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Martin G. Frohberg, Gerhard Betz

SCITRAN
Box 5456
Santa Barbara, CA 93106

National Aeronautics and Space Administration
Washington, D.C. 20546

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By Martin G. Frohberg and Gerhard Betz, Institute for Metallurgy, General Metallurgy - Technical University Berlin*

SUMMARY. A new method was tested for measuring the enthalpies of mixing of liquid metallic alloying systems, involving the combination of two samples in the electromagnetic field of an induction coil. The heat of solution is calculated from the pyrometrically measured temperature effect, the heat capacity of the alloy and the heat content of the added sample. The usefulness of the method was tested experimentally with the iron-copper and niobium-silicon systems. This method should be especially applicable to high-melting alloys, for which conventional measurements have failed, to date.

The immediate calorimetric determination of the enthalpies of mixing of alloy melts requires considerable experimental expense, especially at temperatures above 1000°C. At present the upper limit for such measurements is at 1650°C, conditioned by the limited thermal resistance of the calorimeter's components. Investigations above 1650°C are possible when the alloying process can be carried out without the use of a crucible; for instance, in the magnetic field of an induction coil, or also under weightlessness conditions, with induction, laser or radiation heating [1 - 3]. Using electromagnetic levitation smelting, in principle this


**Numbers in the margin indicate pagination in original foreign text.
temperature range can be extended to above 3000°C. This would facilitate a large proportion of measurements in the liquid state of high melting alloys. Such was the goal in the development of a suitable method.

MEASUREMENT PRINCIPLE

The two alloy partners are combined in a levitation coil in such a manner that the smaller sample (subsequently designated sample 2) is added, as a solid or a liquid, to the larger, suspended and molten sample (solvent; subsequently called sample 1) (Figure 1, below). From the measured temperature change $\Delta T$ of the now alloyed but still levitating sample it is possible to calculate the enthalpy of mixing, with the help of the heat capacities of the pure components. The applicability of the method hinges significantly on the duration of the alloying process, since at these high test temperatures the losses due to radiation are substantial.

Figure 1. Levitation coil with two levitating samples
While corrections are made for such losses, too large a radiative proportion may cause unacceptable errors in the evaluation.

To keep evaluation errors small, the specific test conditions are adapted to the anticipated sign and order of magnitude of the heat of solution. It is hence advantageous to add the alloy partner in the liquid state in the case of endothermal reactions, and as a solid in exothermal reactions. By modifying the added mass, further optimization may be achieved. Keeping these considerations in mind, the following method of operation result:

- combination of two drops,
- combination of a solid with a drop.

A further differentiation results on the base of the test conditions for alloying:

- alloying at constant end temperature,
- alloying under stationary heating.

EXPERIMENTAL TECHNIQUES

The combination of two drops can be accomplished in two ways.

When alloying in a double levitation coil, the two samples are heated simultaneously - but separated spatially - in the potential depressions in the magnetic field. Figure 2 (page 5) shows the course of the field lines in a double levitation coil with potential depressions $A_1$ and $A_2$. The current directions must be chosen in such a manner that each levitation area has a stabilizing opposing winding. A weightless sample would levitate at such locations. In practice and depending on its weight and diameter, the sample levitates in a somewhat lower lying position. The exact levitating position can be determined by a calculation of the power variation along the vertical axis [1, 2, 4]. To perform the test, the device shown in Figure 3 (page 5) was used. Initially,
sample 2 is suspended from a thin wire (sample material), being taken within the range of the upper coil by means of a manipulator. The temperatures of the liquid samples are measured pyrometrically. For alloying, the coil in the upper range is short-circuited, so that the magnetic field there collapses and the
upper drop falls onto the one levitating under it. The temperature of the lower sample is measured before, during and after the alloying process by means of an automatic pyrometer and recorded on a potentiometric recorder.

The experimental technique with a double levitation coil is expensive in its execution and somewhat limited for a series of systems. Here a fusion technique is available, with the following advantages:

1. the temperature measurements are not necessary for the upper sample,
2. the coupling of two liquid samples levitating in a magnetic field is avoided,
3. the positioning and combining of the samples is easier.

In the fusion method, the base metal (for instance, iron) is molten in a levitating coil and held in levitation. The alloying partner (sample 2) is fused inductively from a cylindrical rod (Figure 4, below). The coil geometry and the end of the rod must be fashioned in such a manner that the drop generated separates

![Diagram](image.png)

Figure 4. Experimental setup for alloying using the fusion technique
readily without being subject to lateral motions due to field forces. Temperature measurements of the fusing drop showed hardly any deviation from the melting point.

In the combination of a solid sample with a drop, an experimental arrangement such as that shown in Figure 5, above, is used. Here, sample 2 is projected onto the liquid, levitating sample 1 from a watercooled (room temperature) drum magazine. In order to calculate the enthalpy of mixing, in this case the enthalpy difference for sample 2 must be known, between room temperature and the temperature under investigation. One essential advantage is that by using a sample magazine, several compositions can be measured sequentially in a single experiment.

TEMPERATURE MEASUREMENTS

The temperature of sample 1 is measured from a side, using an automatic ratio pyrometer. In this measurement principle, a ratio is computed automatically from radiant power measurements at 450 nm and at 650 nm, which is indicated by the instrument as a
index temperature. A calibration was performed - using a heated filament pyrometer - at the melting points and in the liquid range of the pure metals, since there are no calibrated tungsten lamps for the 450 nm range. The instrument has 300°C measuring ranges up to 2500°C. Measurements are possible in the 2500-3000°C range if a neutral gray filter is used. Temperature variations can be resolved to 1°C differences, as the tests showed. For each measurement the pyrometer was checked at the melting point, to eliminate possible drift problems.

If required, the temperature of sample 2 can be measured from above, through an angle prism, using a heated filament pyrometer.

Error in the temperature measurements can occur if the added alloying partner (sample 2) deviates significantly from the behavior of the gray radiator, thus distorting the ratio. For copper this difference is significant, while iron and other high-melting metals fairly closely approach the gray radiator.

BASES FOR TEST EVALUATION

The heat effect \( \Delta h_L \) measured after the combination of the two samples can be divided into two portions:

1. the enthalpy variation \( \Delta h_p \) of the added sample, between its initial temperature and the test temperature;
2. the isothermal mixing enthalpy sought, \( \Delta h^M \), generated at the - now common to both alloying partners - test temperature.

An enthalpy balance provides the following result:

\[ \Delta h_L = -(\Delta h^M + \Delta h_p) \]  
(1)

where

\[ \Delta h_L = (n_1 + n_2) \cdot C_{p,1,2} \cdot \Delta T \]  
(2)

and

\[ \Delta h_p = n_1 [h_2(T_2) - h_2(T_1)] \]  
(3)
If we solve for $\Delta h^M$ we obtain from (1), with (2) and (3):

$$\Delta h^M = -[(n_1 + n_2)C_{p1,2} \cdot \Delta T + n_1 (H_2(T_2) - H_2(T_0))].$$

The molar heat capacity of the alloy, $C_{p1,2}$, usually is not known and is calculated, neglecting the higher order terms, by the Neumann-Kopp rule

$$C_{p1,2} = x_1 C_{p1} + x_2 C_{p2}$$

where

$\Delta T$ = corrected temperature increase (a temperature decrease is recorded negatively),

$H_2$ = molar enthalpy of sample 2,

$T_E$ = solvent test temperature prior to alloying,

$T_0$ = initial temperature of sample 2,

$n$ = number of moles.

If an experimental technique is used in which several samples are added sequentially to the solvent, then the individual alloying steps no longer provide the integral enthalpy of mixing directly, but a difference quantity $\Delta h^M_{\Delta}$:

$$\Delta h^M_{\Delta} = -[(n_1 + n_2)C_{p1,2} \cdot \Delta T + n_1 (H_2(T_2) - H_2(T_0))].$$

This alloying step is elucidated graphically in Figure 6, below.

Figure 6. Schematic change in the free energy of mixing as a function of the number of moles of added material.
The integral molar enthalpy of mixing is obtained by means of a summation of the measured $\Delta h^M_\Delta$ values, according to the equation

$$\Delta h^M = \sum \frac{\Delta h^M}{n_1 + n_2}$$

(7)

where $n_1 + n_2$ is the sum of the number of moles in the alloyed sample for those material quantity contents $x_2$ for which the variable $\Delta h^M$ is being calculated.

For small alloy additions ($\Delta x_2 < 0.01-0.02$), the partial molar enthalpy of mixing can be calculated directly from measured quantities:

$$\Delta h^M_2 = \frac{\Delta h^M}{\Delta x_2} = \frac{1}{C_{12}} \left( \frac{\Delta T + (H(T) - H(T))}{\Delta x_2} \right)$$

(8)

The value of $\Delta h^M_2$ is calculated (cf. Figure 6) as the slope of a straight line determined by the two measurement points. It refers to an average composition, corresponding to the number of moles $\bar{n}_2 = n_2 - \Delta n_2/2$.

![Figure 7. Temperature-time curve for an exothermal alloying process (schematic)](image)
The $\Delta T$ values in equations (4), (6) and (8) has been corrected, taking into consideration losses by radiation. This correction of the temperature change is derived below for alloying under constant end temperature, with the aid of Figure 7 (page 10), which shows schematically the course of an exothermal alloying process. According to the equation

$$ \Delta T = T_i - T_c + \Delta T_{corr} $$

(9)

it is necessary to determine $\Delta T_{corr}$ in order to obtain the true temperature increase $\Delta T$. The correction procedure is very similar to the evaluation of the temperature-time curve for an isoperibolic drop calorimeter [3], which assumes the validity of Newton's cooling law. The evaluation, performed numerically here, can be expressed graphically, for elucidation, by means of the condition of surface equality. Thereby we obtain a theoretical course for the curve, from the actual course, in which the heat effect is incorporated into the system without delay. Since in contrast to the calorimeter Newton's cooling law is not satisfied in the present experimental arrangement - because of the predominant radiative portion in the removal of heat - an error is incurred that depends on the test temperature $T_T$ and the temperature difference $T - T_E$. It can be estimated comparing the radiative law

$$ \frac{dq}{dt} = -A \cdot \epsilon_h \cdot \sigma (T^2 - T_i^2) $$

(10)

with Newton's cooling law

$$ \frac{dq}{dt} = -A \cdot a \cdot (T - T_e) $$

(11)

to obtain

$$ a = a_h \cdot \sigma \cdot \left( \frac{T^2 - T_i^2}{T - T_e} \right) $$

(12)

where

$q_v$ = heat loss during the alloying process, in J;
A = sample surface, in cm$^2$;
$\epsilon_h$ = the hemispherical total emission coefficient, and
$\sigma$ = the radiative constant, in JK$^{-4}$s$^{-1}$cm$^{-2}$. 

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The numerical evaluation presented above presupposes that \( a_r \) is constant. However, according to equation (12) this is not the case: it allows for the calculation of the percentage deviation of \( a_r \) for different temperatures \( T_E \) and temperature differences \( T - T_E \). If we start from the most unfavorable case, that the \( \Delta T \) value contains a correction of 50\%, then for an assumed temperature difference of 50\(^\circ\)K, an evaluation error of 1-2\% remains, which is tolerable, in view of other, higher errors. If the evaluation error exceeds 2\%, it is recommended to perform the correction in the temperature increase somewhat more laboriously, with the aid of the substitution

\[
v = \sigma \cdot T^m
\]  

(13)

Replaced in equation (10), this leads to the expression

\[
\frac{dT}{dt} = -A \cdot \sigma \cdot (v - v_i)
\]  

(14)

which now does satisfy Newton's cooling law. The \( v \)-time curve is evaluated in the same manner as the temperature-time curve.

During the alloying process under steady-state heating conditions, it is easy to determine \( \Delta T \) graphically, provided the temperature-time curve is linear during the pre and the after periods. The most favorable case is found when, in addition, the straight lines are parallel. Figure 8, below, shows the original record of an alloying test in the iron-cupper system under steady-state heating.

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![Figure 8. Temperature-time curve for an alloying process in a steady state heating period](image)

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MEASUREMENT METHOD TESTING

The iron-copper and niobium-silicon systems were used to test the measurement method. The first of these systems is very well known experimentally and shows a strong endothermal solution reaction. Thermodynamic data are not known, to date, for the second system, but its phase diagram leads one to expect a strongly exothermal solution reaction. Because of the endothermal reaction, in the iron-copper system we worked with the principle of the combination of two drops, with the copper being added to the molten iron by fusion of a rod. To keep the test temperature under 2000 °K, all measurements except one were taken under steady-state heating conditions. The calculation of the enthalpy of mixing is based on a melting point for copper of 1357 °K [5], as well as molar heat capacities of 31.33 J·K⁻¹·mol⁻¹ [5] for liquid copper, and of 46.02 J·K⁻¹·mol⁻¹ [5] for liquid iron.

Figure 9, below, shows the results graphically, in comparison to the literature. F. Woolley and J. F. Elliott [6] use a solution calorimeter for the direct measurement of the partial enthalpy of mixing.
mixing of copper, in which solid copper samples are projected into molten iron. The "best values" of R. Hultgren et al. [7] are an average of calorimetrically measured enthalpy of mixing data in the liquid state, by F. Woolley and J. F. Elliott [6], W. Oelsen et al. [8] and A. Podgornik [9]. O. Kubashevskij et al. [10] obtained their value by an expanded thermodynamic analysis based on experimental data obtained by direct and indirect measurements. The measurements in the niobium-silicon system were performed after the principle of the combination of a solid sample with a drop, at constant end temperature, with liquid niobium as the solvent. The protective gas was highest purity argon. The niobium purity was 99.96%, while that of silicon attained 99.999%. The thermodynamic data of silicon were taken from the tabulated values in I. Barin and O. Knacke [11]. The $C_p$ value for liquid niobium comes from our own calorimetric measurements [3, 12] ($C_p = 41.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). Figure 10, below, reproduces the results in

![Figure 10](image.png)

**Figure 10.** Integral molar free energy of mixing in the system niobium-silicon
TABLE 1. $\Delta H^M$ and $\Delta H^M_{Si}$ in the niobium-silicon system at 3000°K

<table>
<thead>
<tr>
<th>$x_{Si}$</th>
<th>$\Delta H^M$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^M_{Si}$ (kJ mol$^{-1}$)</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-161.27</td>
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<td>-132.79</td>
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<tr>
<td>0.30</td>
<td>-42.74</td>
<td>-126.00</td>
</tr>
</tbody>
</table>
REFERENCES

9 Oelsen, W., Johannsen, F. and Podgornik, A., as [8], p. 719.