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Enthalpies of formation of Ru–Ge compounds and of the Ge-rich RuGe liquid by direct reaction calorimetry

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Abstract

The enthalpies of formation of RuGe and Ru_2Ge_3 have been measured by direct reaction calorimetry at 1173 K.

$Ru_{0.4}Ge_{0.6}$: $\Delta_f H$ (1173 K) = −34.8 kJ mol^{-1} (±1)
$Ru_{0.5}Ge_{0.5}$: $\Delta_f H$ (1173 K) = −28.7 kJ mol^{-1} (±1.3)

with reference to pure metals in their equilibrium states at the reaction temperature. The Ge rich RuGe liquid was also studied by dissolution of Ru in the liquid alloy of variable composition at 1423 K. The results are compared with the existing literature.

Keywords: Ruthenium–germanium alloys; Calorimetry; Thermochemistry; Enthalpies of formation

1. Introduction

In the course of the systematic study of binary metals systems, we present our calorimetric results for ruthenium–germanium compounds. This work constitutes the first part of a general study of the Ru–Ge system.

Fig. 1 by Massalski [1] is a compilation of previous experimental results about the diagram of this system, which clearly shows occurrence of two intermetallic phases: Ru_2Ge_3 and RuGe.

2. Experimental

Table 1 gives the characteristics of the metals.

2.1. Preparation of samples

All preparations were made in a glove box in a purified Ar atmosphere. Metallic powders were maintained under vacuum for at least 20 h prior to introduction in the glove box in order to remove as much as possible of the adsorbed gases at room temperature. The powders were mixed in suitable proportions in a mortar, then the mixture was compacted under a pressure of few hundred MPa. The compacted pellet was broken into pieces of about 35–50 mg and packed under Ar in a special Ar-tight container. This allowed the transfer of samples from the glove box to the calorimeter, dropping them inside it without any contact with the air. Two mixtures were prepared: $Ru_{0.5}Ge_{0.5}$ and $Ru_{0.4}Ge_{0.6}$ corresponding to RuGe and Ru_2Ge_3 respectively.

2.2. Instrumentation and measurements

Enthalpies of formation of binary compounds

Both method and equipment are already described by Gachon [2] and Selhaoui [3].

In the vertical furnace (a Setaram 2400, ranging from 300–1800K), the calorimetric cell is connected to the special Ar-tight container. This calorimetric cell contains a working crucible surrounded at two different levels by 21 thermocouples (Pt–PtRh 10%) connected in series and supported by alumina tubes. For each series of measurements, alumina samples and pieces of compacted powders were dropped alternatively. Alumina allowed us to check the response of the calorimeter and to calibrate it. The integral of the calorimetric signal was proportional to the heat transfer between the sample and the calorimeter. By comparing the calorimetric effects of alumina cold samples and tabulated data for $Al_2O_3(H_{T_{crucible}} - H_{T_{room}})$ by Ditmars et

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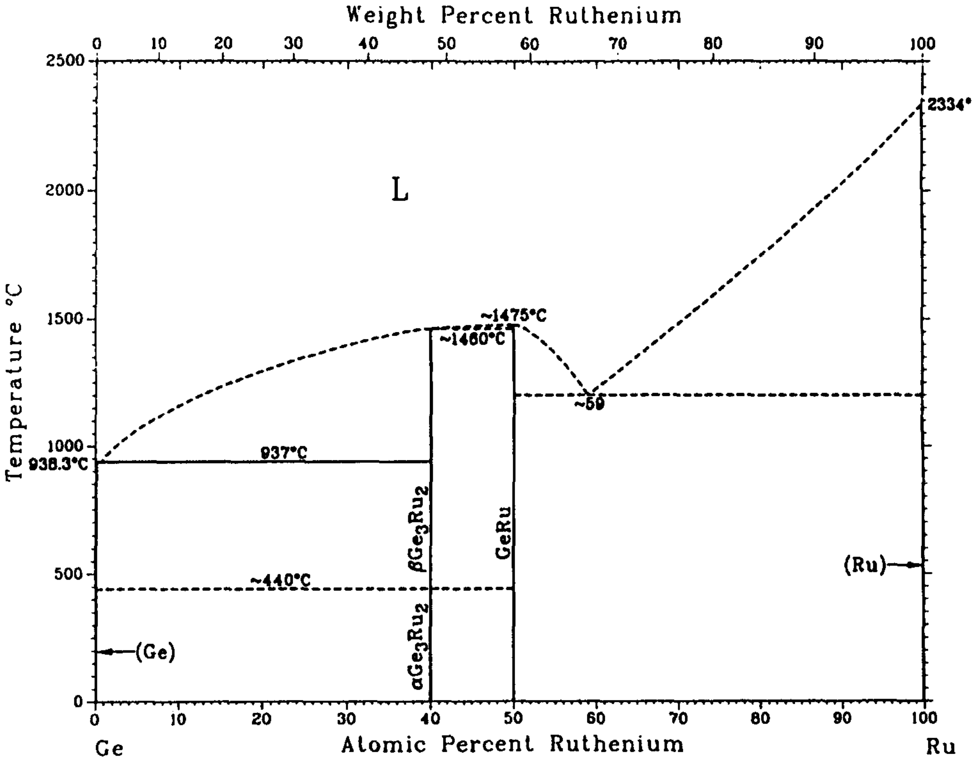

Fig. 1. Ru–Ge system according to Massalski [1].

Table 1
Metals characteristics

Metal	Origin	Purity	Shape and size
Ruthenium	Metalor	99.96% min	Powder 1–25 μm
Germanium	Balzers	99.999% min	Granulates 0.7–0.35 mm [a]

[a] For the calorimetry in the solid state, Ge was grinded into micron size powder.

al. [4], we obtained the sensitivity of the calorimetric cell.

The standard molar enthalpy of formation of the compound Ru_xGe_{1-x} is obtained from the enthalpy effects associated to the following reactions (T_0 = room temperature, T = temperature of the calorimetric cell).

$$xRu(hcp,T_0) + (1-x)Ge(dia,T_0) = Ru_xGe_{1-x}(solid,T) \quad (1)$$

measured by our method and decomposed into two contributions:

$$xRu(hcp,T_0) + (1-x)Ge(dia,T_0) = xRu(hcp,T) + (1-x)Ge(dia,T) \quad (2)$$

increments of enthalpy of Ru and Ge between T and T_0, tabulated in [6]

$$xRu(hcp,T) + (1-x)Ge(dia,T) = Ru_xGe_{1-x}(solid,T) \quad (3)$$

enthalpy of formation of Ru_xGe_{1-x} at T.

We obtain (3) = (1) − (2), regardless of the true path linking the two states: [$xRu(hcp,T_0) + (1-x)Ge(dia,T_0)$] and [$Ru_xGe_{1-x}(solid,T)$].

As described by Eqs. (1)–(3), there are two contributions to the calorimeter signal: the enthalpy increment of the pure metals between T_0 and T (positive) and the reaction enthalpy at T (negative). Thus, the total signal is small and calibration is not critical, even if we perform it carefully. The experimental uncertainties which are reported in paragraph 3 are the standard deviations of the measurements.

Enthalpies of dissolution

Starting with an empty crucible (in an Ar atmosphere to prevent oxidation) at 1423 K, it was possible to drop into it small samples of pure Ge in order to constitute a bath of liquid Ge (melting point, 1211.4 K [5]). This series of samples allowed us to calibrate the calorimeter by using the enthalpy change of germanium given by Barin and Knacke [6] and to verify the response stability of the calorimeter.

In a second step, cold pieces of Ru were added and the heat effect of each addition was measured and corrected from the enthalpy increment given in [6], in order to finally give the enthalpy of dissolution of ruthenium in the bath at the actual progressive composition.

Data treatment and validity check

Data acquisition (time of acquisition, 12 min) and mathematical treatment were performed on a personal computer. After each experiment the products were checked using X-ray diffraction and electronic microprobe analysis. X-Ray diffraction studies were performed on a Philips PW1370 diffractometer using Cu $K_{\alpha 1}$ ($\lambda = 1.54060$ Å) and $K_{\alpha 2}$ ($\lambda = 1.54438$ Å) radiations with 2Θ between 5° and 145°. Microprobe analysis was performed on an ARL-SEMQ device using to Magic IV [7] correction software.

XRD reference samples were induction melted and annealed at 900 °C for 50 days in silica tubes under Ar atmosphere. These standards are in agreement with JCPDS (15-589 and 30-594) [8] and the Lazy Pulverix calculation [9] according to the structural description of RuGe (Raub [10]) and Ru_2Ge_3 (Poutcharovsky [11,12]).

3. Results

3.1. Formation of $Ru_{0.4}Ge_{0.6}$ (Ru_2Ge_3)

Formation was at 1173 K $\Delta_f H(Ru_{0.4}Ge_{0.6}) = -34\ 800 \pm 1000$ J mol^{-1} after five measurements.

Examination of the XRD patterns (Fig. 2) confirmed that the formation of Ru_2Ge_3 was complete (absence of Ru or Ge peaks).

3.2. Formation of $Ru_{0.5}Ge_{0.5}$ (RuGe)

Formation was at 1173 K $\Delta_f H(Ru_{0.5}Ge_{0.5}) = -28700 \pm 1300$ J mol^{-1} of atoms after five measurements.

XRD (Fig. 3) showed a predominance of RuGe with traces of Ru and some Ru_2Ge_3. The presence of Ru_2Ge_3 could be explained by its higher enthalpy of formation. We checked that the enthalpy result is not significantly distorted by this Ru_2Ge_3 because, first, the enthalpies of formation of both phases (RuGe and Ru_2Ge_3) are of the same order of magnitude and secondly, the formation of Ru_2Ge_3 dictates that a part of Ru didn't react. If we consider that only 50% of the right product were formed, the enthalpy change would be only 1 kJ, which is the experimental standard deviation.

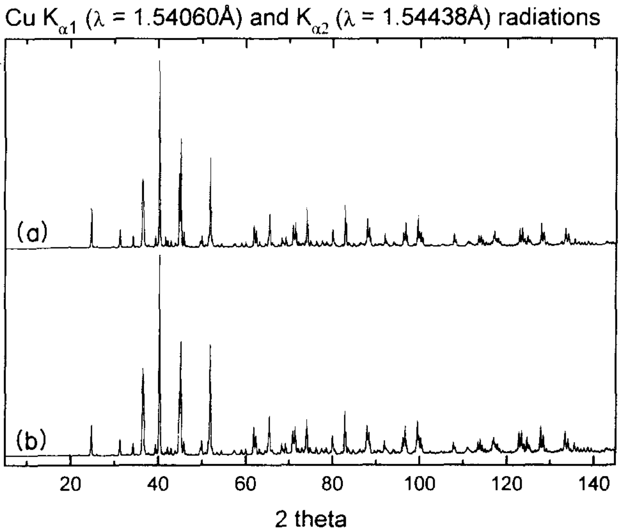

Fig. 2. Comparison between the experimental X-ray pattern of Ru_2Ge_3 obtained by (a) calorimetry and (b) induction melted and annealed sample.

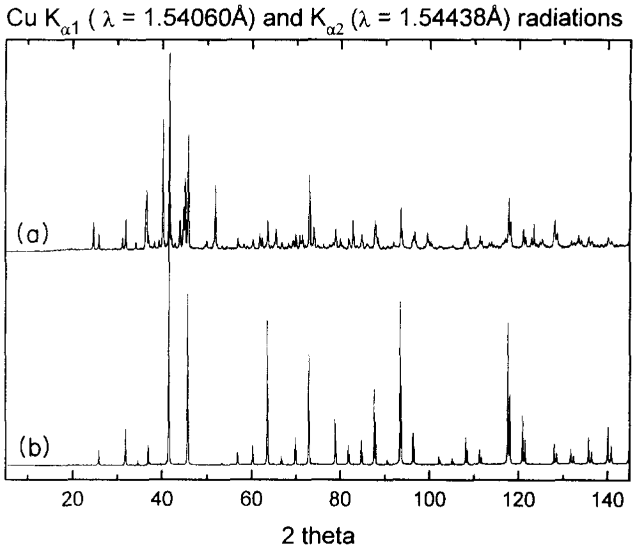

Fig. 3. Comparison between the experimental X-ray pattern of RuGe obtained by (a) calorimetry and (b) induction melted and annealed sample.

These results are compared with Jung and Kleppa's [13] values and Miedema's semi empirical model [14] in Table 2.

Microprobe analysis performed on RuGe and Ru_2Ge_3 samples didn't give coherent results with XRD, the small grain sizes of the products could explain the difficulty of analysis.

3.3. Enthalpies of dissolution of Ru solid in Ge liquid at 1423 K

The aim of this experiment was to determine the partial enthalpy of Ru as a function of the composition in the liquid and liquid + solid domains at 1423 K, and to check the enthalpy of formation of the solid $Ru_{0.4}Ge_{0.6}$. Below a concentration of 75 at.%Ge, the dissolution became too slow and results began to be meaningless. Fig. 4 presents the partial enthalpy of Ru vs. composition for different at.%Ge.

4. Discussion and conclusion

This study confirms the results obtained by Jung and Kleppa [13] and assesses a value for the enthalpy of formation of $Ru_{0.4}Ge_{0.6}$. In addition, results are obtained in the liquid state. For the solid compounds, the results contradict Miedema's results [14]. It has to be mentioned that in Miedema's model, Ge (as with H, B, C, Si, N and P) is a non metal element which has to be transformed into a metal by the general equations of the

Table 2
Enthalpy results

Intermetallic phases	$\Delta_f H$ present work [a] (standard deviation) kJ (mole of atom)$^{-1}$	Jung and Kleppa [13] (kJ (mole of atom)$^{-1}$)	Miedema's model [14] (kJ (mole of atom)$^{-1}$)
$Ru_{0.5}Ge_{0.5}$ [a]	−28.7 (1)	−28.4 [b]	−14
$Ru_{0.4}Ge_{0.6}$ [a]	−34.8 (1.3)	–	−9

[a] Reference to pure Ru and Ge in their equilibrium states at 1173 K.
[b] At 298 K, refered to pure metals at 298 K.

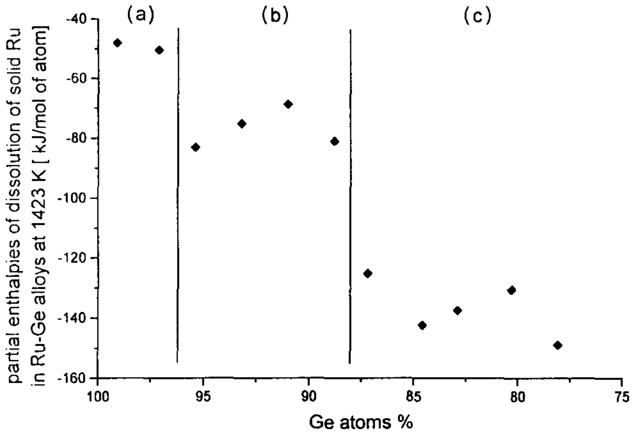

Fig. 4. Results of the calorimetry experiments at 1423 K of dissolution of Ru in liquid Ge and liquid Ge + solid Ru_2Ge_3: region a, enthalpies of dissolution of solid Ru in liquid Ge; region b, phase fluctuations around the liquidus curve; region c, enthalpies of dissolution of solid Ru in (liquid + Ru_2Ge_3).

model. This transformation involves an enthalpy of transformation which is empirically determined. This accounts for an uncertainty of the model results which is certainly broader that the one reported for purely metallic systems. In a previous study, Gachon [15] found that a factor of 2 was possible between the experimental and computed values for the transition–transition systems. In our case, the factor is around 4 for $Ru_{0.4}Ge_{0.6}$. In addition there is a contradiction between the variations between $Ru_{0.5}Ge_{0.5}$ and $Ru_{0.4}Ge_{0.6}$, but the phase diagram study which is under way shows that $Ru_{0.4}Ge_{0.6}$ melts at an higher temperature than $Ru_{0.5}Ge_{0.5}$. This supports the experimental variation of enthalpies of formation: generally the higher the melting temperature, the stronger the enthalpy of formation. Finally we are convinced that our thermodynamic results are firmly established in the solid state. For the liquid state the phase fluctuations in the middle range of composition (Fig. 4) and the difficulties encountered for <75 at.%Ge produce less accurate results than for the solid state.

This calorimetry work constitutes the first part of a more general study of the Ru–Ge system which is under investigation in our laboratories. It will lead to more general results in the near future.

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