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The absolute entropy of $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$ amorphous alloys

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Abstract

The heat capacities of amorphous and crystalline $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$ alloys were measured in the temperature range from ~ 12 K to the crystallization points for the former or to ~ 900 K for the latter. The results together with the data on the thermodynamic properties of the Ni–Zr melt were used for the calculation of the absolute entropy of the amorphous alloys on the assumption that the entropies of a substance in undercooled liquid and glassy states coincide at the glass-transition point. The entropy and heat capacity of the amorphous alloys was found to exceed those of the crystalline ones. The residual entropy of $\text{Ni}_{0.333}\text{Zr}_{0.667}$ and $\text{Ni}_{0.667}\text{Zr}_{0.333}$ amorphous alloys at 0 K is, respectively, 2.7 ± 2.1 and 0.2 ± 1.7 J mol⁻¹ K⁻¹, which is significantly below the residual entropy values typical for traditional oxide glasses (4 – 17 J mol⁻¹ K⁻¹). This points to a much higher degree of order in amorphous metallic alloys as compared to glassy oxides.

1. Introduction

Sufficient experimental information has now been accumulated to give decisive evidence for the metastability of the amorphous state in metallic alloys. Most convincing are the facts that glassy alloys of the same composition, produced by various techniques and/or under different conditions, exhibit, after relaxation, identical properties, which are unchanged over prolonged periods far exceeding the characteristic relaxation times at the same temperatures [1]. The spontaneous transition of a crystalline phase into a vitreous state and *vice versa* under cooling or heating correspondingly [2, 3] also falls into the category of fundamental arguments. The metastability of the amorphous state opens up fresh opportunities for understanding its nature and the regularities of the liquid \leftrightarrow glass transformation in metallic alloys through

the application of thermodynamic methods. However, the current experimental activities in this field are aimed mainly at measurements of heat capacities, enthalpies of formation and crystallization of amorphous alloys. We have not come across any experimental determination of the absolute entropy of amorphous alloys, while the available theoretical assessments (see for example [4, 5]) were carried out under rather rough approximations. At the same time it is precisely this characteristic that is of prime importance for the determination of the thermodynamic functions of amorphous metallic alloys and understanding both the regularities of the liquid \leftrightarrow glass transformation and the ways of subsequent transition to the equilibrium state. This property is also helpful in ascertaining the nature and the degree of disorder in the amorphous state in relation to the crystalline one. The determination of the absolute entropy of metallic alloys in the amorphous state is the objective of this work.

2. Experimental procedure and materials

One possibility to achieve this objective consists of the use of the generally recognized concept that at the glass-transition point, T_g , the entropies of a substance in the undercooled liquid and amorphous states coincide. This means that the entropy value of an amorphous metallic alloy, S_{am} , at any temperature below T_g is equal to

$$S_{am}(T) = S_{ul}(T_g) - \int_T^{T_g} \frac{(C_P)_{am}}{T} dT, \quad (1)$$

where S_{ul} is the entropy of the undercooled liquid and $(C_P)_{am}$ is the heat capacity of the metallic alloy in the amorphous state. Thus the determination of the entropy is connected with heat capacity measurements in the temperature range of 0 K to T_g and with the knowledge of the thermodynamic properties of the undercooled melts. As the transition of molten metallic alloys into the amorphous state occurs under quenching with a rate of the order 10^4 – 10^6 K s $^{-1}$, the direct determination of the thermodynamic properties of an undercooled liquid in the case under consideration seems unfeasible. The only way to obtain the required characteristics involves the extrapolation of the high-temperature thermodynamic properties of liquid over a rather wide temperature range.

In recent research [6], the thermodynamic properties of all crystalline and liquid phases in the Ni–Zr system were carefully measured and an associated solution model was developed that allows adequate extrapolation of the thermodynamic properties of the melt into the region of high undercooling [7, 8]. The alloys of this system exhibit a rather high glass-forming capacity in a wide concentration range and lie at the basis of a variety of bulk metallic amorphous materials [9–11] so that the regularities of the liquid \rightarrow amorphous transformation have been much studied. For the reasons listed, Ni–Zr alloys were chosen for the determination of the absolute entropy of the amorphous state. Along with amorphous alloys the heat capacity of crystalline alloys of the same composition was also measured, in order to have the possibility to evaluate the configurational heat capacity, which is the difference between C_P of a substance in the undercooled liquid and crystalline states, and which plays a decisive role in understanding how the thermodynamic and kinetic characteristics of melts change in the process of undercooling [12].

A vacuum adiabatic calorimeter with a container of 2 cm 3 in volume [13] was used for heat capacity measurements in the range of 12–320 K. The uncertainty was within 0.5% down to 50 K and then gradually increased, reaching 2% at 12 K. Above room temperature, measurements were carried out in a differential scanning calorimeter DSC 111 SETARAM with relative errors of about 0.8%. The mass of samples varied from \sim 2 to \sim 5 g.

The $\text{Ni}_{0.333}\text{Zr}_{0.667}$ and $\text{Ni}_{0.667}\text{Zr}_{0.333}$ amorphous alloys were prepared as bands 2.5–3 mm wide and 0.02 mm thick by melt spinning on a copper disc under a purified helium atmosphere. The initial ingots were smelted from components of purity not worse than 99.8 wt%. The composition of the first alloy corresponded to the NiZr_2 intermetallic compound while that of the second was in the $\text{Ni}_{21}\text{Zr}_8 + \text{Ni}_{10}\text{Zr}_7$ heterogeneous field of the Ni–Zr phase diagram [14].

Preliminary studies in the DSC 111 SETARAM device have revealed that the $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$ amorphous alloys crystallize in the range 817–874 and 628–686 K, with the corresponding maxima of heat evolution at 841 and 655 K. In accordance with this result the amorphous alloys were transformed into the crystalline state by heating in a dynamic vacuum at temperatures 100 K higher than the peaks of the heat evolution. Completeness of the transformation was verified by a second DSC analysis. The experimental data on the heat capacities were approximated with the IVTANTERMO program package [15] by relationships of the type

$$C_P = aT + 0.979D(\theta_1) + 0.979D(\theta_2) + 0.979D(\theta_3) + 0.021E(\theta_E), \quad (2)$$

where D and E are the Debye and Einstein heat capacity functions, θ_i are the corresponding characteristic temperatures, and a is constant.

3. Results and discussion

The measured heat capacities are shown in figures 1(a) and (b), and the coefficients of equation (2) are summarized in table 1. The scatter of the data points around the smoothed curves was $\sim 0.5\%$ at high temperatures and $\sim 0.2\%$ in the range 50–320 K. With further decrease in temperature to 12 K, the scatter progressively increased, and reached $\sim 2\%$ at 12 K. As can be seen, at any temperature studied, the heat capacity of the amorphous alloys is somewhat higher than that of the crystalline alloys. Measurements of the heat effects of the amorphous alloy's crystallization, $\Delta_{\text{cr}}H$, using the DSC 111 SETARAM device, resulted in 3.58 and 2.91 kJ mol^{-1} for $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$, respectively. These values are in agreement with literature data. For example, according to DSC determinations [16, 17] $\Delta_{\text{cr}}H$ for the former alloy is equal to 3.66 ± 0.34 or 3.9 kJ mol^{-1} .

Smith *et al* [18] found the heat capacities of some two-phase crystalline Ni–Zr samples by means of a Perkin-Elmer DSC-2 calorimeter. Figure 1 also shows the C_P values for the $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$ alloys in the crystalline state calculated according to the additivity rule from the data [18] for the heterogeneous fields $\text{Ni}_{21}\text{Zr}_8 + \text{Ni}_{10}\text{Zr}_7$ and $\text{NiZr} + \text{NiZr}_2$. One can see that in the case of $\text{Ni}_{0.667}\text{Zr}_{0.333}$ the C_P values of the two types of determination virtually coincide. For $\text{Ni}_{0.333}\text{Zr}_{0.667}$, agreement is observed only in the range 200–600 K. At lower and higher temperatures, the C_P values [18] differ noticeably from the present ones. Integration of the heat capacity *versus* temperature relations (2) leads to the following absolute entropies of the $\text{Ni}_{0.333}\text{Zr}_{0.667}$ and $\text{Ni}_{0.667}\text{Zr}_{0.333}$ crystalline alloys at standard temperature: 36.95 ± 0.8 and $33.55 \pm 0.7 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The former is somewhat higher than the absolute entropy of NiZr_2 ($34.6 \text{ J mol}^{-1} \text{ K}^{-1}$) reported in [18]. Conversely, the latter is somewhat lower than the value $35.3 \text{ J mol}^{-1} \text{ K}^{-1}$ calculated, by means of the lever rule, from the absolute entropies of $\text{Ni}_{21}\text{Zr}_8$ and $\text{Ni}_{10}\text{Zr}_7$ reported in [18]. The major reason for this discrepancy presumably lies in the extrapolation method used in [18]. The authors of this work assumed that the high-temperature function $C_P(T)$ is obeyed up to ~ 80 K and that, below this temperature, the heat capacity follows a cube law; however, it is well known that this law is, as a rule, valid at considerably lower temperatures.

We can now turn to computing the entropy of the amorphous alloys under investigation. Equation (1) indicates that the knowledge of the glass-transition points and the absolute

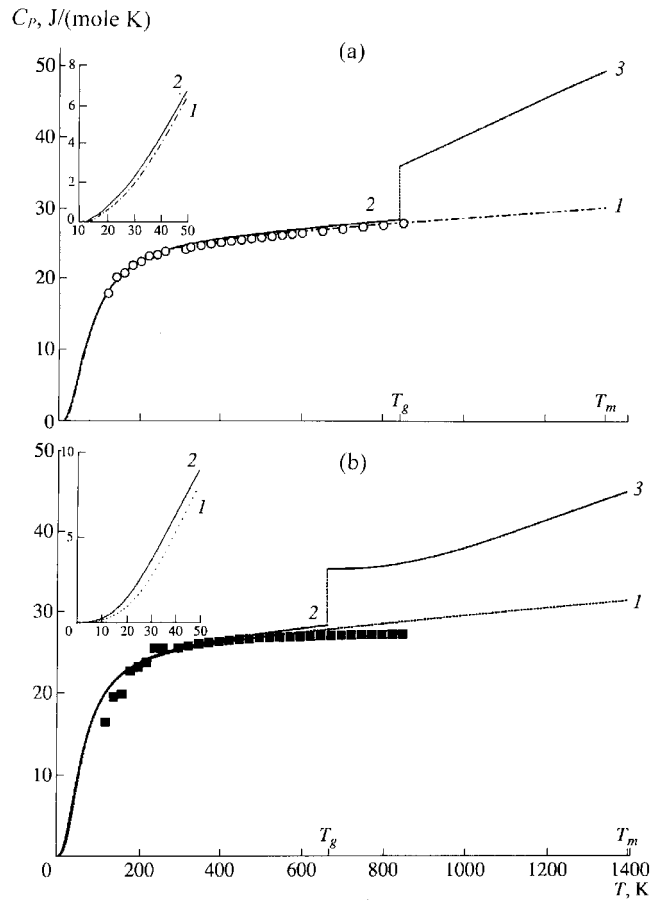


Figure 1. The heat capacity of the alloys (a) $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and (b) $\text{Ni}_{0.333}\text{Zr}_{0.667}$: (1) crystalline state, (2) amorphous state, and (3) undercooled liquid; points—data [18]; T_g —glass-transition point; T_m —melting point.

Table 1. The parameters of the approximating equation (2).

Alloy	State	$a \times 10^3$	θ_1 (K)	θ_2 (K)	θ_3 (K)	θ_E (K)
$\text{Ni}_{0.667}\text{Zr}_{0.333}$	Amorphous	4.6374	217	341	389	600
	Crystalline	4.0799	253	307	391	518
$\text{Ni}_{0.333}\text{Zr}_{0.667}$	Amorphous	5.5249	175	314	321	426
	Crystalline	4.7324	267	267	284	534

entropy of the undercooled liquid are required for this purpose. Experimental studies of the glass \leftrightarrow crystals transition in the Ni–Zr system [17, 19–23] have revealed that the T_g temperature practically coincides with the crystallization point, T_{cr} . The average T_{cr} values are 840 and 666 K for $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$, respectively, which are close to the temperatures of the heat evolution peaks found here by DSC. The above values were used in further calculations. To strengthen the view that an adequate thermodynamic description [6] of the Ni–Zr system can be applied for computing the heat capacity and absolute entropy of the $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$ alloys in the state of a deeply undercooled liquid, the

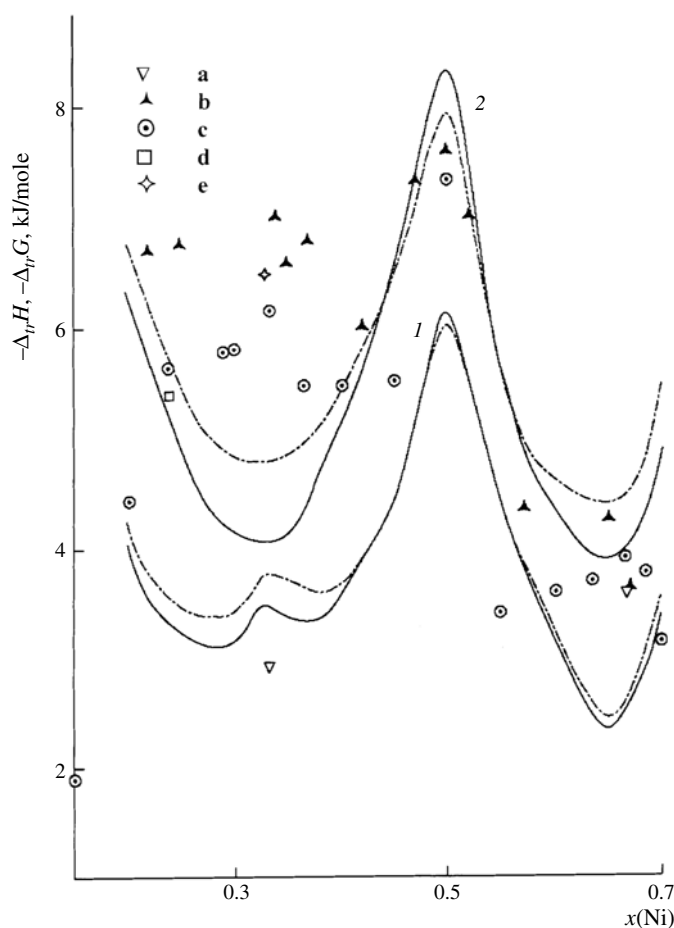


Figure 2. The Gibbs energy $\Delta_{\text{tr}}G$ (1) and enthalpy $\Delta_{\text{tr}}H$ (2) of crystallization of Ni–Zr amorphous alloys according to the present research: solid curves—calculation based on $C_p(\text{cr.})$ from [18], dashed curves—calculation based on the additivity rule, and (a) results of the DSC experiments; and literature data on $\Delta_{\text{tr}}H$: (b) [16]; (c) [17]; (d) [26]; (e) [25].

characteristics of the transformation of the Ni–Zr amorphous alloys into equilibrium crystalline phases at T_{cr} were calculated. The thermodynamic properties of the pure components from [24] were used for the purpose. The resulting values, together with the enthalpies of crystallization measured in [16, 17, 25, 26], are shown in figure 2. It is essential that the heat capacities of the crystalline alloys obtained by extrapolation of the experimental data to temperatures above the temperature range of their determination (>900 K) are virtually the same as the additive values obtained by considering the formation of the alloys from nonmagnetic fcc Ni and bcc Zr. In as much as the C_p values found by the above methods are close to each other, it is hard to unambiguously decide which of these assumptions introduces a larger error. Different methods of representing C_p lead to different thermodynamic characteristics, the larger difference being observed for the enthalpy of crystallization rather than for the Gibbs energy. Figure 2 shows that, within the errors of determination, the calculated enthalpies of crystallization agree with both the data in [16, 17, 25, 26] and our experimental DSC results.

The heat capacity and absolute entropy of the undercooled liquid $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$ alloys in the temperature range from the melting point to the glass transition

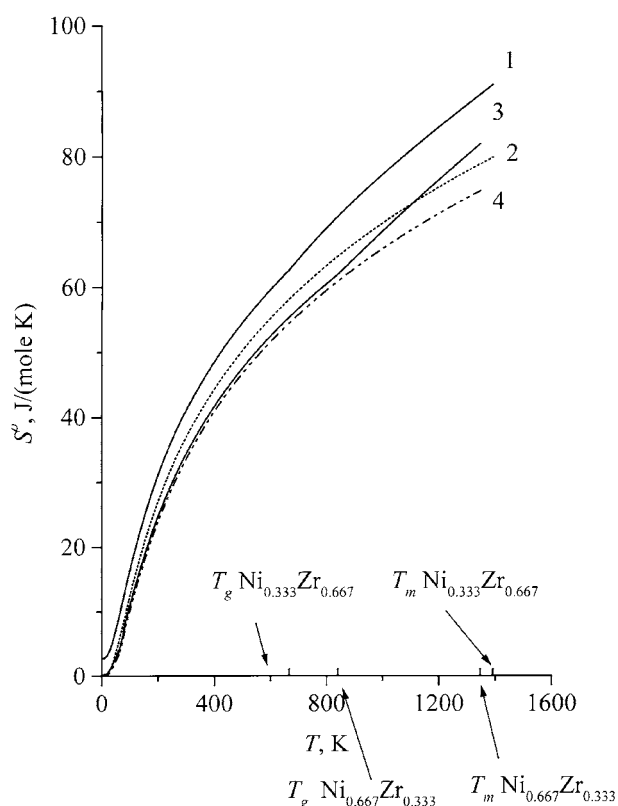


Figure 3. The absolute entropy of the alloys $\text{Ni}_{0.333}\text{Zr}_{0.667}$ (1—amorphous, 2—crystalline) and $\text{Ni}_{0.667}\text{Zr}_{0.333}$ (3—amorphous, 4—crystalline).

point, calculated using the data [24] for pure components, are given in figures 1 and 3. As the composition of the former alloy corresponds to neither an intermetallic compound nor a eutectic, the solidus temperature was taken as its melting point. At the T_g point the entropy of the undercooled liquid was found to be 62.1 and 62.7 $\text{J mol}^{-1} \text{K}^{-1}$ for $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$, respectively. The uncertainty in these values was estimated from the calculated and measured $\Delta_{tr}H$ given in figure 2 under the assumption that the relative errors in the entropy and enthalpy of the undercooled liquid found by means of the model [6] coincided. The distinction between the calculated and average measured $\Delta_{tr}H$ values was considered as the error in the enthalpy of the undercooled liquid alloys in spite of the fact that the heat of crystallization is the difference between the enthalpy of the alloys in the undercooled liquid and solid states and, therefore, the error should be divided between these two terms; thus the most unfavourable conditions were used in the estimation. The corresponding computations revealed that the sought-for relative errors amounted to 1.5 and 2.5% for $\text{Ni}_{0.667}\text{Zr}_{0.333}$ and $\text{Ni}_{0.333}\text{Zr}_{0.667}$, which correspond to ± 0.9 and $\pm 1.6 \text{ J mol}^{-1} \text{K}^{-1}$.

The measured heat capacities of the amorphous alloys were then used to establish the absolute entropy of these alloys in the glassy state in the temperature range from the glass-transition (crystallization) point to 0 K. The results obtained (figure 3) show that, at any temperature, the entropy of the amorphous alloys is higher than the entropy of the crystalline ones. At T_g , this difference, which characterizes the configurational or positional entropy of the

amorphous alloy ($S^{\text{pos}}(T_g)$), is small: $4.4 \text{ J mol}^{-1} \text{ K}^{-1}$ for Ni_{0.333}Zr_{0.667} and $1.0 \text{ J mol}^{-1} \text{ K}^{-1}$ for Ni_{0.667}Zr_{0.333}. At the same time, the configurational heat capacity, $C_p^{\text{conf}}(T_g)$, that is, the difference between the C_p values for an undercooled liquid and a crystal [12], is rather large: 7.5 and $7.9 \text{ J mol}^{-1} \text{ K}^{-1}$ for the alloys studied, respectively (figure 1); and it increases with temperature. This relationship between the $S^{\text{pos}}(T_g)$ and $C_p^{\text{conf}}(T_g)$ functions leads to a rapid decrease in configurational entropy on undercooling the melt and, thus, to a rapid increase in both the viscosity and activation energies of viscous flow and crystallization [12].

With allowance made for uncertainties in the heat capacity measurements, the residual entropy of the Ni_{0.333}Zr_{0.667} and Ni_{0.667}Zr_{0.333} amorphous alloys at 0 K is, respectively, 2.7 ± 2.1 and $0.2 \pm 1.7 \text{ J mol}^{-1} \text{ K}^{-1}$, which is significantly below the entropy values typical for traditional oxide glasses ($4\text{--}17 \text{ J mol}^{-1} \text{ K}^{-1}$) [27]. This finding points to a much higher degree of order in amorphous metallic alloys as compared to glassy oxides. Also of crucial importance is the fact that the residual entropy is a function of the composition of an amorphous alloy, and it decreases with an increase in chemical short-range order in the melt and its propensity to turn into the amorphous state. According to the conclusions of [6], it is precisely the Ni_{0.667}Zr_{0.333} composition that corresponds to the extremes of these characteristics.

4. Conclusions

The combination of the results of thermodynamic research of Ni–Zr alloys in liquid, crystalline and amorphous states has allowed calculation of the absolute entropy of the Ni_{0.333}Zr_{0.667} and Ni_{0.667}Zr_{0.333} amorphous alloys on the assumption that the entropies of a substance in the undercooled liquid and glassy states coincide at the glass-transition point. The entropy and heat capacity of the amorphous alloys were found to exceed those of the crystalline ones. The residual entropy of the Ni_{0.333}Zr_{0.667} and Ni_{0.667}Zr_{0.333} amorphous alloys at 0 K is, respectively, 2.7 ± 2.1 and $0.2 \pm 1.7 \text{ J mol}^{-1} \text{ K}^{-1}$, which is significantly below the residual entropy values typical for traditional oxide glasses ($4\text{--}17 \text{ J mol}^{-1} \text{ K}^{-1}$). This suggests a much higher degree of order in amorphous metallic alloys as compared to glassy oxides.

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