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Journal of Nuclear Materials 376 (2008) 366–370

journal of nuclear materials

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Studies on phase diagram of Pb–Cr–O system

Sulata Kumari Sahu, Rajesh Ganesan, T. Gnanasekaran *

Liquid Metals and Structural Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Abstract

Equilibrium phase fields of the Pb–Cr–O ternary system were identified by long-term equilibrations and characterization of phases by XRD. Existence of the following phase fields was identified: (1) $PbCrO_4$–Pb_2CrO_5–Cr_2O_3, (2) Pb_2CrO_5–Pb_5CrO_8–Cr_2O_3 (3) Pb_5CrO_8–PbO–Cr_2O_3, (4) Pb–PbO–Cr_2O_3 and (5) Pb–Cr–Cr_2O_3. Based on these results, a partial phase diagram of Pb–Cr–O system has been reported.

PACS: 64.75.−g

1. Introduction

Liquid lead and lead bismuth eutectic (LBE) alloy are considered as candidate coolant for fourth generation nuclear reactors and as spallation neutron target as well as coolant in accelerator driven transmutation systems because of their favorable thermal, physical and chemical properties [1]. These properties include high boiling and low melting temperatures, high thermal conductivity, low viscosity, low neutron capture cross section and moderation and high spallation neutron yield [2]. Low chemical reactivity of these coolants with water and air exclude the possibility of fires or explosions. Though these coolants are highly corrosive towards structural steels, a protective oxide layer that prevents this corrosion can be formed over the steel by controlling the oxygen concentration in the coolant. An optimum oxygen concentration in the coolant can be achieved by the use of an oxygen control system, namely, gas phase oxygen control and solid phase oxygen control [3,4]. In this context, study of the interaction of components of structural steels with lead and bismuth in the presence of oxygen is of technological importance. Although many of the ternary compounds involved in Pb (or Bi)–M–O systems (M = Fe, Cr) have been reported, their thermochemical data and equilibrium phase diagrams of the ternary systems are not available. This paper presents the results of the phase equilibration studies on Pb–Cr–O system.

2. Literature data

Preparation and thermal stability of several compounds involved in Pb–Cr–O system and the pseudo binary diagrams of PbO–$PbCrO_4$ and PbO–CrO_3 have been reported in the literature [5–9]. Jaeger and Germs [5] carried out studies on the binary PbO–$PbCrO_4$ system and reported the existence of three additional ternary compounds, viz. Pb_2CrO_5, $Pb_7Cr_2O_{13}$ and Pb_5CrO_8. Negas [6] studied the system by reaction between PbO and Cr_2O_3 in air as a function of temperature and by direct observation of the samples during heating and/or by characterizing the products by X-ray diffraction after quenching them from experimental temperature. Based on the results, the author reported the existence of four ternary compounds, Pb_5CrO_8, Pb_3CrO_6, Pb_2CrO_5 and $PbCrO_4$ in this system. He also reported that $Pb_7Cr_2O_{13}$, a compound that had been reported by Jaeger and Germs [5], was not formed in this system and it was mistaken for Pb_3CrO_6. The experimental results of Negas [6] also indicated that when $PbCrO_4$ was heated in air above 1026 K, it decomposed to Pb_2CrO_5 and Cr_2O_3 with evolution of oxygen. Pb_3CrO_6 was found

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* Corresponding author. Tel.: +91 44 27480302; fax: +91 44 27480065.
E-mail address: gnani@igcar.gov.in (T. Gnanasekaran).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.02.010

to be formed above 1026 K from Pb_2CrO_5 and Pb_5CrO_8 and it congruently melted at 1116 K. DeVries and Roth [7] synthesized a new ternary compound, $PbCrO_3$ which is stable at high pressures and high temperatures (50–65 kbar, 1393–1573 K). The author also derived phase relations in Pb–Cr–O system at high pressure and high temperatures. For these experiments, they had taken the starting materials in the form of cylindrical pellets in a crimped platinum container, which in turn was placed inside a high pressure cell. Then the pressure of the cell was raised to the appropriate value and the temperature of the cell was raised at a programmed rate of 200 °C/min and was held at the desired temperature for 20–30 min and quenched at the rate of 400 °C/s. The samples were then analyzed by XRD.

Mal'tsev et al. [8] studied the phase diagram of PbO–CrO_3 pseudo binary system and reported the formation of Pb_6CrO_9 in addition to Pb_2CrO_5 and $PbCrO_4$. However, the authors did not observe the existence of Pb_3CrO_6 and Pb_5CrO_8. Gadalla and Abadir [9] reported the pseudo binary phase diagram of PbO–Cr_2O_3 system, which shows the existence of the four compounds, viz., $PbCrO_4$, Pb_2CrO_5, Pb_3CrO_6 and Pb_5CrO_8. $PbCrO_4$ was found to be stable in air from 478 K to 1030 K while Pb_2CrO_5 was found to be stable from 873 K to 1197 K. Pb_3CrO_6 and Pb_5CrO_8 were reported to be stable in the temperature range of 1010–1111 K and 948–1108 K, respectively. It is to be noted that Pb_6CrO_9 was not observed by Gadalla and Abadir [9].

3. Experimental

3.1. Materials

Pb_3O_4 powder (99% purity on metal basis, M/s Aldrich Chem. Co., USA), Cr_2O_3 powder (99.999% purity on metal basis, M/s Johnson Matthey Materials Technology, UK) and PbO powder (99.9+% purity on metal basis, M/s Aldrich Chem. Co., USA) were the starting reagents used. Thermogravimetry experiments coupled with evolved gas analysis showed that PbO and Cr_2O_3 contained 1.37 wt% and 0.3 wt% of moisture, respectively. It was also found that PbO contained 2 wt% lead carbonate impurity. The PbO powder was therefore heated in argon atmosphere at 773 K for 2 h while the Cr_2O_3 powder was calcined in air at 523 K for 2 h to remove the moisture before using them in experiments. Lead powder (99.9% purity, M/s Alfa Aesar, USA) and chromium powder (99.8% purity, M/s Alfa Aesar, USA) were also used for phase equilibration studies. The ternary compounds were prepared by the solid-state reaction of mixtures of appropriate molar ratios of lead oxide and chromium oxide powders. The samples were in the form of compacted pellets and were heated in alumina crucibles in ambient air. When Pb_3O_4 was one of the reactant and the product was formed with consumption of oxygen from ambient air, the pellets were first heated at 823 K (which is below the decomposition temperature of Pb_3O_4) for prolonged periods. This was followed by a spell of heating at temperatures above 823 K. During these heating cycles, the pellets were crushed at least once, ground, pelletised and heated in air again. The temperature and duration of heating for preparation of these ternary compounds are given below:

$$2Pb_3O_4 + 3Cr_2O_3 + 7/2O_2 \xrightarrow[\text{b. 923 K, 2 h}]{\text{a. 823 K, 18 h}} 6PbCrO_4, \qquad (1)$$

$$2PbO + Cr_2O_3 + 3/2O_2 \xrightarrow{\text{923 K, 24 h}} 2PbCrO_4, \qquad (2)$$

$$4Pb_3O_4 + 3Cr_2O_3 + 5/2O_2 \xrightarrow[\text{b. 923 K, 2 h}]{\text{a. 823 K,18 h}} 6Pb_2CrO_5, \qquad (3)$$

$$4PbO + Cr_2O_3 + 3/2O_2 \xrightarrow{\text{923 K, 30 h}} 2Pb_2CrO_5 \qquad (4)$$

$$10Pb_3O_4 + 3Cr_2O_3 \xrightarrow{\text{1023 K, 24 h}} 6Pb_5CrO_8 + 1/2O_2\uparrow, \qquad (5)$$

$$10PbO + Cr_2O_3 + 3/2O_2 \xrightarrow{\text{1023 K, 24 h}} 2Pb_5CrO_8, \qquad (6)$$

$$Pb_3O_4 + 1/2Cr_2O_3 + 1/4O_2 \xrightarrow{\text{1048 K, 24 h}} \text{No } Pb_3CrO_6 \text{ formation (only a mixture of } Pb_5CrO_8\text{–}Pb_2CrO_5), \qquad (7)$$

$$2Pb_3O_4 + 1/2Cr_2O_3 \xrightarrow[\text{b. 923 K, 2h}]{\text{a. 823 K, 18 h}} \text{No } Pb_6CrO_9 \text{ formation (only a mixture of } Pb_5CrO_8 - PbO), \qquad (8)$$

$$6PbO + 1/2Cr_2O_3 + 3/4O_2 \xrightarrow{\text{923 K, 24 h}} \text{No } Pb_6CrO_9 \text{ formation (only a mixture of } Pb_5CrO_8 - PbO). \qquad (9)$$

The resulting products were characterised by X-ray diffraction using a Siemens D500 X-ray powder diffractometer with Cu K_α radiation and graphite monochromator.

3.2. Phase equilibration studies

In order to obtain first information regarding the phase fields in the Pb–Cr–O system, the individual ternary chromates namely, $PbCrO_4$, Pb_2CrO_5, Pb_5CrO_8 were allowed to get reduced partially under (i) H_2 atmosphere at 823 K for 2 h and (ii) moist Ar–1% H_2 atmosphere at 723 K for half an hour (Table 1). During this process, the overall composition of the sample shifts towards lower oxygen content with Pb/Cr ratio remaining constant. The samples were then analyzed by X-ray diffraction to deduce the possible co-existing phases. Except for experiments 4 and 5 listed in Table 1, the products formed were then mixed thoroughly and pelletised. The pellets were placed inside an alumina crucible that was then sealed in a quartz ampoule under vacuum and allowed to equilibrate at 923 K for 240 h and quenched in liquid nitrogen. The products were then characterised by XRD.

Based on the above preliminary results, a detailed phase equilibrations were carried out. Mixtures from pure metals, oxides and the ternary compounds with different overall compositions, shown in column 2 of Table 2 and in

Table 1
Results of partial reduction of chromates followed by equilibration

Experiment no.	Starting compound	Temperature and duration of reduction	Temperature and duration of equilibration after reduction	Phases identified after equilibration
Reduction under pure hydrogen				
1	$PbCrO_4$	550 °C, 2 h	700 °C, 240 h	$Pb–PbO–Cr_2O_3$
2	Pb_2CrO_5	550 °C, 2 h	700 °C, 240 h	$Pb–Cr_2O_3$
3	Pb_5CrO_8	550 °C, 2 h	700 °C, 240 h	$Pb–PbO–Cr_2O_3$
Reduction under moist Ar–1%H_2 mixture				
4	$PbCrO_4$	450 °C, 1/2 h	–	$Pb_2CrO_5–Pb_5CrO_8–Cr_2O_3$
5	Pb_2CrO_5	450 °C, 1/2 h	–	$PbCrO_4–Pb_2CrO_5–Cr_2O_3$
6	Pb_5CrO_8	450 °C, 1/2 h	700 °C, 240 h	$Pb–Cr_2O_3$

Table 2
Results of phase equilibration studies in Pb–Cr–O system

Sl. no	Phases taken before equilibration	Overall composition of the sample (in molar scale)	Co-existing phases after equilibration at 973 K
1	$Pb_2CrO_5–PbCrO_4–Cr_2O_3$	$Pb_{0.04}Cr_{0.35}O_{0.61}$	$Pb_2CrO_5–PbCrO_4–Cr_2O_3$
2	$PbCrO_4–PbO–Cr_2O_3$	$Pb_{0.08}Cr_{0.30}O_{0.62}$	$Pb_2CrO_5–Cr_2O_3$
3	$PbCrO_4–PbO–Pb$	$Pb_{0.33}Cr_{0.12}O_{0.55}$	$Pb_5CrO_8–PbO–Cr_2O_3$
4	$PbCrO_4–PbO–Cr$	$Pb_{0.16}Cr_{0.26}O_{0.58}$	$Pb_5CrO_8–PbO–Cr_2O_3$
5a	$Pb_5CrO_8–Pb_2CrO_5–Cr_2O_3$	$Pb_{0.15}Cr_{0.25}O_{0.60}$	$Pb_5CrO_8–Pb_2CrO_5–Cr_2O_3$
5b	$PbCrO_4–PbO–Cr_2O_3$	$Pb_{0.15}Cr_{0.25}O_{0.60}$	$Pb_5CrO_8–Pb_2CrO_5–Cr_2O_3$
6	$PbCrO_4-PbO-Cr$	$Pb_{0.20}Cr_{0.38}O_{0.42}$	$Pb–Cr–Cr_2O_3$
7	$Pb–Cr–Cr_2O_3$	$Pb_{0.05}Cr_{0.65}O_{0.30}$	$Pb–Cr–Cr_2O_3$
8	$PbCrO_4–PbO–Cr_2O_3$	$Pb_{0.16}Cr_{0.20}O_{0.64}$	$Pb_2CrO_5–PbCrO_4–Cr_2O_3$
9	$PbO–Cr–Cr_2O_3$	$Pb_{0.35}Cr_{0.20}O_{0.45}$	$Pb–PbO–Cr_2O_3$

Fig. 1 were prepared by thorough grinding of the component phases. They were also compacted into pellets, taken in alumina crucibles and encapsulated in evacuated quartz ampoules by following the usual procedure described earlier. Each sample was first equilibrated at 973 K for a total period of ≈200 h after which it was quenched in liquid nitrogen. The products were thoroughly ground and characterised by XRD. They were recompacted and sealed under vacuum in quartz ampoules followed by equilibration at 973 K for another spell of 200 h. After equilibration, the quartz ampoules were again quenched in liquid nitrogen. The samples were then retrieved and analyzed by X-ray diffraction.

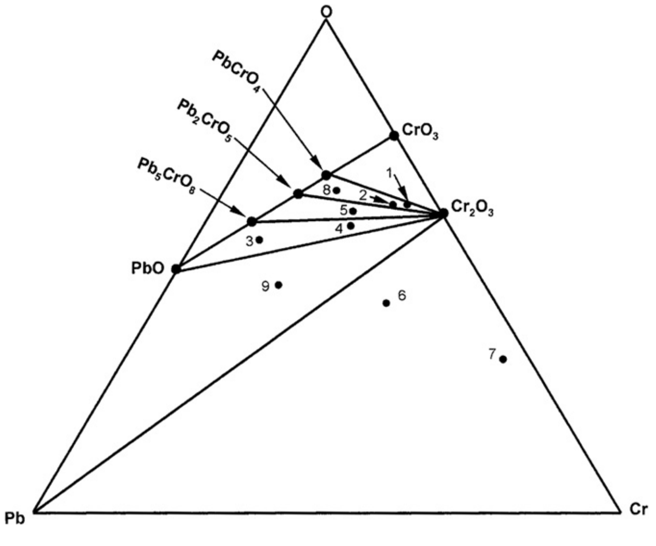

Fig. 1. Partial phase diagram of Pb–Cr–O system at 973 K.

In order to identify the existence of any ternary compounds in the pseudo binary $PbO–Cr_2O_3$ system, compacts of PbO and Cr_2O_3 corresponding to the molar ratios of 2:1, 1:1 and 10:1 were also equilibrated at 923 K for 240 h in vacuum sealed quartz ampoules with one intermediate grinding and recompaction. The samples after equilibration were analyzed by XRD.

4. Results and discussion

The obtained XRD patterns of Pb_5CrO_8, Pb_2CrO_5 and $PbCrO_4$ matched with the patterns reported in JCPDS files of these compounds, viz., 49-0970, 29-0768, 73-2059, respectively. Attempts to prepare Pb_3CrO_6 always resulted in a mixture of Pb_2CrO_5 and Pb_5CrO_8. Although Pb_3CrO_6 is reported to be a stable phase in the temperature range 1010–1111 K, pure phase could not be quenched due to kinetic reasons. Our attempts to prepare Pb_6CrO_9 that was reported by Mal'tsev et al. [8] to be stable up to 1077 K always resulted in a mixture of Pb_5CrO_8 and PbO. This result clearly showed that the compound of composition Pb_6CrO_9 is not formed in this system and it was mistaken for Pb_5CrO_8 by Mal'tsev et al. [8]. It is also to be pointed out that Pb_6CrO_9 was not observed by Negas [6] and Gadalla and Abadir [9].

Equilibrations of phase mixtures of PbO and Cr_2O_3 taken in different molar ratios always showed the co-existence of PbO and Cr_2O_3 only and no ternary compounds were formed. These results showed that in Pb–Cr–O system, under atmospheric conditions ternary compounds exist along PbO–CrO_3 pseudo binary line only.

Table 1 gives the conditions employed for the reduction of the ternary compounds under pure hydrogen and moist Ar–1% H_2 mixture and the phases identified after these partial reduction followed by prolonged equilibration. As seen from the table, the reduction process continued till metallic lead was formed, when pure hydrogen was used. Experiments with $PbCrO_4$ and Pb_5CrO_8 revealed the possible coexistence of the phase field Pb–PbO–Cr_2O_3 while the experiment with Pb_2CrO_5 revealed the possible existence of Pb–Cr_2O_3 line in the phase diagram. Oxygen potential of moist Ar–1% H_2 mixture gas will be higher than in the case of H_2. Reduction under this condition is expected to yield insight into phase fields with higher equilibrium oxygen potential. Reduction of $PbCrO_4$ revealed the possible existence of the phase field $PbCrO_4$–Pb_2CrO_5–Cr_2O_3 while that of Pb_2CrO_5 revealed the possible coexistence of Pb_2CrO_5–Pb_5CrO_8–Cr_2O_3. Reduction of Pb_5CrO_8 revealed the possible coexistence of Pb and Cr_2O_3 while the third equilibrium phase could not be identified.

Table 2 summarizes the details of the samples taken for phase equilibration studies and the results obtained. Since the melting temperatures of the ternary compounds involved are close to the experimental temperature of 973 K, achievement of equilibrium under the prolonged heating periods is expected to be complete. This has been confirmed by the identical XRD patterns of the products obtained at the end of the intermediate equilibration for 200 h and after equilibration for total duration of 400 h. This is also seen from the formation of equilibrium phases when phases of different composition were taken in the initial samples. Fig. 2 shows XRD pattern of the sample mixture of composition $Pb_{0.20}Cr_{0.38}O_{0.42}$ (equilibration experiment no. 6) before and after its equilibration. As the chosen composition $Pb_{0.08}Cr_{0.30}O_{0.62}$ fell on the pseudo binary line of Cr_2O_3 and Pb_2CrO_5, the resultant equilibrium phases were Cr_2O_3 and Pb_2CrO_5 only. From the results indicated in Table 2, the existence of the following

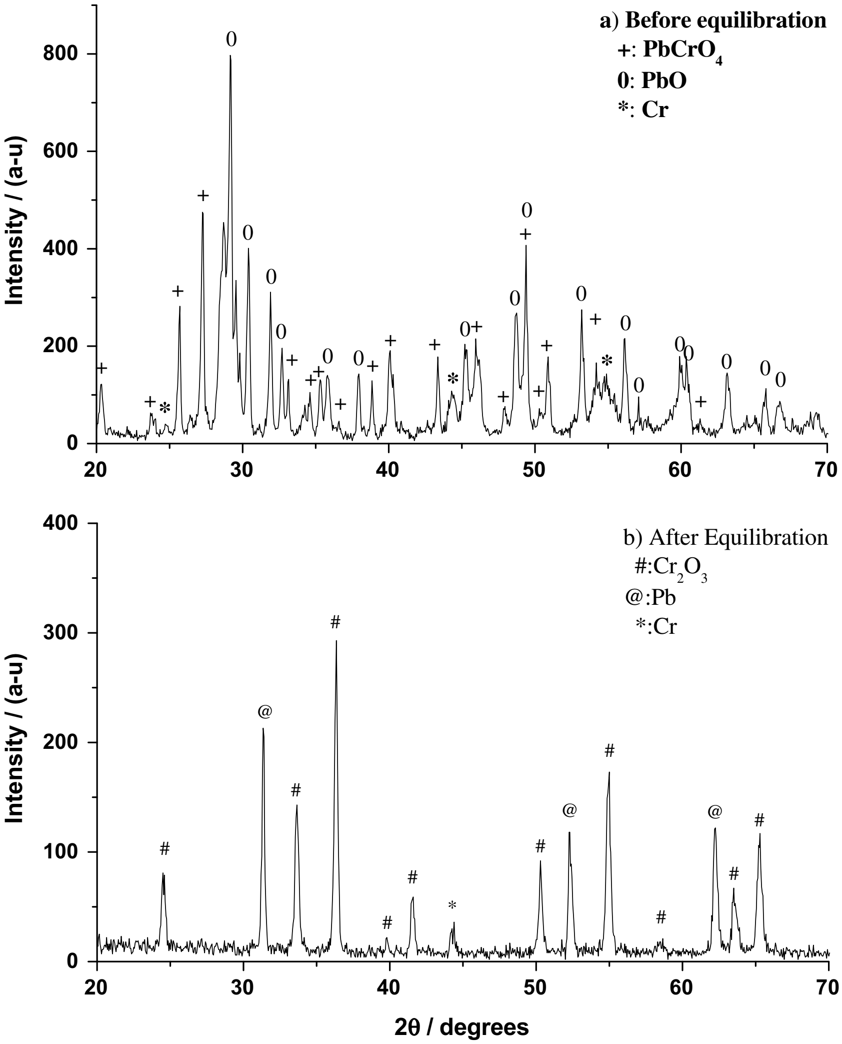

Fig. 2. XRD pattern of the sample of composition $Pb_{0.20}Cr_{0.38}O_{0.42}$ before and after equilibration (a) before equilibration, $PbCrO_4$–PbO–Cr and (b) after equilibration, Pb–Cr–Cr_2O_3.

phase fields at 973 K could be identified: (1) $PbCrO_4$–Pb_2CrO_5–Cr_2O_3, (2) Pb_2CrO_5–Pb_5CrO_8–Cr_2O_3, (3) Pb_5CrO_8–PbO–Cr_2O_3, (4) Pb–PbO–Cr_2O_3 and (5) Pb–Cr–Cr_2O_3.

Based on the above results, the partial phase diagram of Pb–Cr–O system was constructed and is shown in Fig. 1.

5. Conclusions

The partial phase diagram of the ternary Pb–Cr–O system at 973 K has been established. This phase diagram reveals that Cr_2O_3 would first precipitate on increasing oxygen concentration in liquid lead. Further increase in oxygen concentration will lead to precipitation of PbO and no Pb–Cr–O ternary compounds would be formed. This is of significance in understanding the corrosion behavior of alloy steels in lead coolant circuit. Further studies on ternary systems such as Pb–Fe–O need to be carried out to understand the formation of protective oxide layer over the structural steels.

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