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MODERN METHODS IN HIGH TEMPERATURE CALORIMETRY

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High temperature calorimetric methods used in metallurgy are discussed. Two types of isoperibolic mixing calorimeters are presented. They allow to determine directly the enthalpy of mixing of liquid alloys as a function of concentration and temperature and to measure the derivative as a function of concentration for temperatures up to 1300 K and 2000 K, respectively. A high temperature solution calorimeter in which a liquid metal or alloy is used as the bath (maximum temperature 1800 K) can be used to determine the heat of formation of solid alloys and to measure the partial enthalpy of mixing at infinite dilution. With a drop calorimeter it is possible to measure the thermodynamic properties of highly reactive alloy systems. Thermodynamic measurements of high melting refractory metals and alloys for temperatures up to 4000 K can be achieved with levitation calorimetry.

The calorimetry generally provides important data of thermophysical properties of gases, liquids and solids. Several books and review articles have been published on calorimetry. [e.g. 1–3]. This paper is concerned with methods of high temperature calorimetry in metallurgy. The experimental investigation of thermodynamic properties of alloys is the basis to under-

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stand the energetics of alloy formation and to solve technological problems of alloy production and application. Reviews on the development of calorimetry of alloy thermochemistry have been presented previously [4÷6]. Recent progress in this area has mainly been achieved in application of well known principles resulting in improved accuracy of the measurements and extended scope. This paper presents several exemplary calorimetric methods in detail and representative experimental results.The important thermodynamic properties which can be obtained directly by calorimetry are: The integral and partial enthalpies of formation as a function of concentration and temperature for liquid and solid alloys. They can also be determined from the temperature dependence of the partial free energy of formation obtained, for example, by partial vapor pressure measurements or e.m.f. measurements on suitable galvanic cells. The precision, however, is in general relatively poor. The optimal assesment of thermodynamic properties of an alloy is obtained via the free energy determined from the mentioned measurements and the enthalpy of formation obtained by calorimetry.

Mixing calorimeter

For the determination of integral enthalpies of mixing (ΔH) of liquid alloys a calorimeter which operates isothermally is especially suitable. The experimental design described in the following (Fig. 1) allows for a direct measurement of ΔH on mixing of the liquid components at temperatures up to 1300 K. Two crucibles (1) (2) are necessary which contain initially two liquid components at the measuring temperature. Both crucibles are accomodated by a stainless steel block consisting of several massive segments (3). Due to the massive calorimeter block temperature gradients occuring in the central part of the long furnace (4) are minimized. The temperature gradient inside the furnace can already be reduced by three heating coils (Kanthal) which are arranged and regulated separately. Temperature equality between upper and lower crucible after stabilization of the system is controlled by thermocouples (5). A stirrer (6) guarantees for a complete and rapid mixing of the components. The temperature change occuring during the mixing process is determined by a Ni-NiCr thermopile (7) directly

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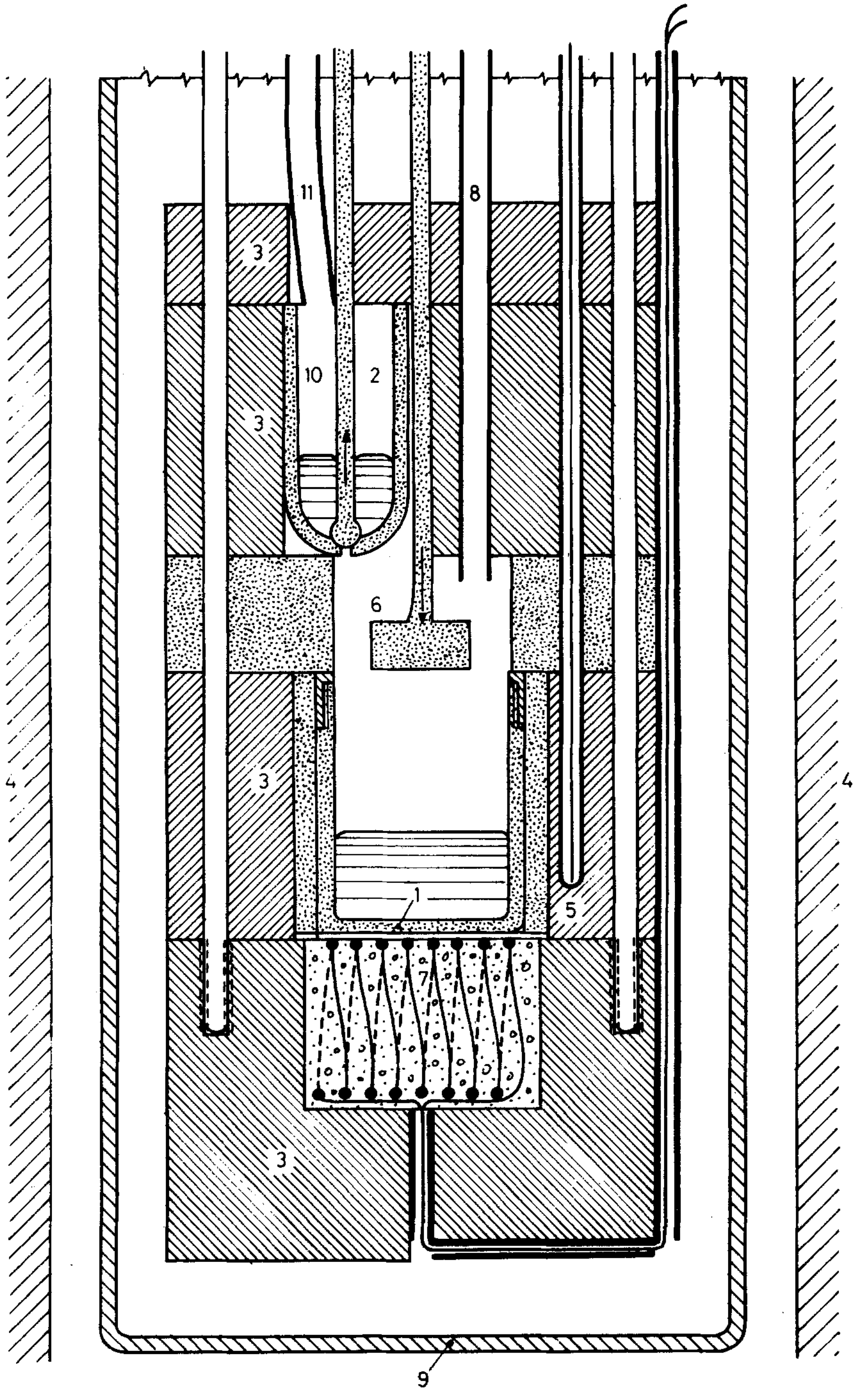
Fig. 1 Calorimeter for determination of enthalpies of mixing as a function of concentration and temperature: 1) reaction crucible 2) melting crucible 3) stainless steel blocks 4) furnace 5) thermocouple 6) stirrer 7) thermopile 8) calibration tube 9) reaction tube 10) stopper 11) addition tube.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mounted below the lower (reaction) crucible. The area under the ΔT-time curve is a measure for the heat effect of the reaction. Calibration can be done alternatively by addition of cylindrical samples of the bath material before starting a series of measurements or by addition of metal samples (e.g. Ta, Mo), which do not react with the alloy melt, between the additions of the second components during the measurement. Calibration samples are droped down the calibration tube (8) into the reaction crucible. It is possible to achieve a standard error of ± 1% for the calibration factor. The choice of the material for the crucibles depends on the alloy system investigated (e.g. alumina, graphit, boron nitride, iron). The calorimeter block is suspended in a reaction tube (9) which is closed below and on top of the calorimeter the supporting connections are situated. With a reaction tube made of stainless steel it is possible to keep the calorimeter free of oxygen by evacuation, heating out and flushing with argon before the measurement starts under argon atmosphere. Three radiation shields are situated above the calorimeter block to reduce fluctuations of the argon gas and heat loss by radiation. The samples are added under a slight argon overpressure using a quartz valve chamber at the top of the addition and calibration tube (11). An advantage of the construction shown in Fig. 1 is, that the upper crucible (2) can be refilled after any measurement. The orifice in the crucible is closed by a stopper (10) and the second component is added through the addition tube. For several alloy concentrations ΔH can be determined in this way by a single experimental run by summation of all previous thermal effects. If the change in concentration is small for each successive step (i.e. < 1 at.%), also $\mathrm{d}\Delta H(x)/\mathrm{d}x$ can be determined in good approximation by

$$\frac{\mathrm{d}\Delta H(x)}{\mathrm{d}x}\left(x_1+\frac{\Delta x}{2}\right)=\frac{\Delta H_2\,(x_1+\Delta x)-\Delta H_1\,(x_1)}{\Delta x} \qquad (1)$$

The $\Delta H\,(x)$ and the $\mathrm{d}\Delta H\,(x)/\mathrm{d}x$ curve for liquid In-Sb alloy [7] is shown in Fig. 2 a, b, for example. From $\Delta H\,(x,T)$ measurements also the values for the mean excess molar heat ΔC_p can be derived via

$$\Delta\bar{C}_\mathrm{p}\,(x,\bar{T})=\frac{\Delta H(x,T_2)-\Delta H(x,T_1)}{T_2-T_1} \qquad (2)$$

whith $\bar{T}=(T_2-T_1)/2$. Fig. 2c shows $\Delta\bar{C}p$ curves for the same alloy [8].

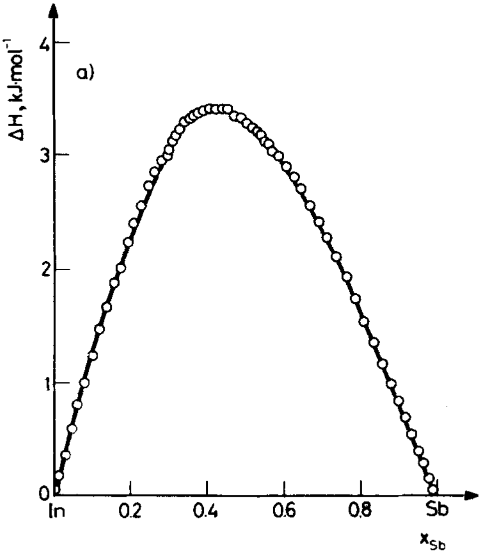

Fig. 2a Enthalpy of mixing of liquid In-Sb alloys at 953 K [7].

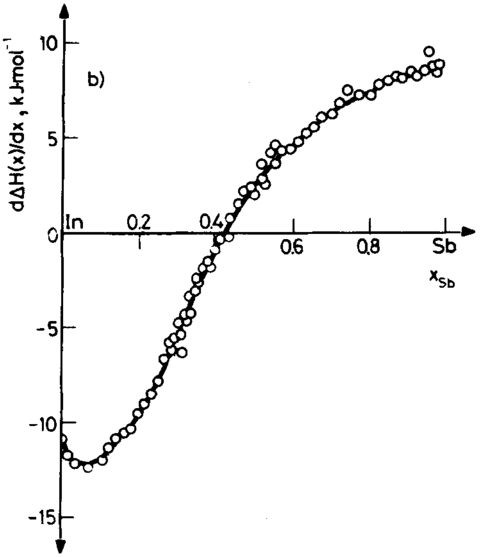

Fig. 2b Derivative of the enthalpy of mixing of liquid In-Sb alloys at 953 K [7].

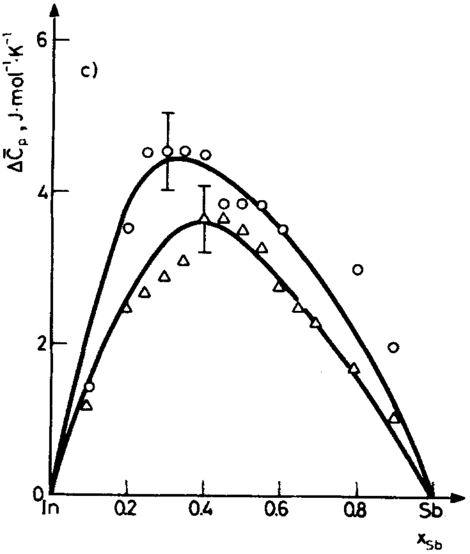

Fig. 2c Mean excess molar heats of liquid In-Sb alloys [8] (o at 971 K; Δ at 1158 K).

Experimental information for ΔC_p and $\mathrm{d}\Delta H(x)/\mathrm{d}x$ are particularly useful for the investigation of chemical short range order tendencies in liquid alloys with compound forming tendencies [18]. Even in systems with weak compound forming tendencies such as in Sb–Sn alloy melts, due to the small ΔH-values ($\leqslant -1.5$ kJ mol^{-1}), $\Delta \bar{C}_p$-values can be obtained (Fig. 3). The values of $\Delta H/x_{\mathrm{Sb}}x_{\mathrm{Sn}}$ shown here demonstrate also the deviations from a regular solution behaviour.

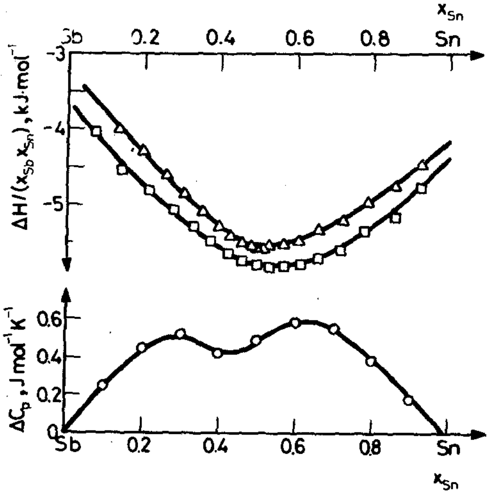

Fig. 3 Mean excess molar heats of liquid Sb-Sn alloys at 988 K and $\Delta H(x,T)/x_{\mathrm{Sb}}x_{\mathrm{Sn}}$ (o at 968 K; Δ at 1108 K) [9].

If the components of an alloy have a high vapor pressure above the melting point and if they are especially sensitive to oxygen like e.g. Li, Mg, Ca or Sr, a special design of the crucible has been used [10]. Two opposing Fe-crucibles tightened together via a screw thread act as the reaction crucible are sealed off with tantalum foils and oxidation as well as vaporization of the components during sample handling outside the argon box and the heating process of the calorimeters can essentially be avoided. By removing the tantalum foils with the strirrer the mixing process is started.

Solution calorimeter

The enthalpy of formation (ΔH^f_{AxBy}) of solid alloys can be measured by solution calorimetry in an analogous manner like the determination of ΔH using the same calorimeter. At room temperature the solid alloy samples and those of the components are droped down the calibration tube into a given bath (e.g. consisting of liquid aluminium). The experimental results for the thermal effects of dissolution ΔH^E extrapolated to $x_{\mathrm{Al}} = 1$ to obtain values of the thermal effects for infinite dilution $\Delta H^{E,O}$. The ΔH^f values of the compounds at room temperature are calculated directly from these $\Delta H^{E,O}$ values

$$\Delta H^f_{A_xB_y} = x\Delta H^{E,O}_A + y\Delta H^{E,O}_B - \Delta H^{E,O}_{A_xB_y} \qquad (3)$$

The partial enthalpies of mixing at infinite dilution on the liquid components A and B in the liquid bath metal $\Delta \bar{H}^o_{A,B}$ can obtained by subtracting the heat content of the elements between room temperature and the temperature of the solution experiment from $\Delta H^{E,O}_{A,B}$. Table 1 shows results for some technologically important intermetallic phases with a very low standard error.

Table 1 Heat of formation of Ni-Al and Fe-Al and Fe-Si intermetallic phases at room temperature and partial enthalpies of mixing at infinite dilution of Ni, Fe and Si in liquid Al [11].

	ΔH^f kJ mol^{-1}	$\Delta \bar{H}^o$ kJ mol^{-1}
$Fe_{0.75}Al_{0.25}$	-14.1 ± 1.1	$\Delta \bar{H}^o_{\mathrm{Ni}} = -153.3 \pm 1.1$ T = 1023 K
$Ni_{75}Al_{25}$	-37.3 ± 2	$\Delta \bar{H}^o_{\mathrm{Fe}} = -123.3 \pm 1.6$ T = 1073 K
$Ni_{76}Al_{24}$	-37.6 ± 1.7	$\Delta \bar{H}^o_{\mathrm{Si}} = -14.2 \pm 0.4$ T = 1073 K
Fe_3Si	-25.8 ± 2	

A schematic construction of a solution calorimeter operating up to temperatures of 1800 K is shown in Fig. 4. Sample addition is carried out inside the calorimeter in vacuum or under argon. A revolving container with 36 holes is used for addition of the calibration samples and of the components or the compound, respectively. The molybdenum calorimeter block (1) is suspended in an alumina reaction tube (7) both (1) and (7) being put in the temperature constant zone of a rhodium wound furnace (8). The PtRh6–PtRh30 thermopile (2) and an alumina reaction crucible (2) complete the calorimeter.

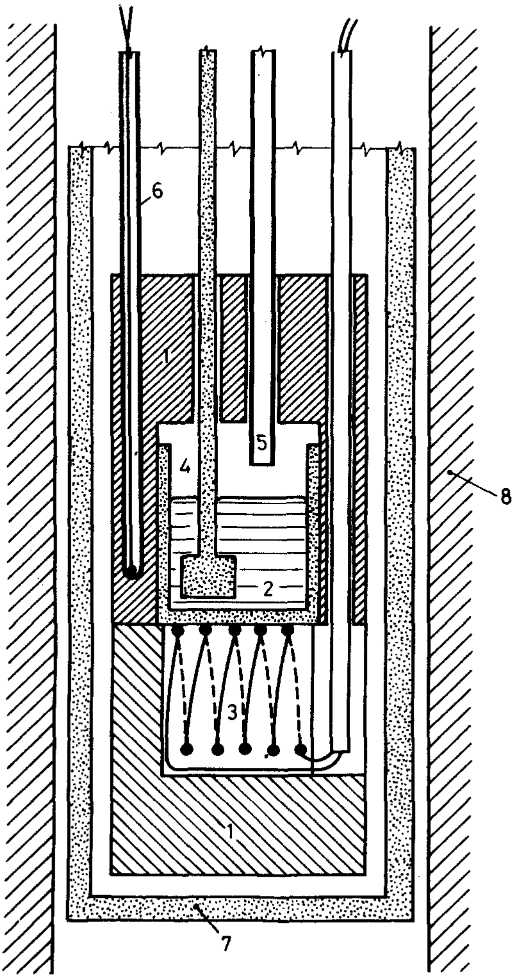

Fig. 4 High-temperature solution calorimeter: 1) moliybdenum blocks 2) reaction crucible 3) PtRh6-PtRh30 thermopile 4) stirrer 5) addition tube 6) thermocouple 7) Al_2O_3 reaction tube 8) rhodium furnace.

At high temperatures a liquid alloy can also be used as a bath for the solution of high melting compounds and components. Pure metals are often not useful at high temperatures because of possible high vapor pressure involved and/or because of small solubilities of component and compounds. For the determination of ΔH^f for Ni_2Ta and CrNiTa a liquid $Cr_{50}Ni_{50}$ alloy at 1700 K was used as the bath [12]. Calibration was done by adding alternatively Cr- and Ni-samples. The change of $\Delta H(x)$ for liquid CrNi alloys is very small compared to the heat content of the calibration samples. The results obtained from Eq. (3) are ($\Delta H^f_{\mathrm{CrNiTa}} = -17.9 \pm 2$ kJ mol^{-1}, $\Delta H^f_{\mathrm{Ni_2Ta}} = -35.5 \pm 1.4$ kJ mol^{-1}).

With additional results for the enthalpy of melting ΔH^m of a intermetallic phase it is possible to calculate additonally ΔH of the liquid alloy at the melting temperature of the congruently melting compound T^m for the composition of the compound

$$\Delta H(x,T^m) = \Delta H^f_{A_xB_y}(T^m) + \Delta H^m_{A_xB_y} - x\Delta H^m_A(T^m) - y\Delta H^m_B(T^m) \quad (4)$$

Where $\Delta H^m_{A,B}$ are the extrapolated enthalpies of melting at T^m. The ΔH value obtained from Eq. (4) allows for checking the results obtained by measuring ΔH directly as e.g. with the calorimeter given in Fig. 1.

High-temperature mixing calorimeter

A high temperature calorimeter, based on the principles of quantitative differential analysis for measurint ΔH of liquid alloys, has recently been improved for measurements up to 1900 K [13]. The construction of the calorimeter is shown schematically in Fig. 5. The high temperatures are obtained by using a molybdenum short circuit heater. The heater and the calorimeter componenets are mounted within a water cooled vacuum container (7). The operation principle is similar to that of the calorimeters described above. Two revolving containers with 48 holes provide for the addition of the samples. Three thermocouples (PtRh6–PtRh30) control the temperatures i.e. one in the reaction crucible, another for the reference in the molybdenum block and the third in the upper crucible. The measurements must be carried out in vacuum. Data of ΔH for liquid Fe-Sn alloys obtained at 1820 K are shown in Fig. 6. The positive values for ΔH show the tendency to segregate these alloys in the liquid state. A fit of the data can be obtained via the quasichemical approximation by replacing mole fractions by atomic surface area concentrations [13].

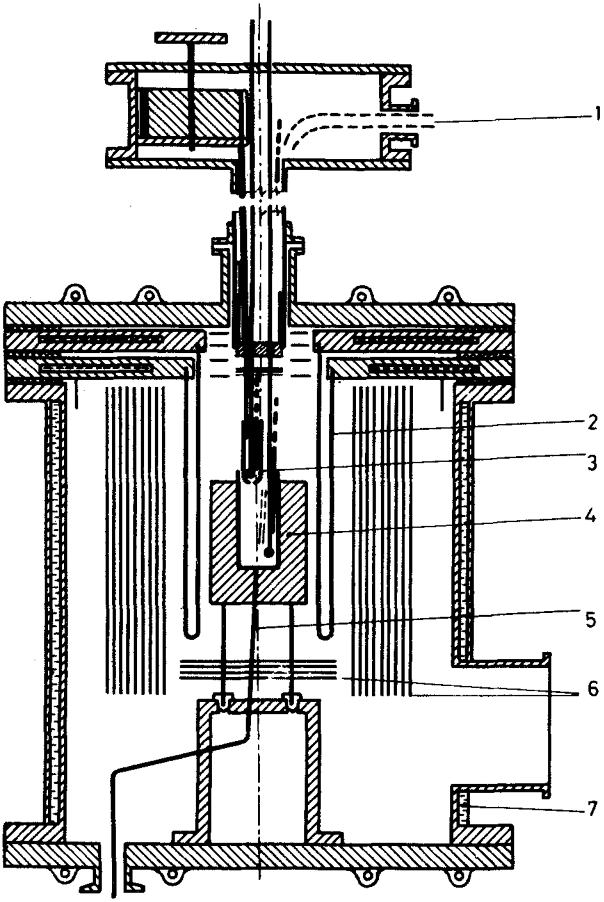

Fig. 5 High-temperature calorimeter for determination of enthalpy of mixing at temperatures up to 1900 K [13]. 1) sample addition 2) molybdenum short circuit heater 3) addition crucible with stopper 4) molybdenum block with reaction crucible, stirrer and thermocouple 5) reference thermocouple 6) radiation shields 7) water cooled vacuum container.

Drop calorimetry

Direct measurement of $\Delta H\ (x,T)$ by mixing of pure liquid components is often not possible if one of the components is e.g. an alkali metal due to the high vapor pressure and the high reactivity of these metals. By employing drop calorimetric heat content measurements $\Delta\bar{C}_p$ and ΔH^m can

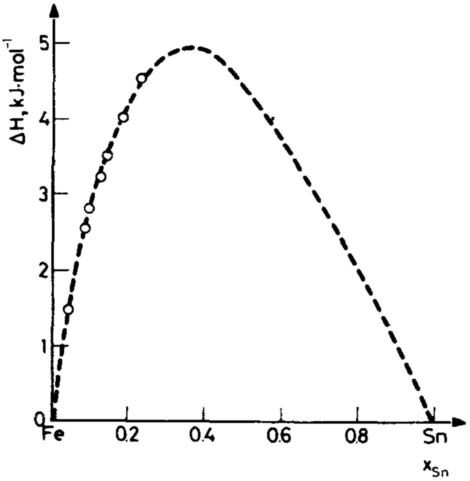

Fig. 6 Enthalpy of mixing of liquid Fe-Sn alloys at 1820 [13].

be determined. This, however, requires that the liquid alloys always reach the same final state when they are cooled to room temperature. According to the phase diagram this condition applies only to the composition of congruent melting compounds. The experimental apparatus consists basically of a furnace for heating the samples up to the measurement temperature and a calorimeter which operates at room temperature for the heat content measurements. The alloys are contained in tightly closed molybdenum ampules. For the calibration a sample container is filled with tin and this tin sample is measured together with the alloy sample at each temperature [14]. Figure 7 shows the results for the heat contents of Li_7Pb_2 alloy. Using C_p-data for Li and Pb the excess molar heats for liquid Li_7Pb_2 alloys is $\Delta\overline{C}_p = 15.7 \pm 2.4$ J mol^{-1} K^{-1} ($1004 \text{ K} \leqslant T \leqslant 1110 \text{ K}$), which highlights the strong temperature dependence of ΔH for this alloy system. From the ΔH^m value and $\Delta H^f_{Li_7Pb_2} = -31.4 \pm 1.7$ kJ mol^{-1} obtained by solution calorimetry, the value for ΔH calculated with Eq. (4) results in -31 ± 2.5 kJ mol^{-1}. The ΔH value measured by direct mixing of the components amounts to -29 ± 1.4 kJ mol^{-1} [15]. Considering the experimental uncertainties, the comparison shows the internal consistency of ΔH^m, ΔH^f and ΔH obtained by different calorimetric methods.

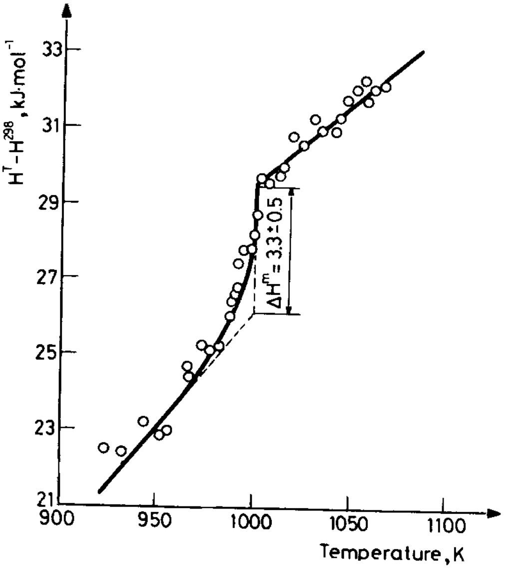

Fig. 7 Heat content of Li_7Pb_2.

Levitation mixing calorimetry

Electrical resistance heating of solid conductors sets an upper temperature limit of about 2000 K for the calorimetric devices of the type considered so far. The use of "levitation calorimetry" which is a levitation melting apparatus with a drop calorimeter has overcome this limit. A metallic specimen is hereby levitated and at the same time heated without any contact by an alternative electromagnetic field. The temperature is measured by using a pyrometer. With this well known technique C_p-values of high melting metals and alloys can be measured in the liquid and solid state. Frohberg *et al.* [16] have developed this method to also measure ΔH and $\Delta\bar{H}_i^0$ of liquid refractory alloys. The specimens to be alloyed are mixed within a levitation coil. A small liquid component is droped onto a different larger liquid component or liquid alloy specimen. From the temperature change of the levitating and alloyed specimen $\Delta\bar{H}_i^0$ or $\Delta H(x)$ can be calculated by using the C_p-values of the components. To mix two liquid components a double levitation coil can be used (Fig. 8) of which the application is expensive and restricted to the choice of the systems. As an alternative a melt-off technique can be used, which includes melting of the base metal and keeping it levitating. A drop of the alloying component is obtained by melting it off a cylindrical solid specimen using induction heating (Fig. 8). Temperature measurements of the melting drop show no deviation from the corresponding melting temperature. A third method is the combination of a solid second component with a drop again in levitating condition. Results obtained for Mo-Si alloys in the temperature range of 2960 to 3224 K are shown in Fig. 9 [17]. The errors for $\Delta H(x)$ and $\Delta \bar{H}_i^o$-values are of the order of 10 to 20%. These methods are limited to systems with metallic solvents showing pronounced exothermal and endothermal reactions.

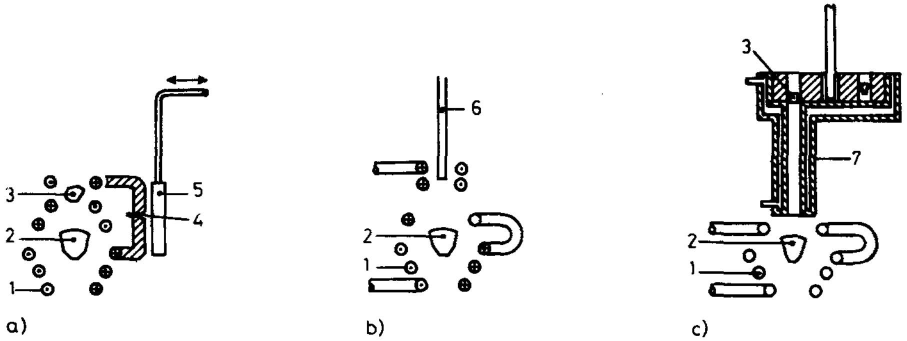

Fig. 8 Experimental set up for combining liquid and solid samples with a liquid solvent [16]: 1) levitation coil 2) liquid solvent 3) second component 4) teflon insulator 5) short circuit bow 6) cylindrical sample 7) water cooled sample magazin.

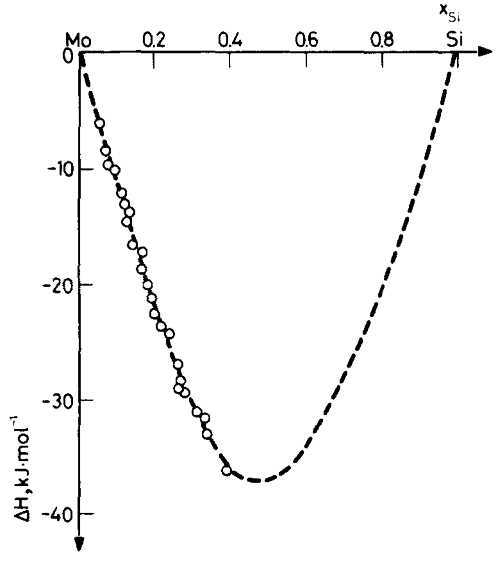

Fig. 9 Enthalpy of mixing of liquid Mo-Si alloys between 2960 K and 3224 K [17].

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Zusammenfassung — Kalorimetrische Hochtemperaturmethoden zur Anwendung in der Metallurgie werden diskutiert. Zwei isoperibole Mischungskalorimeter werden vorgestellt. Sie erlauben die direkte Bestimmung der Mischungsenthalpie flüssiger Legierungen in Abhängigkeit von der Konzentration und Temperatur und ihrer Ableitung nach der Zusammensetzung bei Temperaturen bis 1300 bzw. 2000 K. Ein Hochtemperatur-Lösungskalorimeter, in dem ein flüssiges Metall oder eine flüssige Legierung als Badflüssigkeit dient (Maximaltemperatur 1800 K), kann zur Bestimmung der Bildungswärme fester Legierungen und zur Messung der partiellen Mischungsenthalpie bei unendlicher Verdünnung verwendet werden. Mit einem Einwurf-Kalorimeter können thermodynamische Eigenschaften sehr reaktiver Legierungssysteme gemessen werden. Thermodynamische Messungen schwerschmelzbarer Metalle und Legierungen bei Temperaturen bis 4000 K sind möglich mit der Schwebe-Kalorimetrie.

РЕЗЮМЕ — Обсуждены высокотемпературные калориметрические методы, используемые в металлургии. Представлено два типа изопериболических калориметров, позволяющих непосредственно определять энтальпию смещения жидких сплавов в зависимости от концентрации и температуры, а также измерять концентрационную зависимость ее производной до температур, соответственно, 1300 и 2000 K. Высокотемпературный жидкостной калориметр, где в качестве ванны используется жидкий металл или сплав, может быть использован для определения теплоты образования твердых сплавов и для измерения парциальной энтальпии смещения при бесконечном разбавлении. С капельным калориметром представляется возможным измерять термодинамические свойства очень реакционноспособных сплавов. Термодинамические измерения высокоплавящихся тугоплавких металлов и сплавов могут быть осуществлены метдом поплавковой калориметрии до температуры 4000 K.