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The Establishment, Plotting and Statistic–Mathematical Interpretation of the Liquidus Surface from the Phase Equilibrium Diagram of the Ternary System Al-Cu-Si

The paper forwards the conclusions of a survey performed on a mathematical model of the phase equilibrium from the ternary system Al-Cu-Si. The author presents the calculus of the statistic equation of the liquidus surface model from this diagram, the plotting and statistical-mathematical interpretation of the results obtained.

1. Introduction

The model of obtaining a liquidus surface through thermodynamic-mathematical computerised modelling consists of a thermodynamic analysis and a mathematical complex treatment of the pure components and of their interaction in the binary systems and in the ternary system. The phase equilibriums liquid-solid from the binary diagram Al-Si [1], Al-Cu [6], Cu-Si [7] were treated analytically, rigorously deducing he equations of the phase transformation curves delimiting the monophase liquid domain form the biphase liquid-solid domain based on the models of the regular un-ideal solutions.

2. The computerised generation of the liquidus surface

In order to establish the liquidus curve that forms the perimeter of the liquidus surface of the ternary system Al-Cu-Si, we mathematically processed - through concatenation - the following functions (Table 1) inferred from the phase equilibrium of the binary systems Si-Al, Al-Cu, Si-Cu, valid in the specified sub-intervals of the x variable (% atomic) [4]:

Table 1 *The mathematical functions of the fragments of liquidus curve from the binary diagrams Al-Si, Si-Cu, Cu-Al*

Binary system	Interval	Equation	Coefficients
Al-Si	$x_{Al} \in [0 \div 89]$	$T = \frac{12100 - 3000\left(x_{Al}^{L}\right)^2}{7{,}189 - 1.987 \cdot \ln\left(1 - x_{Al}^{L}\right)}$	
	$x_{Al} \in (89 \div 100]$	$T = \frac{2570 - 3000\left(1 - x_{Al}^{L}\right)^2}{7{,}189 - 1.987 \cdot \ln\left(x_{Al}^{L}\right)}$	
Al-Cu	$x_{Cu} \in [0 \div 17]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$ y=Temp (K) x=atomic fraction Cu	$a = 933.54386$ $b = -612.93$ $c = 58.049536$ $d = -2407.9807$
	$x_{Cu} \in (17 \div 32]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$	$a = 582.7285$ $b = 2329.2222$ $c = -6472.7855$ $d = 6053.0285$
	$x_{Cu} \in (32 \div 36]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$	$a = 21163.327$ $b = -178178.43$ $c = 518571.02$ $d = -499999.6$
	$x_{Cu} \in (36 \div 52]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$	a =607.53922 b =350.58049 c =1289.9897 d =-128.99897
	$x_{Cu} \in (52 \div 60]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$	a =10908.29 b =-57118.803 c =108281.59 d =-66600.059
	$x_{Cu} \in (60 \div 66]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x$	$a = 17156.008$ $b = -84609.564$ $c = 146785.78$ $d = -83333.367$
	$x_{Cu} \in (66 \div 83]$	$y = a + b \cdot \cos(c \cdot x + d)$	$a = 1301.3147$ $b = 22.765299$ $c = 19.183136$ $d = -1.7903553$

	$x_{Cu} \in (83 \div 100]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3$	$a = -7916.6496$ $b = 28158.738$ $c = -28631.32$ $d = 9746.5882$
Si-Cu	$x_{Cu} \in [0 \div 7]$	$y = a + b \cdot x + c \cdot x^2 + d \cdot x^3 + e \cdot x^4$ y=Temp (K) x=atomic fraction Cu	$a = 1682.8106$ $b = -262.72908$ $c = -1658.5227$ $d = 3296.7172$ $e = -3087.1212$
	$x_{Cu} \in (7 \div 8]$	$y = a + b \cdot x + c \cdot x^2$	a =-8649.5116 b =25778.253 c = -16990.83
	$x_{Cu} \in (8 \div 8{,}2]$	$y = \frac{1}{a + bx^c}$	$a = 0.0010221998$ $b = -0.0001547649\ 5$ $c = 1.4769895$
	$x_{Cu} \in (8{,}2 \div 8,$	$y = ax + b$	$a = 693$ $b = 500$
	$x_{Cu} \in (8{,}6 \div 10$	$y = \frac{a}{1 + b \cdot e^{-cx}}$	$a = 1376.8063$ $b = 1038913.7$ $c = 17.978334$

We studied the binary diagrams Si-Al, Al-Cu, Cu-Si, determining the analytical equations and the optimised empirical statistical functions of the liquidus curves, with the experimental data from the literature [1],[6],[7].

In order to establish the analytical equations of the liquidus curves separating the liquid monophase domain from the bi-phase domain where the solid component has known thermal and thermodynamic properties, we applied three computation models for: the ideal liquid solution ($\Delta C_p=0$ and $\Delta C_p \neq 0$) and for the non-ideal solution of the regular type [1], [4]. The empirical equations of the liquidus curves were established for the cases where there were no thermal and thermodynamic data of the solid phases [4],[3],[6], [7].

The selection of the optimum equations of the equilibrium curves was performed with the help of the computer, based on the *correlation coefficient r* and on the *estimated standard error S*, by statistically-mathematically processing the experimental data from the literature, using the statistic software *CurveExpert*

The liquidus surface form the system Al-Cu-Si modelled on the computer with the 3D software StudioMax, using the concatenation of functions (table 1), is presented in fig.1 .

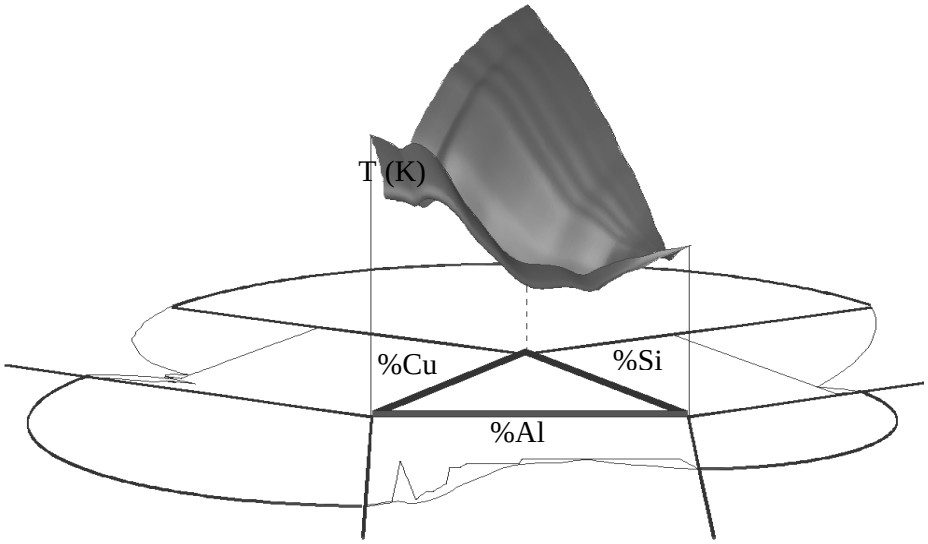

Figure 1 The computerised generation of the liquidus surface from the ternary diagram Al-Cu-Si

The generation of the liquidus curved surface from the spatial diagram of phase equilibrium of the ternary system Al-Cu-Si was performed on a computer using the mathematical instruments that utilise sets of complex mathematical functions which define the surface through a set of control points specified by the user (Fig.2).

These points resulted through the mathematical processing of the liquidus and solidus curves of the binary systems Si-Al, Al-Cu, Cu-Si, with the graphic software *3D Studio Max*.

The plotting (Fig.2) starts from the Gibbs triangle with the concentration expressed in atomic %, and the axis perpendicular on the triangle plane represents the temperature in Kelvin degrees. The acknowledged term for discretisation is „mesh".

The projection of isotherms of the liquidus surface (Fig.3) on the plane of the Gibbs triangle, obtained through the computerised slicing of the surface with horizontal parallel planes offers information on the physical shape and thermal characteristics of each point on these surfaces.

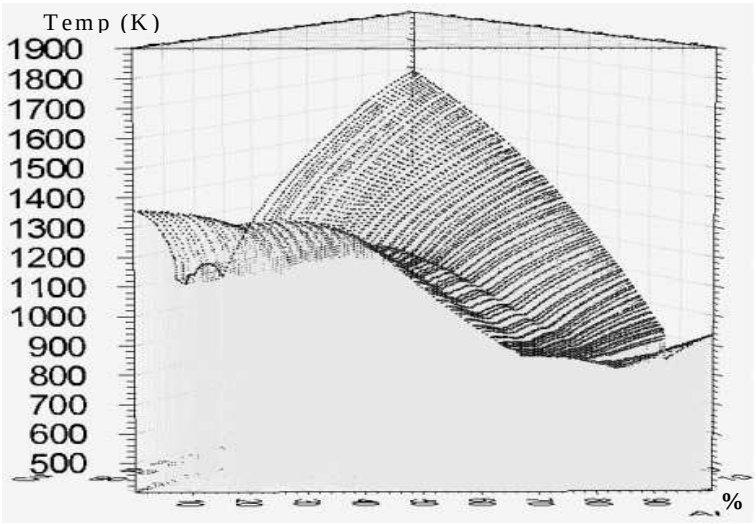

Figure 2 The liquidus surface mathematically modelled, in the system Al-Cu-Si.

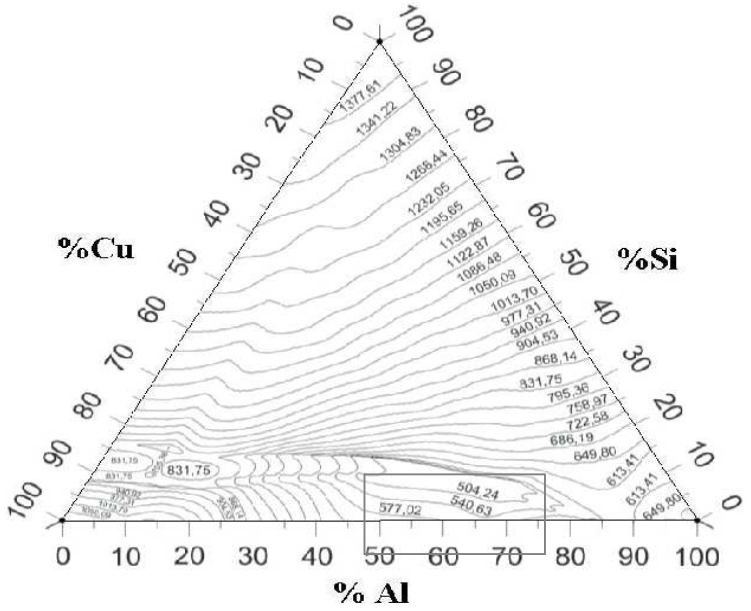

Figure 3 The projection of the liquidus surface on the plane of the Gibbs triangle and the delimitation of the ternary eutectic area.

The study of the mathematically modelled diagram under the temperature of 504°C (Fig.4) leads us to the conclusion that the ternary system Al-Cu-Si has four zones of composition where there may exist ternary eutectic, at the temperature of 476,4°C [4].

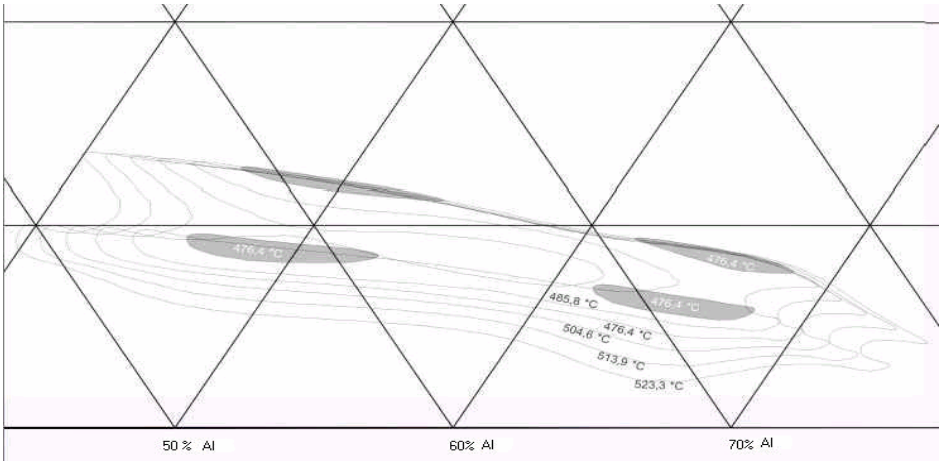

Figure 4 The projection on the Gibbs triangle of the isotherms form the zone of the ternary eutecticles. The area delimited by the isotherm of 476,4°C.

3. The statistical-mathematical equation of the surface

From the database of the mathematical model of the liquidus surface (Fig.2) we selected with the help of the computer 15467 points on the surface having the co-ordinates : *concentrations* x_{Al}, x_{Si}, x_{Cu}, (*atomic %) and temperature (K)*. With these data [4], with the *Statistica 5* software, we established the approximation equation (1) of the liquidus surface through non-linear multiple regression with the full-cubic approximation model [5].

The specific graph offered is a scatterplot with a 95% confidence interval, after a correlation analysis is run [4].

$$T = 918{,}959 \cdot x + 1491{,}086 \cdot y + 1355{,}557 \cdot z + 409{,}962 \cdot x \cdot y - 249{,}939 \cdot x \cdot z - 811{,}233 \cdot y \cdot z - 1354{,}968 \cdot x \cdot y(x-y) - 1396{,}364 \cdot x \cdot z(x-z) + 2416{,}135 \cdot y \cdot z(y-z) + 2564{,}369 \cdot x \cdot y \cdot z \quad (1)$$

where, T- temperature (K); x- at.% Al; y- at.% Si; z- at.% Cu

4. Conclusions

The practical applicability of the equation of the *statistical model* (1) presented in this paper and of the plotting (Fig. 2, Fig. 3) is that it allows the approximation of the melting temperature of any alloy of the (Al-Cu-Si) type, provided we know its chemical composition (at.%). Furthermore we may approximate the alloy's composition knowing only the melting temperature and the concentration of one of the components. Through the thermodynamic-mathematical analysis of the binary systems and determination of the functions of the separation curves of the phase domain from the equilibrium diagrams, we may represent the separation surface of the domains, in the 3D space of the ternary diagram between the components present in the binary systems.The theoretical calculus of the diagrams of phase equilibrium has the advantage of using a small amount of thermo-dynamic data and the possibility of utilising computation techniques, with appropriate software. This considerably reduces the research time and expenses. It is necessary to create mathematical methods, software and even special languages that could simplify the computerised calculus of the phase equilibrium diagrams and in general the calculus in the domain of the thermodynamics of the physical-chemical systems. [1],[2]. The theoretical thermodynamic computations of the equilibrium diagrams, based on the physical and chemical properties of substances and using the new technique, adequate mathematical and graphic software, allow [2]:

The tentative, expected construction of the equilibrium diagrams which haven't been experimentally determined yet;
The completion of the partially plotted equilibrium diagrams;
The correction of the experimental equilibrium diagrams;
The qualitative analysis and systematic classification of the possible type of equilibrium diagrams; The crystallisation process in alloys differs from that in pure metals and depends on the number and nature of phases separating from the melted material as a result of the way the atoms of the composing elements interact. Being a mixture of different atoms, alloys solidify within a temperature range to be found in the thermal range between the liquidus and solidus surfaces. This range may be different in value, depending on the experiment conditions. Possible causes of differences may be: researchers' errors, different sensitivities of the experimental methods used for the diagram plotting, different purity of the initial materials (impurities can provoke the apparition of eutectic
Each theoretical study must nevertheless be sustained by the experimental confirmation through appropriate methods.

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