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EXPERIMENTAL STUDY ON THERMODYNAMICS OF Cu-Pb-Ti AND Cu-Pb-V ALLOYS

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Summary

The thermodynamic activity of Pb in liquid Cu-Pb-Ti and Cu-Pb-V alloys has been determined by the equilibrium saturation method at T = 1473K. The Cu-Pb alloy was accepted as a reference mixture. The interaction parameters of titanium and vanadium on the lead activity, ε_{Pb}^{Ti} and ε_{Pb}^{V}, were calculated on the basis of experimental results. Negative values of these parameters suggest that titanium and vanadium decrease lead activity in the studied alloys

Keywords: copper alloys, thermodynamic activity, interaction parameter

Badania właściwości termodynamicznych stopów Cu-Pb-Ti oraz Cu-Pb-V

Streszczenie

Aktywność termodynamiczną ołowiu w ciekłych stopach Cu-Pb-Ti oraz Cu-Pb-V wyznaczono metodą równowagowego nasycania. Badania prowadzono w temperaturze 1473 K. Roztworem wzorcowym był ciekły stop Cu-Pb. Na podstawie wyników wykonanych doświadczeń obliczono wartości parametrów oddziaływania tytanu i wanadu na aktywność ołowiu, ε_{Pb}^{Ti} oraz ε_{Pb}^{V}. Ujemne wartości parametrów oddziaływania sugerują, że tytan i wanad zmniejszają aktywność termodynamiczną ołowiu w badanych stopach Cu-Pb-Ti i Cu-Pb-V.

Słowa kluczowe: stopy miedzi, aktywność termodynamiczna, parametr oddziaływania

1. Introduction

Lead shows a very negative influence on the physical properties of copper, because it is insoluble in the alloy matrix. Microadditions of metals, which effectively increase the solubility of lead in copper or fix it into high-melting compounds, will allow the neutralization of that negative influence. Nevertheless, usually copper makes intermetallic phases with the same metals as lead [1-3].

It has been decided to make a selective study by the determination of the thermodynamic properties of ternary Cu-Pb-Ti and Cu-Pb-V alloys. Lead activity and the influence of titanium and vanadium on lead activity in the investigated alloys were analyzed. Metal, that the most effectively decreases Pb activity should be the most efficient neutralizer.

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2. Experimental

The analyzed alloys show considerable differences between vapour pressures of their elements. For instance at T = 1473K: $p_{Cu} = 3.95*10^{-3}$ hPa, $p_{Pb} = 19.32$ hPa, $p_{Ti} = 1.16*10^{-4}$ hPa, $p_V = 4.1*10^{-6}$ hPa, [4]. As the vapor pressure of Pb is much higher than that of other elements, the activity measurements of Pb were carried out by the comparative method of equilibrium vapor saturation [5-8]. Apparatus used in experiments is presented in Figure 1.

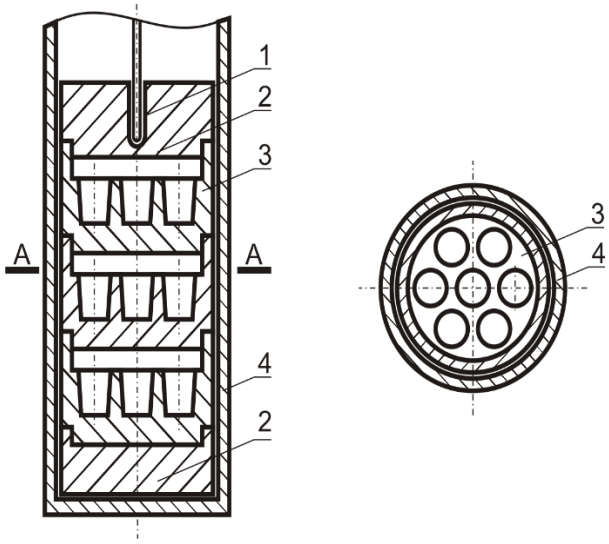

Fig. 1. Apparatus for equilibrium saturation, 1 – [Ni-(Ni-Cr)] thermocouple and alundum sheath for thermocouple, 2– graphite cover, 3 – graphite blocks with grooves for alloys, 4 – vacuum chamber

The studied Cu-Pb-Ti and Cu-Pb-V alloys and the reference Cu-Pb alloy were placed inside a graphite cells in a isothermal zone of a resistance furnace under a reduced argon pressure and saturated with the lead vapor until equilibrium was reached. At the equilibrium state, the activity of Pb is the same in all alloys inside a closed system. If the activity of Pb in the reference Cu-Pb alloy is known, it is possible to calculate the activity of Pb in the Cu-Pb-Ti and Cu-Pb-V alloys:

$$a_{Pb(Cu\text{-}Pb)} = a_{Pb(Cu\text{-}Pb\text{-}Ti)} \tag{1}$$

$$\gamma_{Pb(Cu\text{-}Pb\text{-}Ti)} = x_{Pb(Cu\text{-}Pb)} * \gamma_{Pb(Cu\text{-}Pb)} / x_{Pb(Cu\text{-}Pb\text{-}Ti)} \tag{2}$$

$$a_{Pb(Cu\text{-}Pb)} = a_{Pb(Cu\text{-}Pb\text{-}V)} \tag{3}$$

$$\gamma_{Pb(Cu\text{-}Pb\text{-}V)} = x_{Pb(Cu\text{-}Pb)} * \gamma_{Pb(Cu\text{-}Pb)} / x_{Pb(Cu\text{-}Pb\text{-}V)} \quad (4)$$

where $x_{Pb(Cu\text{-}Pb)}$, $x_{Pb(Cu\text{-}Pb\text{-}Ti)}$ and $x_{Pb(Cu\text{-}Pb\text{-}V)}$ denote the equilibrium mole fraction of Pb in Cu-Pb, Cu-Pb-Ti and Cu-Pb-V, respectively, and $\gamma_{Pb(Cu\text{-}Pb)}$, $\gamma_{Pb(Cu\text{-}Pb\text{-}V)}$ and $\gamma_{Pb(Cu\text{-}Pb\text{-}V)}$ are the corresponding activity coefficients of Pb.

Alloys were prepared from copper MOOB grade (oxygen free) rolls (99.99 mass per cent), lead in the form of pellets (99.99 mass per cent) and titanium and vanadium in small pieces of purity estimated at more than 99 mass per cent. Graphite elements were made of EK-412 type graphite (ash residue < 0.1 mass per cent supplied by Ringsdorf Co). The reference and the studied alloys of appropriate compositions were prepared by melting carefully weighed masses of metals at an argon pressure of 0.1 Pa. The equilibrium compositions of the alloys were determined by the weighing method. The accuracy of weighing was $\pm 10^{-4}$g.

The essential part of apparatus (see Fig.1) consisted of a set of graphite blocks with grooves for alloys and orifices which allowed free evaporation and migration of the vapor of lead inside the system. The shape of the block ensured maximum tightness and made the evaporation of the metal outside the system more difficult. The set of blocks was placed inside a tube made of extra-fine, creep-resistant steel, which served as a vacuum chamber. The tube was placed inside the resistance furnace. Blocks with alloys were placed in the isothermal zone of the furnace. Temperature was measured by the Ni-(Ni-Cr) thermocouple. The pressure in the furnace was measured by a vacuum meter APG-010 manufactured by Balzers. The quantities determined experimentally, i.e. argon pressure and equilibration time were meant to guarantee the attainment of equilibrium between Pb (g) in the reference and the studied alloys. In the preliminary tests all alloys in the grooves were Cu and Pb alloys. The equilibrium state was attained when the mole fraction of Pb was the same in all alloys. The argon pressure was especially chosen to be higher than the vapour pressure of lead. The evaporation process was limited to lead with the sufficient rate. It was established, that at the temperature 1473 K, the time necessary to reach equilibrium was 75 minutes. The argon pressure was 2.7 kPa, which was taken a priori. It is higher than the vapour pressure of Pb, and thus would have prevented boiling of the liquid alloys in the crucible. The escape of Pb(g) from the crucible varied from 2 to 25 per cent. The loss of lead did not upset the equilibrium state.

Determination of the activity of Pb required the experimental assigning of the equilibrium mole fraction of Pb in the reference and the studied aloys. The vapor pressure of lead is more than 100 times higher, than the pressure of the remaining elements. Therefore, the weighing method was accepted for the determination of the composition of alloys.

3. Results

The activity of lead in Cu-Pb-Ti and Cu-Pb-V at 1473 K was determined by the equilibrium saturation method. The activity coefficient of lead, γ_{Pb} in those alloys was calculated on the basis of equation (2) or (4). Experimental values of Pb activity coefficient are presented in Tables 1 and 2. For describing the activity coefficient of lead γ_{Pb} in the reference alloy Cu-Pb the equations proposed by Wypartowicz [9] and Esdaile et.al. [10] were accepted:

$$\ln \gamma_{Pb} = (3360/T - 0.6)\,(1-x_{Pb})^{2.1} \tag{5}$$

$$\log \gamma_{Pb} = [-1.1293 + 263.5/T + (1.156 - 2375/T)\,x_{Pb}]\,x_{Cu}^2 \tag{6}$$

Table 1. Experimental values of $\ln\gamma_{Pb}$ in Cu-Pb-Ti alloys calculated on the basis of equation 2. Values of Pb activity in the reference Cu-Pb mixture calculated according to equations (5) and (6)

$x_{Pb\,(Cu-Pb)}$	$X_{Pb(Cu-Pb-Ti)}$	$X_{Ti(Cu-Pb-Ti)}$	**$\ln\gamma_{Pb}$ acc.to eq.(5)**	**$\ln\gamma_{Pb}$ acc.to eq.(6)**
0.0044	0.0099	0.0204	0.848	0.862
0.0074	0.0260	0.0198	0.373	0.398
0.0134	0.0225	0.0206	1.115	1.180
0.044	0.0116	0.0302	0.705	0.668
0.0109	0.0159	0.0297	1.266	1.337
0.0015	0.0067	0.0416	0.186	0.078
0.0033	0.0139	0.0386	0.227	0.255
0.0023	0.0096	0.0598	0.265	0.265

Table 2. Experimental values of $\ln\gamma_{Pb}$ in Cu-Pb-V alloys calculated on the basis of equation 2. Values of Pb activity in the reference Cu-Pb mixture calculated according to equations (5) and (6)

$x_{Pb\,(Cu-Pb)}$	$X_{Pb(Cu-Pb-V)}$	$X_{V(Cu-Pb-V)}$	**$\ln\gamma_{Pb}$ acc.to eq.(5)**	**$\ln\gamma_{Pb}$ acc.to eq.(5)**
0.0081	0.0107	0.0081	1.374	1.381
0.0274	0.0291	0.0274	1.525	1.545
0.0078	0.0078	0.0078	1.649	1.645
0.0062	0.0066	0.0062	1.589	1.579
0.0092	0.0101	0.0092	1.555	1.493
0.0042	0.0075	0.0042	1.093	0.978
0.0049	0.0074	0.0049	1.256	1.323

As the solutions, are diluted ones, they can be described by means of the Wagner equation [1, 2]:

$$\ln\gamma_{Pb} = \ln\gamma^{0}_{Pb} + \varepsilon^{Pb}_{Pb} x_{Pb} + \varepsilon^{Ti}_{Pb}\, x_{Ti} \quad (7)$$

$$\ln\gamma_{Pb} = \ln\gamma^{0}_{Pb} + \varepsilon^{Pb}_{Pb} x_{Pb} + \varepsilon^{V}_{Pb}\, x_{Ti} \quad (8)$$

where γ^{0}_{Pb} is the activity coefficient of Pb in Cu-Pb-Ti or Cu-Pb-V at $x_{Pb}\to 0$, $\varepsilon^{Pb}_{Pb} = (\partial \ln\gamma_{Pb} / \partial x_{Pb})$, $x_{Pb}\to 0$, $x_{Ti}\to 0$, or $x_{V}\to 0$ is the interaction parameter of Pb in Cu-Pb-Ti or Cu-Pb-V, $\varepsilon^{Ti}_{Pb} = (\partial \ln\gamma_{Pb} / \partial x_{Ti})$ $x_{Pb}\to 0$, $x_{Ti}\to 0$ is the interaction parameter of Ti in Cu-Pb-Ti and $\varepsilon^{V}_{Pb} = (\partial \ln\gamma_{Pb} / \partial x_{V})$, $x_{Pb}\to 0$, $x_{V}\to 0$, is the interaction parameter of V in Cu-Pb-V.

In equation (7, 8) values of mole fractions of components and lead activity coefficient were determined experimentally, whereas values of $\ln\gamma^{0}_{Pb}, \varepsilon^{Pb}_{Pb}, \varepsilon^{Ti}_{Pb}$ and ε^{V}_{Pb} were calculated by means of the least–squares method.

Calculations were performed in two ways:

I. Values $\ln\gamma^{0}_{Pb}$ and ε^{Pb}_{Pb} parameters were accepted from the binary Cu-Pb system.

According to equation (5):

$$\ln \gamma_{Pb} = 1.681\text{-}3.55x_{Pb} \quad (9)$$

According to equation (6):

$$\log \gamma_{Pb} = 0.659 - 1.36x_{Pb}] \quad (10)$$

The ε^{Ti}_{Pb} and ε^{V}_{Pb} parameters were calculated on the basis of experimental results by the least-squares method.

II. Values of all parameters, that is $\ln\gamma^{0}_{Pb}, \varepsilon^{Pb}_{Pb}, \varepsilon^{Ti}_{Pb}$ and ε^{V}_{Pb} were calculated on the basis of experimental results by the least-squares method.

Values of parameters calculated by both methods are presented in Table 3.

Values of interaction parameters ε^{Ti}_{Pb} and ε^{V}_{Pb} calculated by methods I and II do not differ significantly (see Tables 3 and 4). Moreover, the choice of the description of the reference alloy [9 or 10] does not influence values of interaction parameters in studied mixtures (see Table 3 and 4).

On the basic of experimental results the following the following expressions for the Pb activity in studied alloys were obtained.

T = 1473K:
Cu-Pb-Ti alloys

$$\ln\gamma_{Pb} = 1.681 - 1.56x_{Pb} - 30.74x_{Ti} \quad (11)$$

Cu-Pb-V alloys

$$\ln\gamma_{Pb} = 1.681 + 0.2x_{Pb} - 10.31x_{V} \quad (12)$$

Table 3. Values of $\ln\gamma_{Pb}^{0}$, and ε_{Pb}^{V} parameters calculated by methods I and II. Values of Values of Pb activity in the reference mixture ($\ln\gamma_{Pb}$ in Cu-Pb) calculated according to equations (5) and (6)

$\ln\gamma_{Pb}$ in Cu-Pb	ε_{Pb}^{Ti}, method I	$\ln\gamma_{Pb}^{0}$, method II	ε_{Pb}^{Ti}, method II
According to eq. (5)	-34.35	-1.56	-30.74
According to eq. (6)	-30.23	-1.27	-30.79

Table 4. Values of $\ln\gamma_{Pb}^{0}$ and ε_{Pb}^{V} parameters calculated by methods I and II. Values of Values of Pb activity in the reference mixture ($\ln\gamma_{Pb}$ in Cu-Pb) calculated according to equations (5) and (6)

$\ln\gamma_{Pb}$ in Cu-Pb	ε_{Pb}^{V}, **method I**	$\ln\gamma_{Pb}^{0}$, **method II**	ε_{Pb}^{V}, **method II**
According to eq.(5)	-9.24	0.20	-10.31
According to eq. (6)	-9.55	0.77	-10.67

The comparision between the calculated and experimental Pb activities in Cu-Pb-Ti and Cu-Pb-V alloys at 1473K are presented in Figs. 2, 3.

4. Conclusions

Using the vapor saturation method, the Pb activities in Cu-Pb-Ti and Cu-Pb-V alloys at the temperature 1473 K were determined and interaction parameters were calculated. Negative values of interaction parameters suggest that both titanium and vanadium decrease lead activity in the studied alloys. Values of interaction parameters calculated by two methods do not differ significantly (only 10 per cent), what speaks for consistency of the results.

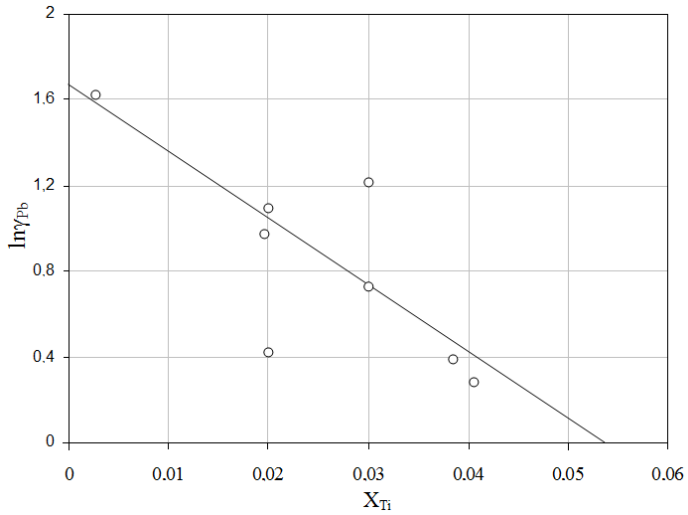

Fig. 2. Activity coefficient of Pb in Cu-Pb-Ti alloys at T = 1473 K

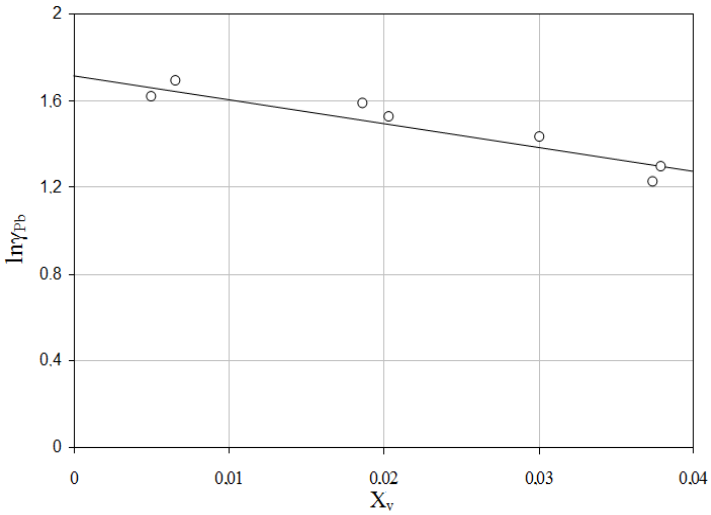

Fig. 3. Activity coefficient of Pb in Cu-Pb-V alloys at T = 1473 K

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