ENERGY OF PRECIPITATION OF Al$_2$Cu AND α-AlFeSi PHASE FROM THE AlCu3 ALLOY AND THE SHAPE OF PRECIPITATES

AlCu3 alloy was examined with the triple simple thermal analysis (TETA), the simultaneous thermal analysis (STA), the computer simulation using Thermo-Calc program and with the metallographic analyses. The energy of solidification and melting of the primary and the eutectic phase, and the energy of the Al$_2$Cu precipitation were determined, and these can be evidently seen from the curves of simultaneous thermal analysis.

Key words: Al-alloys, thermodynamics, thermal analysis, differential scanning calorimetry (DSC), precipitation

Energija precipitacije Al$_2$Cu i α-AlFeSi faze u AlCu3 leguri i oblici precipitata. Legura AlCu3 je istražena sa trojnom jednostavnom toplinskom analizom (TETA), simultanom toplinskom analizom (STA), kompjuterskom simulacijom Thermo-Calc i metalografskom analizom. Izmjerena je energija skrućivanja i taljenja primarne i eutektičke faze i energija precipitacije Al$_2$Cu faze što je vidljivo iz krivulja simultane toplinske analize.

Ključne riječi: Al-legure, termodinamika, toplinska analiza, diferencialna pretražna kalorimetrija (DSC), precipitacija

INTRODUCTION

During the equilibrium solidification all the precipitated phases are in an equilibrium state. But when cooling and solidification are very fast (non-equilibrium state), the equilibrium is not reached and some elements stay trapped in single phases. In certain conditions precipitation from solid solutions can occur and this hardens the alloy [1]. Essential property of the precipitation–hardening alloy system is a temperature–dependent equilibrium solid solubility characterized by the increased solubility with increasing temperature [1].

Precipitation in aluminium-copper alloys

If an alloy with the composition Al-3 wt. % Cu is heated to the temperature of about 540 °C all copper will be dissolved in the solid solution as a stable fcc α phase, and when quenching such specimen in water there is no time for any transformation to occur so that the existing solid solution is retained mainly unchanged to the room temperature. The solid solution is now supersaturated with Cu and there exists a driving force for precipitation of the equilibrium θ phase, Al$_2$Cu.

In the case of Al-Cu alloys the equilibrium θ phase is preceded by the θ'' and θ' phases. The total precipitation process takes place in the following sequence [2]:

$$\alpha_0 \rightarrow \alpha_1 + GP \rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \theta,$$
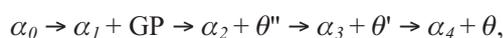
α_0 is the original supersaturated solid solution, α_1 is the composition of the matrix in equilibrium with GP zones, α_2 the composition in equilibrium with the θ'' phase etc. [2, 3, 4]. The transition phases are formed since they have lower activation energy barrier for nucleation than the equilibrium phases [4, 5, 6].

EXPERIMENTAL

The aim of this research was to determine how much energy is liberated during the aging of Al-Cu alloy when cooled at different cooling rates. The intention was also to determine the energy of the precipitation process after different periods of natural aging.

The Al-Cu alloy was made of aluminium electrolytic blocks of purity 99,998 mass %, and of 99,98 mass % pure copper. The prepared alloys were melted in graphite crucibles in an induction furnace. As the temperature 750 °C was reached, the melt was poured from the graphite crucible into the three measuring cells (Figure 1) [7, 8]. The K-type thermocouples were inserted in the centre of each measuring cell and were positioned at the same heights. Different geometries and materials of the measuring cells caused various heat transmissions, and as consequence different cooling rates were achieved.

Simultaneous thermal analysis (STA) of specimens of starting materials was performed with the STA 449c Jupiter NETZSCH device. STA represents the method

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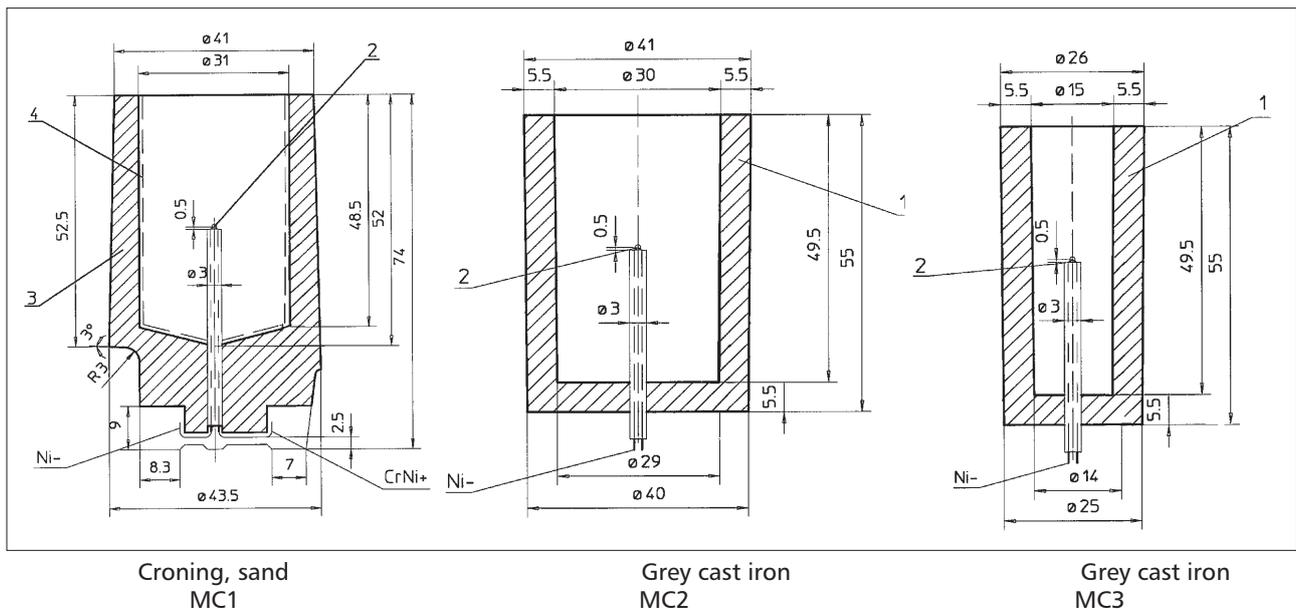
Figure 1. Measuring cells for the triple simple thermal analysis. [7,8]

Table 1. **Chemical composition of the AlCu3 alloy after the TETA**

Element	Al	Si	Fe	Cu	Mn	Mg	Zn	Cr	Ni	Ca
Mass / %	96,7901	0,0333	0,0566	3,055	0,0010	0,0031	0,0019	0,0047	0,0500	0,0150

of thermal analysis that records thermal effects (DSC) and the change of the specimen's mass (TG) during heating and during cooling. The measurements were carried out in protective atmosphere of 99,99 % Ar inert gas. The specimens were heated up to 720 °C with a heating rate of 0,167 K/s and cooled with the same cooling rate to the room temperature. The specimens from the small grey cast iron cell were also heated to 350 °C and 500 °C to determine the energy of segregation of precipitates. After two months of natural aging the specimens from the small grey cast iron cell were again artificially aged at 550 °C and 530 °C. Each time DSC curves were recorded.

A correction factor had to be determined. From the cooling DSC curve the energy of solidification of pure electrolytic aluminium (L_{t_M}) was determined. In the second step, the latent heat of pure aluminium (L_{t_L}) was determined from data in the reference [9]. The correction factor was calculated according to the equation 1:

$$\frac{L_{t_L}}{L_{t_M}} = \frac{397,0}{417,3} = 0,9513 \qquad (1)$$

The correction factor from STA was 0,9513.

The specimens after TETA and STA were examined with electron microanalysis that included SEM, JEOL 5610 with EDS, and electron microanalyzer JEOL SUPERPROBE 733 with two WDS spectrometers.

Specimens were chemically analyzed after the TETA.

Thermodynamic equilibrium of the AlCu3 alloy was simulated with the computer Thermo-Calc application. The program enables to record all the thermodynamically possible equilibrium phases that exist at defined conditions (temperature, pressure, composition) and it enables the construction of the equilibrium binary phase diagram.

RESULTS AND DISCUSSION

Chemical composition is presented in Table 1.

The solidification of the AlCu3 alloy started at temperature of 653 °C with the formation of αAl primary crystals. This process lasted to the temperature of 610 °C when the $Al_{13}Fe_4$ phase started to solidify next to the α_{Al} primary phase (Figure 2). The solidification was completed with the solidification of α_{Al} + Al_2Cu eutectic at the temperature of 586 °C, where the solidus temperature was reached. At 475 °C the precipitation of θ-Al_2Cu phase with 52,9 mass % Cu and 47,1 mass % Al started. The composition of the primary crystals at this temperature was 96,88 mass % Al, 3,03 mass % Cu with some Fe, Si and Ni. The precipitation of the α-AlFeSi phase took place at temperature of 369 °C from the original $Al_{13}Fe_4$ phase. At room temperature, α_{Al} primary crystals, α-AlFeSi phase, and θ-Al_2Cu phase can be traced in the microstructure.

In the triple simple thermal analysis the slowest cooling rate was achieved in the MC1 sand cell, or mould, made by the Croning process (2,3 °C/s). Faster cooling was achieved in the MC2 grey cast iron mould of bigger diameter (19 °C/s), and the fastest one was obtained in the smallest MC3 grey cast iron mould (55 °C/s).

In MC1 mould the solidification started at the temperature $T_{L/min}$ = 649,5 °C or $T_{L/max}$ = 651,5 °C (Figure 3).
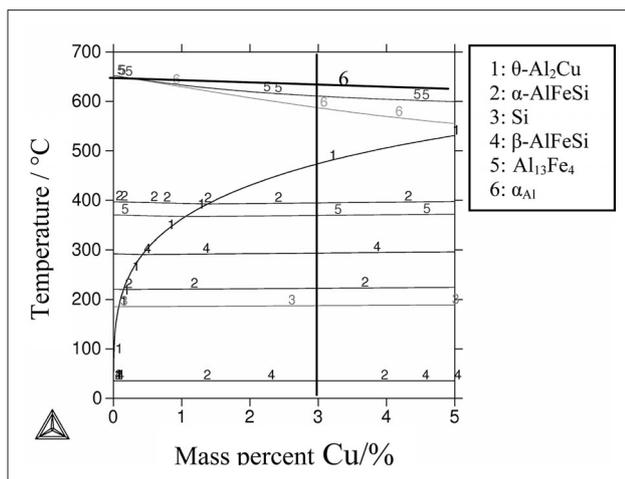
Figure 2. Isopleth equilibrium phase diagram of Al-Cu alloy.

Figure 3. The cooling curve and the differential cooling curve of AlCu3 alloy, cast into MC1 mould.

The undercooling was 305 °C, and recalescence was 2 °C. The eutectic solidification took place because of non-equilibrium solidification conditions at the temperature $T_{E/min} = 540,5$ °C or $T_{E/max} = 541,5$ °C where the solidification was completed.

At faster cooling rate (MC2) the minimum liquidus temperature $T_{L/min}$ was 645 °C, and the maximum liquidus temperature $T_{L/max}$ was 645,5 °C, the liquidus undercooling 9 °C, and recalescence was 0,5 °C. The eutectic temperature was also slightly lower than that in the MC1 mould, and it was $T_E = 520$ °C.

The fastest cooling was achieved in the MC3 mould. The minimum $T_{L/min}$ and the maximum $T_{L/min}$ liquidus temperatures were 639 °C and 643 °C. Undercooling was 14 °C, recalescence dT_L was here 4 °C. The eutectic temperature was $T_E = 509$ °C.

The DSC signal as a function of temperature was plotted. The heating DSC curves of the STA gave the information about the heat that was needed for melting the specimens after the thermal analysis and it determined the purity of the alloy. In melting of the primary crystals the lowest amount of liberated heat was obtained with the specimen that was cooled in the MC1 mould(-338,7 J/g, Figure 4.a), the highest heat was observed with the specimen that was cooled in the MC3 mould (-390,4 J/g) because there was the highest amount of the primary

phase. From the heating curve it can be determined that the greatest amount of eutectic was in the specimen that was cooled in the MC1 mould because of the highest peak on the heating curve. On the heating curves there can be traced two other peaks that indicate the melting of two other phases.

Figure 4.b indicated that solidification started at the temperature of 646,7 °C and it was completed at the temperature of 588,9 °C for the specimen from the sand mould. The temperatures 605,6 °C from MC1 (Figure 4.a) or 611,5 °C from MC2 or 611 °C from MC3 during the heating process can represent the solidification of the $Al_{13}Fe_4$ phase. The first small peak that appeared at higher temperature could be ascribed to the precipitation of the θ-Al_2Cu phase, the second peak that was found at lower temperature could be ascribed to the precipitation of the α-AlFeSi phase (Figure 4.a).

The STA was made also with the specimens from the MC3 mould after the TETA. The specimens were once (curve A) and twice (curve B) heated to the temperature of 350 °C and once heated to the temperature of 500 °C (curve C). The results from this analysis are presented in Figure 5.a.

With the specimen that was heated once the thermal peak appeared because of the precipitation of precipitates from the supersaturated solid solution that was rich

a)

b)
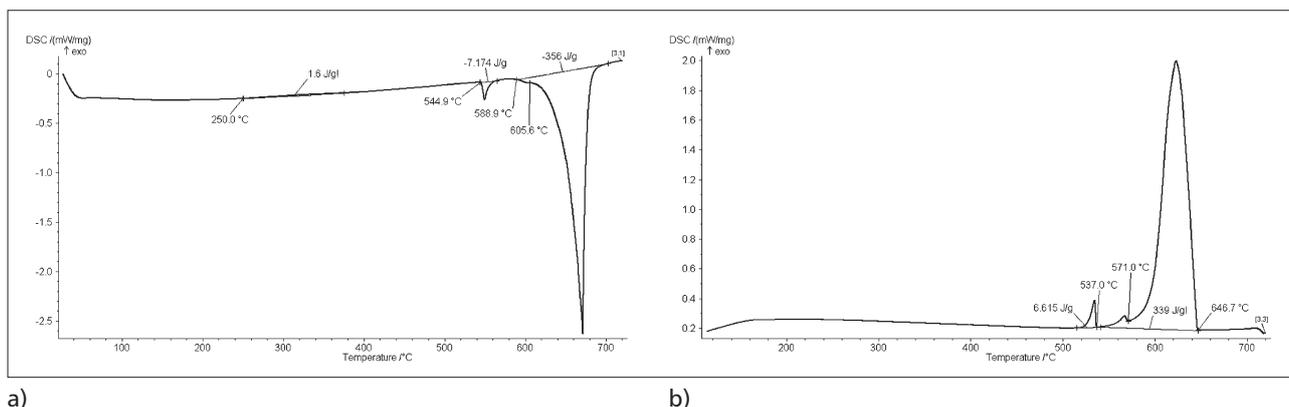
Figure 4. DSC curves of STA of the specimens from MC1: a) heating and b) cooling
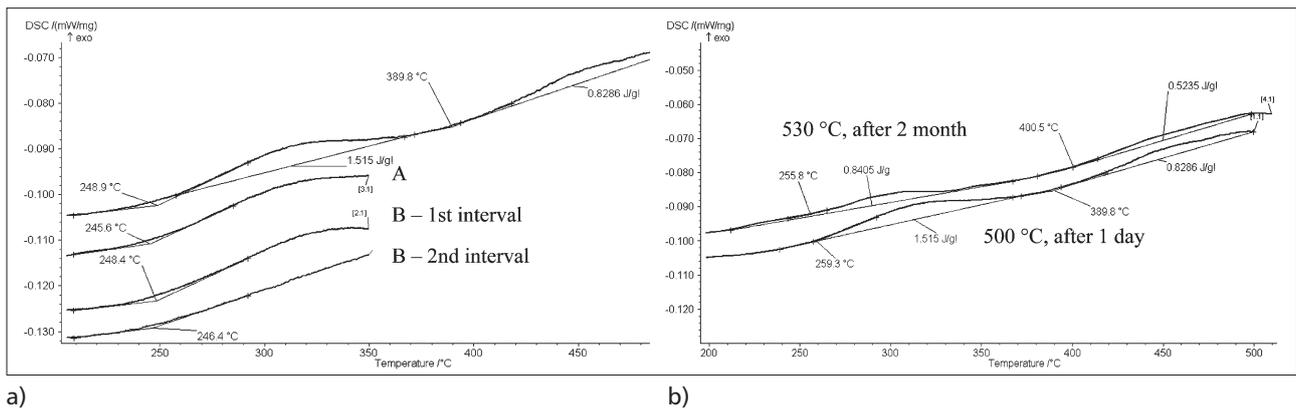
Figure 5. a) DSC curves of ageing AlCu3 specimens after the TETA and b) The comparison of DSC curves of specimens aged at 500 °C for 1 hour, and repeatedly aged after two months at 530 °C for 1 hour.
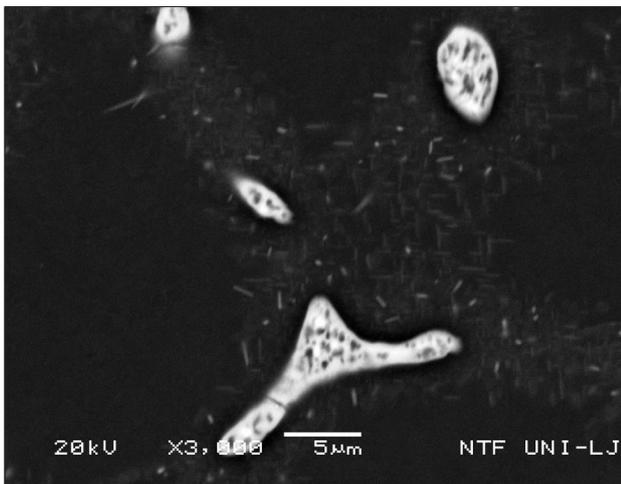
SEM of AlCu3 specimen aged at 350 °C for 1 hour   SEM of AlCu3 specimen aged at 500 °C for 1 hour
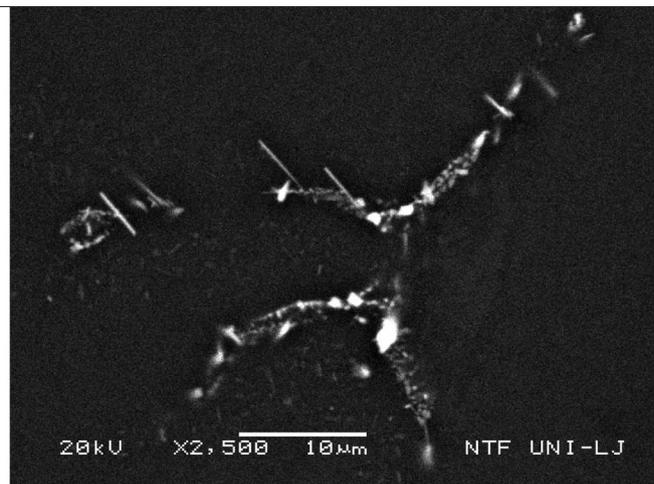
Figure 6. SEM analyses of aged AlCu3 alloy specimens.

on aluminium and contained some iron and silicon. In ageing at the temperature of 500 °C two peaks of liberated heat appeared on the DSC curve, what indicated the precipitation of the second phase.

After two months of natural aging the STA was again made with the specimen from the MC3 mould. The specimens were again aged at the temperature of 530 °C. The results of the STA after cooling in the MC3 mould and after two months of natural aging are presented in Figure 5.b. After natural aging less energy was liberated in artificial aging (aging to the temperature of 530 °C) because some precipitates precipitated already during the natural aging. The energy of precipitation of Al$_2$Cu precipitates was reduced to such an extent that the peak was hardly traceable on the heating curve after two months of natural aging. It can also be seen that the precipitation started at lower temperature than before.

The examination with the electron microscope (SEM) showed that the precipitation takes place in the aging process to the temperatures 350 °C and 500 °C and precipitates are observed among the α_{Al} primary crystals (Figure 6). At bigger magnifications, precipitates of smaller sizes that are composed of aluminium, iron and silicon can be found in the specimens aged at

350 °C. In the specimen aged at 500 °C, short sticks that also precipitated among the α_{Al} primary crystals of aluminium were traced next to the precipitates of smaller sizes. They are composed only of aluminium and copper.

CONCLUSIONS

Based on the results of Thermo-Calc, TETA, STA, light microscopy and SEM analysis the conclusion can be made that the precipitates in the non-equilibrium solidification process appear at lower solidification temperatures. At higher cooling rates copper remains dissolved in the α_{Al} primary crystals.

During the process of heating heat was liberated due to the precipitation process of precipitates from the supersaturated solid solution. At repeated heating peaks representing the liberated heat appeared on the DSC curves due to the precipitation too. The amount of the precipitation energy of the α-AlFeSi precipitates was ~1,45 J/g. After two months of natural aging less energy was liberated (0,8 J/g) and the heat liberation started at lower temperature. The precipitation energy of the θ-Al$_2$Cu precipitates was reduced with natural aging

to such an extent that the peak was no longer traced on the DSC heating curve after four months of natural aging. SEM analysis confirmed that the diffusion of copper from supersaturated solid solution takes place at the temperature of 500 °C, the precipitates of the θ-Al$_2$Cu phase are shaped like small sticks of 3 μm in length. In ageing at the temperature of 350 °C the precipitation of α-AlFeSi takes place and precipitates have shape of small rounded particles of 1 μm diameter.

It is necessary to know the nature of precipitation-hardenable alloys because the precipitation causes great changes of properties of such materials. Hard and tough material can be transformed into hard and fragile material when precipitation is too intensive.

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