The $p$–$T$–$x$ Phase Diagram of the Cu–Mg System

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Abstract

The phase equilibria in the copper-magnesium system with participation of the gazex phase were analyzed. Various graphic variants of the equilibria image, the line projections of the maximal solubility on the plane temperature-composition, isobar and isotherm sections of the $p$–$T$–$x$ phase diagram and $p_{Mg}$–$T$ phase diagram were proposed.

The findings of the analysis can be useful during optimization of the melting, casting, heat treatment and operation processes of the copper-magnesium system alloys.

Keywords

Phase equilibria; phase diagrams; copper-magnesium alloys; intermetallics.

Alloys of copper and magnesium – magnesium bronzes – find technical applications, in particular, slip rings, collector plates, cables are made from them [1–4]. When melting, casting, and heat treating articles made of magnesium bronze, it is necessary to take into account the evaporation of them having high vapor pressure of magnesium. In this regard, the analysis of equilibrium in the copper-magnesium system acquires importance not only taking into account temperature, but also pressure.

The purpose of this article is to build phase diagrams of the copper-magnesium system at various temperatures and pressures.

Two phases are formed in the copper-magnesium system: Mg$_2$Cu (Pearson symbol oF48, space group Fddd) and MgCu$_2$ (Pearson symbol cF24, space group Fd-3m). The projection of curvilinear lines of maximum solubility located in three-dimensional $p$–$T$–$x$ space onto the temperature-composition plane is shown in Fig. 1 [5].

The equilibrium gas above the pairs of Cu–Mg alloys consists mainly of magnesium atoms. The total vapor pressure above the alloys, with the exception of very dilute copper solutions, can be taken equal to the partial vapor pressure of magnesium. The equilibrium pressure of magnesium vapor over the melts in a wide range of concentrations and temperatures is given in Table 1 according to the data of [6–8]. The extrapolation of the temperature dependences of the magnesium vapor pressure given in Table 1, before intersecting with the liquidus lines in the diagram in Fig. 1, determines the parameters of three-phase equilibria: (Cu $\rightleftharpoons$ L $\rightleftharpoons$ G); (Cu$_2$Mg $\rightleftharpoons$ L $\rightleftharpoons$ G), (CuMg$_2$ $\rightleftharpoons$ L $\rightleftharpoons$ G) and (Mg $\rightleftharpoons$ L $\rightleftharpoons$ G).

The diagram in Fig. 1 is a projection of the lines of maximum solubility located in the $p$-$T$-$x$ space of the lines of non-invariant equilibria on the temperature-composition plane. At pressures above 500 Pa, this diagram coincides with the basal section.

Taking these parameters and the data of [5–8] into account, Fig. 2 shows the $p$–$T$ phase diagram of the copper-magnesium system, which is the projection of the spatial lines of three-phase equilibria of this system on the pressure-temperature plane.

In this diagram, curves 1–10 and 10–17 represent the evaporation and boiling of pure magnesium, respectively, and curves 10–15 represent its melting.

Four-phase equilibria are indicated by points 5, 6, and 7. The parameters of these points and the phases involved in them are given in Table 2.

At each point of the invariant four-phase equilibria, four curves of univariate three-phase
Fig. 1. The projection of the lines of maximum solubility of the copper-magnesium system on the temperature – composition plane [5]

Table 1

Temperature dependence of the partial vapor pressure of Mg over equilibrium melts Cu–Mg \[\lg P_{Mg}(Pa) = -\frac{A}{T} + B\]

| Composition, Mg at. % | A    | B    | Temperature, °C | Source  |
|-----------------------|------|------|-----------------|---------|
| 22.4                  | 7760 | 9362 | 815 – 927       |  [6]    |
| 33.0                  | 7630 | 9705 | 823 – 888       |         |
| 52.1                  | 6910 | 9607 | 669 – 781       |         |
| 58.1                  | 6850 | 9609 | 652 – 729       |         |
| 66.7                  | 6760 | 9682 | 618 – 683       |         |
| 76.5                  | 6670 | 9710 | 608 – 687       |         |
| 85.7                  | 6630 | 9726 | 599 – 668       |         |
| 93.6                  | 6590 | 9728 | 592 – 667       |         |
| 11.0                  | 8720 | 9460 | 900 – 1069      |         |
| 18.0                  | 8520 | 9736 | 875 – 959       |         |
| 22.0                  | 8420 | 9896 | 740 – 948       |         |
| 29.0                  | 8260 | 10127| 800 – 915       |         |
| 37.0                  | 8000 | 10202| 812 – 866       |         |
| 42.0                  | 7830 | 10159| 775 – 837       | [7]     |
| 50.0                  | 7630 | 10123| 776 – 837       |         |
| 66.0                  | 7390 | 10213| 572 – 749       |         |
| 76.0                  | 7260 | 10228| 640 – 730       |         |
| 90.0                  | 7190 | 10279| 619 – 730       |         |
| 17.29                 | 8337 | 9550 | 900 – 974       | [8]     |
| 23.36                 | 8097 | 9570 | 886 – 957       |         |
| 30.07                 | 7867 | 9709 | 829 – 963       |         |
| 37.04                 | 7670 | 9733 | 809 – 870       |         |
| 44.49                 | 7463 | 9794 | 789 – 876       |         |
| 50.53                 | 7299 | 9902 | 833 – 848       |         |
| 67.28                 | 7004 | 9920 | 707 – 800       |         |
| 65.52                 | 6905 | 9936 | 683 – 778       |         |
| 90.05                 | 6840 | 9964 | 706 – 783       |         |
Fig. 2. $p$–$T$ phase diagram of the Cu–Mg system

Table 2

| Point number | Temperature, °C | Pressure, Pa | Equilibrium phases                        |
|--------------|----------------|-------------|-------------------------------------------|
| 5            | 485            | 10          | Mg, CuMg$_2$, G, L                        |
| 6            | 552            | 10          | Cu$_2$Mg, CuMg$_2$, L, G                  |
| 7            | 725            | 30          | Cu, Cu$_2$Mg, L, G                       |

Equilibria end. The phases involved in these equilibria are shown in Fig. 2. In the diagram in Fig. 2, there are two more points of non-invariant equilibria 8 and 9, which correspond to congruent melting of Cu$_2$Mg and CuMg$_2$.

The isobar $p = 100$ Pa crosses the curves of three-phase equilibria $5 – 12$, $5 – 10$, $6 – 13$, $6 – 9$, $7 – 10$, $9 – 7$ and $7 – 11$ on the $p$–$T$-diagram (the point of intersection of the isobar with the melting curve of copper is not shown) In accordance with this, eight contour lines of non-invariant equilibria are shown in the isobaric section of Fig. 3. A characteristic feature of this diagram is the presence of three closed regions of the liquid. Of interest is also the heating behavior of mixtures of intermetallic compounds Cu$_2$Mg and MgCu$_2$. First, when mixtures are heated, they melt at a temperature of 552 °C, then at a temperature of 660 °C, the formed melt solidifies with the release of magnesium vapor, then at a temperature of 700 °C the remaining Cu$_2$Mg melts again to form a liquid already rich in copper, which in turn at a temperature of 840 °C hardens again with the release of magnesium vapor and copper-based solid solutions. At an even higher temperature close to the melting point of copper, these solutions, enriched with magnesium, melt again.

The isotherm $T = 740$ °C intersects the equilibrium curves $7 – 11$, $7 – 9$, $6 – 9$ on the $p$–$T$ diagram. In accordance with this, in the isothermal section at a temperature of 740 °C (Fig. 4) there are three horizontal horizons of unvariant equilibria. As follows from Fig. 4, in the indicated pressure range there is a region of a solid solution of magnesium in copper, a solid intermetallic compound Cu$_2$Mg, and two liquid regions, one of which is rich in copper and the other is rich in magnesium.

Of practical interest is the diagram of the first kind [7] for the Cu–Mg system in $p_Mg–T$ coordinates, which is shown in Fig. 5. Taking into account the fact that the total equilibrium pressure of solutions based on copper gas over all alloys, except for very dilute solutions based on copper, can be replaced without partial error by partial pressure of magnesium, the diagram in Fig. 5 can easily be transformed from the diagram in Fig. 2, removing all equilibrium curves involving only condensed phases.
Examples of isobaric and isothermal sections of the phase diagram of the copper-magnesium system are shown in Figs. 4 and 5.

The whole diagram of Fig. 5 is divided into five single-phase regions (two regions of solid solutions based on copper and magnesium, liquid, regions of solid phases Cu$_2$Mg and CuMg$_2$), separated by the boundaries of two-phase equilibria. The compositions of the phases located in these equilibria can be determined using the diagram in Fig. 1. To determine the composition of alloys in single-phase regions of Fig. 5, the presence of isobars or isotherms of solubility of magnesium is necessary. In particular, the compositions of alloys, in particular liquids, in the diagram of Fig. 5, limited by the curve 10–5–6–7–8, can be calculated from the information given in Table 1.

The presented options for graphic equilibrium in the copper-magnesium system can be useful in choosing the optimal conditions for melting, casting, and heat treatment of alloys of the copper-magnesium system.
Conclusions

Based on the analysis of equilibria involving the gas phase in the copper-magnesium system, a $p-T$ diagram of this system, examples of isobaric and isothermal sections of a triple $p-T-x$ phase diagram and a $p_{\text{Mg}}-T$ phase diagram are presented.

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