

THERMODYNAMIC CALCULATION OF PHASE EQUILIBRIA OF THE Cu-Al-Mn ALLOYS

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Keywords: Thermodynamic modeling, CALPHAD method, Cu-Al-Mn alloys

ABSTRACT

Cu-alloys have been intensively studied because of their high thermal conductivity, good electrical and shape memory properties and low cost. Cu-Al-Mn alloys show a higher ductility and elongation in relation to the other Cu-based alloys, as well as a good potential for a cold drawing. Therefore, the investigation of these alloys is still a challenge, especially from a thermodynamic point of view due to a lack of thermodynamic data of Cu-Al-Mn ternary system in the literature.

Thermodynamic calculation of phase diagrams of $\text{Cu}_{0.73}\text{Mn}_{0.10}\text{-Al}$ and $\text{Cu}_{0.70}\text{Mn}_{0.30}\text{-Al}$ vertical sections and isothermal sections at 25 and 400°C is presented in this work. Calculations were done using optimized thermodynamic parameters for binary sub-systems Cu-Al, Cu-Mn, Al-Mn and ternary system Cu-Al-Mn according to CALPHAD method and obtained results were discussed.

1. INTRODUCTION

Phase diagrams are very important for designing and development of materials with target functional properties as well as for prediction of microstructure and phase stability under specific conditions. Thermodynamic modeling offers valuable information for equilibrium thermodynamics, modeling of diffusion processes and grain growth, and represents the advantage according to expensive and time-consuming experimental investigations, especially for complex multicomponent metal systems [1-4]. Reliable thermodynamic databases, with optimized parameters, are crucial for thermodynamic calculations of Gibbs energy of all phases existing in investigated system and accuracy of calculated phase equilibria. CALPHAD method is based on the minimization of total Gibbs energy for a set of

independent variables, such as temperature, pressure and concentration [5-8]. Gibbs energy for any phase is given as a sum of different contributions:

$$G_m^\phi = G_{ref}^\phi + G_{id}^\phi + G_E^\phi + G_p^\phi + G_m^\phi + \dots \quad \dots(1)$$

The contribution of mechanical mixing of pure components for substitutional solid solutions or liquid phase is expressed as:

$$G_{ref}^\phi = \sum_{i=1}^n x_i {}^0G_i^\phi \quad \dots(2)$$

Where ${}^0G_i^\phi$ is a Gibbs energy of the pure component i in the standard state. Temperature dependence is given by equation (3):

$$G = a + bT + cT \ln(T) + \sum d_i T^n \quad \dots(3)$$

Contribution from ideal random mixing of the constituents is given by:

$$G_{id}^\phi = RT \sum_{i=1}^n x_i \ln(x_i) \quad \dots(4)$$

The excess Gibbs energy term is usually expressed using Muggianu extension of the Redlich-Kister formalism:

$$G_E^\phi = \sum_{\substack{i,j=1 \\ i \neq j}}^n x_i x_j \sum_{z=0}^m {}^zL(x_i - x_j)^z + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^n x_i x_j x_k L_{ijk} \quad \dots(5)$$

where zL is temperature dependent interaction parameter between constituents.

Contribution to the Gibbs energy due to magnetic properties of the phase is given by following equation:

$$G_m^\theta = RT \ln(\beta^\theta + 1) f(\tau) \quad \dots(6)$$

where β^θ is related to magnetic entropy and τ is given by T/T_C , where T_C is the critical temperature of magnetic ordering.

Thermodynamic descriptions of binary systems Cu-Al, Al-Mn and Cu-Mn are given in a number of references, but there is a lack of relevant experimental and optimized thermodynamic data for ternary Cu-Al-Mn alloy [9-13]. According to wide application of Cu-Al-Mn alloys in engineering, medicine, electronic devices, etc., it seems very interesting to analyze thermodynamic properties of this ternary system, especially in Cu-rich region and low content of aluminum, i.e. alloys with a low degree of order β -phase, which show a shape

memory effect and martensite structure by quenching as well as excellent ductility and cold workability [14-15].

2. THERMODYNAMIC CALCULATION

Thermodynamic calculations of phase equilibria were done by Thermo-Calc 5 software, on the basis of CALPHAD method. Calculations were done for alloys along two vertical sections $\text{Cu}_{0.73}\text{Mn}_{0.10}\text{-Al}$ and $\text{Cu}_{0.70}\text{Mn}_{0.30}\text{-Al}$. Isothermal sections were determined for 25 and 400 °C.

3. RESULTS AND DISCUSSION

The calculation of phase equilibria of the Cu-Al-Mn ternary system was performed on the base of the thermodynamic parameters of sub-systems Cu-Al, Cu-Mn, Al-Mn and ternary phase τ . Gibbs energies of pure metals in their stable phases were taken from Dinsdale SGTE database [16], except for Cu in the bcc and cub phases. Gibbs energies for Cu in bcc and cub phases were assumed as those of pure nickel [17]. Pure copper and aluminum was taken as fcc phase structure and pure manganese as a bcc phase structure in the standard state. Optimized thermodynamic parameters due to experimental measurements, for ternary phase were taken from Miettinen [17].

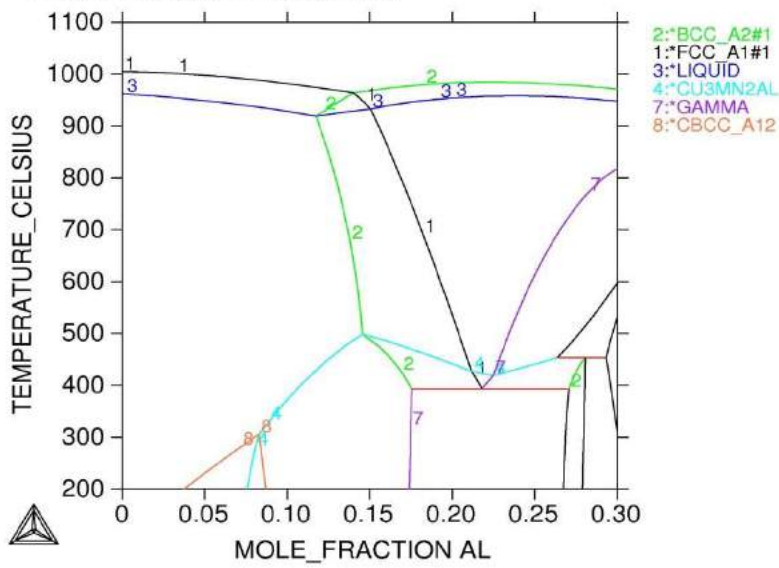
Phases in Cu-Al-Mn system that are considered for calculation are given in Table 1.

Table 1. Phases in Cu-Al-Mn system taken in calculation

Phase	TD database name	Pearson symbol
Liquid	L	-
fcc (Cu)	FCC_A1	<i>cF4</i>
β	BCC_A2 \neq 1	<i>cI2</i>
γ	GAMMA	<i>cF4</i>
cub (βMn)	CUB_A13	<i>cP20</i>
bcc (αMn)	CBCC_A12	<i>cI58</i>
τ_3	$\text{Cu}_3\text{Mn}_2\text{Al}$	<i>cF24</i>

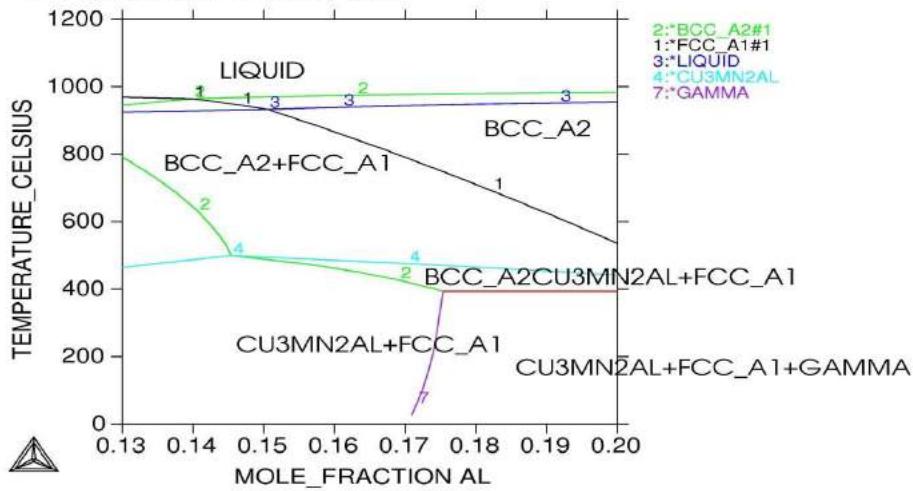
Disordered solution phases were described with the substitutional solution model, while the ternary phase, τ_3 , $\text{Cu}_3\text{Mn}_2\text{Al}$, was described with the sublattice model. Contribution of magnetic ordering was also taken in calculation of Gibbs energy for Cu-Al-Mn system, according to equation (6).

THERMO-CALC (2016.02.28:14.48) :
 DATABASE:USER
 P=1.01325E5, N=1, X(MN)=0.1;



a)

THERMO-CALC (2016.02.28:14.58) :
 DATABASE:USER
 P=1.01325E5, N=1, X(MN)=0.1;

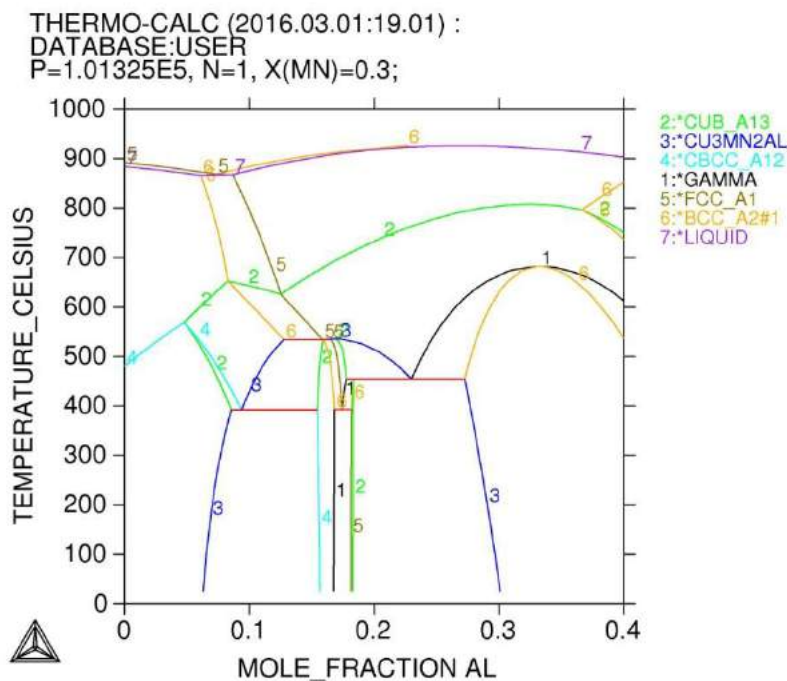


b)

Figure 1. Calculated phase diagram for $\text{Cu}_{0.73}\text{Mn}_{0.10}\text{-Al}$ vertical section (a, b)

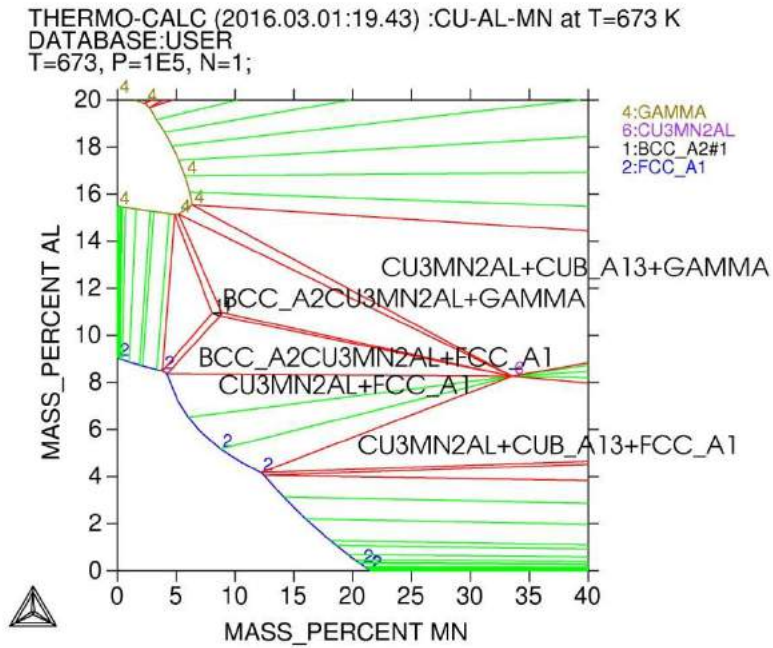
Phase stability diagram of the $\text{Cu}_{0.73}\text{Mn}_{0.10}\text{-Al}$ section is given at the Figures 1. a) and b). TCW diagram at Figures 1. a) shows primary crystallization at the aluminium content 0.17 Al: $L + \text{bcc}$. At the lower content of Al there is a second area of primary crystallization: $L + \text{fcc}$. β -phase in Cu-Al-Mn system could forms two different superstructures cP2 (β') and cF16 (β''), Heusler phase. Beside these superstructures, there are also known three intermetallic phases that exist in Cu-Al-Mn ternary system [6]. From Figures 1. a) and b) it could be seen the intermetallic phase, τ_3 , $\text{Cu}_3\text{Mn}_2\text{Al}$, which exists in Cu-rich region of Cu-Al-Mn alloy. τ_3 phase in $\text{Cu}_{0.73}\text{Mn}_{0.10}\text{Al}_{0.17}$ alloy solidify at temperature 475 °C and fcc at temperature 790 °C. β -phase is stable from 976 °C to 423 °C, while at the room temperature stable phases are fcc and $\text{Cu}_3\text{Mn}_2\text{Al}$ phase.

The invariant reaction $\text{bcc} \leftrightarrow \text{fcc} + \gamma + \tau_3$ occurs at the temperature 392 °C for higher content of aluminum (> 0.18). β -phase undergoes to order-disorder transition: A2 (bcc β) \rightarrow B2 (CuAl) \rightarrow DO3 (Cu₂Al) or L21 (in CuAlMn). Decomposition of β -phase can be suppressed by rapid quenching and in that case martensitic transformation occurs below M_s temperature. Calculated diagram for Cu-Al-Mn system for $x_{\text{Mn}} = 0.30$ in the Cu-rich region, is shown in Figure 2. It can be seen three invariant reactions containing τ_3 phase: at 534 °C, 454 °C and at 392 °C, what is in agreement with calculations presented in the literature [6,17,18]. Phase stability at 25 °C and 400 °C can be seen from isothermal calculations of Cu-Al-Mn system given at Figures 3. and 4.



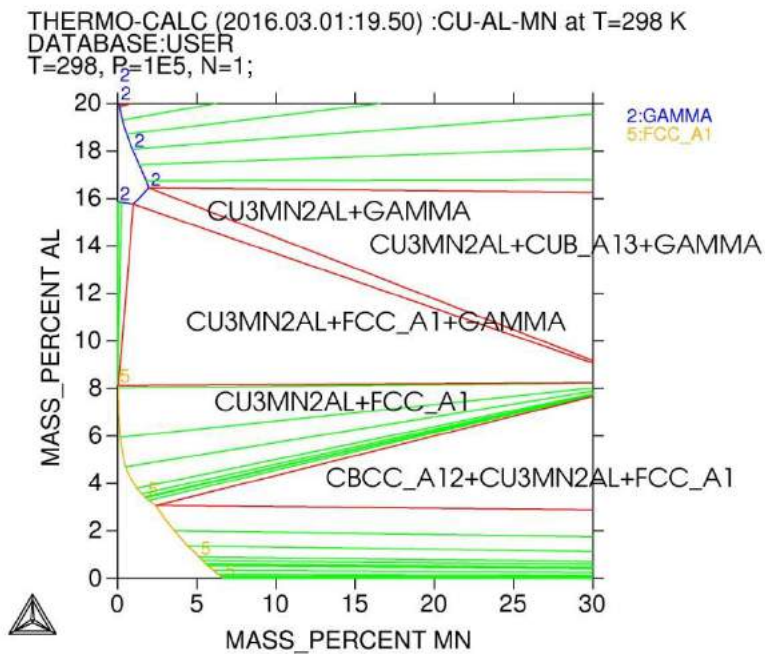
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Figure 2. Calculated isopleth in Cu-rich region at $x_{\text{Mn}} = 0.30$



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Figure 3. Isothermal section at 400°C in the Cu-rich region of the Cu-Al-Mn ternary system



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Figure 4. Isothermal section at 25°C in the Cu-rich region of the Cu-Al-Mn ternary system

4. CONCLUSION

Thermodynamic calculation of phase equilibria of the Cu-Al-Mn alloys was performed by CALPHAD method. Calculations were done for different sections in the Cu-rich corner. Calculations point to stability of intermetallic phase τ_3 , $\text{Cu}_3\text{Mn}_2\text{Al}$, in the investigated range of compositions, which is stable under 550 °C. In calculations it was assumed as a stoichiometric ternary phase, and it was described by sublattice model. Invariant reactions containing ternary τ_3 phase, were found at temperatures 534°C, 454°C and at 392°C for vertical section of Cu-Al-Mn system with $x_{\text{Mn}} = 0.30$.

Acknowledgements

This work has been fully supported by Croatian Science Foundation under the project IP-2014-09-3405.

5. REFERENCES

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