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Thermodynamic properties of liquid alloys of 3d transition metals with metalloids (silicon, carbon and boron)

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Abstract

A survey of the experimental investigations of the thermodynamic functions of formation of liquid binary and ternary alloys of 3d transition metals (Tr ≡ Cr, Mn, Fe, Co, Ni, Cu) with metalloids (Si, C and B) is presented. The thermodynamic data for 19 ternary (such as Tr–Fe–C, Tr–B–C, Tr–Si–C and Tr–Si–B) and 17 border binary systems are reviewed. The effects of the microheterogeneous structure of liquid binary and ternary alloys of iron and chromium with carbon and boron are described. The experimental data indicate the existence of attractive forces between unlike atoms in all systems studied. The cobalt-rich regions in Fe–Co–C and Co–Si–C melts, where athermal solutions exist and repulsive forces take place, are an exception. The correlation between structural parameters of the liquid metals and excess thermodynamic functions at infinite dilution is discussed. Model calculations of glass-forming tendency (GFT), based on the concentration dependence of the integral enthalpy of mixing and the stoichiometry of associates in liquid ternary systems, allow the range of glass formation to be estimated.

1. Introduction

The principal thermodynamic properties of liquid binary alloys of 3d transition metal (Tr) with metalloids, such as silicon, carbon and boron, have been established. The Fe–Si system has been studied most extensively. For these alloys, calorimetric [1–7] and activity data [8–14] are available. The thermodynamic activity in Tr–Si systems shows large negative deviations from Raoult's law and reflects the strong chemical interaction between the components in the alloy melts. The activity data measured by different methods are in good agreement. The enthalpies of mixing in Mn(Co, Ni, Cu)–Si systems [15–22] are scarce, and further investigations are required, especially in the Cr–Si system [23]. For the liquid binary alloys Tr–C, only activity data [24–31] are available. Experimental thermodynamic functions of liquid alloys containing boron are few in the literature. Activity data are absent; the only calorimetric data were obtained by Esin *et al.* [32–35] and Batalin *et al.* [36] in single experimental series. The activities of components and the interaction parameters in Fe–Si–C-based alloys, at compositions which correspond to steel and grey iron, have been studied [37–42]. Nevertheless, some high-temperature binary and all ternary alloys of 3d metals are as yet unexplored by calorimetry. The investigation of the thermodynamics of ternary melts of these metals with metalloids is the basis to the understanding of the energies of alloy formation and is necessary to solve the technological problems of materials production and application, especially for the newly developing branch of the alloy industry, *i.e.* metallic glasses. Real progress in this field will be made by the collection of reliable thermodynamic data in computer systems banks. In this paper, a description of the method of measurement of the heat of formation in high-temperature ternary alloys and the results of 17 binary and 19 ternary systems are presented.

2. Experimental and systematic details

An isoperibolic high-temperature calorimeter, provided with a system of data accumulation and mathematical treatment by personal computer and operational up to 2200 K, was used for the measurement of the enthalpies of formation in the systems containing 3d metals and metalloids. The apparatus was applied as a drop calorimeter with constant temperature. The heats of formation were measured by successive introductions of samples (3d metal or metalloid) placed at standard temperature into a liquid bath (pure metal, binary or ternary alloy). The initial mass of metal or alloy in the calorimetric crucible was 40–60 g. A stirrer guarantees complete and rapid dissolution or mixing of the components. Temperature measurements were carried out using a thermocouple (WRe5–WRe20) pro-

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tected by a high-resistance ceramic tube and placed into the melt. The thermocouple was calibrated using pure substances recommended by International Practical Temperature Scale, 1968. The construction and general principles of this calorimeter have been described previously [43, 44]. The experimental method is based on the measurement of the temperature dependence difference (ΔT) *vs.* time (t) between the bath in which the sample was added and the reference specimen. The heat effect may be calculated from the ΔT *vs.* t curves by integration using a personal computer.

The measurements in ternary systems were carried out on ray sections (the concentration ratio of the initial components in the alloy was maintained constant for the total run time). To obtain the partial molar enthalpies of alloy formation, the dropping sample mass was controlled by computer so that the concentration changes in the bath did not exceed 1 at.%. The experiments were carried out in purified helium at an excess pressure of 5×10^3 Pa. The purities (%) of the metals and metalloids were as follows: Cr, 99.83, Mn and Fe, 99.6; Cu, 99.996; monocrystalline Si. 99.999; graphite, 99.95; crystalline B, 99.5.

The results of the calorimetric measurements were presented as the temperature of the melt (T) and the squares of the thermal figures (F) *vs.* concentration (x). To obtain the smoothed enthalpies of formation of the liquid alloys, these values were transformed by polynomial series expansions. In general, the calorimetric calculations in binary and ternary systems may be carried out using the equations given in refs. 45 and 46, but in long time runs the isoperibolic conditions do not hold rigorously, so that temperature drift exists, especially at very high temperatures ($T > 2000$ K), due to changes in the thermophysical properties of the melt. In this case, for a ternary system, if the concentration ratio $y/(1-y)$ is constant within the run, the enthalpies of mixing may be expressed as follows

$$\Delta\bar{H}_i(x) = -\Delta H^{\mathrm{To}}_{298,i} - \Delta c_{p,i}\,\Delta T(x) + W(x)F_i(x) \qquad \mathrm{i}=1, 2, 3 \tag{1}$$

$$\Delta H(x) = (1-x)(1-y)\Delta\bar{H}_1(x) + (1-x)y\Delta\bar{H}_2(x) + x\Delta\bar{H}_3(x) \tag{2}$$

$$\mathrm{d}W = -[\Phi_\Sigma(x)]^{-1}\left[W(x)\mathrm{d}\Phi_\Sigma(x) + W(x)\,\frac{\Phi_\Sigma(x) - F_3(x)}{1-x}\,\mathrm{d}x - \Delta C_{p,\Sigma}(x)\,\mathrm{d}T(x)\right] \tag{3}$$

$$\Phi_\Sigma(x) = (1-x)(1-y)F_1(x) + (1-x)yF_2(x) + xF_3(x) \tag{4}$$

$$\Delta C_\Sigma(x) = (1-x)(1-y)\Delta c_{p,1} + (1-x)y\Delta c_{p,2} + x\Delta c_{p,3} \tag{5}$$

where $\Delta\bar{H}_i(x)$, $\Delta H^{\mathrm{To}}_{298,i}$, $\Delta c_{p,i}$ and $F_i(x)$ are the partial enthalpy of formation, the standard enthalpy of heating, the heat capacity and the square of the thermal figure (referred to 1 mol) of the i component respectively, $\Delta H(x)$ is the integral enthalpy of formation of alloys on the ray section with constant ratios $y/(1-y)$ and $W(x)$ is the thermal equivalent of the calorimeter. The value $\Delta T(x) = T(x) - T_0$ is the difference between the temperature values at each drop ($T(x)$) and the initial temperature (T_0) fixed at $x=0$; x is the mole fraction of the third component in the ternary solution and y is the mole fraction of the second component in the initial binary melt.

The differential equation (eqn. (3)) does not allow the variables to be divided; therefore the numerical method of solution was applied. The initial expression for $x = x_0$ stands

$$W(x_0) = \frac{\Delta H(x_0) + \Delta H^{\mathrm{To}}_\Sigma(x_0) + \Delta C_{p\Sigma}(x_0)\Delta T(x_0)}{\Phi_\Sigma(x_0)} \tag{6}$$

where

$$\Delta H^{\mathrm{To}}_\Sigma(x) = (1-x)(1-y)\Delta H^{\mathrm{To}}_{298,1} + (1-x)y\Delta H^{\mathrm{To}}_{298,2} + x\Delta H^{\mathrm{To}}_{298,3}$$

$\Delta H(x_0)$ is the integral enthalpy of the ternary alloy at a concentration x_0. To determine the initial value of the thermal equivalent at the beginning of the experimental series ($x=0$) we obtain

$$W(0) = \frac{(1-y)\,\Delta H^{\mathrm{To}}_{298,1} + y\Delta H^{\mathrm{To}}_{298,2} + \Delta H^\circ}{(1-y)F_1(0) + yF_2(0)}$$

where ΔH° is the integral enthalpy of formation of an initial alloy.

As can be seen from eqn. (3) difficulties in the numerical integration may arise when $\phi_\Sigma(x_0)$ is equal or near to zero. However, in all 3d metal-based melts studied this was not observed.

The excess thermodynamic functions taken at the standard state of the liquid metals and for a hypothetical supercooled liquid (HSL) metalloid (C and B) were calculated using the well-known equations [47]

$$\Delta_{\mathrm{m}}\bar{H}_i = \Delta_{\mathrm{s}}\bar{H}_i - \Delta_{\mathrm{f}}H_i - \int_T^{T_{\mathrm{f}}} \Delta c_{p,1}\,\mathrm{d}T$$

$$\Delta_{\mathrm{m}}\bar{S}^{\mathrm{ex}}_i = \Delta_{\mathrm{s}}\bar{S}^{\mathrm{ex}}_i - \Delta_{\mathrm{f}}H_i/T_{\mathrm{f}} - \int_T^{T_{\mathrm{f}}} \Delta c_{p,i}/T\,\mathrm{d}T$$

$$\Delta_{\mathrm{m}}\bar{G}^{\mathrm{ex}}_i = \Delta_{\mathrm{s}}\bar{G}^{\mathrm{ex}}_i - \Delta G'_i$$

$$\Delta G'_i = \Delta_{\mathrm{f}}H_i(1 - T/T_{\mathrm{f}}) + \int_T^{T_{\mathrm{f}}} \Delta c_{p,i}\,\mathrm{d}T - \int_T^{T_{\mathrm{f}}} \Delta c_{p,i}/T\,\mathrm{d}T$$

$$a_{\mathrm{m},i} = a_{\mathrm{s},i}\exp(\Delta G'_i/RT)$$

where i stands for metalloid, s and m indicate that the standard state is liquid metal, solid metalloid and liquid metal, HSL metalloid respectively, $\Delta_f H$ is the enthalpy of fusion of the metalloid, $\Delta\bar{H}$, $\Delta\bar{S}^{ex}$, $\Delta\bar{G}^{ex}$ and a are the partial enthalpy, excess entropy, free energy and activity of the components respectively and Δc_p is the difference between the heat capacity of the metalloid in the liquid state (at temperature T_f) and the solid state (at the temperature of the calorimetric measurements T). Standard values of the enthalpy of heating, heat capacity temperature dependence and enthalpy of fusion for each component were taken from refs. 48–50.

3. Thermodynamics of binary liquid systems

3.1. 3d transition metal–silicon systems

For calorimetric measurements of the enthalpies in ternary systems, as follows from eqn. (2), reliable data for border binary alloys are needed. These functions for Tr–Si systems were measured in detail (more than 100 experimental points in three separate experiments were obtained for each system). These results, in common with statistically treated activity or free energy data, are sufficient to determine reliable values of the excess entropy of mixing in Tr–Si alloys, because the optimum assessment of the thermodynamic functions of an alloy can be obtained via the Gibbs energy and of the enthalpy of formation from calorimetric data [44]. Our results are presented in Fig. 1. The characteristic features of liquid Tr–Si alloys are the large negative enthalpy values and the negative entropies of mixing. Thus, in the silicon-rich region in Cu–Si melts, $\Delta_m S^{ex}$ is slightly positive. This reflects the strong atomic interaction and ordering effects in these melts in comparison with an ideal solution. This phenomenon is associated with the chemical nature of the components resulting in the filling of the incomplete 3d shell of the transition metal. Thus, it has been proven that the large negative entropy of mixing is due to electron contribution [51–53]. The interaction of transition metals with silicon is accompanied by the transfer of the valence electrons of silicon, with the last ones filling the d shell of the metal leading to a decrease in entropy due to an increase in the density of states near the Fermi level. The atomic interaction between 3d metals and p elements is stronger, the more completely filled the d shell becomes. This tendency is in agreement with the values of the partial enthalpy of mixing of silicon ($\Delta\bar{H}^{\circ}_{Si}$) with the 3d metals (Table 1). However, copper and chromium show a different behaviour conditioned by the half-filled ($3d^5 4s^1$) and completely filled ($3d^{10} 4s^1$) d shell. Chromium, whose external 4s shell is incomplete, interacts more actively with silicon than manganese. This effect is observed for copper in comparison with zinc.

3.2. 3d transition metal–carbon systems

The activity data for binary melts Mn(Fe, Co, Ni)–C have, in most cases, been obtained by vapour pressure measurements [24–31]. The lack of data available for Cr–C melts may be due to its chemical reactivity at very high temperatures. The thermodynamic properties

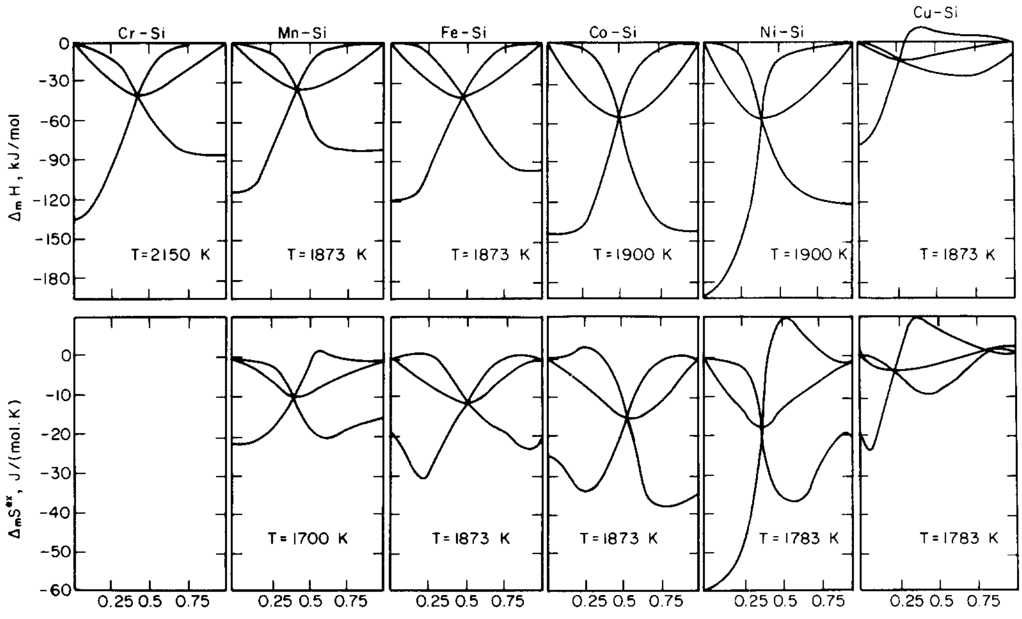

Fig. 1. Concentration dependence of enthalpies (upper row) and excess entropies (lower row) of mixing of silicon with 3d metals.

TABLE 1. Thermodynamic parameters of mixing for liquid Tr–Si alloys

Parameter	Cr–Si	Mn–Si	Fe–Si	Co–Si	Ni–Si	Cu–Si
$\Delta_m\bar{H}^\circ_{Si}$ (kJ mol^{-1})	-135 ± 11	-115 ± 5	-120 ± 9	-144 ± 8	-189 ± 8	-85 ± 4
$\Delta_m\bar{H}^\circ_{Tr}$ (kJ mol^{-1})	-82 ± 3	-78 ± 7	-92 ± 6	-140 ± 11	-123 ± 10	-11 ± 3
$-\Delta_m H_{min}$ (kJ mol^{-1})	39.5 ± 2.1	36.2 ± 2.1	40.7 ± 2.0	55.0 ± 2.2	56.0 ± 2.1	14.0 ± 0.6
x_{Si} ($_{min}\Delta_m H$) (at.%)	43	43	47	50	39	25
$\Delta_m\bar{S}^{\circ,ex}_{Si}$ (J mol^{-1} K^{-1})	–	-22 ± 2	-18 ± 3	-25 ± 3	-65 ± 5	-20 ± 2
$\Delta_m\bar{S}^{\circ,ex}_{Tr}$ (J mol^{-1} K^{-1})	–	-14 ± 1	-21 ± 2	-34 ± 3	-22 ± 2	2.3 ± 1.5
$\Delta_m S^{ex,min}$ (J mol^{-1} K^{-1})	–	-11 ± 1	-11 ± 2	-15 ± 2	-17 ± 3	-4.0 ± 0.5
x_{Si} ($_{min}\Delta_m S^{ex}$) (at.%)	–	40	51	52	38	20
T (K)	2160	1700	1873	1873	1783	1773

of binary systems at the standard state (liquid 3d metal and β-graphite, liquid 3d metal and HSL carbon) were calculated from activity and calorimetric data [43, 54–58]. The activities of the components at the standard state of HSL carbon in alloys with Mn, Fe, Co and Ni reveal negative departures from Raoult's law, thus reflecting the strong interaction between the components in solution. Partial enthalpies of mixing for HSL carbon are given in Fig. 2(a). This function shows a concentration dependence with a horizontal portion and a minimum at concentrations of 24 at.% C and 12 at.% C for Cr and Fe respectively; this may be associated with the microheterogeneous structure of the melts themselves. This is in agreement with other experimental results which prove the existence of complexes of Cr_3C [59] as well as the nucleation and growth of Fe_3C particles at temperatures exceeding the temperature of the liquidus according to the cluster association mechanism [60]. The results of the structural investigation of the samples, obtained by the rapid quenching of melts, may also be given as proof of complex formation in liquid chromium–carbon alloys. Indeed, it has been established [61] that carbon is combined into the metastable carbide Cr_3C. As shown in Fig. 2(b) the atomic interaction energy between 3d metal and carbon increases in the order Co → Ni → Fe → Mn → Cr.

The excess entropy of mixing of manganese and iron with HSL carbon is negative (Fig. 2(c)), the minimal values of -5.0 ± 1.1 and -1.6 ± 0.6 J mol^{-1} K^{-1} being located at 24 and 18 at.% C respectively. These binary liquid alloys are indeed the most ordered in the studied group. The mixing of cobalt and nickel with carbon results in positive excess entropy values, as a result of the significant non-configurational (electronic, magnetic) contribution to the entropy of alloy formation.

The partial thermodynamic functions of mixing at infinite dilution of carbon (enthalpy $\Delta_m\bar{H}^\circ_C$, free energy $\Delta_m\bar{G}^{\circ,ex}_C$ and entropy $\Delta_m\bar{S}^{\circ,ex}_C$) vary through the series of transition metals in agreement with the variation of the heat capacity, viscosity, electric resistivity and first coordination number [62]. These dependences are due to the nature of the melt, the extreme values for cobalt being caused by the awkward short-range structure of the liquid cobalt matrix into which the carbon is incorporated. Calorimetric measurements of the limiting

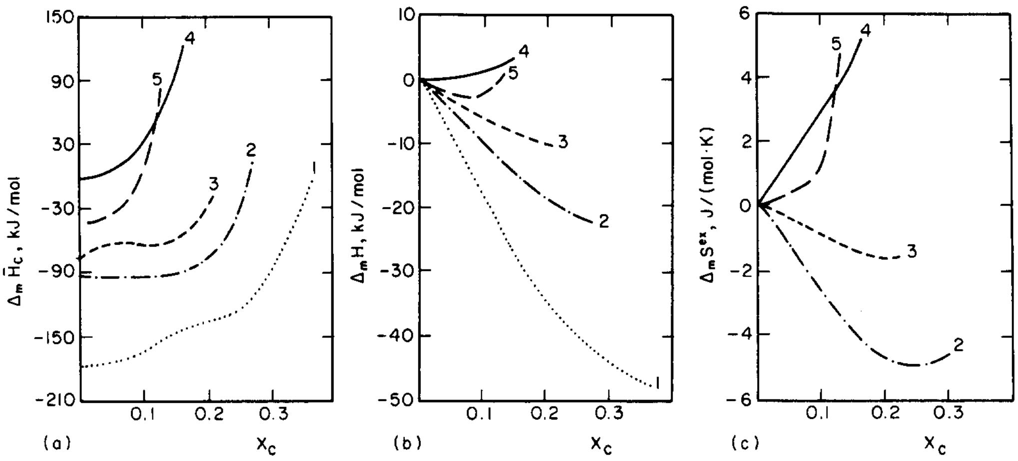

Fig. 2. Concentration dependence of partial enthalpies (a), integral enthalpies (b) and integral excess entropies (c) of mixing for HSL carbon with 3d metals: curve 1, Cr (2160 K); curve 2, Mn (1673 K); curve 3, Fe (1873 K); curve 4, Co (1873 K); curve 5, Ni (1873 K).

TABLE 2. Limiting values of the partial thermodynamic functions of alloy formation in binary Tr–C systems

Parameter	Cr–C	Mn–C	Fe–C	Co–C	Ni–C
$\Delta_s\bar{H}_C^\circ$ (kJ mol^{-1})	-92 ± 12	-5.3 ± 3.4	7.9 ± 2.1	93 ± 10	43 ± 4
$\Delta_m\bar{H}_C^\circ$ (kJ mol^{-1})	-185 ± 20	-98 ± 16	-84 ± 15	1 ± 18	-49 ± 17
$\Delta_s\bar{G}_C^{\circ,ex}$ (kJ mol^{-1})	–	-10.5 ± 0.5	-5.6 ± 1.1	2.3 ± 1.2	-19 ± 3
$\Delta_m\bar{G}_C^{\circ,ex}$ (kJ mol^{-1})	–	-65 ± 8	-56 ± 8	-48 ± 7	-69 ± 9
$\Delta_s\bar{S}_C^{\circ,ex}$ (J mol^{-1} K^{-1})	–	3.1 ± 2.7	7.2 ± 1.9	48 ± 6	33 ± 5
$\Delta_m\bar{S}_C^{\circ,ex}$ (J mol^{-1} K^{-1})	–	-20 ± 5	-15 ± 5	26 ± 8	11 ± 6
T (K)	2160	1673	1873	1873	1873

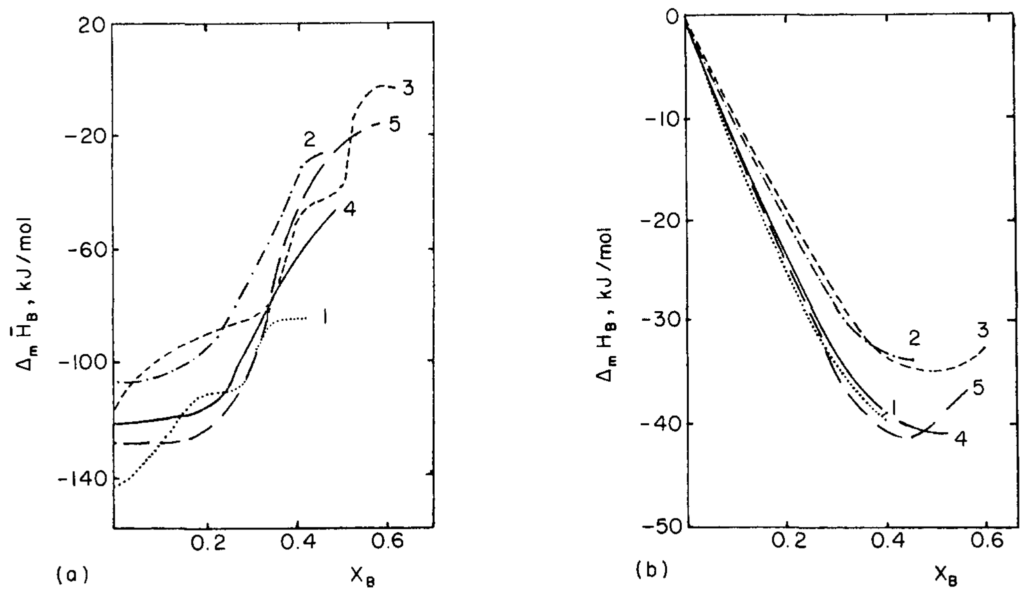

Fig. 3. Partial (a) and integral (b) enthalpies of mixing of HSL boron with 3d metals: curve 1, Cr (2160 K); curve 2, Mn (1873 K); curve 3, Fe (1900 K); curve 4, Co (1900 K); curve 5, Ni (1900 K).

TABLE 3. Limiting values of the enthalpies of liquid alloy formation in binary Tr–B systems

Parameter	Cr–B	Mn–B	Fe–B	Co–B	Ni–B	Cu–B
$\Delta_s\bar{H}_B^\circ$ (kJ mol^{-1})	-92 ± 5	-59 ± 5	-63 ± 6	-67 ± 7	-76 ± 9	95 ± 10
$\Delta_m\bar{H}_B^\circ$ (kJ mol^{-1})	-142 ± 6	-109 ± 6	-115 ± 7	-117 ± 8	-127 ± 10	45 ± 10
$\Delta_s H^{min}$ (kJ mol^{-1})	–	-14 ± 1	-14 ± 1	-19 ± 1	-21 ± 1	–
x_B ($_{min}\Delta_s H$) (at.%)	–	33	37	38	35	–
$\Delta_m H^{min}$ (kJ mol^{-1})	–	-34 ± 2	-36 ± 2	-41 ± 2	-41 ± 3	–
x_B ($_{min}\Delta_m H$) (at.%)	–	43	50	50	43	–
T (K)	2160	1873	1900	1900	1900	1873

partial enthalpies correlate with the excess Gibbs energies calculated from the carbon activities reported in the literature (Table 2).

3.3. Melts of 3d metals with boron

As carried out for melts of 3d metals with Si, a detailed investigation of the mixing enthalpies in the alloy systems Mn(Fe, Co, Ni)–B and in Cr–B solution is required. Generally, the results obtained are in agreement with previous data [32–35]; however, horizontal portions in the concentration dependence of the partial functions of Fe–B and Cr–B systems arise (Fig. 3(a)). This effect may be associated with the microscopic heterogeneous structure of Fe–B and Cr–B melts owing to the formation of associates Fe_4B, Fe_3B, Fe_2B and Cr_3B. Direct investigation of the liquid structure by X-ray diffraction confirmed the microheterogeneous structure [63] and the existence of structural groups, such as Fe_4B at 14 at.% B, Fe_4B and Fe_3B at 25 at.% B and Fe_4B and FeB or FeB_2 at 33 at.% B

[64]. The horizontal portion of the partial enthalpy of mixing at high metalloid content is also due to compound formation, *e.g.* the borides Cr_2B, MnB, Fe_2B, CoB and NiB. It is of interest to note that the variations in the initial values of the partial enthalpy of mixing of HSL boron in liquid chromium, manganese and iron (Table 3) approach those obtained for the mixing of silicon in these metals (see Table 1). For the Cu–B liquid alloys, the limiting value of $\Delta_m\bar{H}^\circ_B$ in copper was determined to be 45 ± 10 kJ mol^{-1}. These results are in accordance with the mean value of certain experimental data points in the copper-rich region presented in ref. 36; however, Batalin *et al.* [36] failed to determine the enthalpy variation in the middle concentration region because of the low solubility of crystalline boron in liquid copper. Thus, in ref. 36, amorphous boron was used.

The integral enthalpies of mixing in Tr–B systems (Fig. 3(b)) approach minimal values at 45 at.% B for Mn and Ni and at 50 at.% B for Fe and Co. In Cr–B alloys, at the temperature of the experiment, the minimum of ΔH is located in the heterogeneous concentration region and so it was not determined.

3.4. *Correlation between thermodynamic functions and the structure of liquid 3d metals*

The variation in the partial enthalpies at infinite dilution of C, Si and B and the structural parameters (first coordination number z_1, nearest interatomic distance r_1 [65]) through the 3d transition metal series is shown in Fig. 4. Silicon and boron display an analogous behaviour slightly different from that of carbon, whose enthalpies of mixing with 3d metals show a more pronounced dependence on the location of the 3d metal in the Periodic Table. The electronegativity, ionization energy and metallic radii of boron and silicon are close [66, 67], in contrast with carbon, whose minimal metallic radius promotes an interstitial mechanism of alloy formation which seems to be preferred for the melts studied. Manganese has a half-filled 3d shell and, with the metalloids, forms liquid solutions with almost equivalent interaction energies between the components. Chromium interacts with carbon more significantly than with boron and silicon. This tendency should be retained for melts of other carbide-forming elements of the 3d metal series (Sc, Ti and V). In contrast, those transition metals located to the right of manganese show stronger interaction with silicon and boron than with carbon. In addition, the phase diagrams of the above-mentioned metals with carbon do not show the existence of carbide phases.

The data presented in Fig. 4 were treated by polynomial regression analysis using

$$\Delta_m\bar{H}_i^\circ = Ar_1 + Bz_1 + Cn_d + Dn_s + E \qquad (7)$$

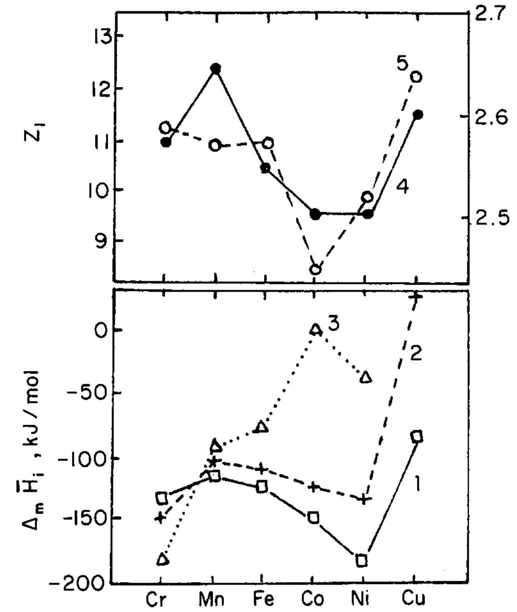

Fig. 4. Variation of the limiting partial enthalpies of mixing and the structural parameters of liquid 3d metals *vs.* atomic mass number for the series of 3d metals from Cr to Cu: curve 1, $\Delta_m\bar{H}^\circ_{Si}$; curve 2, $\Delta_m\bar{H}^\circ_B$; curve 3, $\Delta_m\bar{H}^\circ_C$; curve 4, r_1 [65]; curve 5, z_1 [65].

where A, B, C, D and E are coefficients and n_d and n_s are the numbers of electrons in the 3d and 4s shells respectively. These values, with correlation coefficients and error limits (considerable level is 0.05), are given in Table 4. The dependence of $\Delta_m\bar{H}^\circ_C$ *vs.* the structural parameters may be described through the 3d transition metal series using only the first coordination number; $\Delta_m\bar{H}^\circ_{Si}$ and $\Delta_m\bar{H}^\circ_B$ depend on the nearest interatomic distance. These correlations reflect the special nature of the liquid solution of the 3d metals with metalloid elements. The mechanism of liquid alloy formation is considered to be strongly influenced by the metalloid atom size factor and its electronic structure. Two interactions are possible: the substitution of a solvent atom by a metalloid atom, or the incorporation of a solute atom into the interatomic vacancies.

If the first type of interaction occurs, the alloy formation energy should be due to the destruction of interatomic bonds and the creation of bonds between the metal and metalloid. In this case the mixing enthalpy may correlate with the nearest interatomic distance which is generally treated as a direct characteristic of the cohesive energy. Table 4 shows that this type is realized in melts of 3d metals with boron and silicon.

If the metallic radius of a metalloid atom is small we may safely consider the interstitial mechanism to be dominant. This process provides the thermodynamic profit by increasing the entropy due to distortion of the liquid solvent structure. The metalloid atom interaction with the liquid metal matrix is determined

TABLE 4. Coefficients of eqn. (7) and adequate description indices for the enthalpies of metalloids

Parameter	A	B	C	D	E	Error limit (kJ mol^{-1})	Correlation coefficient
$\Delta_m\bar{H}_C^\circ$	–	−32.4	4.1	80.0	77.8	3.2	0.998
$\Delta_m\bar{H}_{Si}^\circ$	3709	–	5.2	−13.8	−1100	9.2	0.820
$\Delta_m\bar{H}_B^\circ$	5268	–	32.2	−16.6	−1640	8.6	0.963

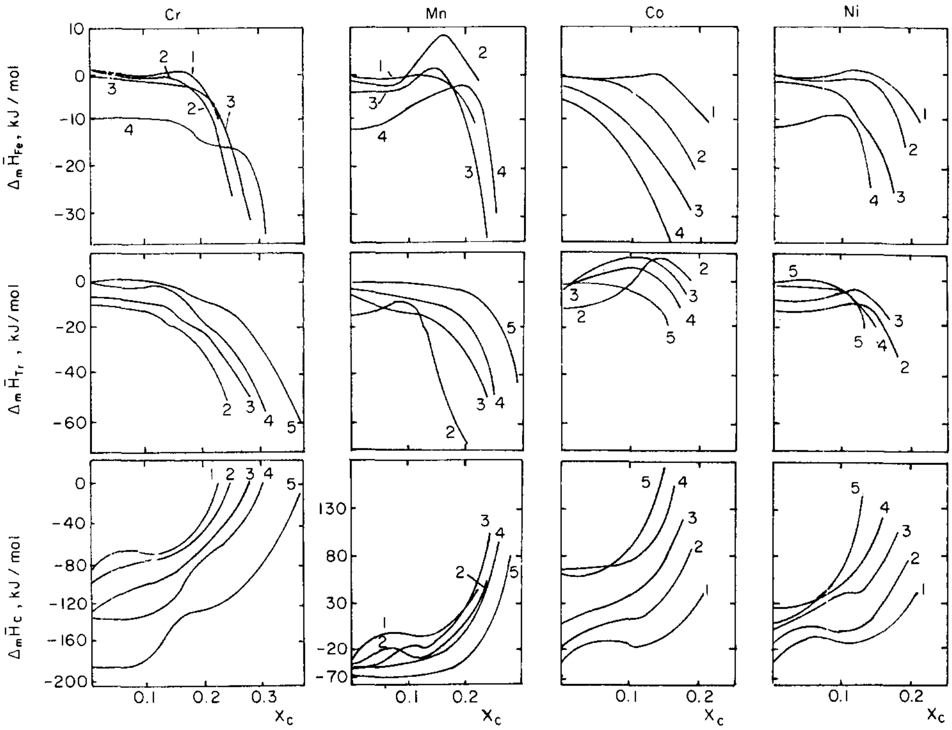

Fig. 5. Concentration dependence of the partial enthalpies of mixing of iron (upper row), 3d transition metals (middle row) and HSL carbon (lower row) in ternary Tr–Fe–C systems for ray sections with the ratio x_{Tr}/x_{Fe}: curve 1, 0/1.0; curve 2, 0.25/0.75; curve 3, 0.5/0.5; curve 4, 0.75/0.25; curve 5, 1.0/0.

mainly by the coordination number of the solvent as observed for liquid alloys of 3d metals with carbon.

Thus the correlation of the thermodynamic function of mixing with the short-range order parameters explains the nature of the studied melts.

4. Thermochemistry of ternary melts

4.1. Ternary melts of 3d metal with iron and carbon

The partial and integral enthalpies of mixing for liquid Fe–Mn–C, Fe–Co–C and Fe–Ni–C were determined at 1900 ± 10 K; the Fe–Cr–C system was investigated in the temperature range 1900–2160 K [46, 68]. As the thermodynamic properties of binary Fe–Cr, Fe–Mn, Fe–Co and Fe–Ni melts have been studied recently in detail, we selected the most reliable data [14, 69–71] of the integral enthalpies of mixing to calculate the thermal equivalent of the calorimeter.

The partial enthalpies of mixing of HSL carbon in these ternary systems are shown in Fig. 5. For many melts, at low carbon concentration, the dependences of the enthalpies may be described with a simple dilute solution model; the sharp changes in the concentration dependences indicate the presence of a microheterogeneous structure for several ternary liquid alloys, as mentioned previously for the binary systems Fe–C and Cr–C. However, an increase in the second 3d metal concentration to more than 30 at.% promotes further homogenization of the melts.

The projection of the isoenthalpy sections of the integral mixing enthalpy surfaces for the mentioned liquid alloys on the concentration triangles is given in Fig. 6. This function indicates the existence of attractive forces between unlike atoms ($\Delta_m H < 0$). The cobalt-rich region in the Fe–Co–C system, where athermal solutions exist ($\Delta_m H = 0$) and repulsive forces take place ($\Delta_m H > 0$), is an exception.

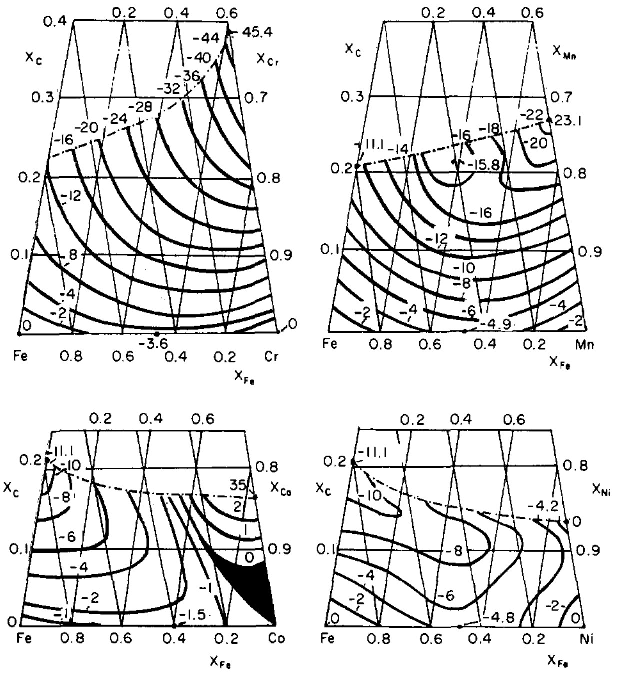

Fig. 6. Integral enthalpies of mixing (kJ mol^{-1}) of liquid components in ternary Tr–Fe–C systems.

4.2. Ternary 3d metal–silicon–carbon systems

The mixing enthalpies of the ternary liquid alloys of Mn(Fe, Co, Ni) with silicon and carbon at 1900 ± 10 K [72–74] and Cr–Si–C at 2160 ± 15 K [75] were studied over the concentration regions corresponding to the existence of homogeneous solutions. The partial enthalpies of mixing are presented in Fig. 7. The ternary melts studied may be subdivided into two groups, determined from the ray section in the Gibbs–Rosebohm concentration triangle. This ray joins the point of pure carbon with the concentration of the binary Tr–Si melt which has the minimal integral enthalpy of mixing. It should be noted that there are some distinguishing features in the melt behaviour caused by the equilibrium of the liquid with graphite (in the 3d metal-rich melts) the liquid silicon carbide equilibrium (in the silicon-rich region). The first equilibrium occurs when the carbon atoms are introduced into a short-range medium, but this effect is significantly limited by the strong interaction of the 3d metal with silicon causing a sharp increase in the partial enthalpy of mixing of HSL carbon (the last to saturate within the melt). The mixing of carbon with the silicon-rich melt shows that the substitutional type of interaction actually exists; however, there is a slight difference between the bonding energy in homogeneous Si–C solution and in crystalline silicon carbide. Therefore, the partial enthalpies of the components do not depend on the carbon content.

In Fig. 8, the projection of the isosections of the integral enthalpy of mixing surfaces on the concentration triangles is given. These systems, in general, possess significant negative values of the enthalpy of mixing.

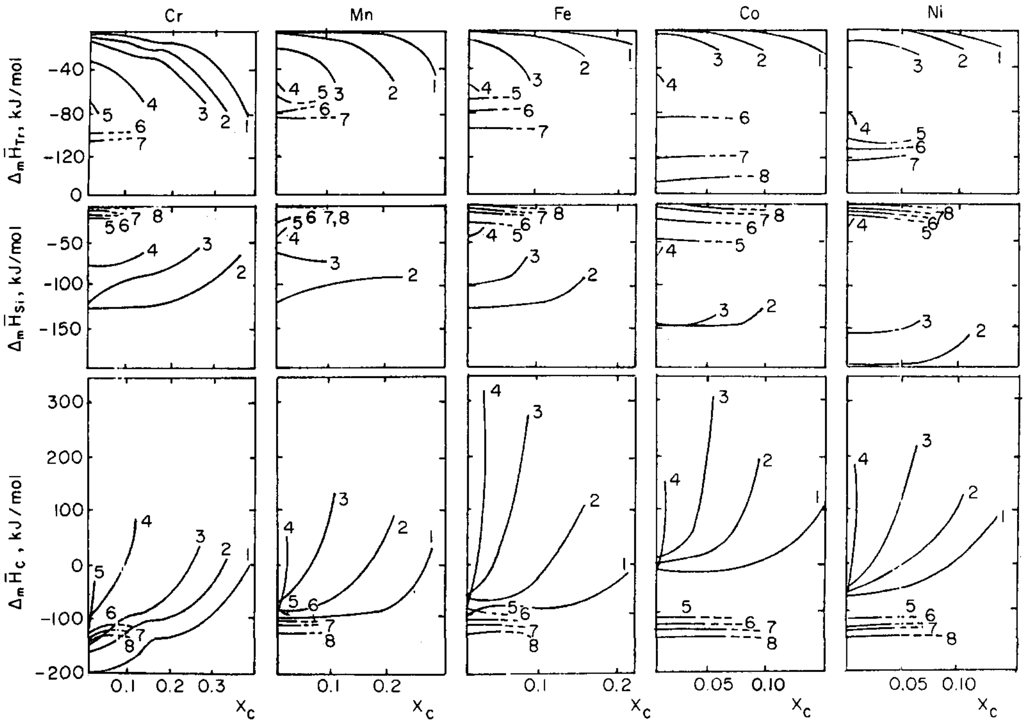

Fig. 7. Concentration dependence of the partial enthalpies of mixing of liquid 3d transition metals (upper row), silicon (middle row) and HSL carbon (lower row) in ternary Tr–Si–C systems for ray sections with the ratio x_{Si}/x_{Tr}: curve 1, 0/1.0; curve 2, 0.1/0.9; curve 3, 0.2/0.8; curve 4, 0.33/0.67; curve 5, 0.5/0.5; curve 6, 0.67/0.33; curve 7, 0.82/0.18; curve 8, 1.0/0.

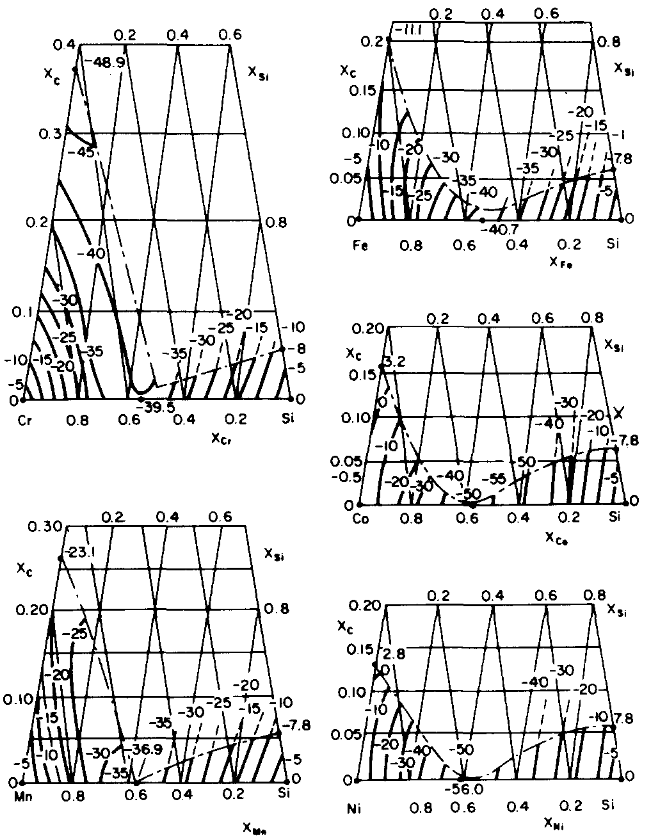

Fig. 8. Integral enthalpies of mixing (kJ mol^{-1}) of liquid components in ternary Tr–Si–C systems.

Only two systems (Co–Si–C and Ni–Si–C) show narrow fields where the enthalpies take a positive value at the 3d metal-rich composition range, approaching the solution saturated with carbon.

4.3. Ternary Tr–B–C systems

Ternary melts of 3d transition metals with the metalloid elements boron and carbon may be used in the synthesis of amorphous materials having a zero value of the magnetostriction [76]. In recent years, Rongxian *et al.* [77] have reported the thermodynamic activity data; however, the measurements in such melts were only obtained for the carbon-saturated concentration region. We measured the partial and integral mixing enthalpies in these liquid 3d metal alloys from chromium to nickel (Fig. 9) [78–80].

The integral enthalpies of mixing (Fig. 10) for systems with constant metalloid content show that the largest exothermic effect is observed for the Cr–B–C melt whereas the smallest exothermic effect is found in the Co–B–C melt. These show positive and zero values of $\Delta_m H$ at some cobalt-rich concentrations.

4.4. Ternary Tr–Si–B melts

Tr–Si–B melts are used for the production of soft magnetic amorphous alloys. Results of calorimetric measurements for these alloys are presented in refs. 81–84. The partial enthalpy of mixing for Si–B melts

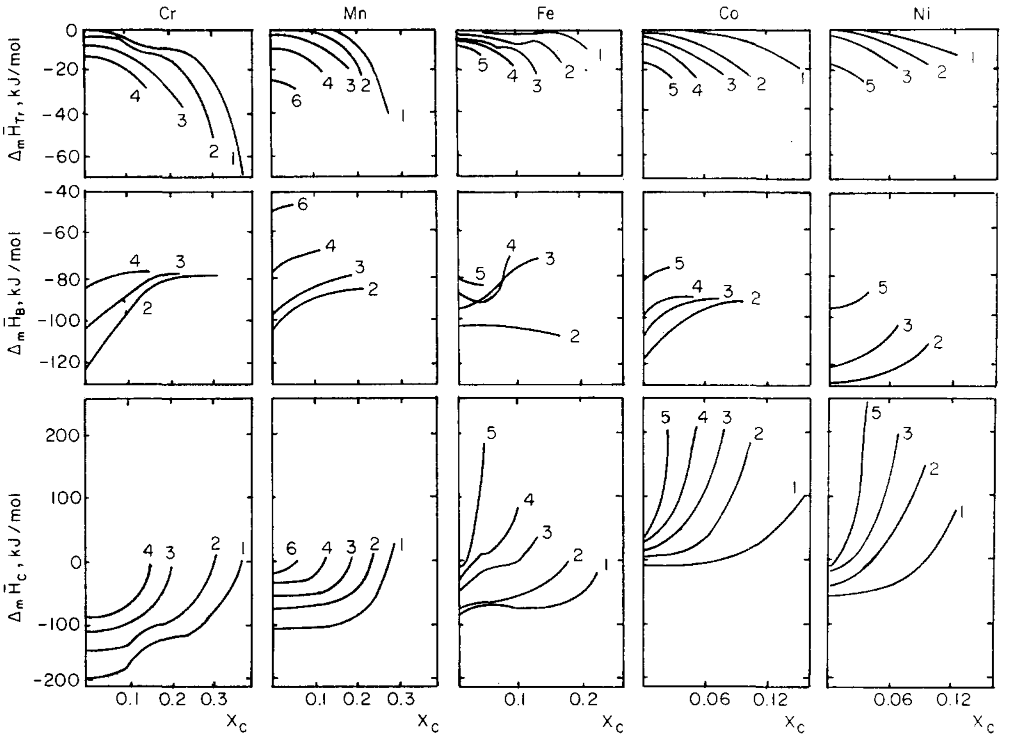

Fig. 9. Concentration dependence of the partial enthalpies of mixing of liquid 3d transition metals (upper row), HSL boron (middle row) and HSL carbon (lower row) in ternary Tr–B–C systems for ray sections with the ratio x_B/x_{Tr}: curve 1, 0/1.0; curve 2, 0.1/0.9; curve 3, 0.2/0.8; curve 4, 0.25/0.75; curve 5, 0.33/0.67; curve 6, 0.4/0.6.

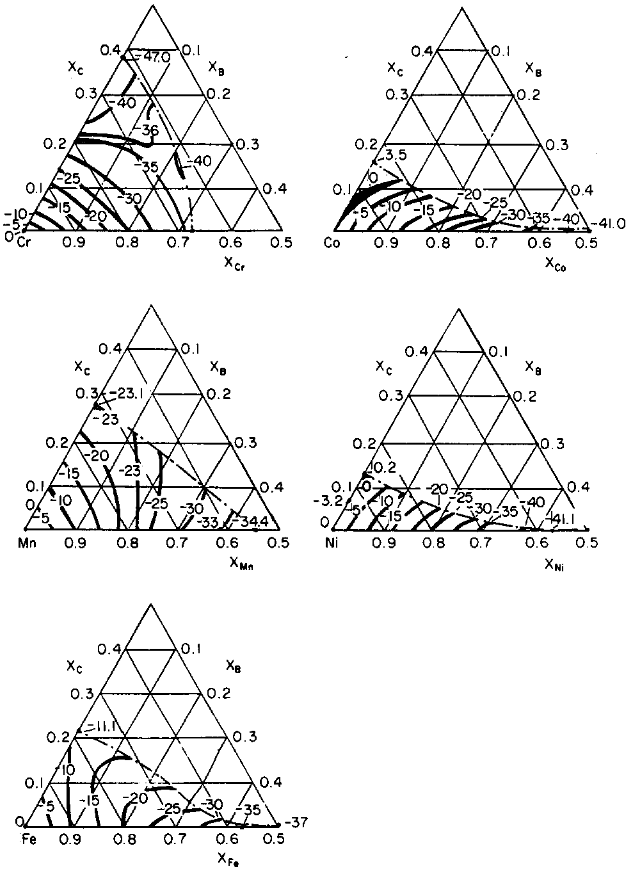

Fig. 10. Integral enthalpies of mixing (kJ mol^{-1}) of liquid components in ternary Tr–B–C systems.

decreases from 30±10 kJ mol^{-1} to −63±5 kJ mol^{-1}. This effect seems to be associated with the formation of associates such as Si_2B in liquid alloys. The effect of the microheterogeneous structure of the ternary liquid alloys Fe–Si–B and Cr–Si–B (as well as the recently studied Fe–B and Cr–B) on the partial enthalpies is shown in Fig. 11. At high concentrations of silicon, the horizontal portion tends to move to a lower content of boron confirming that silicon takes part in the formation of three-component associates. A similar effect on the enthalpies was found for each Tr–Si–B system, confirming the formation of borides and silicoborides when the concentration approaches the phase separation limits.

The isolines of the integral enthalpy of mixing in liquid Tr–Si–B alloys are given in Fig. 12. These alloys show a strong exothermic effect of formation which is larger than for the other liquid alloys discussed; this reflects significant changes in the energetic spectra of the valence electrons of pure components on interaction. The minimum value in Mn-, Fe-, Co- and Ni-based alloys corresponds to the binary composition Tr–Si, whereas in the Cr–Si–B system it corresponds to the ternary composition $Cr_{0.53}Si_{0.37}B_{0.10}$.

4.5. *Regularities in infinitely dilute solutions*

Limiting values of the enthalpies of mixing of boron and carbon in the initial binary melts Tr–Fe, Tr–B and Tr–Si are presented in detail in Fig. 13. The melts

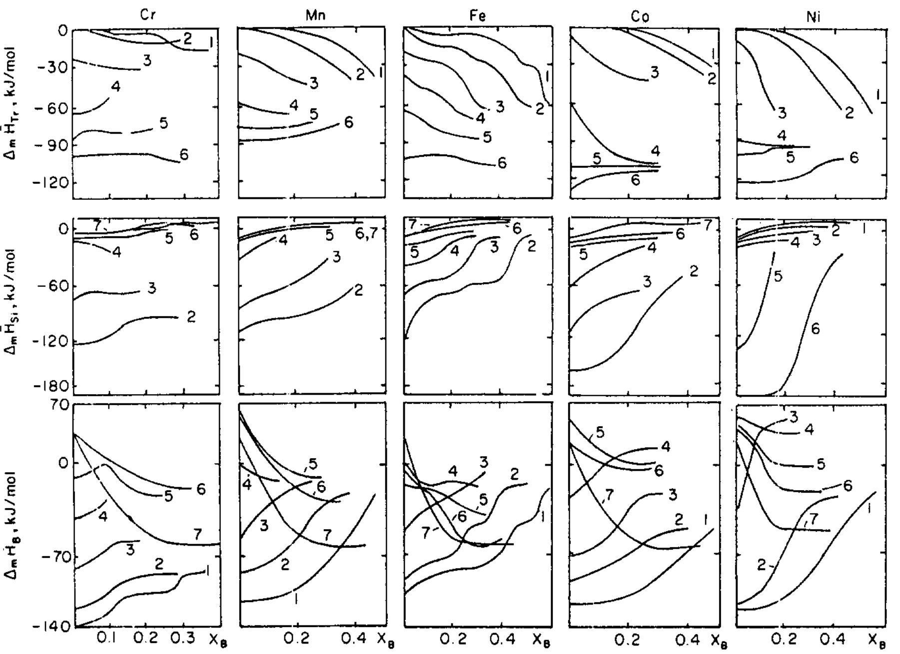

Fig. 11. Concentration dependence of the partial enthalpies of mixing of liquid 3d transition metals (upper row), silicon (middle row) and HSL boron (lower row) in ternary Tr–Si–B systems for ray sections with the ratio x_{Si}/x_{Tr}: curve 1, 0/1.0; curve 2, 0.15/0.85; curve 3, 0.33/0.67; curve 4, 0.5/0.5; curve 5, 0.67/0.33; curve 6, 0.83/0.17; curve 7, 1.0/0.

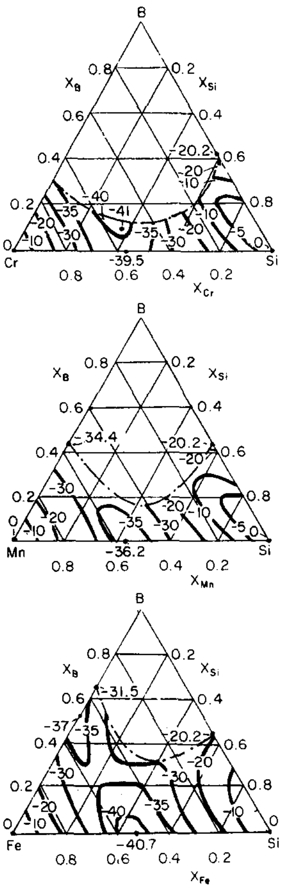

Fig. 12. Integral enthalpies of mixing (kJ mol^{-1}) of liquid components in ternary Tr–Si–B systems.

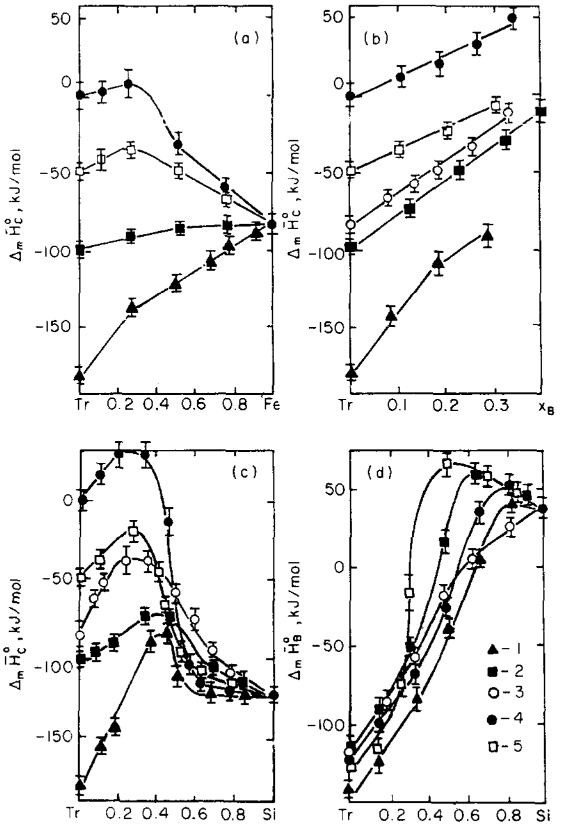

Fig. 13. Concentration dependences of the limiting enthalpies of mixing of HSL carbon (a, b, c) and boron (d) in binary alloys: (a) Tr–Fe; (b) Tr–B; (c) and (d) Tr–Si. 1, Cr; 2, Mn; 3, Fe; 4, Co; 5, Ni.

studied possess a common feature: the $\Delta \bar{H}_i^\circ$ values over the wide concentration regions rich in both first and second components show a linear concentration dependence within the error bars. However, the extension of these portions does not coincide with the analogous regions in binary systems, for which Henry's law applies. As can be seen from Fig. 13, between the two linear portions, a region exists where the functions depend strongly on concentration and the maximal variation of $\Delta_m \bar{H}_i^\circ$ correlates with the minimal value of $\Delta_m H$ in the initial binary system.

The Tr–Si systems show strong interaction between unlike atoms and the dependences are displayed more sharply than for weakly interacting Tr–Fe systems. For Fe(Mn, Co, Ni)–B solutions, the $\Delta_m \bar{H}_C^\circ$ values vary almost linearly *vs.* boron concentration up to 30–40 at.% B. It is difficult to assume the variation in these data at higher boron contents because of the low solubility of carbon at higher concentrations of boron.

The limiting partial enthalpies of mixing in the systems studied generally show a positive deviation from the weighted sum values. This behaviour indicates that the interaction energy in binary liquid alloys of unlike atoms exceeds the interaction energy between like atoms. This effect prevents the graphite and boron dissolution process.

Finally, the complex dependences of $\Delta_m \bar{H}_i^\circ$ obtained even for the weakly interacting liquid alloys (Fig. 13(a)) show that the simple models of Kohler [85], Bonnier and Gaboz [86] and Toop [87], usually applicable for the description of ternary melts using the thermodynamic parameters from the corresponding binary systems, are incorrect for these systems.

5. Glass-forming tendency in Tr-Si-B and Tr-B-C alloys

The amorphous metallic state is known to be greatly influenced by the liquid state. The existence of atoms, associated into small groups within the total volume of liquid alloys, results in glass-forming ability at high cooling rates. In recent years, several approaches for the estimation of glass-forming tendency (GFT) have been developed. Some consider the peculiarities of metallic systems (eutectics, supercooling ability, etc.) and estimate reliably the possibility of formation of amorphous alloys. From the thermodynamic point of

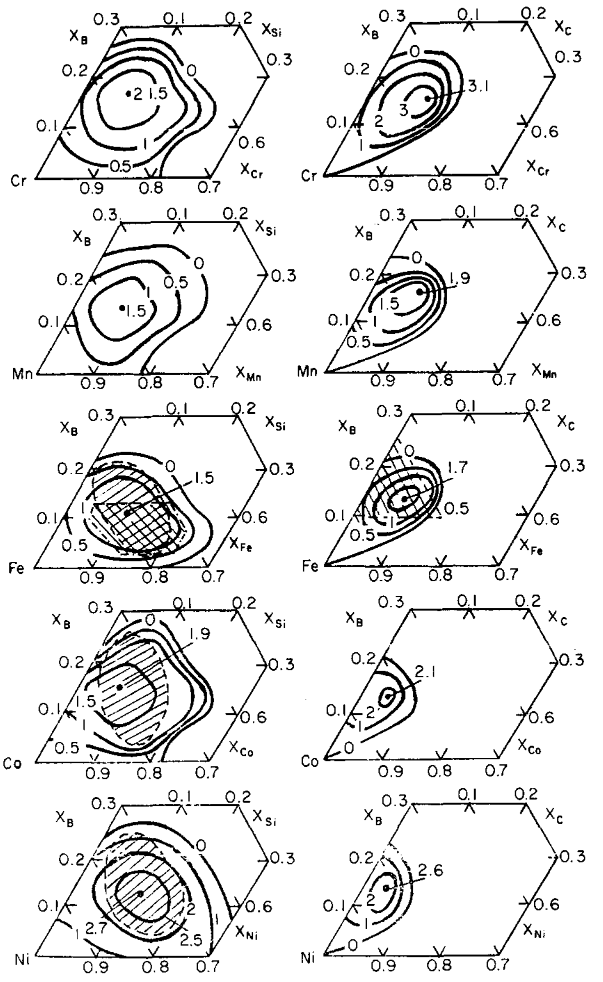

Fig. 14. Glass-forming tendency of Tr–Si–B (left column) and Tr–B–C (right column) melts (in shaded regions the metallic glasses were obtained by the splat cooling technique with a thickness of more than 50 μm [76]).

view the model propounded by Zielinski and Matyja [88] seems to be of special interest. The model developed for binary systems using the theory of nucleation and crystal growth processes, takes into account the strong attractive interactions between unlike particles responsible for cluster formation in liquid alloys. Experimental research by Biletski *et al.* [89] has shown that this model may be applied to the calculation of GFT in ternary melts. For this purpose the principal equation [88] may be written as

$$\mathrm{GFT} = -\log\left[1 - \frac{2\Delta H(x,y)}{(x_a+y_a)RT}\right] - 0.434\left[\frac{\Delta H(x,y)}{(x_a+y_a)RT} + \left(\frac{x+y}{x_a+y_a}\right)(m+n+l)\log\left(\frac{N}{m+n+l}\right)\right]$$

where $\Delta H(x, y)$ is the integral enthalpy of mixing in ternary liquid alloys, x and y are the concentrations of the second and third components (the latter refers to metalloid elements in this case) respectively, x_a and y_a are the concentrations corresponding to the formation of the structural group which promotes nucleation, m, n and l are the stoichiometric coefficients of the structural group, R is the gas constant, T is the absolute temperature (in ref. 88 it was assumed that a liquid can be supercooled about 200 K below the solidus temperature in binary systems; however, in the present paper, for all systems, T was taken to be equal to 1000 K) and N is Avogadro's number.

The concentration dependences of the enthalpies of mixing, described earlier in this paper, allow the GFT for the liquid systems Tr–Si–B and Tr–B–C, which are important in the metallic glasses industry, to be calculated [76]. The stoichiometric indices of the complexes in Tr–Si–B melts were determined from the partial enthalpy curves and from the location of the minimum excess integral entropy. The complex itself was considered to act as an embryo of crystallization (preventing amorphization) if the solid intermetallic compound at the corresponding concentration point exists according to the phase diagrams of stable and metastable equilibrium. If not the complex of given stoichiometry may increase the glass-forming ability. In ternary liquid Tr–B–C alloys, in the carbon-rich region ($x_C/x_B > 0.5$), the graphite groups are considered to act as embryos when approaching the melt–graphite equilibrium line; the values of x_a and y_a depend on the location of this line in the concentration triangle. Thus the calculations assume that the characteristic properties of the melts are the degree of component interaction, the existence of complexes in the liquid state and the stoichiometric phases in the solid state. The calculated GFT surface in a certain concentration region shows a maximum which indicates the most favourable concentration for the formation of amorphous alloys.

The projection of the GFT surface isosections (positive values) is given in Fig. 14. There is satisfactory agreement between the estimated results and the experimental literature data concerning the concentration range within which amorphous alloys are obtained in the Fe–Si–B, Co–Si–B, Ni–Si–B and Fe–B–C systems, corresponding to the formation of thick (more than 50 μm) amorphous metallic ribbons [76].

Finally, despite the progress in theoretical calculations, direct calorimetric measurements remain the most reliable source of thermochemical information in ternary systems. A combination of experimental data and theoretical models allows glass-forming ability to be estimated in amorphous alloys of 3d transition metals with metalloid elements.

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