KINETICS OF PHASE TRANSFORMATIONS IN Cu-2wt.%Al-8wt.%Ag AND Cu-4wt.%Al-6wt.%Ag ALLOYS

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Abstract

The investigations of Cu-2wt.%Al-8wt.%Ag and Cu-4wt%Al-6wt%Ag alloys from Cu-Al-Ag system, known for exhibiting shape memory effect, are presented in this work. Based on performed experimental measurements, done using differential thermal analysis under non-isothermal conditions, phase transformation kinetics in chosen alloys of selected system was examined and activation energy values were determined using Borchardt and Daniels method.

Keywords: *Shape memory alloys, Cu-Al-Ag alloys, thermal analysis, kinetics, activation energy*

1. INTRODUCTION

Shape memory alloys (SMAs) such as Ni-Ti-based, Cu-based and Fe-based alloys are commercially attractive for the practical applications of superelasticity (SE), the shape memory effect (SME) and two-way memory effect (TWME) [1]. Shape memory refers to the ability of certain plastic deformed metals and alloys to regain their original shape during the heating process due to complete or almost complete absence of deformation [2]. These characteristics are result of martensitic phase transformation. SMAs have some common characteristics, such as order of atoms and thermoelastic martensitic transformations [3]. These alloys are used for various applications such as pipe couplings, various actuators in electric appliances, automobile applications, antennae for cellular phones, medical implants etc. Besides, since they have the function of an actuator as well as a sensor, they are considered as promising candidates for miniaturization of actuators, i.e. as microactuators, micromachines or robots [4]. Among these alloys, the Cu-based SMAs are most attractive for practical applications [1,5,6], being lower in cost than Ni–Ti-based alloys and showing better SME and SE comparing to Fe-based alloys.

Therefore, investigation of kinetics of phase transformation in typical representative alloys in Cu-Al-Ag system, already proved in literature as interesting new shape memory alloy [7,8] was the main aim of this paper.

2. THEORETICAL FUNDAMENTALS

Phase transformations in alloys occur by nucleation and growth and there are two types of them [9] - *phase transformation of nucleation and growth* if grain grows very slowly, depending on diffusion rates, and *martensite phase transformation* if grain grows very fast, without diffusion and with elastic transformation going with elastic strain. Each of mentioned processes possesses characteristic energy of activation [9,10].

The activation energy values in this work were determined using Daniels and Borchardt method [11,12]. The Borchardt and Daniels kinetics approach was originally described for solutions and

was subsequently refined for solids by other researchers [13]. The Borchardt and Daniels approach assumes that the reaction follows n^{th} order kinetics and obeys the general rate equation:

$$d\alpha/dt = k(T)\,[1-\alpha]^n \quad \ldots (1)$$

where $d\alpha/dt$ presents reaction rate (1/sec); α is fractional conversion; k(T) is specific rate constant at temperature T; and n is reaction order. The Borchardt and Daniels approach also assumes Arrhenius behavior [12]:

$$k(T) = Z \cdot e^{-Ea/RT} \quad \ldots (2)$$

where Ea presents activation energy; Z is pre-exponential factor or Arrhenius frequency factor; and R is gas constant.

3. EXPERIMENTAL

The alloys selected from Cu-Al-Ag system and studied in this work, were Cu-2wt.%Al-8wt.%Ag (sample A1) and Cu-4wt%Al-6wt%Ag alloy (sample A2). The samples were prepared by induction melting of the starting metals (Cu, Al and Ag metals of 99.99% purity) in graphite crucible under argon atmosphere. In order to improve compositional homogeneity, the alloys were melted and cooled repeatedly for three times. The sample mass was 3g, with total metal losses less than 1%.

The phase transformation temperatures of the as-cast alloy samples were determined by DTA method using instrument NETZSCH STA 449F1 Jupiter, under following conditions: argon atmosphere, heating rate 10^0C/min, and alumina as referent material.

4. RESULTS AND DISCUSSION

DTA curve of the investigated Cu-2wt.%Al-8wt.%Ag (sample A1) and Cu-4wt%Al-6wt%Ag alloy from Cu-Al-Ag system is shown in Fig.1.

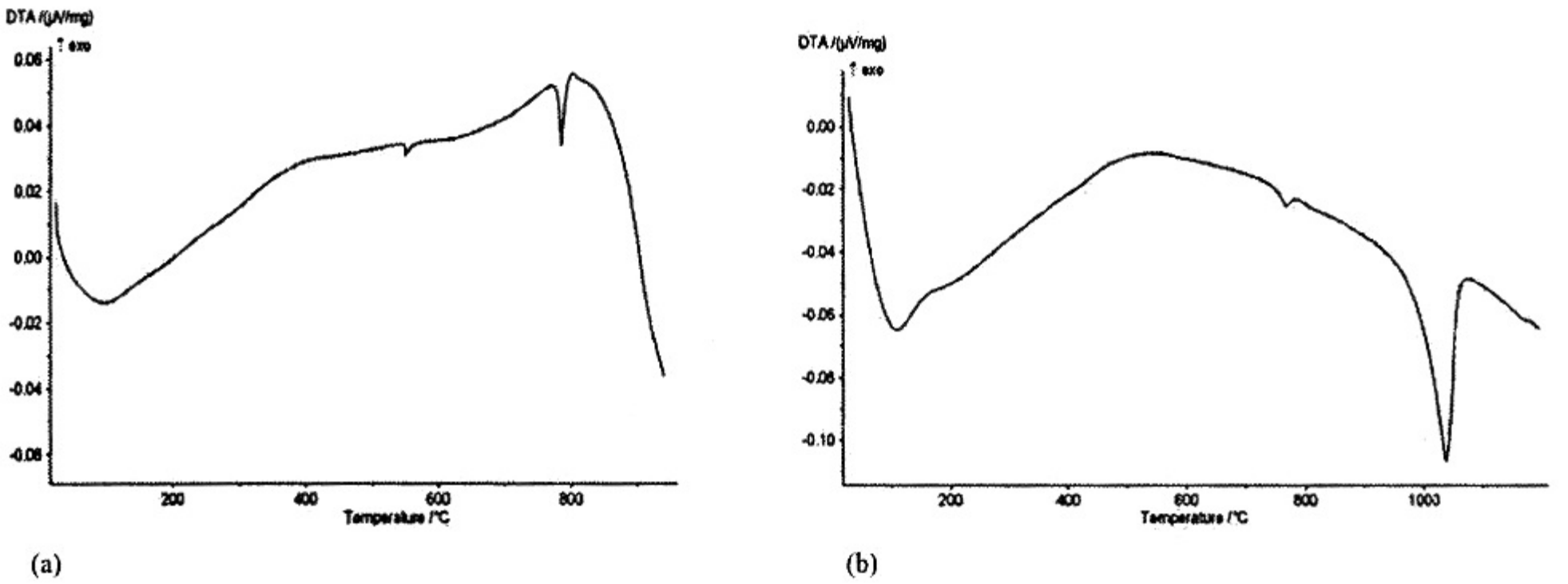

Figure 1 *– DTA curves of investigated samples:*
a) sample A1 (Cu-2wt.%Al-8wt.%Ag) and b) sample A2 (Cu-4wt%Al-6wt%Ag alloy)

As can be seen from DTA curves, two characteristic endothermic peaks were noticed for both investigated alloys. For sample A1, the peaks are presented at the temperatures of 551.8 and 785°C, while for sample A2 the peaks are at 752.7 and 958.5°C. Obtained peaks respond to the start and ending of melting process, which is in accordance with literature phase diagram [5]. Maximum in DTA curves is related to the temperature in which maximum of phase transformation occurs. Such thermal event became more intense with the increase of Ag content, indicating that transition may be attributed to the total dissolution of silver in matrix [7,8].

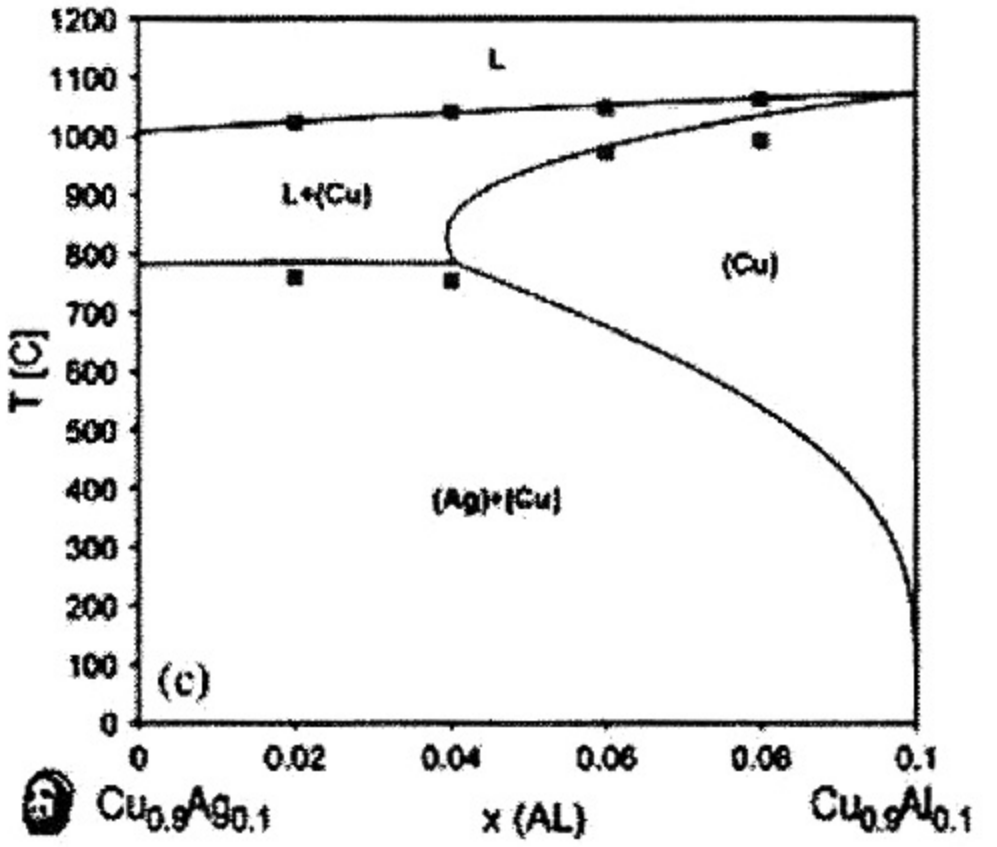

***Figure 2** – Phase diagram of the vertical section with Cu = 90 at% in the Cu–Al–Ag ternary system*

The Borchardt and Daniels method was applied to obtained DTA measurements results according to standard procedure. Finally, the Arrhenius plots were constructed for both peaks and both alloys - the dependencies of $\ln k_i$ on $1000/T_i$ presented in Figs. 3 and 4 – which enabled determination of adequate activation energy values, shown in Table 1.

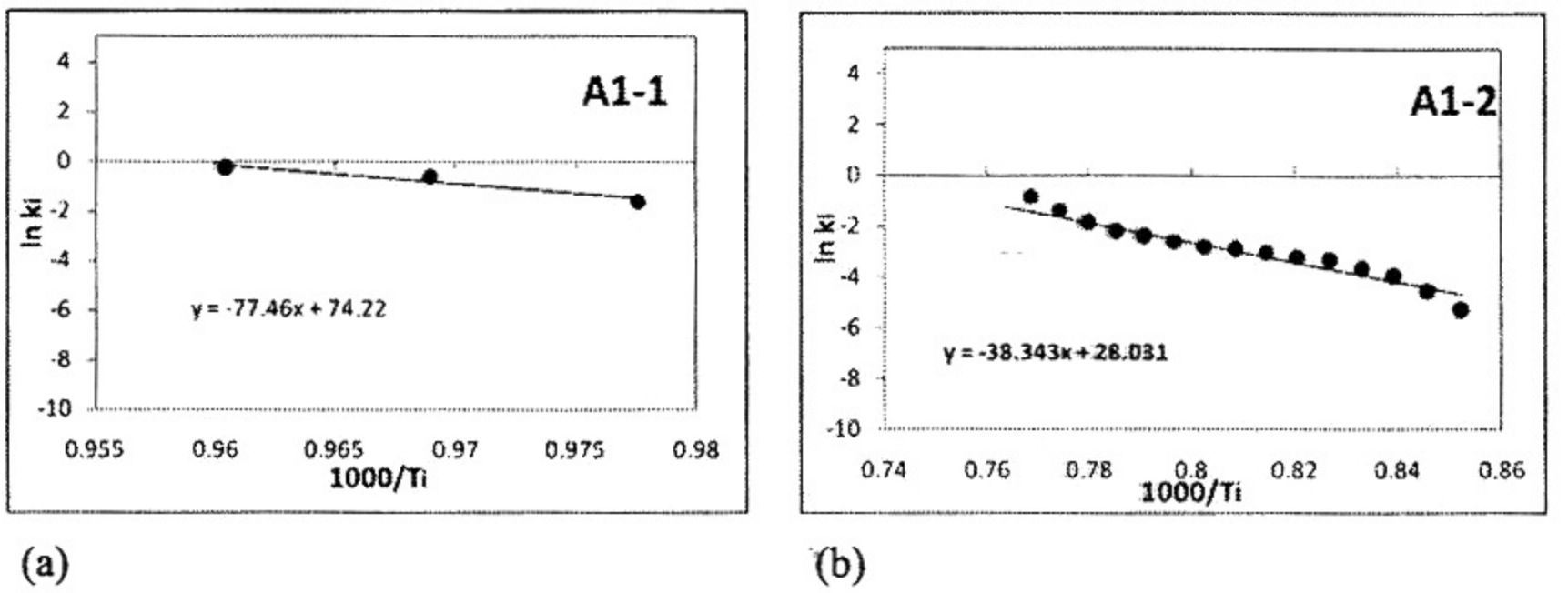

***Figure 3** – Sample A1: $\ln k_i$ vs. $1000/T_i$ for (a) the first DTA peak and (b) the second DTA peak*

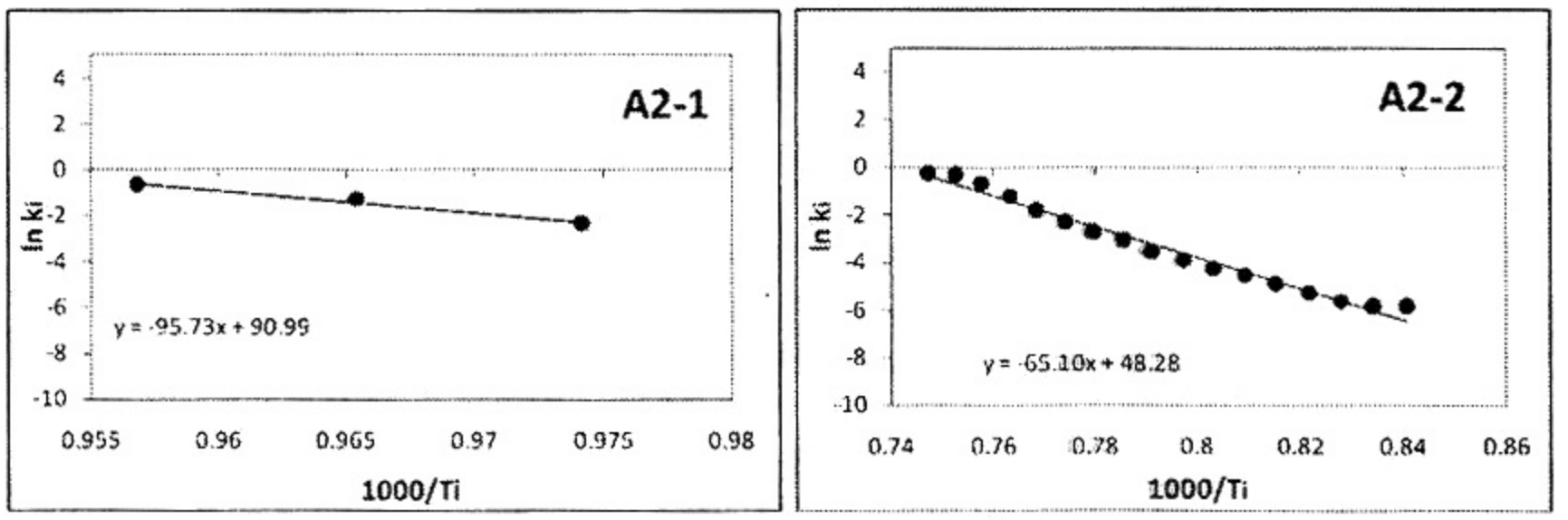

***Figure 4** – Sample A2: $\ln k_i$ vs. $1000/T_i$ for (a) the first DTA peak and (b) the second DTA peak*

Considering obtained results, higher values of energy of activation was obtained for sample A2 comparing to sample A1. Similar results were obtained by Adorno et.al [8] in their research of Cu-Al system kinetics, in which they noticed influence of silver content to kinetic parameters.

Table 1 – Activation energy

Sample	A1		A2	
Peak in DTA curve	I	II	I	II
Ea (kJ/mol)	**644**	**319**	**796**	**541**

5. CONCLUSION

Based on performed experimental DTA measurements of Cu-2wt.%Al-8wt.%Ag and Cu-4wt.%Al-6wt.%Ag alloys and using Daniels and Borchardt method, activation energy (Ea) values were determined. The results show diferent activation energy acording of content of Ag in system. Lower contents of Ag in system bring along higher values of activation energy for same phase transformation. Thermal event became more intense with the increase of Ag content, thus indicating that this transition can be attributed to the total dissolution of Ag in matrix.

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