World Scientific
www.worldscientific.com

Structural state and thermodynamic stability of Al–Cu alloys

Nataliia Filonenko

Department of Medical and Biological Physics and Informatics,
State Institution "Dnipropetrovsk Medical Academy of Health Ministry of Ukraine",
9 Vernadsky Street, Dnipro UA 49044, Ukraine

Z. I. Nekrasov Iron and Steel Institute of National Academy of Sciences of Ukraine,
1 Ak. K. F. Starodubova Square, Dnipro UA 49107, Ukraine
natph2016@gmail.com

It is known that processes occurring in binary system melts affect the crystallization process and the phase composition of alloys. To predict these processes, we should determine the region of thermodynamic stability of the melt. In this paper, the structural properties of hypoeutectic and hypereutectic alloys in Al–Cu system are studied depending on the heating temperature above the liquidus line and aftercooling rate. It is shown that overheating of Al–Cu melts to 150 K above the liquidus line and further cooling leads to complete suppression of the process of formation of primary aluminum crystals in hypoeutectic alloys and Al_2Cu phase in hypereutectic alloys. For the first time, by accounting in Gibbs energy of binary Al–Cu alloy for the first degree approximation of high-temperature expansion of thermodynamic potential, the dependence of temperature of line of the melt thermodynamic stability on copper content in alloy is obtained.

Keywords: Al–Cu alloys; Al_2Cu phase; eutectics; thermodynamic stability of a liquid.

PACS numbers: 61.50.Ah, 64.70.kd

1. Introduction

The interest in Al–Cu system alloys over the last few decades arises from the widespread use of these alloys in the aircraft industry and in transport. According to the state diagram of Al–Cu system proposed by Murray, the eutectics is formed at copper content of 33 wt.% and aluminum content of 67 wt.% and is represented structurally by α-solid solution of copper in aluminum and intermetallic Al_2Cu compound.[1,2]

It is known that at temperatures exceeding the crystallization temperature, in Al–Cu melts, the microconcentration inhomogeneity is observed.[3–7] The

structure-sensitive methods, one of which is viscosity-temperature study of the melt,[8,9] are known to detect the occurrence of microcomplexes or short-range order in the liquid of Al–Cu alloys. The study of the viscosity-temperature dependence of Al–Cu alloys revealed the divergence of the heating and cooling curves (hysteresis loops); these loops are associated with the formation of complexes in the alloy liquid.[8–13] For the alloy of eutectic composition (copper content is of 17.0 at.%), the intersection of heating and cooling viscosity curves occurs at the temperature of 1123 K,[8] and in Ref. 10, it is stated that the branching temperature for pure aluminum is 1173 K, for 10 at.% and 17.1 at.% Cu alloys — 1223 K, 1323 K for 25 at.% and 40 at.% Cu and 1123 K for 32.2 at.% Cu. The authors of Ref. 11 think otherwise and point out that there is a hysteresis on the temperature-density curves of the melt for the 17 at.% Cu eutectic alloy below a temperature of 1023 K and for the alloy with copper content of 23 at.% below a temperature of 1073 K. It should be noted that experimental study of the temperature dependence of the viscosity of alloy with copper content of 30 at.% shows that when the melt is heated upto a temperature above 1023 K, there is a sharp decrease in the coefficient of viscosity of the alloy, indicating that heating of alloys above this temperature is unpractical, since the homogeneous melt is already formed in the given range.[12]

Investigation of density of the melt with copper content of 0–100 wt.% by the method of penetrating gamma-radiation in the range from the room-temperature to 1573–1673 K shows that the dependence of the melt density on aluminum content in the alloy is non-monotonic with extrema near temperatures of the melts of the composition of Cu_3Al, Cu_2Al, $CuAl$ and $CuAl_2$, which indirectly indicate the conservation of these atomic groups in the liquid phase across the entire temperature range under consideration, and for real alloys, the approximation of viscosity-temperature dependence will not be a linear function.[13]

Study of dependence of function value of the structural parameter on temperature and copper content in alloy shows that for the alloy of eutectic composition ($Al_{83}Cu_{17}$), there is a decrease in structural parameter within the temperature range of 1023–1253 K, and occurrence of sharp peak shows that there is an ordered structure.[14] In Ref. 15, occurrence of the peak was observed in the temperature range of 835–935 K, and in Ref. 3, in the study of $Al_{83}Cu_{17}$ and $Al_{80}Cu_{20}$ melts, peaks were detected at 885 and 1000 K, respectively. The authors of these papers note that a slight overheating of alloys above the liquidus line leads to significant decrease of complexes in the liquid.

Similar results were obtained by the authors of Ref. 16, who indicate that below a temperature of 1000 K, the number of icosahedral clusters in the $Al_{80}Cu_{20}$ melt rises sharply, and the change in melt viscosity when the temperature decreases illustrates the anomalous structural dynamics and the occurrence of locally-arranged clusters.

The existence of complexes in eutectic and peritectic melts affects the structure and properties of corresponding solid alloys, which is important for casting, brazing, welding and in making of composite materials based on eutectic matrix. The effect on formation of complexes in the melt enables to improve the properties of solid

alloys, both crystalline and amorphous. Nowadays, all available information on temperature dependence of Al–Cu structural state is not sufficient to allow general conclusions about the relationship between liquid and solid states near the phase, transition point.

Thus, the purpose of this work is to investigate the structural properties of Al–Cu alloys depending on the temperature of alloy heating above the liquidus line and cooling rate, and to determine the homogeneity limit of the melt.

2. Materials and Methods

The investigation was carried out for the specimens of Al–Cu alloys with copper content of 25.0–36.0 wt.%, the rest was aluminum. To obtain such alloys, we used the furnace charge of the composition: 99.9 wt.% aluminum and 99.9 wt.% copper. Smelting of specimens was performed in a Tammann furnace with graphite heater in alundum crucibles. The cooling rate of alloys was 10 K/s. Some specimens were prepared in a similar way, but after heating were casted into V-shaped molds; as a result, in the process of cooling in the wide part of the wedge, the cooling rate was 10^2 K/s and in the edge it was 10^4 K/s.

To determine the chemical composition of alloy, chemical and spectral analyses were used.[17] To determine the temperature of phase transformations, differential thermal analysis by derivatograph with heating rate of 2 K/min was used.

The phase composition of alloys was determined by X-ray microanalysis, by means of JSM-6490 microscope, as well as by means of optical microscope, "Neophot-21". The X-ray structure analysis was performed with DRON-3 diffractometer in monochromated Cu_α radiation.

3. Results and Discussion

The structure of hypoeutectic alloys of Al–Cu system after heating to 873 K and further cooling with rate of 10^2 K/s consists of primary Al dendrites and regular Al + Al_2Cu eutectics, which corresponds after crystallization to the phase composition of the system state diagram.[1] As the cooling rate rises to 10^3–10^4 K/s, the volume fraction and size of primary aluminum dendrites decrease and those for the eutectics increase.

The microstructure of Al–Cu hypoeutectic alloys after heating to 100 K above the liquidus line and cooling with rate of 10^2 K/s is represented by primary aluminum dendrites and eutectics. By increasing the cooling rate to 10^3–10^4 K/s, the volume fraction and size of primary aluminum dendrites decrease and those for the eutectics increase compared with pretreatment of specimens, which correlates with the results of authors of Ref. 18.

Preheating of hypoeutectic alloys to 150 K above the liquidus line and aftercooling with rate of 10^3–10^4 K/s results in the formation of eutectics with more dispersed structure compared to specimens cooled at lower rate (Fig. 1). Besides, there are no primary aluminum crystals in the structure.

N. Filonenko

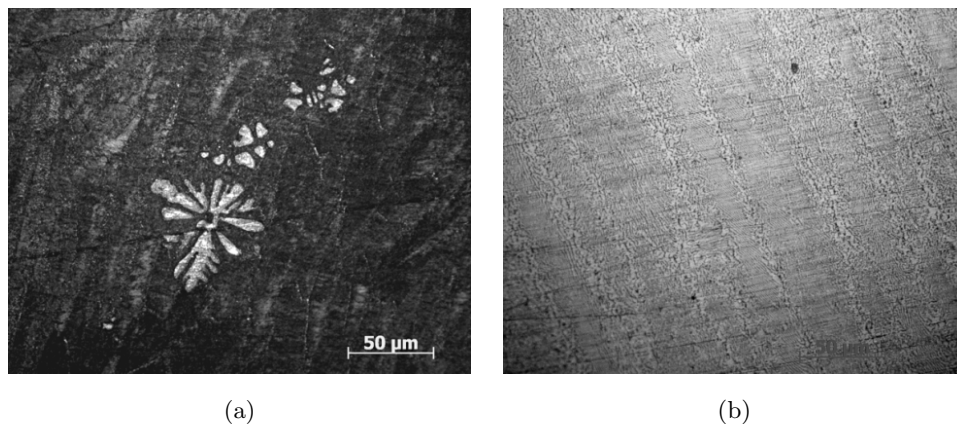(a)   (b)

Fig. 1.   Microstructure of alloy wedge after presuperheating of 71.0 wt.% Al alloy liquid to 150 K and aftercooling with rate of (a) 10^2 K/s and (b) 10^4 K/s.

In the heating thermogram of hypoeutectic alloy obtained after overheating of the melt above the liquidus line to 150 K and further cooling with rate of 10^4 K/s, the eutectics smelting occurs at 823 K. However, there is no transformation in the alloy thermogram that would correspond to the formation of primary crystals.

According to the results of X-ray, diffraction analysis of Al–Cu alloys with overheating to 150 K and aftercooling at different speeds ranging from 10^2 to 10^4 K/s, a slight shift of lines for the solid solution of aluminum and Al_2Cu phase towards high angles is observed [Fig. 2(a)]. The results obtained can be explained by the fact that the formation of supersaturated solid solution of copper occurs.

For hypereutectic 34.0–40.0 wt.% Cu alloys overheated to 50 K above the liquidus line and cooled with rate of 10^2 K/s, the formation of primary Al_2Cu crystals and eutectics is observed, which corresponds to the Al–Cu state diagram.
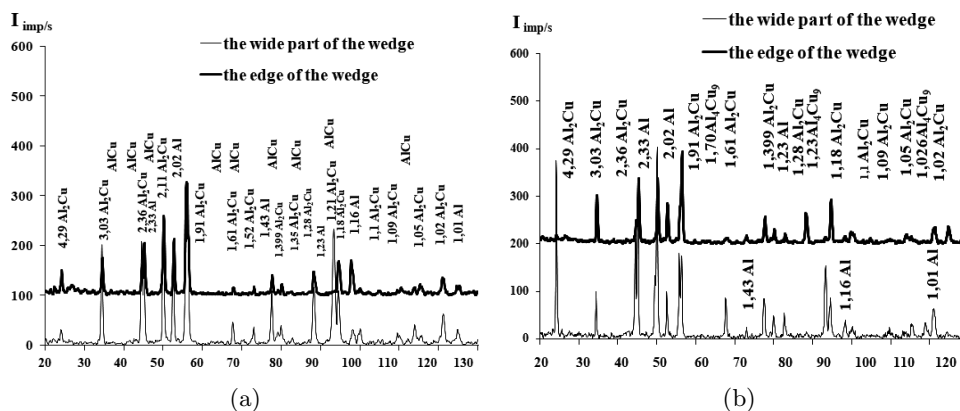

(a)   (b)

Fig. 2.   Diffractogram of alloys with aluminum content of (a) 71.0 wt.% and (b) 63.0 wt.%.
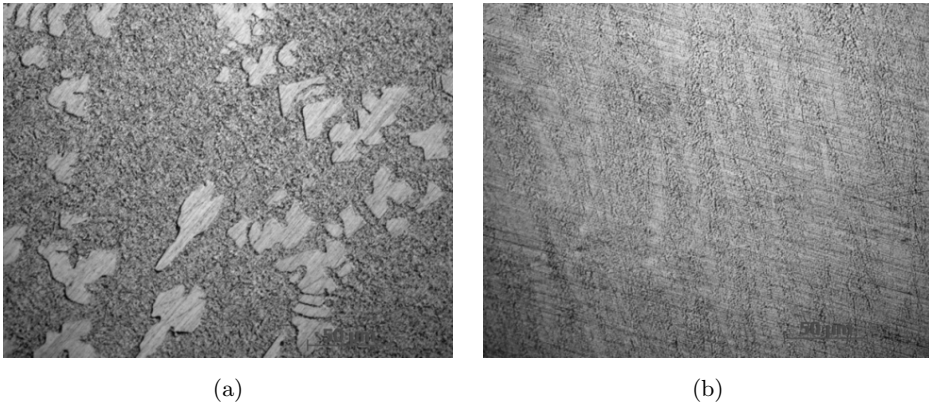
(a) (b)

Fig. 3. Microstructure of alloy wedge after presuperheating of the melt with Al–content of 63.0 wt.% to 150 K and aftercooling with rate of (a) 10^2 K/s and (b) 10^4 K/s.

The same sort of situation is observed in the study of microstructure after overheating of hypereutectic alloys to 100 K above the liquidus line, to be exact, there is further decrease in sizes of primary Al_2Cu phase and increase in volume fraction of the eutectics. While cooling of hypereutectic alloys with rate of 10^4 K/s, the formation of quasi-eutectics and complete suppression of formation of primary Al_2Cu crystals are observed.

The consequent increase in the melt overheat temperature to 150 K and cooling at 10^2 K/s is accompanied by significant decrease in size and volume fraction of primary Al_2Cu crystals [Fig. 3(a)]. Increase in cooling rate to 10^3–10^4 K/s leads to complete suppression of the formation of primary Al_2Cu crystals [Fig. 3(b)].

When the cooling rate is increased to 10^4 K/s, there is a slight shift of the lines for aluminum and Al_2Cu phase in the diffractogram [Fig. 2(b)]. These results can be explained by the fact that the process of formation of primary phases is suppressed by increasing the volume fraction of eutectics, possibly by changing the solubility of copper in aluminum and aluminum in Al_2Cu phase.

Thus, the melt overheating above the liquidus line and rapid cooling enabled to investigate the high-temperature state of the melt.

The overheating of the hypoeutectic and hypereutectic Al–Cu alloys above the liquidus line to 50–100 K and further cooling leads to decrease in volume fraction of primary crystals and increase in volume fraction of the eutectics. The consequent overheating of the alloys is accompanied by suppression of the formation of primary aluminum crystals in hypoeutectic alloys and to suppression of Al_2Cu phase in hypereutectic alloys.

In this paper, it is shown experimentally that to obtain a homogeneous melt, which lacks any microcomplexes, it is necessary to perform the overheating of the melt to 100–150 K above the liquidus line in accordance with copper content in the alloy. Our outcomes are in good agreement with the results of works, in which

the findings of structure-sensitive methods for determining the structural state of Al–Cu melts are presented.[10–16]

One of the important factors affecting the formation of alloys structure during cooling is determining the stability of the liquid, namely the temperature at which the liquid is homogeneous and there are no microcrystalline formations.

The Gibbs energy of the phase is known to be a function of independent variables $G = G(p, T, x_i)$, where p is pressure, T is temperature, x_i is chemical content of elements in the compound, $i = 1, 2$ ($x_1 = x_{Al}$, $x_2 = x_{Cu}$). Provided that there are no external force and change in pressure ($p = $ const.), the total differential of Gibbs energy is

$$dG = dU - d(TS) + d(pV) = -SdT + \sum_{i=1,2} \mu_i dx_i,$$

where U is internal energy.[19]

Correspondingly, the thermodynamic forces are

$$S = -\left(\frac{\partial G}{\partial T}\right)_{x_1 x_2}$$

and chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial x_i}\right)_T.$$

To determine the stability of the phase,[20] we find the variation of Gibbs energy

$$\delta G = \sum_{n=1}^{\infty} \frac{1}{n!} \left[\delta T \frac{\partial}{\partial T} + \delta x_1 \frac{\partial}{\partial x_1} + \delta x_2 \frac{\partial}{\partial x_2}\right]^n G. \tag{1}$$

The general condition of phase stability by Gibbs is that arbitrary variations of the internal energy and external parameters of the system should not cause both reversible and irreversible processes in the system (to keep the system in equilibrium), so they must be such that

$$\delta U - T\delta S + p\delta V - \sum_{i=1,2} \mu_i \delta x_i > 0, \tag{2}$$

taking into consideration the relation between internal energy and free Gibbs energy $U = G + TS - pV$ and the fact that

$$\delta S = -\delta \left(\frac{\partial G}{\partial T}\right)_{x_i} = -\left(\frac{\partial \delta G}{\partial T}\right)_{x_1 x_2}, \quad p = \text{const.}$$

Let us expand the Gibbs energy as a power series in δT and δx_i (1):

$$\delta G = \left(\frac{\partial G}{\partial T}\right)_{x_1 x_2} \delta T + \left(\frac{\partial G}{\partial x_1}\right)_{T x_2} \delta x_1 + \left(\frac{\partial G}{\partial x_2}\right)_{T x_1} \delta x_2 + \frac{1}{2}\left[\left(\frac{\partial^2 G}{\partial T^2}\right)_{x_1 x_2} \delta T^2\right.$$

$$+ \left(\frac{\partial^2 G}{\partial x_1^2}\right)_T \delta x_1^2 + \left(\frac{\partial^2 G}{\partial x_2^2}\right)_T \delta x_2^2 + 2\left(\frac{\partial^2 G}{\partial T \partial x_1}\right)_{x_2} \delta T \delta x_1$$

$$+ 2\left(\frac{\partial^2 G}{\partial T \partial x_2}\right)_{x_1} \delta T \delta x_2 + 2\left(\frac{\partial^2 G}{\partial x_1 \partial x_2}\right)_T \delta x_1 \delta x_2 \bigg] + \cdots$$

$$\delta G = -S\delta T + \mu_1 \delta x_1 + \mu_2 \delta x_2 + \frac{1}{2}\left[-\left(\frac{\partial S}{\partial T}\right)_{x_1 x_2} \delta T^2 + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T x_2} \delta x_1^2\right.$$

$$+ \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T x_1} \delta x_2^2 + 2\left(\frac{\partial \mu_1}{\partial T}\right)_{x_1 x_2} \delta T \delta x_1 + 2\left(\frac{\partial \mu_2}{\partial T}\right)_{x_1 x_2} \delta T \delta x_2$$

$$+ 2\left(\frac{\partial \mu_2}{\partial x_1}\right)_{T x_2} \delta x_1 \delta x_2 \bigg] + \cdots . \tag{3}$$

To determine the derivative

$$\left(\frac{\partial \delta G}{\partial T}\right)_{x_1 x_2},$$

we consider only the first- and second-order terms in expansion (3)

$$\left(\frac{\partial \delta G}{\partial T}\right)_{x_1 x_2} = -\left(\frac{\partial S}{\partial T}\right)_{x_1 x_2} \delta T + \left(\frac{\partial \mu_1}{\partial T}\right)_{x_1 x_2} \delta x_1 + \left(\frac{\partial \mu_2}{\partial T}\right)_{x_1 x_2} \delta x_2$$

$$+ \frac{1}{2}\left[-\left(\frac{\partial^2 S}{\partial T^2}\right)_{x_1 x_2} \delta T^2 + \left(\frac{\partial^2 \mu_1}{\partial T \partial x_1}\right)_{x_2} \delta x_1^2 + \left(\frac{\partial^2 \mu_2}{\partial T \partial x_2}\right)_{x_1} \delta x_2^2\right.$$

$$+ 2\left(\frac{\partial^2 \mu_1}{\partial T^2}\right)_{x_1 x_2} \delta T \delta x_1 + 2\left(\frac{\partial^2 \mu_2}{\partial T^2}\right)_{x_1 x_2} \delta T \delta x_2$$

$$+ 2\left(\frac{\partial^2 \mu_2}{\partial T \partial x_1}\right)_{x_2} \delta x_1 \delta x_2 \bigg] + \cdots . \tag{4}$$

In Eq. (4), we take into account the equalities of mixed derivatives:

$$\left(\frac{\partial^2 G}{\partial x_1 \partial T}\right)_{x_2} = \left(\frac{\partial^2 G}{\partial T \partial x_1}\right)_{x_2} = -\left(\frac{\partial S}{\partial x_1}\right)_{T x_2} = \left(\frac{\partial \mu_1}{\partial T}\right)_{x_1 x_2},$$

$$\left(\frac{\partial^2 G}{\partial x_2 \partial T}\right)_{x_1} = \left(\frac{\partial^2 G}{\partial T \partial x_2}\right)_{x_1} = -\left(\frac{\partial S}{\partial x_2}\right)_{T x_1} = \left(\frac{\partial \mu_2}{\partial T}\right)_{x_1 x_2},$$

$$\left(\frac{\partial^2 G}{\partial x_1 \partial x_2}\right)_T = \left(\frac{\partial^2 G}{\partial x_2 \partial x_1}\right)_T = \left(\frac{\partial \mu_1}{\partial x_2}\right)_{x_1 T} = \left(\frac{\partial \mu_2}{\partial x_1}\right)_{x_2 T}.$$

Inserting expressions (1), (3) and (4) in the stability condition (2) and considering the second-order terms, we obtain the inequality

$$\left(\frac{\partial S}{\partial T}\right)_{x_1 x_2} \delta T^2 + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{Tx_2} \delta x_1^2 + \left(\frac{\partial \mu_2}{\partial x_2}\right)_{Tx_1} \delta x_2^2 + 2\left(\frac{\partial \mu_1}{\partial T}\right)_{x_1 x_2} \delta x_1 \delta T$$

$$+ 2\left(\frac{\partial \mu_2}{\partial T}\right)_{x_1 x_2} \delta x_2 \delta T + 2\left(\frac{\partial \mu_2}{\partial x_1}\right)_{Tx_2} \delta x_1 \delta x_2 \geq 0.$$

If we have a quadratic form $a_{11}x_1^2 + a_{12}x_1x_2 + a_{13}x_1x_3 + \cdots + a_{nn}x_n^2 \geq 0$, then it will be positive when the determinant consisting of coefficients a_{ij} and all its principal minors (Sylvester's criterion) will be positive.

Thus, we obtain the determinant of stability[21]:

$$D = \begin{vmatrix} \left(\dfrac{\partial S}{\partial T}\right)_{x_1 x_2} & \left(\dfrac{\partial \mu_1}{\partial T}\right)_{x_1 x_2} & \left(\dfrac{\partial \mu_2}{\partial T}\right)_{x_1 x_2} \\ \left(\dfrac{\partial \mu_1}{\partial T}\right)_{x_1 x_2} & \left(\dfrac{\partial \mu_1}{\partial x_1}\right)_{Tx_2} & \left(\dfrac{\partial \mu_2}{\partial x_1}\right)_{Tx_2} \\ \left(\dfrac{\partial \mu_2}{\partial T}\right)_{x_1 x_2} & \left(\dfrac{\partial \mu_1}{\partial x_2}\right)_{Tx_1} & \left(\dfrac{\partial \mu_2}{\partial x_2}\right)_{Tx_1} \end{vmatrix}. \tag{5}$$

In order for system to be in equilibrium, D and leading elements in determinant need to be positive.

The case $D = 0$ was first defined by Gibbs as a critical state of matter.[22] During supercritical transitions, the determinant and coefficients of stability pass through finite minima that correspond to the growth of fluctuations. The locus of these minima is low-stability line. It should be noted that for different coefficients of stability, the low-stability lines may differ. This is why the line of lowered stability for D, which includes all equilibrium characteristics of the system and therefore best describes its stability, is used as a basis.[23] The threshold case of supercritical transitions, when fluctuations in the system reach the maximum level, and D and stability coefficients pass zero minima, is the critical state. So, it is necessary to study the condition $dD = 0$.

When calculating thermodynamic functions of the phases for the high-temperature region, we take into consideration the first degree approximation of high-temperature expansion for thermodynamic potential of binary alloy in the form of infinite series in powers of $1/T$.[24]

The energy of interaction between elements L_{12} depends on temperature. Let us represent the temperature dependence of interaction energy as $L_{12} = a + bT + cT \ln T$. Using G_1^0 and G_2^0 data for pure components,[25,26] and data for interaction energy between components in the phase (a, b and c values),[3] we obtained the temperature dependence of Gibbs energy of the melt:

$$G_m = x_1 G_1^0 + x_2 G_2^0 + RT(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2 L_{12} - \frac{L_{12}^2 x_1^2 x_2^2}{2RTZ}. \tag{6}$$

Then the determinant of stability (5) with accounting for (6) is equal to

$$
\begin{aligned}
D = &\left[-\frac{cx_1x_2}{T} + \frac{x_1^2x_2^2(b+c+c\ln T)^2}{RTZ} - \frac{x_1^2x_2^2(a+bT+cT\ln T)(2b+c+2c\ln T)}{RT^2Z} \right. \\
&\left. + \frac{x_1^2x_2^2(a+bT+cT\ln T)^2}{RT^3Z} \right] \left[\left(\frac{RT}{x_1} - \frac{x_2^2(a+bT+cT\ln T)^2}{RTZ} \right) \right. \\
&\times \left(\frac{RT}{x_2} - \frac{x_1^2(a+bT+cT\ln T)^2}{RTZ} \right) \\
&\left. - \left(a+bT+cT\ln T - \frac{2x_1x_2(a+bT+cT\ln T)^2}{RTZ} \right)^2 \right] \\
&- \left[R(\ln x_1 + 1) + x_2(b+c+c\ln T) + \frac{x_1x_2^2(a+bT+cT\ln T)^2}{RT^2Z} \right. \\
&\left. - \frac{2x_1x_2^2(a+bT+cT\ln T)(b+c+c\ln T)}{RTZ} \right]^2 \left(\frac{RT}{x_2} - \frac{x_1^2(a+bT+cT\ln T)^2}{RTZ} \right) \\
&- \left[R(\ln x_2 + 1) + x_1(b+c+c\ln T) + \frac{x_1^2x_2(a+bT+cT\ln T)^2}{RT^2Z} \right. \\
&\left. - \frac{2x_1^2x_2(a+bT+cT\ln T)(b+c+c\ln T)}{RTZ} \right]^2 \left(\frac{RT}{x_1} - \frac{x_2^2(a+bT+cT\ln T)^2}{RTZ} \right) \\
&+ 2\left[a+bT+cT\ln T - \frac{2x_1x_2(a+bT+cT\ln T)^2}{RTZ} \right] \\
&\times \left[R(\ln x_1 + 1) + x_2(b+c+c\ln T) + \frac{x_1x_2^2(a+bT+cT\ln T)^2}{RT^2Z} \right. \\
&\left. - \frac{2x_1x_2^2(a+bT+cT\ln T)(b+c+c\ln T)}{RTZ} \right] \left[R(\ln x_2 + 1) + x_1(b+c+c\ln T) \right. \\
&\left. + \frac{x_1^2x_2(a+bT+cT\ln T)^2}{RT^2Z} - \frac{2x_1^2x_2(a+bT+cT\ln T)(b+c+c\ln T)}{RTZ} \right].
\end{aligned}
$$

In order for state of the system to be stable, the condition $dD = 0$ should be fulfilled:

$$
dD = \left(\frac{\partial D}{\partial T} \right)_{x_1 x_2} dT + \left(\frac{\partial D}{\partial x_1} \right)_{x_2 T} dx_1 + \left(\frac{\partial D}{\partial x_2} \right)_{x_1 T} dx_2 = 0.
$$

This condition works when

$$
\left(\frac{\partial D}{\partial T} \right)_{x_1 x_2} = 0, \quad \left(\frac{\partial D}{\partial x_1} \right)_{x_2 T} = 0, \quad \left(\frac{\partial D}{\partial x_2} \right)_{x_1 T} = 0. \tag{7}
$$

The solution of system of Eqs. (7) is shown in Fig. 4.

Thus, the calculated line of thermodynamic stability of the liquid is in good agreement with the results of experimental studies,[4–6,12,14–16] to be exact with the
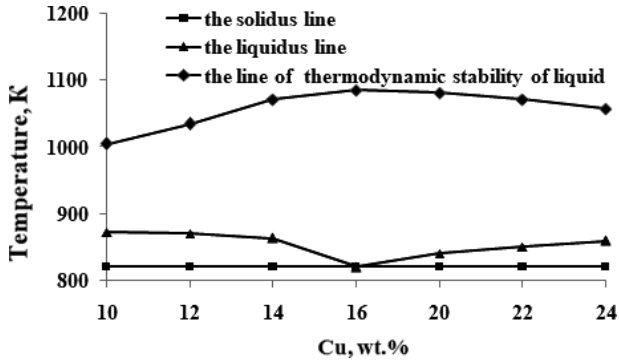
N. Filonenko

Fig. 4.   The line of thermodynamic stability in the Al–Cu state diagram.

line of concentration anomaly obtained for Al–Cu alloys. The analysis of results showed that in order to obtain a homogeneous liquid of Al–Cu alloys without microheterogeneous structure in the form of short-range micro-areas, it is necessary to perform overheating to 100–150 K depending on the copper content in alloy (Fig. 4).

4. Conclusions

The Al–Cu alloys with copper content of 25.0–36.0 wt.% (the rest is aluminum) are investigated in this paper and the obtained results are as follows:

- Overheating of the alloy liquid to 50–100 K above the liquidus line leads to the formation of finely-dispersed eutectic structure, the size and volume fraction of primary aluminum crystals in hypoeutectic alloys decrease along with those for Al_2Cu phase in hypereutectic alloys.
- Overheating of the melt to 150 K above the liquidus line and aftercooling with rate of 10^3–10^4 K/s leads to complete suppression of formation of primary aluminum crystals in hypoeutectic alloys and Al_2Cu phase in hypereutectic alloys, correspondingly.
- For the first time, taking into consideration the contribution of the first-degree approximation of high-temperature expansion of thermodynamic potential for binary alloy to the Gibbs energy, we obtain the dependence of temperature of thermodynamic stability for the melt on copper content in alloy.

The obtained results are relevant because they enable to explain the features of crystallization process depending on overheating temperature.

Acknowledgments

of railway wheels for different application and their maintainability" of National Academy of Sciences of Ukraine.

References

1. J. J. Murray, *Int. Mater. Rev.* **30**, 211 (1985).
2. A. Meetsma, J. L. De Boer and S. Van Smaalen, *J. Solid State Chem.* **83**, 370 (1989).
3. M. E. Trybula, *Comput. Mater. Sci.* **122**, 341 (2016).
4. M. Schick *et al.*, *J. Mater. Sci.* **47**, 8145 (2012).
5. C. Stinn and A. Allanore, *Metall. Mater. Trans. B* **49**, 3367 (2018).
6. J. Dziedzic, S. Winczewski and J. Rybicki, *Comput. Mater. Sci.* **114**, 219 (2016).
7. I. Shtablavyi *et al.*, *J. Non-Cryst. Solids* **354**, 4469 (2008).
8. Y. Plevachuk *et al.*, *Metall. Mater. Trans. A* **39**, 3040 (2008).
9. N. Yu. Konstantinova *et al.*, *Russ. Metall. (Met.)* **2016**, 144 (2016).
10. N. Y. Konstantinova and P. S. Popel, *J. Phys. Conf. Ser.* **98**, 062022 (2008).
11. N. Konstantinova, A. Kurochkin and P. Popel, *EPJ Web Conf.* **15**, 01024 (2011).
12. S. G. Men'shikova *et al.*, *Met. Sci. Heat Treat.* **59**, 133 (2017).
13. A. R. Kurochkin *et al.*, *High Temp.* **51**, 197 (2013).
14. J. Brillo *et al.*, *J. Non-Cryst. Solids* **352**, 4008 (2006).
15. S. Mudry, I. Shtablavyi and I. Shcherba, *Arch. Mater. Sci. Eng.* **34**, 14 (2008).
16. W. Y. Wang *et al.*, *Acta Mater.* **97**, 75 (2015).
17. S. V. Tverdokhlebova, *Visn. Dnipropetr. Univ., Ser. Fiz. Radioelektron.* **14**, 100 (2007).
18. D. Eskin *et al.*, *Mater. Sci. Eng.* **405**, 1 (2005).
19. V. V. Sychev, *The Differential Equations of Thermodynamics* (Hemisphere, New York, 1991).
20. E. D. Soldatova, *J. Mol. Liq.* **127**, 99 (2006).
21. R. B. Griffiths, *Phys. Rev. A* **2**, 1047 (1970).
22. J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Scribner's Son, New York, 1902; Reprinted by Dover, New York, 1960).
23. O. M. Galdina, *Visn. Dnipropetr. Univ., Ser. Fiz. Radioelektron.* **14**, 68 (2007).
24. L. A. Girifalco, *Statistical Mechanics of Solids* (Oxford, University Press, 2000).
25. R. A. Roble and D. R. Waldbaum, *Thermodynamic Properties of Minerals and Related Substances at 298.15 K (25.0°C) and One Atmosphere (1.013 Bars) Pressure and at Higher Temperatures* (Orton Memorial Library, The OHIO State University, 1970).
26. A. T. Dinsdale, *SGTE Data for Pure Elements* (NPL Materials Centre, Division of Industry and Innovation, National Physical Laboratory, Teddington, Middlesex, 1991).