KINETICS OF PHASE TRANSFORMATIONS IN SI-RICH ALUMINUM ALLOYS

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1. Introduction

Addition of Si to Al is promising way to enhance mechanical properties of resulting alloy as compared to pure Al or other construction Al alloys[1]. Solubility of Si in Al is very low (about 1 at. %), but it can be increased by process of rapid quenching. Addition of transition metal such as Ni further increases content of dissolved Si in alloy and in certain compositional range even results in fully amorphous alloy [2].

In this work we have examined kinetics of phase transformations and evolution of phase composition during heating of rapidly quenched Al-Ni-Si alloys with variable content of Ni (5, 10, 15 at.%).

2. Experimental

Rapidly quenched alloys of $Al_{75}Ni_5Si_{20}$, $Al_{70}Ni_{10}Si_{20}$ and $Al_{70}Ni_{15}Si_{15}$ were prepared atthe Institute of Physics SAS.Master alloys were inductively melted in Ar atmosphere to ensure compositional homogeneity. Rapidly quenched alloys were prepared in form of 10 mm wide and 20 μm thick ribbons by planar flow casting on copper wheel with tangential speed of approximately 40 m/s. The phase characterization of as-cast and annealed alloys was performed by in-situ X-ray diffraction (Bruker D8, Cu/Cr K_α radiation) during linear heating with rate of 5 K/min. Reaction kinetics of transformations from as-cast state was characterized by differential scanning calorimetry (DSC, Perkin-Elmer DSC7) during linear heating with rate of 1 - 40 K/min and by measurements of temperature dependence of electrical resistivity using linear heating with rate of 10 K/min.

3. Results

It was discovered that increasing content of transition metal in alloy increases glass forming ability of the alloy [3]. As is clearly seen in Fig. 1, displaying X-ray diffraction patterns of alloys in as-cast state, alloy with 5 at.% of Ni has mixed amorphous and crystalline structure composed of amorphous matrix with embedded fcc-Al and Si crystals. In contrast, alloys containing 10 and 15 at.% of Ni have fully amorphous structure. However, small diffraction peak atposition of Si reflexion is present in alloy containing 10 at. % of Ni.Alloys with higher Ni content show bimodal diffraction plateau. Presence of this plateau can be explained by coexistence of amorphous phases similar to eutectic alloy[4]. According to the paper of [5], this plateau is explained by ultra-fine crystalline structure which mimics diffraction of amorphous structure.

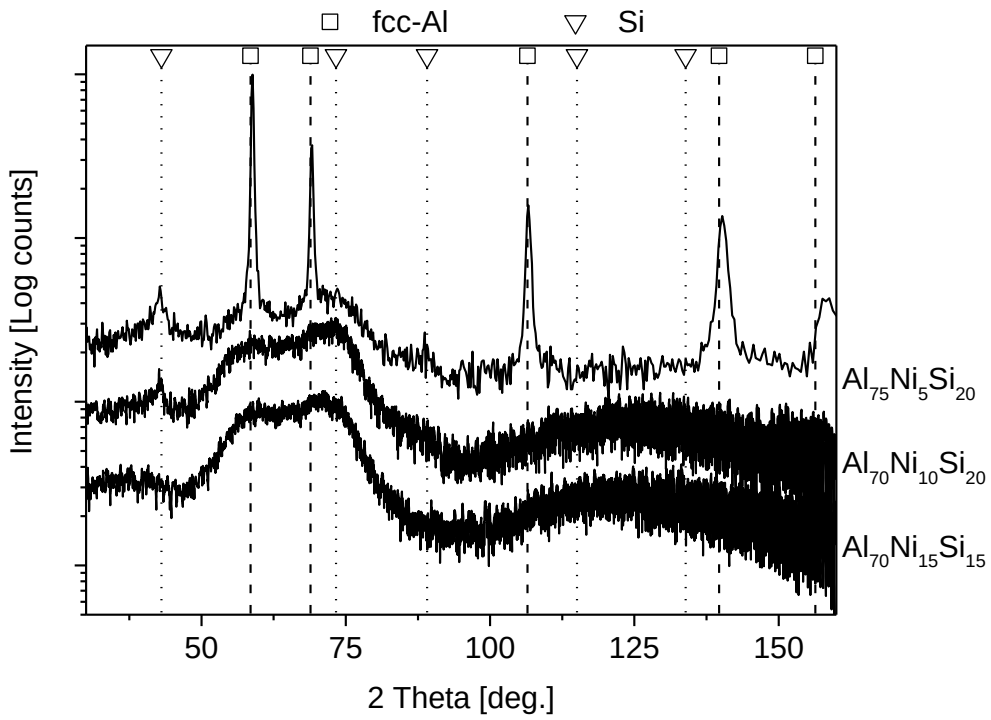

Fig. 1: *X-ray diffraction patterns (Cr K_α) of as-cast rapidly quenched Al-Ni-Si alloys. Squares and triangles mark positions offcc-Al and diamond cubic Si peaks, respectively. Data are shifted vertically for clarity.*

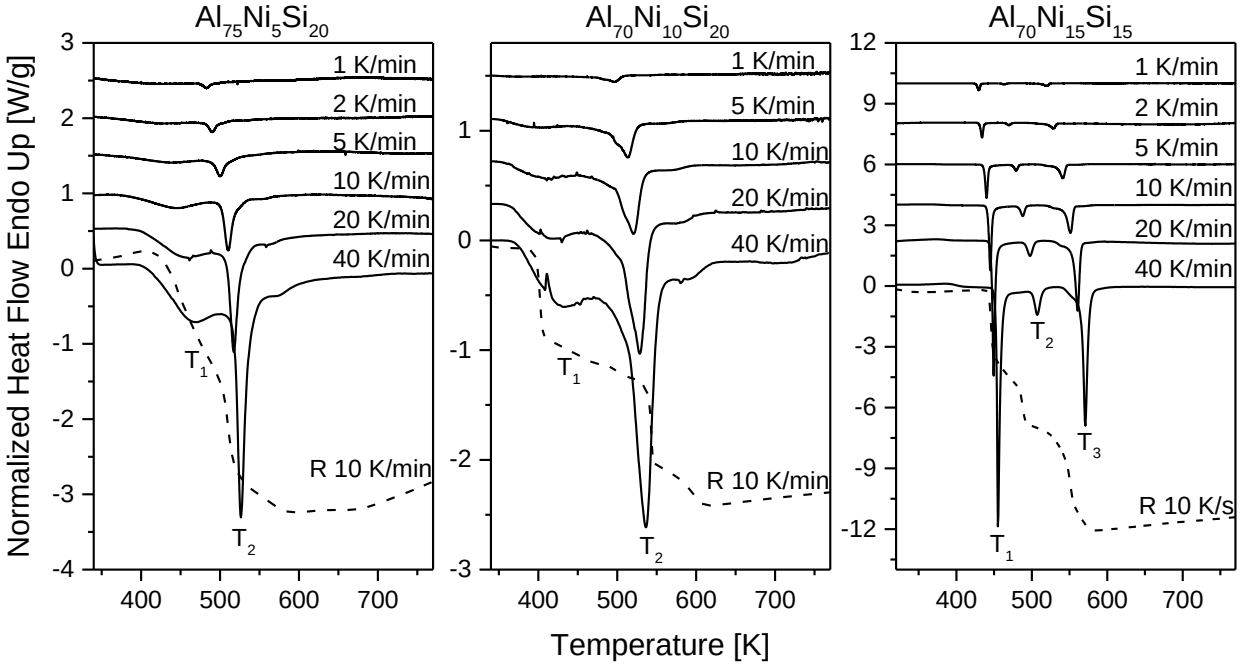

Fig. 2: *Differential scanning calorimetry (solid line) and electrical resistivity measurements (dashed lines) of rapidly quenched Al-Ni-Si alloys measured with heating rates in range of 1 - 40 K/min. T_n denotes heat flow peaks used in kinetic analysis. Other unmarked peaks were not taken into account. Data are shifted vertically for clarity.*

Fig. 2 shows DSC and electrical resistivity data. Alloys upon linear heating with rates (β) in the range of 1 – 40 K/min undergo 3 – 5 consecutive transformations. In order to calculate activation energies of reactions, peaks of heat flowmarked as T_1, T_2, T_3 which correspond to maximum reaction speeds, were used in Kissinger analysis [6]. Other unresolved peaks of heat flow observed in DSC data were excluded from analysis. Dashed line represents measurement of relative electrical resistivity of alloys under linear heating which is consistent with DSC data.

Kissinger plot obtained from DSC data is displayed on Fig 3. Series of data for each alloy and peak position were linearly fitted. Activation energies (Tab. 1) were calculated from slopes of these fits.

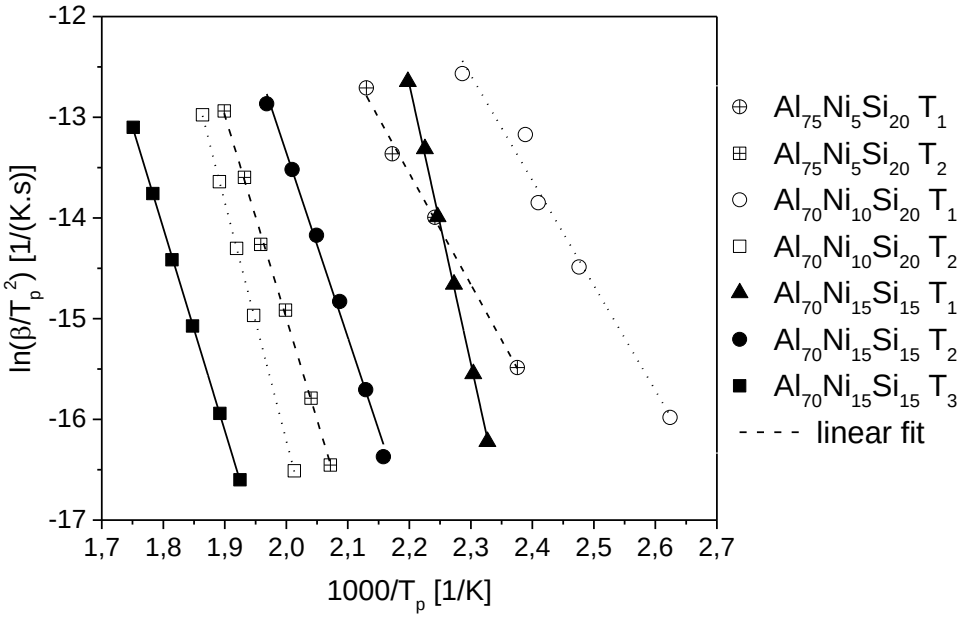

Fig.3:*Kissinger plots for peak positions acquired from differential scanning calorimetry.*

Tab. 1: *Activation energies of phase transformations according to Kissinger analysis of differential scanning calorimetry data.*

	peak	$T_{10\ K/min}$ (K)	E_a (kJ/mol)
$Al_{75}Ni_5Si_{20}$	T_1	446	92
	T_2	511	168
$Al_{70}Ni_{10}Si_{20}$	T_1	415	87
	T_2	521	197
$Al_{70}Ni_{15}Si_{15}$	T_1	440	231
	T_2	479	152
	T_3	541	167

Fig. 4 shows evolution of XRD diffraction patterns during linear heating. At temperature of about 450 K the formation of fcc-Al phase took place, in both $Al_{70}Ni_{10}Si_{20}$ and$Al_{70}Ni_{15}Si_{15}$ alloys. At this temperature, also other diffraction peaks appeared with no match in powder diffraction database files. At about 550 K other unknown phase(s) and final phases of Al_3Ni and $Al_{3,21}Si_{0,47}$ are observed. Diffraction pattern of $Al_{70}Ni_{15}Si_{15}$ after final stage of heating is depicted in Fig. 4d with marked positions of Al_3Ni and $Al_{3,21}Si_{0,47}$ phase

peaks. $InAl_{75}Ni_5Si_{20}$ (Fig 4c), at about 530 K polycrystalline fcc-Al and Si in amorphous matrix started to transform to Al_3Ni and $Al_{3,21}Si_{0,47}$ phases, which coalesced during further heating [7].

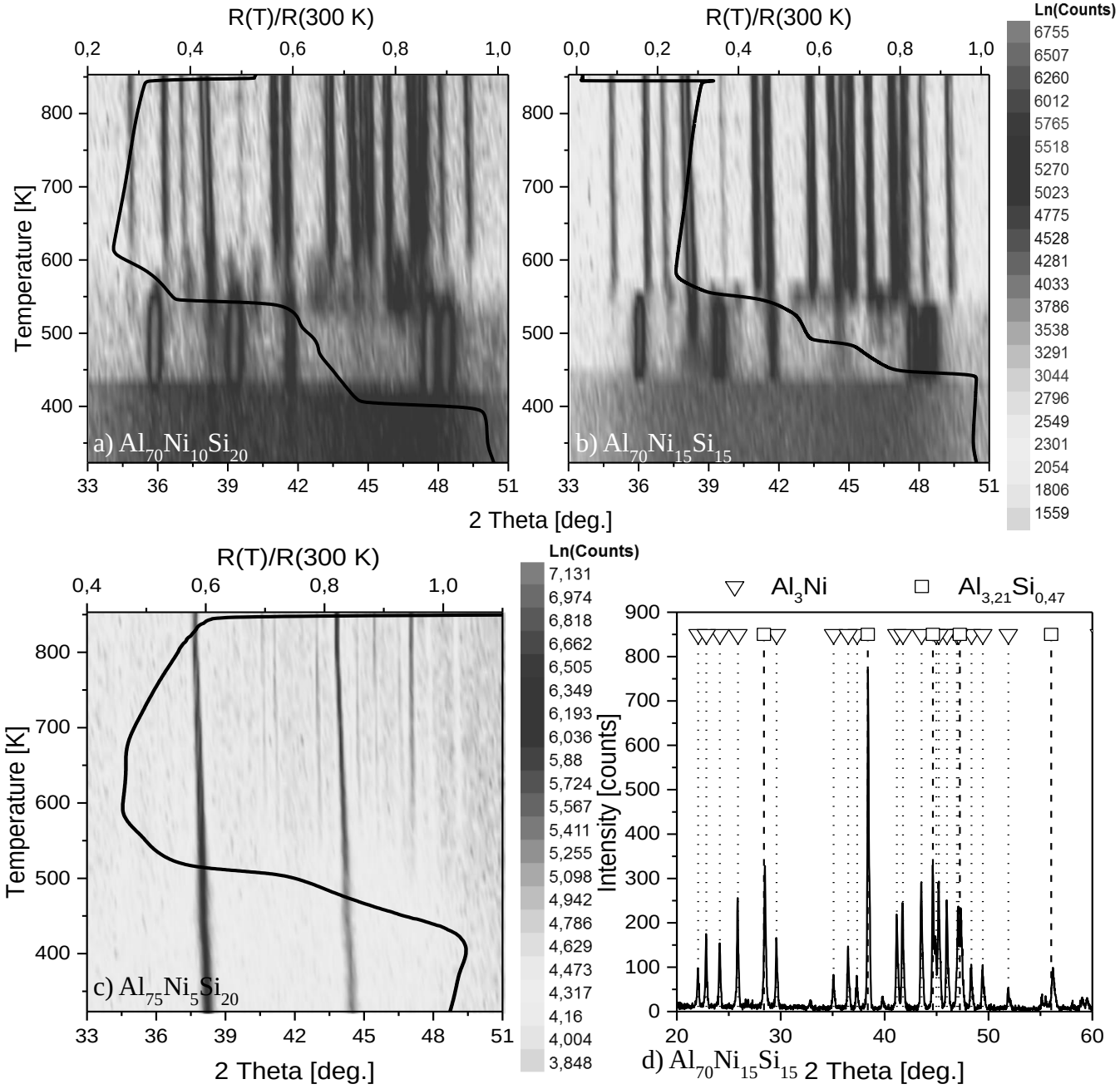

Fig. 4: *Evolution of X-ray diffraction patterns (Cu K_α) during linear heating of 5 K/min compared to evolution of relative resistivity. Phases Al_3Ni and $Al_{3,21}Si_{0,47}$ are present in all studied alloys after final heating. This is illustrated in d) which is X-ray diffraction pattern of $Al_{70}Ni_{15}Si_{15}$ after final heating.*

4. Discussion

Addition of Ni to alloy of Al-Si has the effect of increasing glass forming ability of Al-Ni-Si alloys. In alloys of $Al_{70}Ni_{10}Si_{20}$ and $Al_{70}Ni_{15}Si_{15}$sufficient content of Ni in combination with rapid quenching resulted in amorphous structure in as-cast state. In $Al_{75}Ni_5Si_{20}$ structure is not fully amorphous, due to lower content of Ni and contains fine crystalline fcc-Al and Si in amorphous matrix is present in as-cast state.

DSC data of Al-Ni-Si alloys shows 3 – 5 peaks that correspond to phase transitions. Kissinger analysis of these peaks was made, however further experiments should be performed to assign activation energies to particular phase transformations.

Evolution of XRD patterns during linear heating show formation of several phases as was expected from DSC data. In all three alloys formation of unknown phase(s) takes place at about 530 K. Formation of this phase can be assigned to DSC peak T_2 for $Al_{75}Ni_5Si_{20}$ and $Al_{70}Ni_{10}Si_{20}$. For $Al_{70}Ni_{15}Si_{15}$ it is questionable whether formation of this unknown phase can be assigned to T_2 or other unresolved peak in DSC data.Upon further heating (530K-$Al_{75}Ni_5Si_{20}$, 550K -$Al_{70}Ni_{10}Si_{20}$ and $Al_{70}Ni_{15}Si_{15}$,) formation of final Al_3Ni and $Al_{3,21}Si_{0,47}$ phases occurred.

Acknowledgement

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