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Thermodynamical analisys of Al-Cu-Mn system using RKM model

Termodinamična analiza sistema Al-Cu-Mn z uporabo modela RKM

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Abstract

The results of thermodynamic analysis of alloys in ternary system Al-Cu-Mn are been presented in these work. Thermodynamic analysis was carried out by applying Redlich-Kister-Muggianu (RKM) method in selected sections from aluminum, copper and manganese corner, in the temperature interval from 1 073 K to 1 873 K. Thermodynamic properties (excess integral Gibbs energy and activity of components) has been calculated using Redlich-Kister parameters of constituent binary systems and presented in form of graphics. Analyzing calculated data it can be concluded that high content of manganese in alloy can significantly lower miscibility of alloy.

Key words: thermodynamics, RKM model, Al-Cu-Mn system

Izvleček

V delu so predstavljeni rezultati termodinamične analize zlitin iz ternarnega sistema Al-Cu-Mn. Termodinamična analiza je bila opravljena z uporabo Redlich-Kister-Muggianujeve (RKM) metode v izbranih področjih aluminijevega, bakrovega in manganovega kota, v temperaturnem območju od 1 073 K do 1 873 K. Termodinamske lastnosti (presežne intergralne Gibbsove energije in aktivnosti komponent) so bile izračunane z uporabo Redlich-Kisterjevih parametrov za komponente binarnih sistemov in so predstavljene v grafični obliki. Iz analize izračunanih podatkov je mogoče sklepati, da lahko visoka vsebnost mangana v zlitini bistveno zmanjša sposobnost mešanja zlitine.

Ključne besede: termodinamika, RKM-model, sistem Al-Cu-Mn

Introduction

Shape memory materials are able to recover their original shape, after being distorted, at the presence of right stimulus. These materials include: a) Shape memory alloys, b) shape memory polymers, c) shape memory composites and newly developed d) shape memory hybrids[1].

Shape memory alloys (SMAs) are characterized by unique properties (pseudo-elasticity and shape memory effect), which enables them to "remember" their original shapes. These alloys are used as activators which change their shape, position and other mechanical characteristics in response to variation in temperature and electromagnetic field[2].

Alloys from ternary system Cu-Al-Mn belongs to wide group of Cu-Al-based shape memory alloys (SMAs)[3, 4].

Thermodynamic data related to ternary Cu-Al-Mn system is, at best, scarce. Termodynamic description of Cu-Al-Mn System in the Cu-rich corner (Al contents up to w = 18 % and Mn contents up to w = 50 %), using available data for binary systems (Cu-Al, Cu-Mn and Al-Mn) was given by Miettinen[5]. Kainuma et al.[6] studied phase equilibria between α, β and γ phase in Cu-rich portion of Cu–Al–Mn system, by means of TEM-EDS, DSC and X-ray diffraction.

Main area of use for alloys which belong to Cu-Al-Mn system is connected to martensitic transformation and shape memory effect, so these properties and possible applications have been primary focus of researchers[7-24].

Additional research have been done on influence of composition and maximum cycling temperature on Cu-Al-Mn shape memory alloys microstructure[25], seismic application of Cu–Al–Mn alloy bars[26, 27], damping capacity of Cu-Al-Mn alloys[28-30] and magnetic properties of chosen Cu-Al-Mn alloys[31, 32].

Objective of this work is to give some information about thermodynamic properties of ternary Al-Cu-Mn system, taking into account current lack of such data in literature.

Theoretical basis

Many different methods for predicting thermodynamic properties of ternary systems based on information about binary systems included in their composition are available in the literature. In this paper, Redlich-Kister-Muggianu model[33] is used for calculation of thermodynamic properties of the investigated ternary system.

$$\Delta G^{E} = x_1 x_2 [L^0_{12} + (x_1 - x_2)\, L^1_{12} + (x_1 - x_2)^2 L_2^{12} + \ldots]$$

$$+ x_2 x_3 [L^0_{23} + (x_2 - x_3)\, L^1_{23} + (x_2 - x_3)^2 L^2_{23} + \ldots]$$

$$+ x_1 x_3 [L^0_{13} + (x_1 - x_3)\, L^1_{13} + (x_1 - x_3)^2 L^2_{13} + \ldots]$$

$$+ L^1_{23}\, x_1 x_2 x_3 \ldots \quad (1)$$

The basic equation of Redlich-Kister-Muggianu[33] model for ternary system is:

For the calculation it is adopted that the value of ternary interaction parameter L_{123} is zero and all the ternary interatomic reactions are ignored due to the lack of experimental data for ternary systems.

In the equation (1), DG^{E} and DG^{E}_{ij} correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of components in investigated ternary system. Partial thermodynamic quantities of aluminum, copper and manganese are calculated according to the equations:

$$G_i^E = G^E + (1\text{-}x_i)(\partial G^E / \partial x_i) = RT \ln \gamma_i \quad (2)$$

and

$$a_i = x_i \gamma_i \quad (3)$$

Results and discussion

From the concentration area of ternary system Al-Cu-Mn sections shown in Figure 1. were selected and thermodynamic prediction was carried out using RKM model[33], with content of the third component x_i = 0, 0.1–0.9, 1 in temperature interval 1 073–1 873 K. Redlich-Kister

Table 1: *Redlich-Kister parameters for the constituent binary systems*

System *ij*	L^{o}_{ij} (T)	L^{1}_{ij} (T)	L^{2}_{ij} (T)	L^{3}_{ij} (T)
Al-Cu[34]	−67 094 + 8.555*T	32 148 − 7.118*T	5 915 − 5.889*T	−8 175 + 6.049*T
Cu-Mn[35]	1118.55 − 5.622 5*T	−10 915.375	0	0
Al-Mn[36]	−66 174 + 27.098 8*T	−7 509 + 5.483 6*T	−2 639	0

parameters of constituent binary systems presented in Table 1, were used for the calculation.

Values of excess integral Gibbs energy and activity for all components, in sections from aluminum, copper and manganese corner of ternary Al-Cu-Mn system, calculated using RKM method and equations (2) and (3) are shown in Figures 2–4.

As can be seen in figures 2–4., values for excess integral Gibbs energy of investigated sections from the corner of aluminum and copper are negative, with minimum values up to −14 kJ/mol, while for the investigated section from the corner of copper Gibbs energy goes up to −15 kJ/mol.

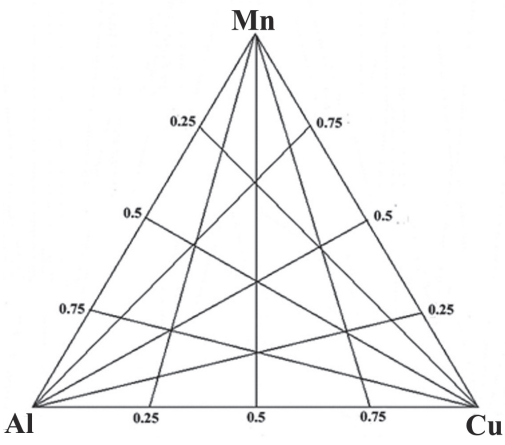

Figure 1: *Schematic diagram of the investigated cross-sections of ternary Al-Cu-Mn system.*

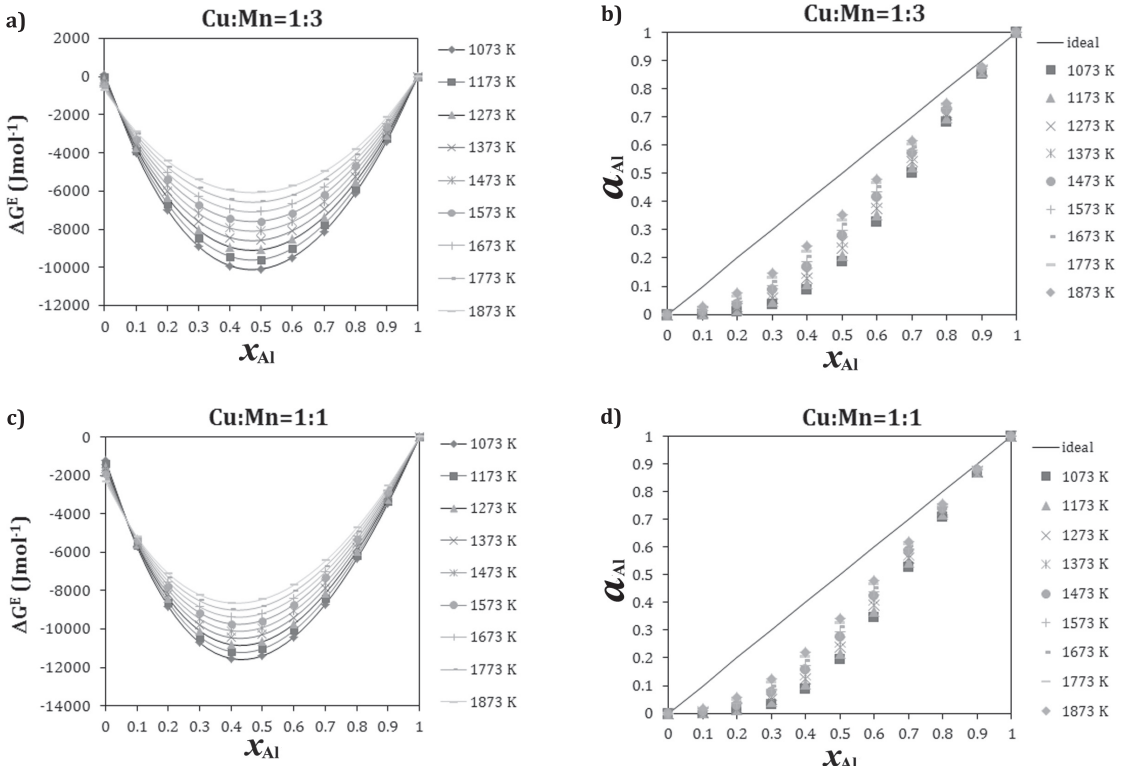

Figure 2: *Results of thermodynamic predicting according to RKM model in temperature range* 1 073-1 873 K *for cross-sections from aluminum corner (part 1).*

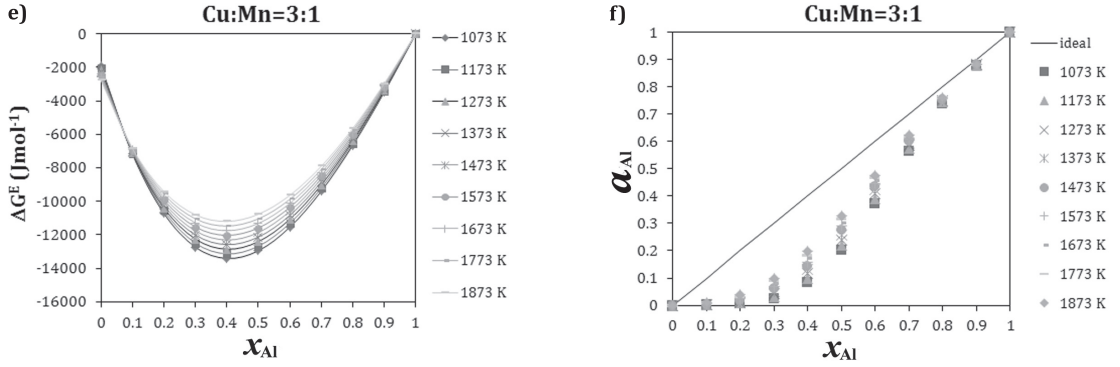

Figure 2: *Results of thermodynamic predicting according to RKM model in temperature range* 1 073-1 873 K *for cross-sections from aluminum corner (part 2).*

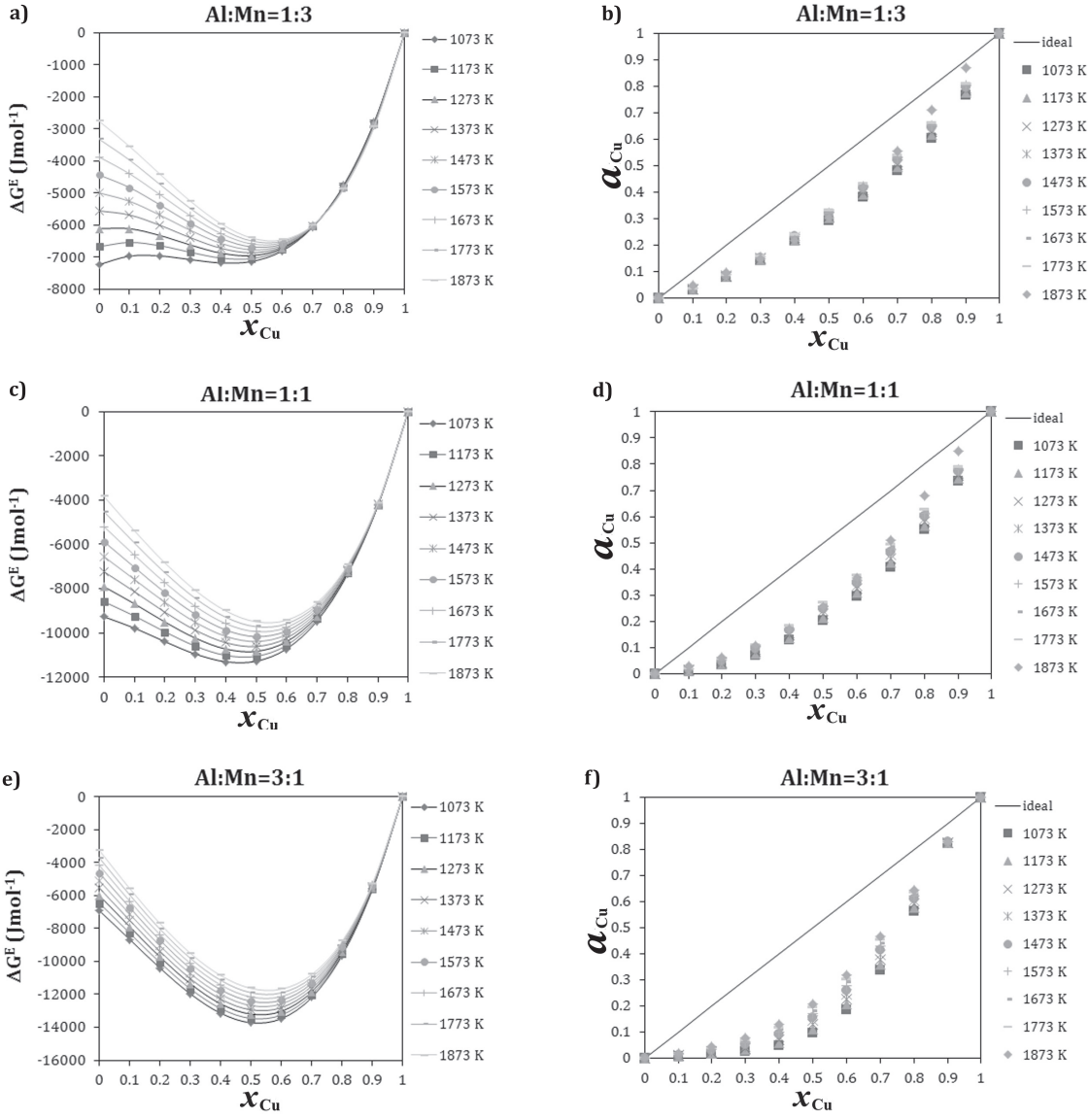

Figure 3: *Results of thermodynamic predicting according to RKM model in temperature range* 1 073-1 873 K *for cross-sections from copper corner.*

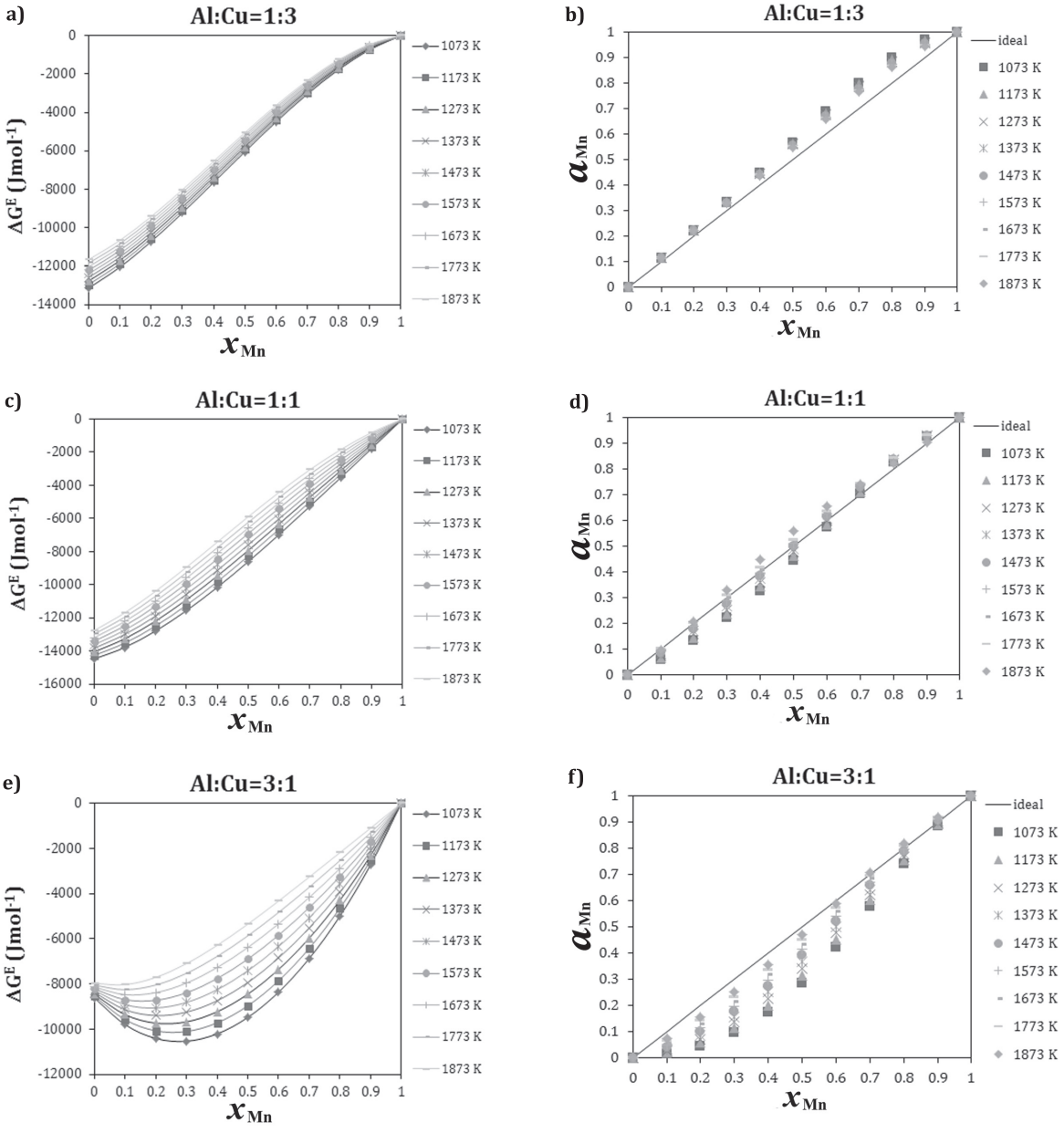

Figure 4: *Results of thermodynamic predicting according to RKM model in temperature range* 1 073–1 873 K *for cross-sections from manganese corner.*

Aluminum and copper activity shows pronouncedly negative deviation from Rault's law for all investigated sections. Different situation can be observed for activity of manganese, where in section Al : Cu = 1 : 3 positive derivation from line of ideal condition is present. For cross section Al : Cu = 1 : 1 manganese activity is near to ideal solution line, while for cross section Al : Cu = 3 : 1 negative deviation can be seen. From all this data it can be concluded that high content of manganese in alloy significantly lowers miscibility of alloy, which can lead to occurrence of layering between different metals. Also it can be noticed that with increasing aluminum content in alloy with simultaneously lowering content of copper, previously positive deviation of manganese activity from Rault's law, gradually changes to negative deviation, as seen in cross section Al : Cu = 3 : 1.

Conclusion

Thermodynamic analysis of alloys in ternary Al-Cu-Mn system has been conducted using the Redlich-Kister-Muggianu model. Thermodynamic properties (excess integral Gibbs energy and activity of components) has been calculated using Redlich-Kister parameters of constituent binary systems and presented in form of graphics. Calculation has been carried out in temperature interval 1 073–1 873 K.
Considering current lack of thermodynamic data about Al-Cu-Mn alloys in literature, thermodynamic data presented in this work could be useful for the further assessment of this system and its phase diagram as well as for completing thermodynamic description of these alloys.

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