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Abstract

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THERMODYNAMIC PROPERTIES OF COPPER-PALLADIUM ALLOYS

By the method of electromotive forces (e.m.f.) we have found the free energy, heat, and entropy of mixing of copper-palladium alloys.

The e.m.f. of the following galvanic cell was measured:

$$\mathrm{Cu}\,|\,\mathrm{Cu}^{+}\ \text{(halide melt)}\,|\,\mathrm{Cu—Pd}\ \text{(alloy)}.$$

The method was described by us earlier ([1]).

As the electrolyte, in some cases a melt of potassium chloride and lithium chloride of eutectic composition was used, and in others sodium iodide and potassium iodide with a minimum melting temperature (about 590°C). In the first case, about 1% CuCl was also added to the electrolyte; in the second, CuI. As the experiments showed, when iodide salts are used as the electrolyte, the scatter is reduced and the reproducibility of the e.m.f. values of the cell is improved. Therefore, in most cases a melt of potassium, sodium, and copper iodides of the indicated composition was used.

The alloys were prepared by mixing definite weight quantities of copper and palladium powders; the mixture was then pressed and annealed at 900—1000°C for 200—250 hr. The alloys were not analyzed. The current leads were tungsten wires 1.2 mm in diameter. After annealing, shallow holes were drilled in the alloys, the current leads were inserted into them, and the alloy was compressed in ordinary dies. As experience showed, such a connection is quite reliable.

The experiments were carried out at temperatures of 600—760°C in an atmosphere of argon purified with metallic sodium. The duration of an experiment was 130—150 hr; constant e.m.f. values were obtained after 30—40 hr from the beginning of the experiment, but subsequently the e.m.f. constant at a given temperature after a change in temperature was established comparatively rapidly (5—10 hr).

Fig. 1. Electromotive forces of Cu–Pd alloys.
1—$N_{\mathrm{Cu}} = 0.887$; 2—$N_{\mathrm{Cu}} = 0.835$;
3—$N_{\mathrm{Cu}} = 0.790$; 4—$N_{\mathrm{Cu}} = 0.740$; 5—$N_{\mathrm{Cu}} = 0.700$; 6—$N_{\mathrm{Cu}} = 0.578$; 7—$N_{\mathrm{Cu}} = 0.0809$

Fig. 1. Electromotive forces of Cu–Pd alloys.

Figure 1: Fig. 1. Electromotive forces of Cu–Pd alloys.

Figure 2

Figure 2: Figure 2

The e.m.f. values obtained experimentally for each composition were plotted on an e.m.f.-temperature graph, and a straight line was drawn through the points. The deviation of individual e.m.f. values from the straight line does not exceed ±0.5—1%.

(see Fig. 1). Further processing of the experimental data has already been described by us [2].

Figure 2 gives the activities of copper and palladium in the alloys at a temperature of 1000° K; Fig. 3 gives the integral heats, free energy, and entropy of formation of Cu–Pd alloys at 1000° K.

With respect to ordering in the solid state in Cu–Pd alloys there is a fairly extensive literature (see, for example, [3–6]). In any case, despite some discrepancies among the results of different investigators concerning the temperature of ordering and the composition of the ordering alloys, it can be stated with confidence that in our investigations, carried out at temperatures above 600° C, we were dealing with disordered alloys. In addition, an extraordinary slowness of the ordering process in Cu–Pd alloys was noted [5].

Fig. 2. Activities of copper and palladium in Cu–Pd alloys at 1000°K. Points are experimental data;
1 –activity of copper; **2** –activity of palladium

Fig. 3. Free energy, heat, and entropy of mixing of Cu–Pd alloys at 1000°K: **1** $-\Delta Z$, **2** $-\Delta Z^{ex}$, **3** $-\Delta H$, **4** $-\Delta S^{ex}$, **5** $-\Delta S$

However, even at the high temperatures of our experiments, the tendency toward ordering is clearly manifested in the negative deviation of the thermodynamic functions from the ideal laws (Figs. 2 and 3), in the large negative heat of mixing (−1780 cal/g-at at $N_{Cu} = 0.65$) and in the shift of the minima of the heat of mixing and of the free energy toward copper (Fig. 3), where a greater tendency toward ordering is observed (in the cited works ordering is noted in alloys of the compositions Cu_5Pd, Cu_3Pd, Cu_5Pd_3, and CuPd, but so far no long-range order has been found in alloys with a content greater than 50 at. % Pd).

Figure 3

Figure 3: Figure 3

Nevertheless, since only short-range order exists in the alloys, the excess entropies of mixing have a comparatively small negative value (of the order of −0.2 e.u./g-at) and vary only slightly with composition. It is possible that other factors also influence the entropy of mixing.

Thus, the thermodynamic properties of Cu−Pd alloys at 1000° K found by us are consistent with the presence of superstructures in these alloys at lower temperatures.

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Note: Figure translations are in progress. See original paper for figures.