental ones, even though $\Delta C_p = \text{constant}$ assumption has been taken in this approach. Other expressions given by various workers either underestimate or overestimate ΔG particularly in large undercooled region. Since ΔG is the driving force for crystallization, its accurate evaluation is important from the view point of alloy design for various applications.

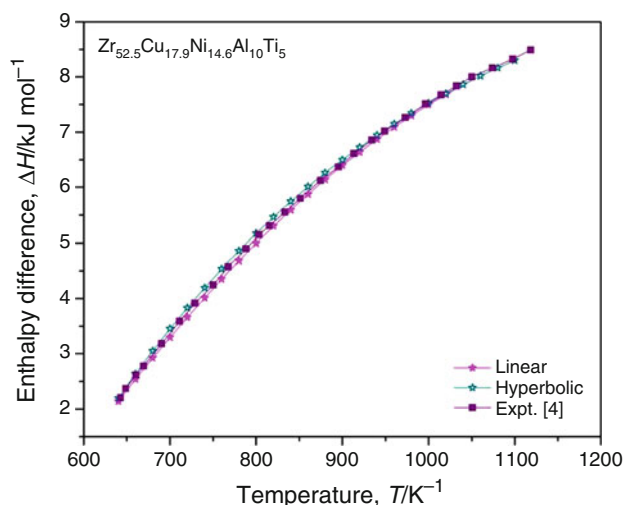
The entropy difference, ΔS between the undercooled liquid and corresponding crystalline solid has been obtained from the derivative of the plotted ΔG using Eqs. 10 and 13 and the same has been shown in Fig. 2 along with experimental results of Glade et al. [4]. It can be seen from the figure that the present approach accounts for accurate ΔS values in the entire temperature range and is matching excellently with the experimental points. Calculations using other theoretical expressions have not been shown as they are expected to show large variation from experiment. This has already been indicated in the ΔG plot and ΔS have been derived using the derivative of ΔG only. ΔH , the enthalpy difference between undercooled liquid and corresponding crystalline solid has been also evaluated from the known values of ΔG and ΔS using Eq. 1. The

Table 1 Parameters used for calculation of thermodynamic quantities ΔG , ΔS , and ΔH and different GFA criteria

| System | T_g/K | T_x/K | T_m/K | T_l/K | T_K/K | $\Delta H_m/kJ \text{ mol}^{-1}$ | $\Delta C_p^m/J \text{ mol}^{-1}K^{-1}$ | $\Delta S_m/J \text{ mol}^{-1}K^{-1}$ | Ref. |
|--|---------|---------|---------|---------|---------|----------------------------------|---|---------------------------------------|------|
| $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ | 675 | 727 | 1085 | 1091 | 638 | 8.2 | 7.02 | 7.6 | [4] |

Table 2 Different GFA criteria

| System | $\delta = \frac{T_K}{T_m}$ | $T_{rg} = \frac{T_g}{T_m}$ | $\gamma_m = \frac{(2T_x - T_g)}{T_l}$ | $\gamma = \frac{T_x}{T_g + T_l}$ | $\frac{T_x}{T_l}$ | $\frac{\Delta C_p^m}{\Delta S_m}$ | $\Delta G(T_K)/\text{kJ mol}^{-1}$ |
|---|----------------------------|----------------------------|---------------------------------------|----------------------------------|-------------------|-----------------------------------|------------------------------------|
| Zr _{52.5} Cu _{17.9} Ni _{14.6} Al ₁₀ Ti ₅ | 0.588 | 0.622 | 0.714 | 0.412 | 0.666 | 0.923 | 2.11 |
| Zr ₅₇ Cu _{15.4} Ni _{12.6} Al ₁₀ Nb ₅ | 0.601 | 0.617 | 0.719 | 0.413 | 0.665 | 1.514 | 2.18 |

**Fig. 3** Enthalpy difference, ΔH as a function of temperature, T for Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅

difference in the enthalpy between the liquid and the crystalline states at the glass transition, should in principle, provide the amount of enthalpy frozen into the liquid at T_g . The changing thermodynamics between the phases has also been recently investigated [12].

Besides the evaluation of ΔG in the undercooled region, various other GFA parameters [13] indicating the tendency of glass formation in this system have been derived and are given in Table 2. For getting an idea of relative glass forming tendency of this system, GFA indicating parameters of another system [3] having Nb in place of Ti have also been listed in the same Table. From the Table, it appears that glass forming ability of both these systems is nearly identical. Addition of an extra element like Nb or Ti does not seem to affect the GFA of Zr–Cu–Ni–Al system [14] reported to have super high glass forming ability (Figure 3).

Conclusions

The theoretical formulations used in this study provide excellent results for thermodynamic parameters ΔG , ΔS , and ΔH in the entire undercooled region of BMG forming alloy, Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅. Among these three parameters, accurate evaluation of ΔG is very important as

its value is an indicator of GFA of BMG's. It is obvious from the ΔG values obtained for this system that it has fairly good glass forming tendency owing to smaller value of ΔG . ΔG is a signature of driving force for crystallization. Other two parameters, ΔS and ΔH follow from ΔG and hence these two also show one to one correspondence with the experiment. Further, the present system exhibits good glass forming tendency as indicated by various GFA parameters.

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