

Standard enthalpy of formation of compounds of the Cd–Zr system

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Abstract

Thermodynamic properties of two intermetallic phases $\text{CdZr}_2(\text{s})$ and $\text{Cd}_3\text{Zr}(\text{s})$ in the binary Cd–Zr system have been investigated. The standard molar enthalpy of formation $\Delta_f H_{298}^0$ of $\text{CdZr}_2(\text{s})$ and $\text{Cd}_3\text{Zr}(\text{s})$ was obtained by measuring the reaction enthalpy of $\text{CdZr}_2(\text{s})$, $\text{Cd}_3\text{Zr}(\text{s})$ and $\text{Zr}(\text{s})$, respectively, using $\text{Cd}(\text{l})$ in a Calvet calorimeter. The values of $\Delta_f H_{298}^0$ of $\text{CdZr}_2(\text{s})$ and $\text{Cd}_3\text{Zr}(\text{s})$ at 298 K were found to be $-(61.7 \pm 1.2) \text{ kJ mol}^{-1}$ and $-(72.3 \pm 0.9) \text{ kJ mol}^{-1}$, respectively.

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1. Introduction

Zircaloy is used as clad for nuclear pins due to its low neutron absorption cross-section, high thermal conductivity, high corrosion resistance and good mechanical strength. Zirconium metal forms one of the major components of the Zircaloy. Under operating conditions of the nuclear reactor, cadmium is formed in moderate amounts inside the fuel pins and remains in elemental state. The gaseous cadmium under the temperature gradient can migrate out of the fuel-clad boundary and interact with Zircaloy. In addition, Cd is used as control rod to control the neutrons at a desired level. Under accidental conditions, Cd vapor from volatilized rods can react with the Zircaloy clad, thus influencing upon the release behavior of Cd vapors. Thermodynamic data of Cd and Zr compounds of and along with their solid solution are important in the assessment of the Cd release behavior into the environment under accidental conditions.

The phase diagram of the binary Cd–Zr system is available in the literature [1]. Four known intermediate compounds with formula Cd_3Zr , Cd_2Zr , CdZr and CdZr_2 are reported. However, thermodynamic properties of these intermediate phases are not available in the literature. In

this paper we describe synthesis, characterization and determination of the standard enthalpy of formation of Cd_3Zr and CdZr_2 by Calvet calorimetry.

2. Experimental

Cd_3Zr was prepared by reacting appropriate amounts of the zirconium powder (Aldrich, 100 mesh, and purity 99.9%) and cadmium turnings (BDH, reagent grade). Zirconium powder stored in paraffin oil was washed with benzene and acetone and dried under vacuum before used. The cleaned and dried Zr powder and the cadmium turnings were taken in a tantalum tube and sealed in an evacuated quartz ampoule. The ampoule was heated at 773 K for 12 h and furnace-cooled to room temperature. The sample was then thoroughly ground under acetone, dried and pelletized and again heated under similar conditions for 12 h. The compound was characterized for its phase purity. The compound CdZr_2 was prepared by thermal decomposition of the Cd_3Zr solid following the Knudsen mass loss. The samples were characterized by vacuum thermogravimetry (Setaram TG-DTA, Model 92-16.18) and the X-ray diffraction method (XRD) using a Philips X-ray diffractometer (Model PW-1820), and energy dispersive X-ray analysis (EDX) model excel 30 (ESEL) techniques.

The standard molar enthalpy of formation of $\text{Cd}_3\text{Zr}(\text{s})$ and $\text{CdZr}_2(\text{s})$ compounds were determined by measuring

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the heat of dissolution of $\text{Cd}_3\text{Zr(s)}$, $\text{CdZr}_2\text{(s)}$, Cd(s) and Zr(s) in liquid Cd using a Setaram Calvet calorimeter Model HT-1000. The calorimeter has an isothermal alumina block which contains two identical one-end closed alumina cells surrounded by a series of thermopiles. The temperature of the isothermal block was measured using a Pt–Pt10% Rh thermocouple (± 0.1 K). The heat flow between the isothermal block and either of the cells was recorded in the form of a millivolt signal. The details of the experimental measurements have been described elsewhere [2]. The heat calibration was carried out using a synthetic sapphire (NIST SRM-720).

About 3 g of pure cadmium metal contained in alumina tube with a quartz insert as a protective liner was introduced into the alumina reaction cell on either side of the calorimeter. The system was evacuated and purged with the purified argon gas three times and then a continuous inert gas flow was maintained for 2 h before and during heating the metal. The calorimeter was programmed and maintained at 655.5 K which is 61 K above the melting point of Cd metal. The reaction cell assembly was slowly lowered into the calorimeter and equilibrated for sufficiently long time till a steady base line signal was achieved. The base line shift in the differential heat flow signal for the endothermic effect due to small vaporization of Cd metal got nullified as the same effect was present in the sample and reference cell. Small pellets containing few milligrams of the reactants were dropped from room temperature to the reaction cell containing liquid Cd and the corresponding enthalpy change signal as a function of temperature was noted. The reaction completion time was determined by recording the heat flow signal as a function of time. After each measurement the sample and reference cells were slowly withdrawn from the calorimeter chamber under flowing argon condition and allowed to cool to room temperature. The characterization of the cooled mass for evolution of the phase was done by XRD and EDX analyses. For each experiment fresh cadmium metal was used so that the similar dilution condition was maintained. The amount of the reactant dropped into the Cd(l) was chosen in such a manner that the concentration of Zr in Cd remained well below 1 at.%. The evolution of phases and the distribution of Zr in the cadmium matrix after the dropping experiment were checked by XRD and EDX analyses of the frozen liquid.

3. Results and discussion

Fig. 1(a) gives the XRD pattern of Cd_3Zr prepared by the direct reaction of Zr powder and cadmium turnings at 773 K. The compound crystallizes in the tetragonal AuCu type structure with the cell parameters as $a = 441.5$ pm, $c = 430.7$ pm and space group $P4/mmm$ (no. 123) [3]. No impurity lines due to ZrO_2 , Zr, and Cd etc. could be found. After indexing the cell parameters are found to be $a = 437.5(2)$ pm, $c = 436.2(2)$ pm. The chemical analysis of Cd_3Zr indicates that the observed

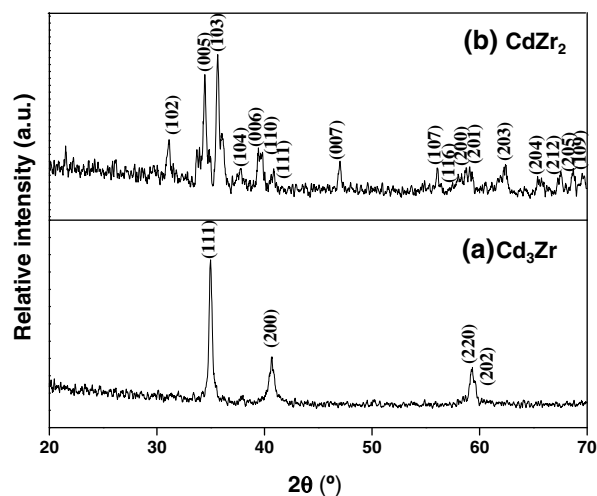


Fig. 1. XRD plots of the prepared compounds (a) Cd_3Zr and (b) CdZr_2 .

atom per cents of Zr and Cd match with the expected values. Our attempts to prepare the other reported compounds in the Cd–Zr system such as Cd_2Zr , CdZr and CdZr_2 did not yield pure phases as they were always contaminated with Cd_3Zr as impurity phase. Therefore, thermal decomposition of pure Cd_3Zr was tried to prepare these phases. Fig. 2 gives the TG plots for the thermal decomposition of Cd_3Zr recorded under pure argon atmosphere. From the plot it can be seen that $\text{Cd}_3\text{Zr(s)}$ decomposes to CdZr(s) and $\text{CdZr}_2\text{(s)}$ in the temperature range of 623–723 K and 748–873 K, respectively, and finally to Zr metal with dissolved cadmium, corresponding to the phase boundary composition [1]. Out of the two TG steps the last one corresponding to the formation of CdZr_2 was distinct. The total mass loss of 65.2% observed in the above steps matches well with the expected mass change for the formation of $\text{CdZr}_2\text{(s)}$. The Cd:Zr ratio seen in EDX corroborated the composition. CdZr_2 in large amount was therefore, prepared by decomposing Cd_3Zr , contained in a tantalum Knudsen cell at 1073 K and online monitoring

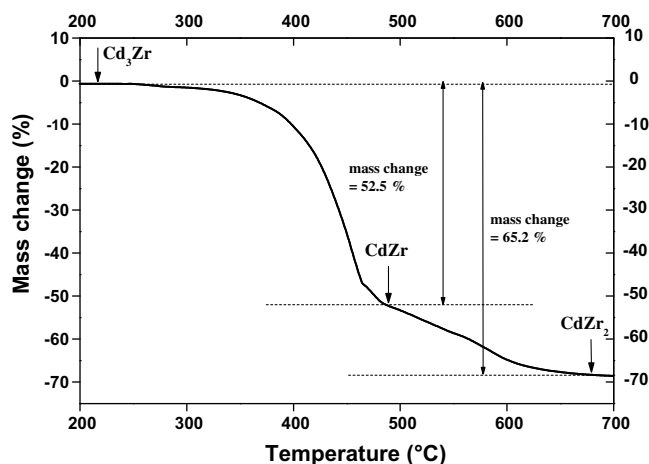


Fig. 2. Thermal decomposition of Cd_3Zr .

its mass loss using a vacuum balance. Fig. 1(b) gives the XRD pattern of CdZr_2 . The XRD lines could be indexed to a MoSi_2 type tetragonal crystal lattice with cell constants $a = 315(1)$ pm, $c = 1330(1)$ pm and space group $I4/mmm$ (no. 139), against the reported data $a = 315$ and $c = 1337$ [4]. However, due to the close decomposition steps the phases Cd_2Zr and CdZr could not be isolated in the pure form by this method.

3.1. Standard enthalpy of formation of $\text{Cd}_3\text{Zr}(s)$ and $\text{CdZr}_2(s)$

Fig. 3(a) gives the heat flow signal for the dropping of Cd from room temperature to liquid Cd maintained at 655.5 K. A single endothermic peak was observed. In this case the steady base line resumed after two hours of dropping of the sample. Hence, 2 h measurement time was chosen for each experiment. Table 1 gives the values of enthalpy change of dropping of $\text{Zr}(s)$, $\text{Cd}(s)$, $\text{CdZr}_2(s)$ and $\text{Cd}_3\text{Zr}(s)$ into the $\text{Cd}(l)$ maintained at 655.5 K. The average enthalpy change for $\text{Cd}(s)$ dropping is found to be (16.11 ± 0.10) kJ mol^{-1} . This enthalpy change was attributed to the sum of the heat effects due to the enthalpy increment for heating $\text{Cd}(s)$ from 298 K to the melting point (594.26 K), the enthalpy of fusion of Cd and the enthalpy for heating liquid Cd from 594.26K–655.5 K. The total enthalpy change (ΔH_T) for the process can be expressed as

$$\Delta H_T = \int_{298.15}^{594.26} C_p(\text{Cd},s)dT + \Delta H_{\text{fus}}(\text{Cd}) + \int_{594.26}^{655.5} C_p(\text{Cd},l)dT \quad (1)$$

Using the values of the heat capacity of solid Cd and liquid Cd and the enthalpy of fusion of Cd from the literature [5], the enthalpy change for Cd dropping could be found to be (16.44 ± 0.35) kJ mol^{-1} which agrees very well with our experimental values.

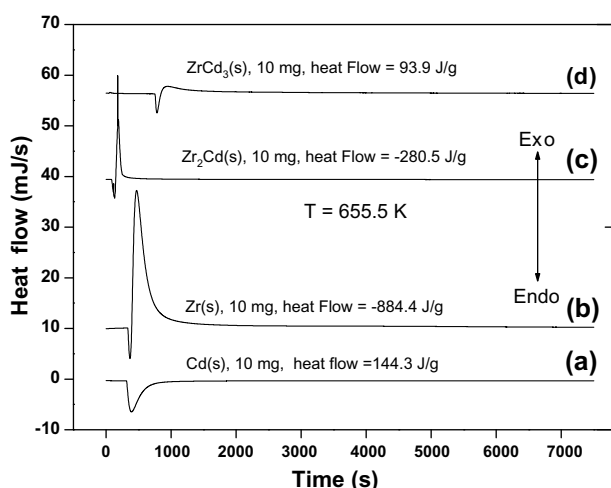


Fig. 3. Plot of heat flow vs. time in calorimetric reactions.

Table 1

The molar enthalpies of dissolution of $\text{CdZr}_2(s)$, $\text{Cd}_3\text{Zr}(s)$, $\text{Zr}(s)$ and $\text{Cd}(s)$ in 3 g of $\text{Cd}(l)$ at $T = 655.5$ K

Compound	Mass m (mg)	ΔH (J/g)	ΔH_T (kJ mol^{-1})
$\text{Zr}(s)$ at. wt. = 91.224	14.2	-884.4	-80.68
	27.5	-869.0	-79.28
	31.3	-891.2	-81.31
	20.5	-879.6	-80.24
			Average: -80.38 ± 0.85
$\text{Cd}(s)$ at. wt. = 112.41	359.2	144.3	16.22
	138.5	142.4	16.01
	183.7	143.7	16.15
	108.5	142.8	16.05
			Average: 16.11 ± 0.10
$\text{CdZr}_2(s)$ mol. wt. = 294.86	49.6	-280.5	-82.71
	66.9	-281.7	-83.06
	27.8	-281.9	-83.12
	15.3	-280.9	-82.83
			Average: -82.93 ± 0.19
$\text{Cd}_3\text{Zr}(s)$ mol. wt. = 428.454	33.0	93.9	40.23
	34.9	93.7	40.15
	9.4	94.0	40.27
	17.2	93.8	40.19
			Average: 40.21 ± 0.05

m denotes the mass of the sample dissolved; ΔH is the measured energy change per unit mass and ΔH_T is the molar enthalpy of solution.

Fig. 3(b) gives the heat flow versus time plot for dropping of Zr metal in liquid Cd. It can be observed that immediately after the dropping an endothermic peak accompanied with another exothermic peak was obtained. The endothermic peak is attributed to the absorption of heat for heating Zr metal from 298 to 655.5 K, while the exothermic effect can be attributed to the reaction of Zr with excess Cd metal to form one Cd-rich solution. The SEM/EDX analysis of the frozen sample indicates that Zr is uniformly distributed in the whole solvent medium (Cd metal) with sparsely distributed small packets having higher concentrations of Zr (Fig. 4). The inset in the

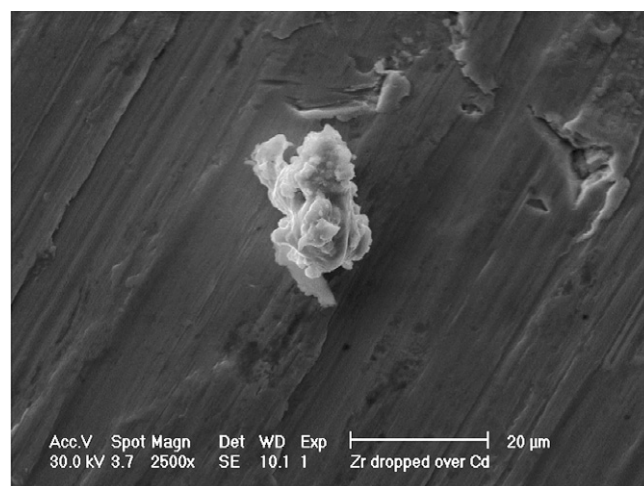


Fig. 4. SEM image showing small packets having higher concentration of Zr in Cd recorded at 655.5 K.

SEM picture shows a Zr-rich composition. The average concentration of Zr in these pockets determined from the EDX analysis was found to be close to 30 at.%, which is near to the Cd_3Zr composition. This intermetallic phase precipitation from the dilute solution can be explained on the basis of the phase diagram of the binary Cd–Zr system. The Cd-rich liquid on cooling below this eutectic temperature of 594.26 °C results in the two-phase mixture of $\text{Cd}_3\text{Zr(s)} + \text{Cd(s)}$. However, due to the small concentration of the Cd_3Zr phase (<1%), the XRD pattern of the alloys after the reaction showed a line due to Cd metal only.

The completion of the reaction between Zr powder and the Cd liquid was monitored by recording the heat flow signal at different time intervals (7200, 14400, 21600 and 28800 s). Steady base lines in the heat flow signal could be obtained from 6000 s onwards. No significant change in the heat flow values could be noticed for different time intervals. For comparison purpose the heat flow signals are shown for 7500 s for all the measurements. The overall heat effect was calculated considering both endothermic and exothermic effects using the SETSOFT software supplied along with the instrument.

Similarly the heat of reaction of $\text{CdZr}_2\text{(s)}$ and $\text{Cd}_3\text{Zr(s)}$ with Cd(l) was calculated considering both the endothermic peak due to sample heating from room temperature to the reaction temperature and the exothermic effect for the heat of reaction (Fig. 3(c) and (d)). It can be noticed from Fig. 3(d) that the overall heat effect in the case of $\text{Cd}_3\text{Zr(s)}$ is endothermic. In this case an endothermic peak followed by a small diffused exothermic peak. The endothermic peak is due to heating of the sample from the drop temperature to 655.5 K, while the small diffused exothermic peak is due to the dissolution of $\text{Cd}_3\text{Zr(s)}$ in Cd forming a dilute solid solution. Table 1 gives the molar heat of reaction of $\text{Cd}_3\text{Zr(s)}$ with Cd(l) and $\text{CdZr}_2\text{(s)}$ with Cd(l).

The thermochemical cycles from which the standard molar enthalpies of formation of $\text{CdZr}_2\text{(s)}$, and $\text{Cd}_3\text{Zr(s)}$ have been derived are given in Table 2 and 3, respectively. The experimentally measured values using the above cycles were combined together to derive the standard molar enthalpy of formation of $\text{CdZr}_2\text{(s)}$, and $\text{Cd}_3\text{Zr(s)}$ at 298.15 K. The values are $-(61.7 \pm 1.2) \text{ kJ mol}^{-1}$ and $-(72.3 \pm 0.9) \text{ kJ mol}^{-1}$ for $\text{CdZr}_2\text{(s)}$, and $\text{Cd}_3\text{Zr(s)}$, respectively (see the tables).

Table 2

Reaction scheme for the standard molar enthalpy of formation of $\text{CdZr}_2\text{(s)}$

Reaction	ΔH_i	ΔH_i (kJ mol^{-1})
$\text{CdZr}_2\text{(s,298 K)} + \text{Cd(sln)} = 2\text{Zr(sln)} + \text{Cd(sln)}$	ΔH_1	-82.93 ± 0.19
$\text{Zr(s,298 K)} + \text{Cd(sln)} = \text{Zr(sln)}$	ΔH_2	-80.38 ± 0.85
$\text{Cd(s,298 K)} = \text{Cd(sln)}$	ΔH_3	16.11 ± 0.10
$2\text{Zr(s,298 K)} + \text{Cd(s,298 K)} = \text{CdZr}_2\text{(s,298 K)}$	$\Delta_f H_{298}^0$	-61.7 ± 1.2

(M(sln) = dilute solution of species M in 3 g Cd(l) maintained at 655.5 K, $\Delta_f H_{298}^0 = -\Delta H_1 + 2\Delta H_2 + \Delta H_3$).

Table 3

Reaction scheme for the standard molar enthalpy of formation of $\text{Cd}_3\text{Zr(s)}$

Reaction	ΔH_i	ΔH_i (kJ mol^{-1})
$\text{Cd}_3\text{Zr(s,298 K)} + \text{Cd(sln)} = \text{Zr(sln)} + 3\text{Cd(sln)}$	ΔH_1	40.21 ± 0.05
$\text{Zr(s,298 K)} + \text{Cd(sln)} = \text{Zr(sln)}$	ΔH_2	-80.38 ± 0.85
$\text{Cd(s,298 K)} = \text{Cd(sln)}$	ΔH_3	16.11 ± 0.10
$\text{Zr(s,298 K)} + 3\text{Cd(s,298 K)} = \text{Cd}_3\text{Zr(s,298 K)}$	$\Delta_f H_{298}^0$	-72.3 ± 0.9

(M(sln) = dilute solution of species M in 3 g Cd(l) maintained at 655.5 K, $\Delta_f H_{298}^0 = -\Delta H_1 + \Delta H_2 + 3\Delta H_3$).

4. Conclusion

The standard enthalpy of formation of $\text{CdZr}_2\text{(s)}$ and $\text{Cd}_3\text{Zr(s)}$ was obtained by measuring the enthalpy of dissolution of $\text{CdZr}_2\text{(s)}$, $\text{Cd}_3\text{Zr(s)}$, Zr(s) and Cd(s) in the Cd(l) maintained at 655.5 K. The values of $\Delta_f H_{298}^0$ of $\text{CdZr}_2\text{(s)}$ and $\text{Cd}_3\text{Zr(s)}$ were found to be $-(61.7 \pm 1.2) \text{ kJ mol}^{-1}$ and $-(72.3 \pm 0.9) \text{ kJ mol}^{-1}$, respectively.

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