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Experimental investigations and thermodynamic description of the $PbO-Bi_2O_3$ system

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ABSTRACT

In the present work, the experimental characterization of the pseudo-binary $PbO–Bi_2O_3$ cut has been performed by differential thermal analysis (DTA), isothermal annealing, powder X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). A thermodynamic assessment according to the Calphad method was also performed based on the present results as well as previous experimental data using the ThermoCalc software.

1. Introduction

The T91 steel (9%Cr1%Mo) is considered as a structural material in the new generation of nuclear reactors named ADS (Accelerator Driven System). In this device, the steel will be in direct contact with the liquid spallation target (which is constituted by lead or lead–bismuth eutectic, 55.2 wt.% Bi). It is necessary to evaluate the corrosion resistance of the T91 steel in the eutectic liquid lead–bismuth environment, under a low oxygen pressure and more particularly in the temperature range of (300 to 600) °C. The first immersion tests had shown that complex oxides of Fe, Bi, and Pb were formed [1] leading to the conclusion that a complete thermodynamic knowledge of the quinary Pb–Bi–O–Fe–Hg system would be useful for the understanding and the interpretation of the corrosion results.

In order to obtain the thermodynamic assessment of the quinary system, it was necessary in a first time to investigate the description of the ternary sub-systems. The study of three ternary sub-systems, Pb–Bi–Hg, Bi–Fe–O, and Pb–Fe–O, has been initiated experimentally in our laboratory [2–5]. In the present work, the efforts are focused on the ternary Pb–Bi–O and more particularly on the investigation on the pseudo-binary $PbO–Bi_2O_3$ cut in order to obtain the most coherent diagrammatic information which is essential to model the system according to a Calphad approach.

2. Experimental data

2.1. Review

The phase diagram of the $PbO–Bi_2O_3$ system was established by Belladen in 1922 who pointed out the existence of the following three compounds: Bi_8PbO_{13}(4:1), $Bi_6Pb_2O_{11}$(3:2), and $Bi_2Pb_2O_5$(1:2) [6]. In 1969, Boivin *et al.* [7] had mentioned the existence of an extensive solid solution between Bi_2PbO_4(1:1) and $Bi_6Pb_7O_{16}$(3:7) at 625 °C by annealings and X-ray diffraction. Later by coupling DTA, XRD, and annealings between (500 and 750) °C, they had confirmed the existence of $Bi_6Pb_2O_{11}$(3:2), $Bi_6Pb_7O_{16}$(3:7), and the solid solution named β_{ss} with a wide range of non-homogeneity. Moreover they had found three new compounds: $Bi_{12}PbO_{19}$(6:1), $Bi_8Pb_5O_{17}$(4:5), and $Bi_2Pb_3O_6$(1:3) [8]. Further investigations carried out by Biefeld and White [9] in 1980, using X-ray diffraction and DTA, confirmed the existence of four phases $Bi_{12}PbO_{19}$(6:1), $Bi_6Pb_2O_{11}$(3:2), $Bi_8Pb_5O_{17}$(4:5), $Bi_2Pb_3O_6$(1:3), and the solid solution β_{ss}. But they did not observed the presence of $Bi_6Pb_7O_{16}$(3:7). In order to avoid the oxidation of PbO to Pb_3O_4, Biefeld and White [9] had heated their samples in reduce atmosphere (N_2) and then they had obtained the forecasted phases without Pb_3O_4. Their results indicated that the $PbO–Bi_2O_3$ phase diagram presented a single eutectic situated at 73 mol.% PbO and 635 °C, a Bi_2O_3 solid solution while undergoes an allotropic α/β transformation at 715 °C, one tetragonal PbO solid solution, γ, and one intermediate solid solution (figure 1). The PbO-L/PbO-M (L = Litharge; M = Massicot) transformation temperature (489 °C) was not indicated because experiments was carried out between (500 and 900) °C. There is also two eutectoids involving

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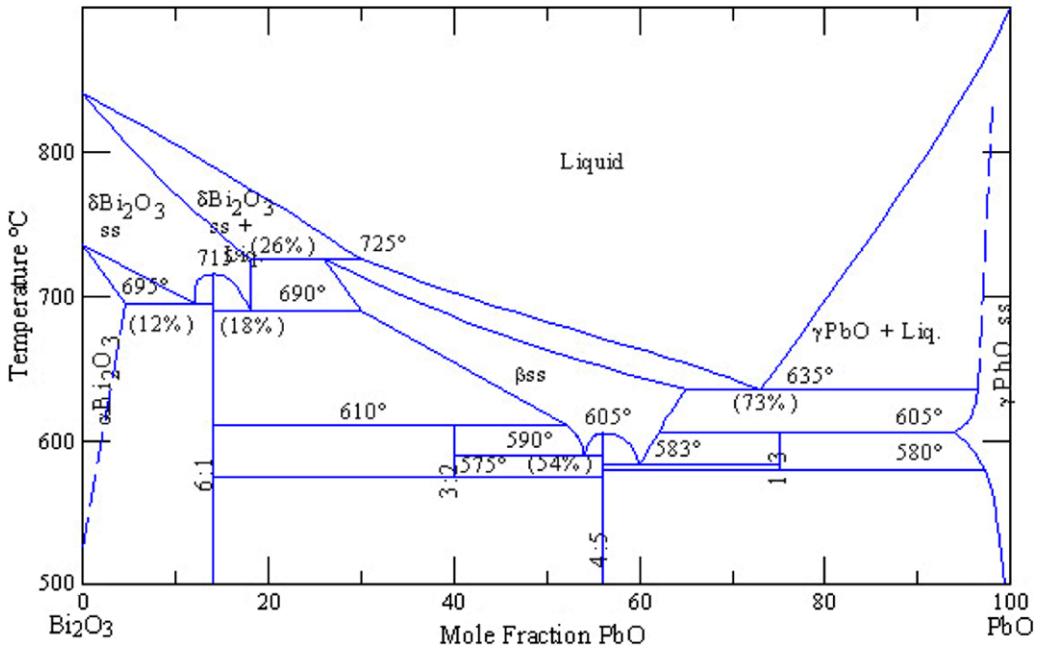

FIGURE 1. The phase diagram of Bi_2O_3–PbO system [9].

$Bi_{12}PbO_{19}$(6:1), one at 12 mol.% PbO and 695 °C (δ-Bi_2O_3 → $Bi_{12}PbO_{19}$(6:1) + α-Bi_2O_3) and the other at 18 mol.% PbO and 690 °C (δ-Bi_2O_3 → $Bi_{12}PbO_{19}$(6:1) + β_{ss}). The compound $Bi_{12}PbO_{19}$(6:1) is formed from δ-Bi_2O_3 at 715 °C. The peritectic formation of β_{ss} from δ-Bi_2O_3 and liquid (liquid + δ-Bi_2O_3 → β_{ss}) occurs at 26 mol.% PbO and 725 °C. The peritectoid and eutectoid for the formation and the decomposition of $Bi_2Pb_3O_6$(1:3), *i.e.* β_{ss} + γ-PbO → $Bi_2Pb_3O_6$(1:3) and $Bi_2Pb_3O_6$(1:3) → $Bi_8Pb_5O_{17}$(4:5) + γ-PbO, occur at (610 and 575) °C, respectively. The $Bi_8Pb_5O_{17}$(4:5) compound is formed at 605 °C on cooling the β_{ss} phase and is involved in two eutectoids, at (590 and 583) °C and related to (54 and 60) mol.% PbO, respectively, *i.e.* β_{ss} → $Bi_6Pb_2O_{11}$(3:2) + $Bi_8Pb_5O_{17}$(4:5) and β_{ss} → $Bi_8Pb_5O_{17}$(4:5) + $Bi_2Pb_3O_6$(1:3).

The $Bi_8Pb_5O_{17}$(4:5) compound presents at least four polymorphs, which structural aspects have been studied in the past. A compilation of literature data was done by Ganesan *et al.* [10]. β_1-$Bi_8Pb_5O_{17}$(4:5), β_2-$Bi_8Pb_5O_{17}$(4:5), and ϕ-$Bi_8Pb_5O_{17}$(4:5) are low temperature phases. β_1-$Bi_8Pb_5O_{17}$(4:5) with monoclinic form is obtained by quenching in liquid nitrogen from (595 to 605) °C. β_2-$Bi_8Pb_5O_{17}$(4:5) with tetragonal structure and ϕ-$Bi_8Pb_5O_{17}$(4:5) with triclinic structure are formed at different temperature. These two phases can be observed as well on heating (β_2 → ϕ → β_{ss}) as on cooling (β_{ss} → β_2 → ϕ). According to Ganesan *et al.* [10], the ϕ-$Bi_8Pb_5O_{17}$(4:5) form is more stable than β_2. The β_{ss} is the high temperature phase with a body-centered cubic form. Ganesan *et al.* [10] indicated that the formation of all these phases depends on the thermal history of the sample and that could be attributed to their comparable thermodynamic stabilities. Some transformations can be irreversible.

Later, in 1993, Vikhreva *et al.* [11] had confirmed the existence of $Bi_8Pb_5O_{17}$(4:5) and also had indicated the existence of $Bi_8Pb_6O_{18}$(4:6). These works [10,11] illustrate the difficulties to interpret the experimental results when the samples are heated in air between (450 and 520) °C, in attempt to reach equilibrium. In this situation, PbO oxidizes into Pb_3O_4. This was announced by Shaaban *et al.* [12] in 1984.

More recently, some other authors had confirmed or infirmed these results. In 1996, Zhongbao *et al.* [13], after having investigated the phase diagram PbO–Bi_2O_3 using the same techniques as [9–12], had proposed a new version of the phase diagram (figure 2). Unlike the works of Belladen [6], Boivin *et al.* [7], Boivin and Tridot [8], and Biefeld and White [9], their results had put in evidence only two compounds. They had confirmed the existence of $Bi_{12}PbO_{19}$(6:1) and $Bi_6Pb_3O_9$(2:3) compounds. The eutectoid decomposition of $Bi_6Pb_3O_9$(2:3) was measured at 55 mol.% PbO and 590 °C ($Bi_6Pb_3O_9$(2:3) → $Bi_{12}PbO_{19}$(6:1) + γ-PbO). One single eutectoid involving $Bi_{12}PbO_{19}$(6:1) was found at 6 mol.% PbO and at 702 °C instead of the two ones identified by Boivin *et al.* [7], Boivin and Tridot [8], and Biefeld and White [9]. A eutectic involving $Bi_{12}PbO_{19}$(6:1) and γ-PbO was observed at 70 mol.% PbO and 615 °C (liquid → $Bi_{12}PbO_{19}$(6:1) + γ-PbO). The decomposition temperature of $Bi_{12}PbO_{19}$(6:1) was measured at 720 °C. The maximum solubility of Bi_2O_3 in γ-PbO phase was reached at 615 °C for about

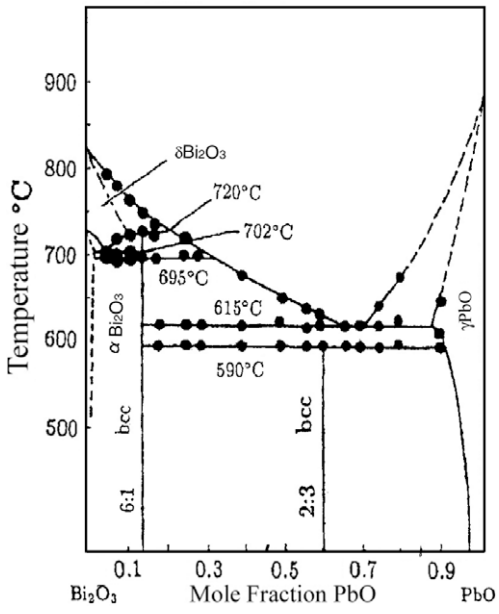

FIGURE 2. The phase diagram of the (Bi_2O_3 + PbO) system [13].