Thermochemical properties and glass forming tendency modeling for the ternary Ge–Mn–Gd melts

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Information on the thermochemical properties may be useful for predicting of the concentration regions of easy glass formation in multicomponent alloys. In present investigation the integral enthalpies of mixing for the Ge–Mn–Gd melts were determined for the entire concentration interval at 1830 K using the Redlich-Kister-Muggianu method. GFT values for binary and ternary alloys of this system were calculated. Size mismatch entropy was estimated within the frameworks of hard spheres model. On the basis of performed calculations the concentration regions in which the melts of the Ge–Mn–Gd system can demonstrate considerable tendency to easy glass formation were suggested.

Introduction

Rare earth intermetallic compounds in ternary RE–Mn–Ge systems (where RE – rare earth metal), in particular GdMnGe, GdMn₂Ge₂, Gd₃Mn₄Ge₄ and GdMn₆Ge₆ [1–5], attract considerable attention due to their unusual electronic and magnetic properties. Such compounds can exhibit antiferromagnetic type of ordering with subsequent transition to a ferromagnetic, paramagnetic or even ferromagnetic state under the influence of a temperature or magnetic field, or when a certain part of the compound atoms is replaced by atoms of some other d- and f-metals. The abovementioned properties of these intermetallics make them promising for use as

magnetic materials. Special mention should be made about magnetic properties of amorphous materials obtained from liquid alloys of the Ge–Mn–Gd system [6]. Therefore, information on the thermochemical properties as well as prediction of the concentration region where easy glass formation can be observed in the Ge–Mn–Gd system may be useful for the purposes of production of amorphous magnetic materials.

Previously, in [7] we have presented the results of the calorimetric experiments for the liquid alloys of the five sections with constant $x_{\text{Ge}} / x_{\text{Mn}}$ ratio equal to 0.25/0.75, 0.4/0.6, 0.5/0.5, 0.7/0.3 and 0.8/0.2 of the Ge–Mn–Gd system at 1830 K. In the present work we have used the Redlich-Kister-Muggianu method of

modeling of thermodynamic properties of the ternary alloys to determine the concentration dependence of integral enthalpies of mixing throughout the whole concentration triangle. The data on the thermochemical properties of binary constituent systems and those of the Ge–Mn–Gd ternary system, experimentally obtained within a limited concentration region, have been used for this purpose. The term of specific "ternary" interaction has been determined in order to obtain the best fit of the simulated data with the experimental ones.

To calculate the thermochemical properties of the ternary Ge–Mn–Gd alloys, we used the data on the enthalpies of mixing of liquid alloys for the binary constituents systems obtained via high-temperature calorimetry, an experimental technique which allows to obtain the most reliable data on the enthalpies of mixing. It should be noted that the data available in the literature up to 2006 are rather completely analyzed in [7]. Since then, three new works have appeared on the properties of constituent binary systems of interest, namely: Ref. [8] on the experimental determination of the enthalpies of mixing in the Gd–Mn system, the 2017 assessment [9] on the same system, and the 2014 assessment [10] on the Ge–Mn system. After thorough analysis of the abovementioned sources, we selected the data that most adequately describe the enthalpies of mixing in the constituent binary systems at high temperature, namely: the data from Ref. [11]

obtained at 1585 K for the Ge–Mn system (according to [7] and [10]); the data from Ref. [12] obtained at 1973 K for the Ge–Gd system (according to [7]); the data from Ref. [8] at 1650 K for the Gd–Mn system (according to [9]). While performing calculations we considered it possible to neglect the temperature dependence of the enthalpies of mixing at such a high temperature.

It should be noted that the data on the enthalpies of mixing of liquid alloys for the binary constituent systems correlate well with their phase diagrams. All three binary phase diagrams demonstrate a significant number of intermediate phases of fixed composition or with extended homogeneity range. The minimum value of the integral enthalpy of mixing ($\Delta_{\text{mix}}H$) in the Ge–Mn alloys is equal to $(-20.9) \text{ kJ mol}^{-1}$ and is observed at $x_{\text{Mn}} = 0.65$ [11]. According to the Ge–Mn phase diagram [10] a series of chemical compounds exists in the same composition region ($x_{\text{Mn}} = 0.6 \div 0.8$). For the liquid alloys of the Ge–Gd system the minimum $\Delta_{\text{mix}}H$ reaches $(-98.4) \text{ kJ mol}^{-1}$ at $x_{\text{Ge}} = 0.45$ [12]. Such a great exothermic effect combined with the existence of a series of the high-temperature solid compounds including congruently melting Gd_5Ge_3 in the same composition region [13] allows concluding existence a short-range order of a chemical compound type in a liquid state. The Gd–Mn system is characterized by small negative values of the enthalpy of mixing (with the minimum

$\Delta_{\text{mix}}H$ value of $(-2.0) \text{ kJ mol}^{-1}$ at $x_{\text{Mn}} = 0.6$) [8]. According to the phase diagram of this system [14], three intermetallic compounds with low melting temperatures (below the melting point of the manganese) exist in Mn-rich composition region.

The calculations of the enthalpies of formation for the ternary system were performed according to the Redlich-Kister-Muggianu formula, which is given by the following equation:

$$\begin{aligned} \Delta H(x_1, x_2, x_3) = & x_1 x_2 \sum_{i=0}^n {}^i L_{\text{Me1-Me2}} (x_1 - x_2)^i + \\ & + x_1 x_3 \sum_{i=0}^n {}^i L_{\text{Me1-Me3}} (x_1 - x_3)^i + \\ & + x_2 x_3 \sum_{i=0}^n {}^i L_{\text{Me2-Me3}} (x_2 - x_3)^i + \\ & + x_1 x_2 x_3 (x_1 {}^0 L_{\text{Me1-Me2-Me3}} + \\ & + x_2 {}^1 L_{\text{Me1-Me2-Me3}} + x_3 {}^2 L_{\text{Me1-Me2-Me3}}), \end{aligned} \quad (1)$$

where ${}^i L_{\text{Me1-Me2}}$, ${}^i L_{\text{Me1-Me3}}$, ${}^i L_{\text{Me2-Me3}}$ are the coefficients of the Redlich-Kister polynomial for the corresponding binary systems, n is the power of this polynomial, ${}^0 L_{\text{Me1-Me2-Me3}}$, ${}^1 L_{\text{Me1-Me2-Me3}}$, ${}^2 L_{\text{Me1-Me2-Me3}}$ are the ternary interaction parameters.

The Redlich-Kister parameters for the binary systems were obtained by conversion of the corresponding simple polynomials for the binary constituent systems into the Redlich-Kister polynomials. The last term of the equation (1) characterizes the specific ternary interaction which is a measure of deviation of the thermodynamic properties of ternary solution from the regular behavior. It is important to know

this term to better understand the nature of the component interaction in liquid state. The ternary parameters were obtained as a result of the statistical treatment of the difference between the experimental data for the ternary system and those calculated from the regular solution model.

Results and discussion

The complete set of binary and ternary parameters is listed in **Table 1**.

Table 1. The binary and ternary interaction parameters for the integral enthalpies of mixing $\Delta_{\text{mix}}H$ ($\text{kJ} \cdot \text{mol}^{-1}$) in liquid alloys of the binary Ge-Mn (Gd), Mn-Gd and ternary Ge-Mn-Gd systems at 1830 K

${}^i L_{\text{Me1-Me2}}$	Me ₁ – Me ₂ system		
	Mn–Ge	Ge–Gd	Gd–Mn
${}^0 L_{\text{Me1-Me2}}$	– 73.103	–387.698	–7.528
${}^1 L_{\text{Me1-Me2}}$	– 72.948	102.108	5.117
${}^2 L_{\text{Me1-Me2}}$	20.693	29.923	3.438
${}^3 L_{\text{Me1-Me2}}$	58.069	–	–4.184
${}^4 L_{\text{Me1-Me2}}$	–3.470	–	–1.530
${}^5 L_{\text{Me1-Me2}}$	– 21.142	–	0.997
${}^i L_{\text{Me1-Me2-Me3}}$	Ge–Mn–Gd system		
${}^0 L_{\text{Me1-Me2-Me3}}$	–386.345		
${}^1 L_{\text{Me1-Me2-Me3}}$	289.476		
${}^2 L_{\text{Me1-Me2-Me3}}$	38.210		

The projections of the obtained isenthalpies of mixing of the ternary Ge-Mn-Gd melts in the entire Gibbs concentration triangle are shown in **Figure 1**. It should be noted that for the binary Gd-Ge melts in the composition range of $0.25 < x_{\text{Ge}} < 0.55$ (in the vicinity of the existence of high-melting binary

compounds) as well as for the ternary alloys with compositions close to the same region the enthalpies of mixing refer to the supercooled liquid state of the alloy. In our opinion, this should not significantly affect the results of subsequent calculations, due to the fact that usually the temperature dependence of the exothermic values of the enthalpies of mixing at sufficiently high temperatures is insignificant.

Figure 1. The projections of isolines of the integral enthalpies of mixing of the ternary Ge–Mn–Gd alloys at 1830 K ($\text{kJ}\cdot\text{mol}^{-1}$), in comparison with experimental values (individual characters, indicated in figure) obtained for this ternary system [7]

From **Figure 1** one can see that the $\Delta_{\text{mix}}H$ surface in this system gradually decreases from the Mn-rich corner to the Ge–Gd side of the concentration triangle. The minimum value of the enthalpy of mixing of the ternary liquid alloys at the composition close to those of the most stable intermetallics in the Ge–Gd system. The topology of the isolines also indicates the effect of the short-range order that exists in the Ge–Mn system at $x_{\text{Mn}} > 0.7$ on the

properties of ternary melts that are close in composition to this binary system.

The simulation of the glass forming tendency of the Ge–Mn–Gd liquid alloys. One of the actual problems of materials science is to perform an estimation of the tendency of certain metal alloy to form glass when rapidly cooling from the liquid phase and to assess the thermodynamic stability of such glass to recrystallization. Of course, it is desirable to evaluate these properties quantitatively, basing on simple criteria and calculations. It is well known, that this problem has both thermodynamic and kinetic aspects. The thermodynamic stability of an amorphous phase with respect to pure components can be considered as a necessary condition for an amorphous alloy formation if the kinetic requirements to formation and growth of nuclei of a crystalline phase are satisfied. One can say that thermodynamic properties determine the general possibility of formation of a disordered amorphous state instead of a stable crystalline state [15]. The thermodynamic properties of supercooled liquid and amorphous alloys at the glass forming temperature (T_g) are very similar. Therefore, the extrapolation of the thermodynamic properties of liquid alloys to the glass transition temperature T_g [16] can be used to estimate the thermodynamic aspects of amorphous alloys formation in a wide range of compositions, including those for which amorphous alloys have not yet been obtained

experimentally. It may be important for assessing the prospects of the formation of new amorphous materials and also the conditions of their exploitation.

Interparticle interaction determines the structure and thermodynamic properties of metal alloy in a liquid state. Therefore, the possibility of metal glass obtaining through the rapid quenching of liquid alloy is also determined by the interaction between atoms of different components. The existence of ordered groups of atoms or atomic associates in the bulk of liquid melt substantially affects its tendency to amorphization. In some cases, the existence of such associates may lead to an increase in glass formation tendency due to the extension of the period of time necessary to rearrange the short-range order inherent in liquid state to that inherent in solid state. In other cases, the similar atomic groups can act as the centres of crystallization.

At the present time the number of methods is used for assessing the ability to easy amorphization. Some of them take into account the peculiarities of the metallic melts (such as the presence of deep eutectics, the ability to significant overcooling of the liquid phase, etc.) another base on their thermodynamic properties (such as great negative enthalpies or free energies of mixing), that makes the estimation much more reliable.

The authors of Ref. [17], basing on the kinetic theory of the nucleation and growth of

crystals, and taking into account the strong interaction between different kinds of atoms, which contributes to the formation of associates (or clusters, in their terminology) and to the changes in diffusion coefficients of atoms of components in melts, proposed the application of the GFT (glass forming tendency) criterion, which determines the tendency for easy glass formation. GFT can be calculated as follows:

$$GFT = -\lg \left(1 - 2 \frac{cH_{AB}^m}{c_m RT_g} \right) - 0.434 \frac{cH_{AB}^m}{c_m RT_g} - 0.145 \left(\frac{c}{c_m} \right)^{m+n} \ln \left(\frac{N}{m+n} \right), \quad (2)$$

where T_g is the absolute temperature, to which it is possible to overcool the liquid alloy; R is the universal gas constant; m and n are the stoichiometric coefficients of the associate (cluster or binary complex); H_{AB}^m – enthalpy of formation of liquid melt at $c_m = n / (m + n)$ concentration, N – Avogadro number. In this form, GFT is the ratio of the tendency of a binary solution to form glass to the same value of the pure component A. GFT demonstrates how much easier and faster can be certain alloy converted into amorphous state as compared to the pure component in the same conditions of rapid quenching. The alloy of the selected composition forms a metallic glass easily than the pure component if the GFT value is greater than zero. Although the model is approximate, the predictions based on it are in good agreement

with many experimental results, as shown in [18, 19].

The model presented in [17] was used to determine the glass formation tendency for the binary constituent Ge–Mn (Gd), Mn–Gd systems and the ternary Ge–Mn–Gd systems. It was assumed that the glass formation temperature was $0.6T_m$ of the component with the lowest melting point, that is 730 K (for Ge–Mn(Gd)) and 910 K (for Mn–Gd). When choosing the composition of the clusters that influence the formation of the amorphous phase the most, we have taken the cluster of composition that corresponds to a congruently melting compound with the highest melting temperature or to a compound that forms the eutectic of the lowest temperature. Input data for GFT calculations in the binary constituent systems of the Ge–Mn–Gd ternary system are presented in **Table 2**. The type of the cluster has been determined according to the phase diagrams of the corresponding binary systems.

Table 2. Cluster compositions for the binary Ge–Mn(Gd) and Mn–Gd constituent systems

System	Variants of considered systems	$c_m = \frac{n}{m+n}$
Ge–Mn	Ge–Mn: Ge–Ge ₃ Mn ₅	0.625
	Mn–Ge: Mn–Mn ₅ Ge ₃	0.375
Gd–Mn	Gd–Mn: Gd–GdMn ₂	0.667
	Mn–Gd: Gd–Mn ₂ Gd	0.333
Ge–Gd	Ge–Gd: Ge–Ge ₃ Gd ₅	0.625
	Gd–Ge: Gd–Gd ₅ Ge ₃	0.375

We have corrected the formula (2) for the GFT calculation proposed by the authors [17]

taking into account that we use the exact values of the integral enthalpies of mixing ($\Delta_{\text{mix}}H(x)$) of the melts according to the experimentally obtained concentration dependences, but not the approximate values of the enthalpies recalculated from the cluster formation enthalpy, i.e.

$$\frac{c}{c_m} H_{AB}^m = \Delta_{\text{mix}}H(x).$$

After simple mathematical transformations, we obtained the following equation (3) for GFT calculation:

$$GFT = -0.434 \left\{ \ln \left(1 - 2 \frac{\Delta_{\text{mix}}H(x)}{RT_g} \right) + \frac{\Delta_{\text{mix}}H(x)}{RT_g} \right\} - 0.145 \left(\frac{c}{c_m} \right)^{m+n} \ln \left(\frac{N}{m+n} \right).$$

(3)

The GFT concentration dependences for the binary Ge–Mn (Gd) and Mn–Gd constituent systems calculated by equation (3) are presented in **Figure 2**.

a)

Figure 2. Composition dependences of GFT for liquid alloys of the binary constituent Ge–Mn (Gd) and Mn–Gd systems.

Figure 2,a demonstrates a strong tendency for easy glass formation in the Ge–Gd melts in comparison with pure germanium and gadolinium. According to our results two areas of easy glass formation can be expected: the first one is in concentration range from nearly pure germanium to $x_{\text{Gd}} = 0.6$ and the second is from $x_{\text{Gd}} = 0.64$ up to nearly pure gadolinium. Calculations were performed for the most likely Gd_5Ge_3 cluster because it corresponds to the most thermally stable compound in this system and thus can provide the best results in predicting the areas of easy glass formation for this system. According to our calculations for the Mn–Gd

alloys (**Figure 2,b**), we do not observe any tendency for easy glass formation as compared with pure components. It means that to obtain glass in this system, it is necessary to apply cooling rates not less, maybe higher, than that for obtaining glass from pure liquid Mn or Gd. From **Figure 2,c** one can see that for the Ge–Mn alloys the tendency to easy glass formation is insignificant. The region of an easy amorphization of liquid alloys as compared to the pure components is rather narrow and is located in the Mn-rich composition range. In this system, GFT calculations were performed for Mn_5Ge_3 cluster, because according to the phase diagram of the Ge–Mn system the melting temperature of such an intermetallic is the highest of those existing in this system, so it can be expected that the best result is achieved when applying this composition of the cluster.

For the calculations in the ternary Ge–Mn–Gd we have assumed that the composition of the clusters which affect the tendency for easy amorphization varies gradually along the line connecting the compositions of Mn_5Ge_3 and Gd_5Ge_3 binary compounds (the most thermally stable in the corresponding binary systems). This is a reasonable assumption, especially taking into account that the Mn_5Ge_3 and Gd_5Ge_3 binary compounds are isostructural. Therefore, along the Mn_5Ge_3 – Gd_5Ge_3 section of the ternary Ge–Mn–Gd system, a series of X_5Ge_3 associates may be formed, where X denotes manganese and gadolinium atoms taken in different ratios close

to the ratio of their concentrations in the corresponding ternary alloy. The validity of such approach is confirmed by the existence of the ternary $\text{Gd}_3\text{Mn}_2\text{Ge}_3$ compound, which was established in [20] (**Figure 3**). **Figure 3** also demonstrates that the great majority of ternary compounds in Ge–Mn–Gd system have compositions close to the line connecting Gd_5Ge_3 and Mn_5Ge_3 compounds.

Figure 3 – Scheme explaining the calculations of GFT of the ternary Ge–Mn–Gd alloys; asterisks and numbers in parentheses correspond to the compositions of ternary compounds determined at 973 K in [20].

GFT was calculated for the germanium-rich alloys for which the mixing enthalpies were obtained experimentally as well as for the gadolinium-rich alloys that were not calorimetrically investigated, but the reliable values of integral enthalpies of mixing for them were obtained due to calculation of ternary interaction term.

For the ternary Ge–Mn–Gd alloys the glass formation temperature T_g was chosen to be 730 K.

The results obtained for the GFT values of the ternary Ge–Mn–Gd alloys are presented in **Figure 4**.

Figure 4. Projections of GFT isolines of the ternary Ge–Mn–Gd melts. The compositions of the alloys for which amorphous ribbons have been experimentally obtained in [6] are given for comparison: ○ – $\text{Gd}_{65}\text{Mn}_{30}\text{Ge}_5$; ● – $\text{Gd}_{65}\text{Mn}_{25}\text{Ge}_{10}$.

Figure 4 demonstrates that the largest positive value of GFT is expected for the alloys with compositions close to the Ge–Gd binary system. With increase in a content of manganese the GFT value is gradually decreases for the alloys of the both parts of concentration triangle, situated to the right and to the left of the line connecting Gd_5Ge_3 and Mn_5Ge_3 compounds. For the alloys located inside the areas defined by lines with $\text{GFT}=2$ one can expect that the glass formation for the ternary Ge–Mn–Gd alloys proceeds much easier than for pure germanium or gadolinium.

In addition, it should be noted that the considered ternary system is not only the one with strong interaction of components in liquid state, but also is characterized by large size

difference of the components. Indeed, according to the data [21] on the radii of the first coordination sphere for metallic melts the radii of component atoms are: $r_{\text{Mn}} = 133$ pm, $r_{\text{Ge}} = 141$ pm, $r_{\text{Gd}} = 183$ pm. The combination for the Ge–Mn–Gd ternary alloys of such characteristics as large exothermic enthalpies of mixing and large component size mismatches may further evidence in favour of the existence of sufficiently wide concentration regions of alloys with easy amorphization in this system.

Within the framework of the liquid state model, known as hard spheres model, which is widely used for the description of metallic melts, the difference between the atomic sizes of the alloy components always leads to the appearance of a positive entropy contribution to the thermodynamic functions of the formation of a disordered phase, the so-called size mismatch entropy S_{σ} [22, 23]. According to the approach of the authors of [24], such a positive contribution is favourable to the appearance of areas of easy amorphization. So, for our ternary system we have calculated the corresponding S_{σ} contribution to the entropy of mixing. The calculations of S_{σ} values were carried out according to the following equation:

$$S_{\sigma} / k_B = \frac{3}{2}(\zeta^2 - 1)y_1 + \frac{3}{2}(\zeta - 1)^2 y_2 - \left\{ \frac{1}{2}(\zeta - 1)(\zeta - 3) + \ln \zeta \right\} (1 - y_3), \quad (4)$$

where k_B is the Boltzmann constant, the ζ parameter is related to the sphere packing

coefficient ξ as $\zeta = 1 / (1 - \xi)$, the coefficient of packing in our calculations was equal to 0.64, that corresponds to the random packing of hard spheres in the amorphous phase according to [24]. Dimensionless parameters y_1 , y_2 and y_3 were determined using the data on diameters d_i of hard spheres and molar fractions x_i of the corresponding components according to the following equations (taking into account that $y_1 + y_2 + y_3 = 1$):

$$y_1 = \frac{1}{\sigma^3} \sum_{j>i=1}^3 (d_i + d_j)(d_i - d_j)^2 x_i x_j \quad (5)$$

$$y_2 = \frac{\sigma^2}{(\sigma^3)^2} \sum_{j>i=1}^3 d_i d_j (d_i - d_j)^2 x_i x_j \quad (6)$$

$$y_3 = \frac{(\sigma^2)^3}{(\sigma^3)^2} \quad (7)$$

$$\sigma^k = \sum_{i=1}^3 c_i d_i^k; k = 2, 3. \quad (8)$$

The isolines of the obtained S_{σ} / k_B values for the ternary Ge–Mn–Gd system plotted in the concentration triangle are shown in **Figure 5** (solid lines).

Figure 5. Projections of the isolines of S_{σ} / k_B parameter for the Ge–Mn–Gd system (solid lines) and the expected regions of easy formation of the amorphous alloys (dashed lines).

Comparison of the topology of S_{σ} / k_B and $\Delta_{\text{mix}}H$ surfaces with the results of the performed GFT calculations allows to reasonably assume that the concentration regions of alloys with the high tendency to amorphization are situated inside the dashed contours, as shown in **Figure 5**. The first of these dashed contours almost completely coincides with the isoline with $\text{GFT} = 0.5$ for alloys located to the left of the Ge_3Mn_5 – Ge_3Gd_5 connecting line, and the second coincides with the isoline with the $\text{GFT} = 1.5$ for alloys located to the right of this line. For the alloys whose compositions lie along the indicated curves, despite the relatively small values of the GFT parameter (0.5 or 1.5), an additional positive effect on the formation of the amorphous phase is provided by the size mismatch entropy S_{σ} / k_B factor, whose value is more than 0.3 in the vicinity of the maximum of the curvature of the indicated GFT curves. The value of $S_{\sigma} / k_B > 0.3$ can contribute to the additional thermodynamic stabilization of the disordered liquid phase. It also can contribute to the formation of the amorphous phase by increasing the period of time necessary for rearrangement of the short-range order inherent in liquid state to that inherent in the crystalline phase of the corresponding composition. It should be noted that the compositions of the

amorphous alloys obtained by rapid quenching in [6] fall into the indicated regions (see **Figure 4**). The composition of the compounds (8) and (6) from **Figure 3** also fall into the region of easy amorphization, which means that one can expect to obtain these magnetic phases in amorphous state.

Conclusions

The integral enthalpies of mixing for the Ge–Mn–Gd melts were determined for the entire concentration interval at 1830 K using the Redlich-Kister-Muggianu method and taking into account the term of a specific ternary interaction. This made possible to calculate the GFT values for the alloys of the binary Ge–Mn(Gd) and Mn–Gd constituent systems and of the ternary Ge–Mn–Gd system and to suggest the concentration regions in which the melts can demonstrate great tendency to easy glass formation when being rapidly cooled. In the ternary system, these regions are located on both sides of the line which connects the compositions of the Ge_3Mn_5 and Ge_3Gd_5 compounds. Also, the calculations of the size mismatch entropy S_{σ} were performed since this ternary system refers to the type of systems with strong component interaction in liquid state and with large atomic size difference of the components. The significant value of S_{σ} can contribute to the appearance of wide areas of easy amorphization for the alloys of the Ge–Mn–Gd ternary system.

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