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Enthalpies of formation of Ru–Si and Ru–Sn compounds by direct reaction calorimetry

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Abstract

The enthalpies of formation of two Ruthenium–Tin (Ru–Sn) and three Ruthenium–silicon (Ru–Si) compounds have been measured by direct reaction calorimetry:

$Ru_{0.4}Sn_{0.6}: \Delta_f H(1173\,K) = -28.1\,kJ/mole(\pm 1.6)$

$Ru_{0.3}Sn_{0.7}: \Delta_f H(1173\,K) = -29.8\,kJ/mole(\pm 0.8)$

$Ru_{0.57}Si_{0.43}: \Delta_f H(1505\,K) = -45.3\,kJ/mole(\pm 0.6)$

$Ru_{0.5}Si_{0.5}: \Delta_f H(1515\,K) = -57.7\,kJ/mole(\pm 1.4)$

$Ru_{0.4}Si0.6: \Delta_f H(1704\,K) = -80.4\,kJ/mole(\pm 1.0)$

refered to pure elements in their equilibrium states at the reaction temperatures.

Keywords: Direct reaction calorimetry; Enthalpy of formation; Ruthenium–Silicon and Ruthenium–Tin alloys; Ruthenium–Silicon and Ruthenium–Tin compounds

1. Introduction

During the general thermodynamic and structural study of the binary systems Ru–Si, Ru–Ge [1,2] and RuSn, calorimetry experiments were made in order to determine the enthalpies of formation of intermediate phases. Results have already been published for RuGe compounds [1] and the purpose of this paper is to give the data for three RuSi and two RuSn intermediate phases, already identified by Massalski et al, Weitzer et al and Schwomma et al [3–6]. Comparison with existing values of the literature and discussion concerning the enthalpies of formation of <RuSi>, <RuGe> and <RuSn> compounds are made.

2. Experimental

2.1. Calorimetric measurements

Preparation of samples, method and equipment have already been described in earlier communica-

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Table 1
Elements characteristics

Element	Origin	Purity	Grain size
Ru	Métalor	99.96%(min)	1–25 μm
Sn	Goodfellow	99.9%	45 μm
Si	Alfa	99.5%	<44 μm

tions [7–9], we simply recall the principle. Fine powders of the two components are mixed and cold compressed in appropriate ratios, under an argon protective atmosphere inside a glove box. Table 1 gives powders characteristics.

The compacted pellets, weighing from 50–100 mg, were dropped into the calorimeter which operated under argon (purity ≥99.995%) (to avoid oxidation) at a sufficiently high temperature to ensure a rapid interdiffusion of the two components. Calibration and stability checks were made with α-alumina samples (20–60 mg) which were introduced into the crucible alternatively with the samples. The calorimeter measured the sum of the heat content of the pure components (between room and calorimeter temperatures) and the enthalpy of formation of the compound at calorimeter temperature starting from the components in their equilibrium states at this temperature. The enthalpy increments of the pure elements and α-Al_2O_3 were taken from Barin [10] and Ditmars et al. [11] respectively. At the end of each series of measurements, the calorimeter cell was slowly cooled.

2.2. Phase characterization

After each experiment, the products were checked by X-ray diffraction (XRD) and electron probe microanalysis (EPMA). XRD studies were performed on a Philips PW1370 diffractometer using Cu $K_{\alpha 1}$ (λ=0.154060 nm) and $K_{\alpha 2}$ (λ=0.154438 nm) radiations and allowed comparisons with patterns calculated by Lazy–Pulverix [12] according to literature data [13–18]. Microprobe analyses were performed using a Cameca SX 50 (Earth Sciences Department, University of Lausanne, Switzerland), coupled with the PAP's routine [19] for matrix corrections.

3. Results

3.1. Ru–Sn system

3.1.1. Formation of $Ru_{0.4}Sn_{0.6}$ (Ru_2Sn_3)

At the temperature of 1173 K, the enthalpy of formation obtained by our method was $\Delta_f H$ $(Ru_{0.4}Sn_{0.6})^1$ = − 28.1 kJ mole^{-1} of atoms (±1.6) (mean of four measurements)

Fig. 1 shows a predominance of the compound $Ru_{0.4}Sn_{0.6}$ with small quantities of Ru and $Ru_{0.3}Sn_{0.7}$. Considering the presence of an amount of 5% of $Ru_{0.3}Sn_{0.7}$ and including its enthalpy of formation given in Section 3.1.2, we checked that the present enthalpy result was not distorted by the formation of this second phase, the enthalpy change would be only 0.6%, which is less than the experimental standard deviation.

3.1.2. Formation of $Ru_{0.3}Sn_{0.7}$ (Ru_3Sn_7)

At the temperature of 1173 K, we found $\Delta_f H$ $(Ru_{0.3}Sn_{0.7})^2$ = − 29.8 kJ mole^{-1} of atoms (±0.8) (mean of four measurements). In Fig. 2, comparison between (a) and (b) shows that the compound obtained by direct reaction calorimetry gives a pattern analogous to the cubic structure calculated by Lazy–Pulverix [12] according to Nial's study [15] and confirmed that the formation of $Ru_{0.3}Sn_{0.7}$ was complete (absence of Ru and Sn peaks).

3.2. Ru–Si system

3.2.1. Formation of $Ru_{0.57}Si_{0.43}$ (Ru_4Si_3)

At the temperature of 1505 K, the enthalpy of formation was $\Delta_f H$ $(Ru_{0.57}Si_{0.43})^3$ = − 45.3 kJ mole^{-1} of atoms (±0.6) (mean of four measurements). The result cannot be considered as an accurate value despite the very small standard deviation. The examination of the XRD pattern of the calorimetry product allowed us to establish at first the presence of $Ru_{0.57}Si_{0.43}$ by comparison with the calculated structure according to Engström [16] and

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[1] With reference to pure metals in their equilibrium states at the reaction temperature: Ru solid and Sn liquid.

[2] With reference to pure metals in their equilibrium states at the reaction temperature: Ru solid and Sn liquid.

[3] With reference to pure metals in their equilibrium states at the reaction temperature: Ru solid and Si solid.

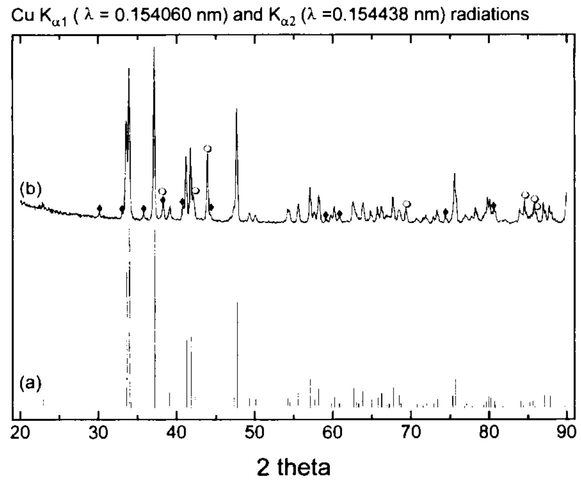

Fig. 1. Comparison between the Lazy–Pulverix computation according to Poutcharovsky's experimental results [13,14] (a) and our X-ray pattern of $Ru_{0.4}Sn_{0.6}$ as obtained by calorimetry (b). (○ Ru peaks, ◆ $Ru_{0.3}Sn_{0.7}$ peaks).

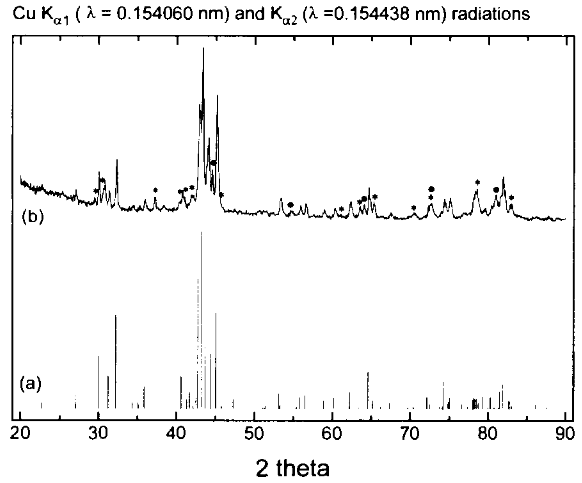

Fig. 3. Comparison between the Lazy–Pulverix computation according to Engström's experimental results [16] (a) and our X-ray pattern of $Ru_{0.57}Sn_{0.43}$ as obtained by calorimetry (b).(● RuSi (CsCl-type) peaks, $Ru_{0.66}Si_{0.33}$ (Ru_2Si) peaks).

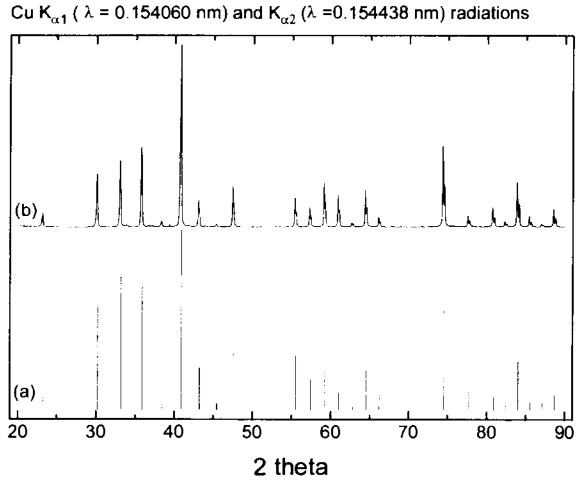

Fig. 2. Comparison between the Lazy–Pulverix computation according to Nial's experimental results [15] (a) and our X-ray pattern of $Ru_{0.3}Sn_{0.7}$ as obtained by calorimetry (b).

secondly the presence of two other phases: Ru_2Si according to Aronsson [20] and RuSi (CsCl-type) [17] and Fig. 3 . These three different phases were also detected by microprobe analysis (see Fig. 4). We have not yet been able to find out the temperature range of stability for Ru_2Si, Morozkin et al. [21] for instance, as well as our own differential thermal analysis (DTA) and XRD experiments contradict the diagram published by Weitzer [3] and assessed by Massalski [4]. As a consequence we have not yet tried to measure the enthalpy of formation of Ru_2Si, and we consider the result about $Ru_{0.57}Si_{0.43}$ as indicative.

3.2.2. *Formation of $Ru_{0.5}Si_{0.5}$ (RuSi)*

At 1515 K, the calorimeter gave Δ_fH $(Ru_{0.5}Si_{0.5})^4$ – -57.7 kJ $mole^{-1}$ of atoms (±1.4) (mean of four measurements). The formation of $Ru_{0.5}Si_{0.5}$ is complete. Fig. 5 clearly shows that the phase was exclusively RuSi (CsCl-type). The other structure of RuSi (FeSi-type) was not found. Microprobe investigations confirmed that the product composition was homogeneous.

3.2.3. *Formation of $Ru_{0.4}Si_{0.6}$ (Ru_2Si_3)*

At the temperature of 1704 K, the enthalpy of formation was Δ_fH $(Ru_{0.4}Si_{0.6})^5 = -80.4$ kJ $mole^{-1}$ of atoms (±1.0) (mean of five measurements) Δ_fH $(Ru_{0.4}Si_{0.6})^6 = -50.3$ kJ $mole^{-1}$ of atoms (±1.0). For

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[4] With reference to pure metals in their equilibrium states at the reaction temperature: Ru solid and Si solid.

[5] With reference to pure metals in their equilibrium states at the reaction temperature: Ru solid and Si liquid.

[6] With reference to pure metals in their solid states.

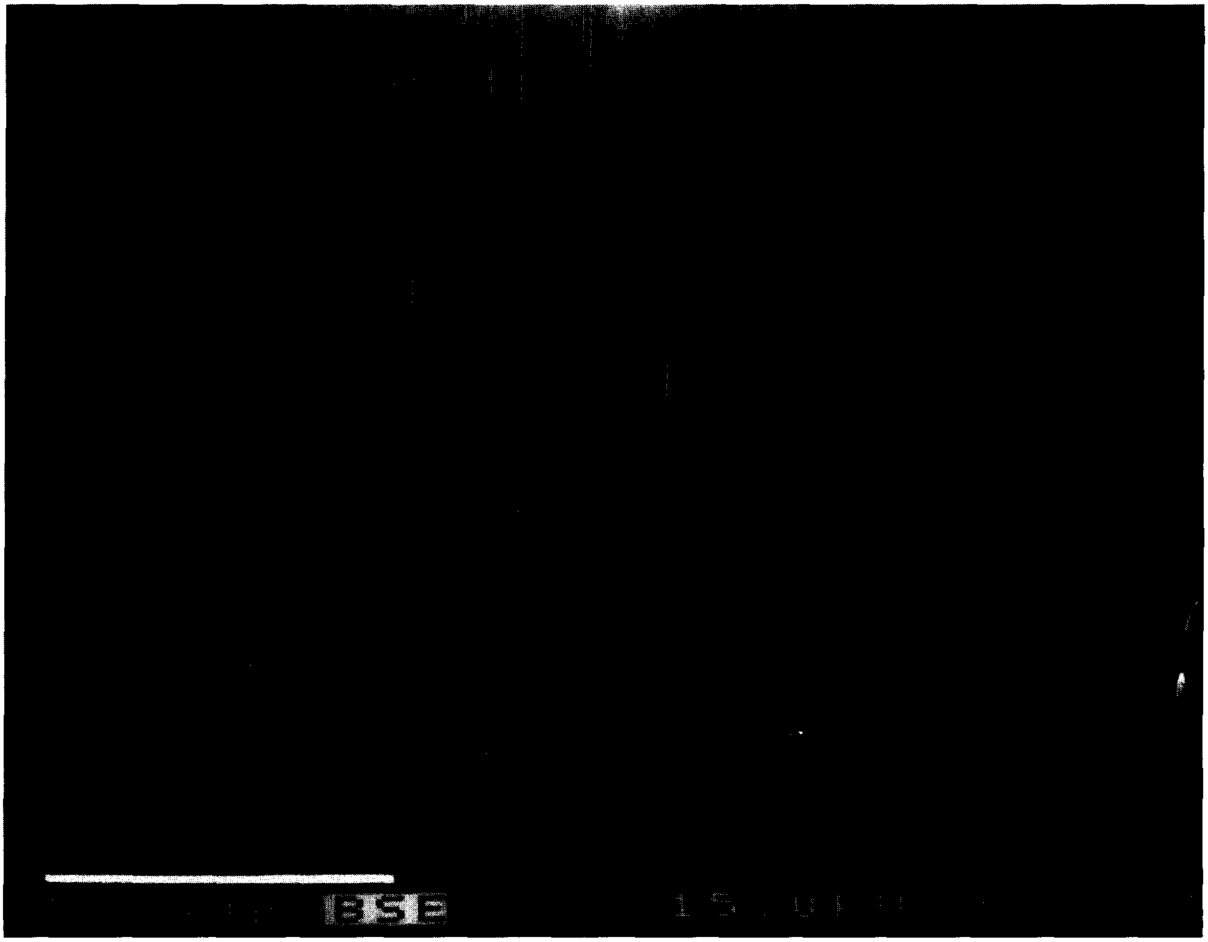

Fig. 4. Back scattered electrons micrography on a $Ru_{0.57}Si_{0.43}$ sample obtained by direct reaction calorimetry. Three phases are detected: light grey, medium grey and dark grey with a composition of 33, 42 and 49 at.% Si respectively. Black spots are holes.

comparison (see Fig. 6) between the XRD pattern of the product obtained by direct reaction calorimetry and the Lazy–Pulverix computation got with the structure of $Ru_{0.4}Si_{0.6}$ as determined by Israiloff [18] confirmed the predominance of the expected compound but also showed small amounts (10% estimated) of RuSi (FeSi type). The presence of these two phases was confirmed by EPMA. By considering the presence of an amount of 10% of $Ru_{0.5}Si_{0.5}$ and including its enthalpy of formation given in Section 3.2.2, we checked that the present enthalpy result was not distorted by the formation of this second phase, the enthalpy change would only be 1.2%, which is less than the experimental standard deviation.

4. Discussion and conclusions

4.1. Comparison with existing values

Table 2 summarizes the available values of enthalpies of formation for Ru–Sn and Ru–Si compounds in the literature. For the enthalpy of formation of $Ru_{0.5}Si_{0.5}$, our result is in very good agreement with Topor and Kleppa value [28], who determined the standard enthalpy of formation at 298.15 K by high temperature mixing calorimetry. The very small difference between the two values seems to indicate that there is no significative ΔCp between the pure elements and the compound.

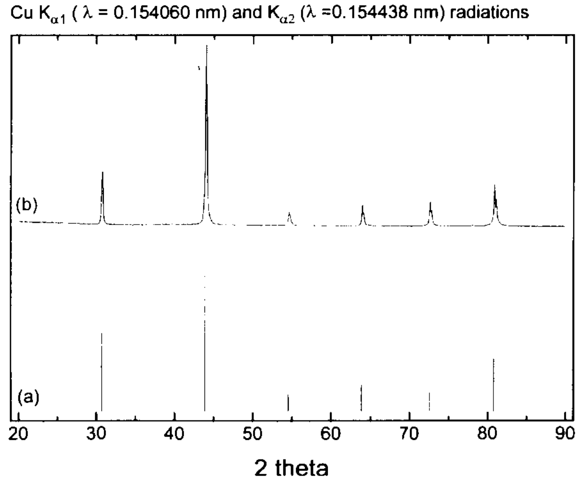

Fig. 5. Comparison between the Lazy–Pulverix computation according to Göransson's experimental results [17] (a) and our X-ray pattern of $Ru_{0.5}Si_{0.5}$ as obtained by calorimetry (b).

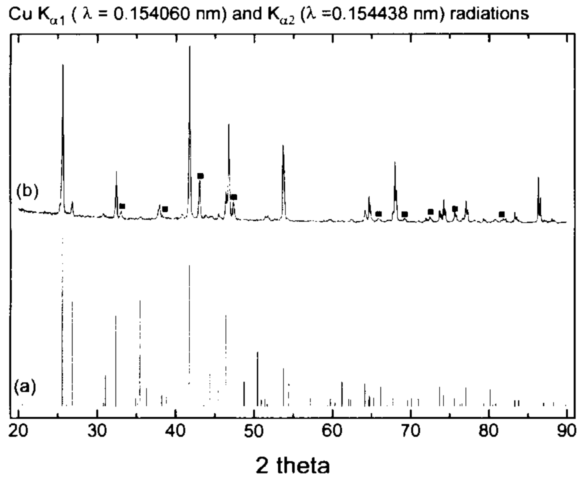

Fig. 6. Comparison between the Lazy–Pulverix computation according to Israiloff's experimental results [18] (a) and our X-ray pattern of $Ru_{0.4}Si_{0.6}$ as obtained by calorimetry (b). (■ RuSi (FeSi-type) peaks).

4.2. Comparison with our preceding results in the RuGe system

Table 3 summarizes our results about the enthalpies of formation of compounds in the RuX systems (X = Si, Ge and Sn). Fig. 7 presents the comparison of the enthalpies of formation of the seven phases reported in table 4 according to the atomic composition of X (X =

Table 2
Comparison between our results and existing values of the literature enthalpies of formation in kJ mol^{-1} of atoms.

Phase	Our results (st.deviation) T measurements	Searcy [22]	Chart [23]	Machlin [24]	Gelatt [25]	Peterson [26]	Miedema [27]	Pasturel [28]	Topor [29] (st. deviation)T measurements
$Ru_{0.4}Sn_{0.6}$	−28.1 (1.6) 1173 K						−11.4		
$Ru_{0.3}Sn_{0.7}$	−29.8 (0.8) 1173 K						−8.8		
$Ru_{0.57}Si_{0.43}$	−45.9 (0.6) 1505 K						−33.0		
$Ru_{0.5}Si_{0.5}$	−57.7 (1.4) 1505 K	−33.4 (10.5)	−42	−39.2	−94.6	33.2	−32.4	−43.9	−58.1. (3.6) 1400–1473K
$Ru_{0.4}Si_{0.6}$	−50.3 (±1.0) (1.0) 1704 K	−23.9 (10.7)				−26.8	−26.0		
Technique	high temp.calorimetry	assessment	assessment	model	model	estimation	model	model	high temp.mixing calorimetry

Table 3

Phase	$\Delta_f H^a$ kJ mole^{-1} of atoms	$\Delta_f H^b$ kJ mole^{-1} of atoms	type of decomposition	T(K) decomposition
$Ru_{0.4}Ge_{0.6}$	−34.8	−34.8 [1]	fusion	1824 [2]
$Ru_{0.5}Ge_{0.5}$	−28.7	−28.7 [1]	fusion	1783 [2]
$Ru_{0.4}Sn_{0.6}$	−28.1	−24.3	peritectic	1539 [30]
$Ru_{0.3}Sn_{0.7}$	−29.8	−25.4	fusion	1530 [30]
$Ru_{0.4}Si_{0.6}$	−80.4	−50.3	fusion	1983 [3,4]
$Ru_{0.57}Si_{0.43}$	−45.3	−45.3	peritectic	1968 [3,4]
$Ru_{0.5}Si_{0.5}$	−57.7	−57.7	fusion	2023 [3,4]

[a] With reference to pure components in their equilibrium states at the reaction temperatures.
[b] With reference to pure components in their solid states at the reaction temperatures.

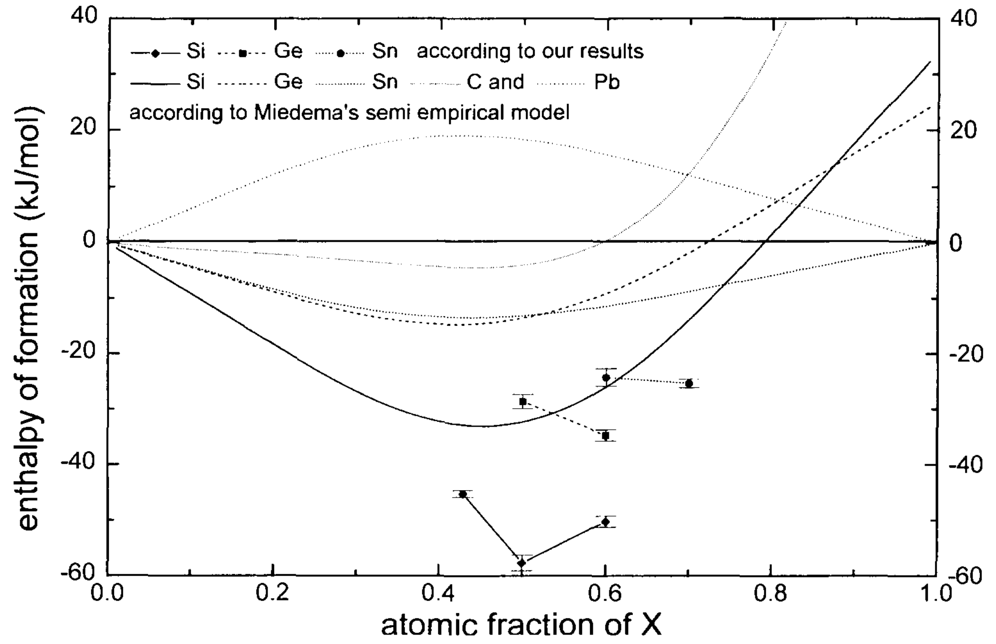

Fig. 7. Comparison of the enthalpies of formation of RuX compounds with reference to pure components in their solid states at the reaction temperatures, according to this present work and [1], with ◆: X = Si,■:X = Ge [1] and ●: X = Sn and the enthalpies of formation of $Ru_{(1-x)}X_x$ (with X = C, Si, Ge, Sn and Pb) compounds versus atomic fraction of X, according to Miedema's semi empirical model.

Si, Ge and Sn). The lighter the associated component to Ruthenium, the higher the enthalpy of formation. Fig. 8 shows the variation of the intermetallic enthalpies of formation versus their decomposition temperatures. The stronger the enthalpy of formation, the higher (negative) the decomposition temperature. Moreover we can notice for semi-metal alloys (RuSi and RuGe), a linear evolution between enthalpies of formation and temperatures of decomposition. RuSn compounds do not seem to follow this linear tendency. According to the general trend shown by this figure, the existence of RuPb compounds seems very uncertain. This is confirmed: firstly by the results of Miedema's semi-empirical model (Fig. 7) which give a positive enthalpy of formation for $Ru_xPb_{(1-x)}$ on the entire range of composition; secondly we never observed any intermetallic phase by direct reaction between Ru powder and melted Pb.

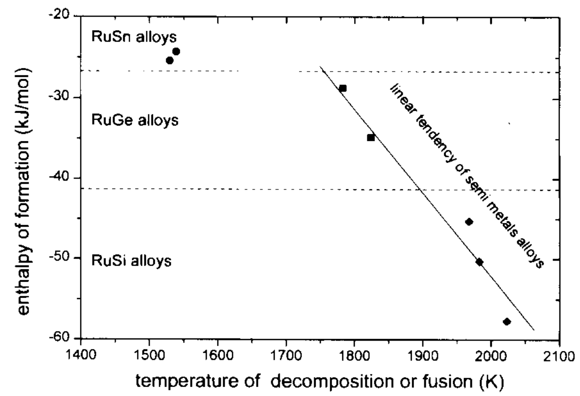

Fig. 8. Enthalpies of formation (refered to pure elements in their solid states at the reaction temperatures) of the RuSi, RuGe and RuSn compounds versus their temperatures of decomposition or fusion. It can be seen that RuSi follow the trend of Kubaschewski's correlation [34] while RuSn doesn't.

4.3. Compounds occurrence

As Topor and Kleppa [28] did, we found only RuSi (CsCl-type) in our $Ru_{0.5}Si_{0.5}$ samples obtained by direct reaction calorimetry. We also found a few traces of the other cubic structure (FeSi-type) but in $Ru_{0.4}Si_{0.6}$ calorimetry samples. Following Buddery [31], Korst [32], Finnie [33], Weitzer [4] and recently Göransson [17], we cannot at the present time give a coherent explanation concerning the mechanisms of formation of these two types of $Ru_{0.5}Si_{0.5}$ (RuSi). The CsCl-type seems to appear in the Ru rich side of <RuSi> while FeSi-type was only observed in equilibrium with $Ru_{0.4}Si_{0.6}$ (Ru_2Si_3).

Furthermore, $Ru_{0.57}Si_{0.43}$ (Ru_4Si_3) formation is still uncertain, we never obtained a single-phase alloy as well by induction melting or powder method (methods described in [2–30]) as by arc furnace.

Studies of the <RuSn> [30] and <RuSi> systems are still under way in our laboratories by means of DTA, XRD and EPMA and will deal complementary information about these two binary systems.

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