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DSC INVESTIGATION OF HIGH-COPPER AlCuMg ALLOYS

DSC-RAZISKAVA ZLITIN AlCuMg Z VISOKIM BAKROM

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The effect of copper content on the microstructure of aluminium-copper-magnesium alloys was examined with DSC (Differential Scanning Calorimeter), X-ray powder diffraction, hardness, compression strength tests and electron microprobe analysis.

Differential scanning calorimetry was carried out for the samples: AlCu5Mg2, AlCu5Mg4, AlCu15Mg2 and AlCu15Mg4, all with addition of 0.25 % Ti. The obtained DSC-curve, showed two endothermal effects which were used for the calculation of the transition enthalpy.

The formation of intermetallic compounds Al_2Cu and Al_2CuMg was monitored with of X-ray powder diffractometry. In the alloy AlCu15Mg2 a tetragonal Al_2Cu was found and in the alloys: AlCu5Mg2, AlCu5Mg4 and AlCu15Mg4 the orthorhombic intermetallic compound Al_2CuMg was found.

Key words: copper-magnesium-aluminium alloys, intermetallic compounds Al_2Cu and Al_2CuMg

Raziskan je bil vpliv bakra na mikrostrukturo zlitin AlCuMg. Uporabljene so bile metode DSC, difrakcija rentgenskih žarkov, merjenje trdote, tlačni preizkus in analiza na elektronskem mikroanalizatorju. Diferenčna vrstična kalorimetrija je bila uporabljena pri zlitinah AlCu5Mg2, AlCu5Mg4, AlCu15Mg2 in AlCu15Mg4 z dodatkom 0,25 % Ti. DSC-krivulje so pokazale endotermne efekte, ki so bili uporabljeni za izračun tranzicijske entalpije. Difraktometrijska analiza je pokazala tetragonalno intermetalno fazo Al_2Cu v zlitini AlCu15Mg2 in ortorombično fazo Al_2CuMg v zlitinah AlCu5Mg2, AlCu5Mg4 in AlCu15Mg4.

Ključne besede: zlitine aluminij-baker-magnezij, intermetalni spojini Al_2CuMg

1 INTRODUCTION

Excellent strength vs. density ratio, formability and corrosion resistance make high-copper AlCuMg alloys a potential candidate for a number of industrial applications[1]. Developed in the early times for use in the aeronautical field, these alloys have been then considered for a wide range of different applications, even though, due to their high strength, they are mainly considered as a substitute of iron-based materials for structural parts in the transportation industry. Several compositions are presently standardized and new alloys based on that metallic system are now being considered and developed[2].

In the binary aluminium-copper system, the aluminium-rich solid solution is in equilibrium with the intermetallic compound θ, with the approximate composition of $CuAl_2$. The addition of magnesium allows the formation of other intermetallic compounds, such as $CuMgAl_2$, $CuMg_4Al_6$, $CuMgAl$ and $Cu_6Mg_2Al_5$, as shown in the isothermal section at 430 °C of the ternary system Al-Cu-Mg in **Figure 1**. The liquidus, solidus and solvus isotherms are shown in **Figure 2**.

To explain the heat treatment of these alloys, we will consider an alloy containing 4 % Cu and 1 % Mg. To visualize the relation of this composition and the isotherms in **Figure 2**, the relation of the liquidus, solidus and solvus projections to the three-dimensional ternary phase diagram is shown. For this composition, the alloy is liquid above 650 °C (point a); in a two-phase

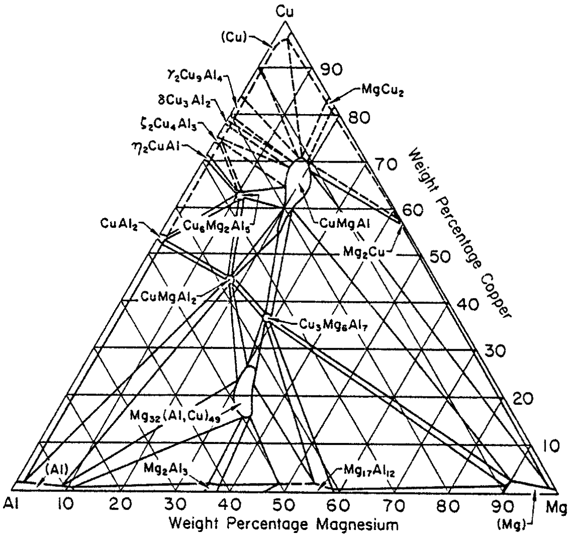

Figure 1: Isothermal section at 430 °C for the Al-Cu-Mg system. (Adapted From Metals Handbook, 8th Ed., Vol 8, American Society for Metals, Metals Park, Ohio, 1973)

Slika 1: Izotermni prerez faznega diagrama Al-Cu-Mg pri 430 °C (Prirejeno iz Metals Handbook, 8th Ed., Vol. 8, ASM, Metals Park, Ohio, 1973)

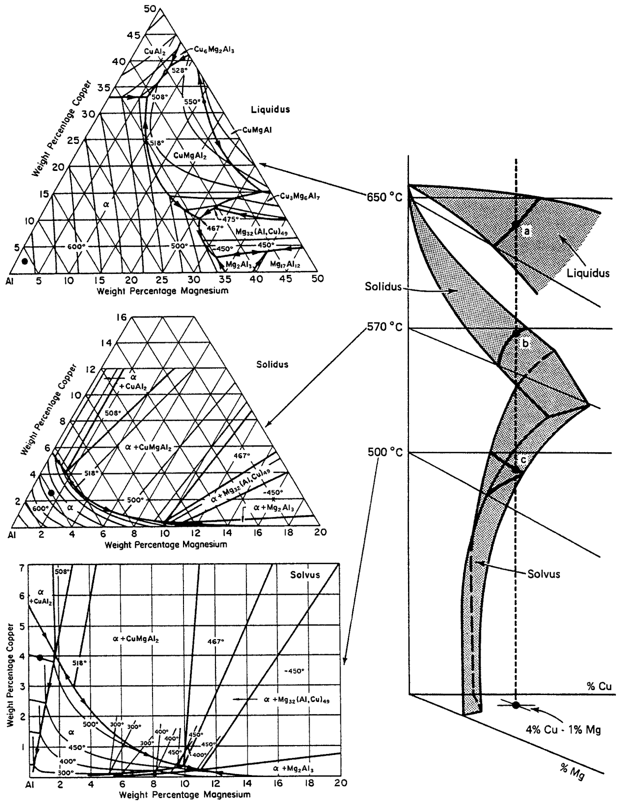

Figure 2: The relation between the projection of the liquidus, solidus and solvus isotherms and the three-dimensional phase diagram. The temperatures noted are for the alloy with 4% Cu and 1 % Mg.

Slika 2: Povezava med projekcijo likvidus, solidus in salvus izoterm in tridimenzionalnim faznim diagramom. Označene so temperature za zlitino s 4 % Cu in 1 % Mg

liquid-solid region between 570 °C (point b) and 650 °C; it is a single-phase α region between 570 °C and 500 °C (point c); and it is in the three-phase region below 500 °C where the α-solid solution is in equilibrium with the compounds Al_2Cu and Al_2CuMg. For the optimal precipitation hardening it is necessary to equilibrate the alloy in the α region and to bring in solution the intermetallic phases. To achieve this the alloy must be annealed between 500 °C and 570 °C for a sufficient time to obtain a homogenous solid solution. After the solution heat treatment, the alloy is cooled to 20 °C at a rate sufficient to suppress any precipitation. The precipitation process begins immediately, with a rate depending upon the tempering temperature. In the investigated Al-Cu-Mg alloy the precipitation rate at 20 °C is sufficiently great to cause significant changes in mechanical properties.

Depending on the alloy composition (say Cu content and Cu/Mg ratio), different phase distributions and consequently different material characteristics can be obtained. In this paper a DSC study of four different AlCuMg alloys with a high copper content (w = 5 % and 15 %) and a Cu/Mg ratio 2,5 and 1,25; 7,5 and 3,75 respectively, is reported in order to determine the effect of copper contents on the microstructure of AlCuMg alloys.

2 EXPERIMENTAL

The experimental work can be divided in two phases. The first phase consists of melting and casting of samples with different compositions in the aluminium-copper-magnesium system covering the region of standard, but also higher copper contents, with addition of 0,25% Ti (AlTi5B1) as a modifier. The second phase includes the characterization of samples obtained with the previous melting and casting with differential scanning calorimetry, X-ray powder diffractrometry and electron microprobe analysis. The properties of these materials have been also examined including the determination of hardness and compression strength.

The composition of the alloys was determined with wet analysis and the results are reported in **Table 1**. DSC analyses have been performed in a differential scanning

Table 1: Chemical composition of the investigated alloys (in w/%)
Tabela 1: Kemična sestava zlitin (masni delež w/%)

Type of sample	%Fe	%Si	%Ti	%Cu	%Zn	%Mg	%V	%Cr	%Mn
AlCu5Mg2 (0.25%Ti)	0.16	0.06	0.265	4.903	0.061	1.924	0.005	0.002	0.009
AlCu5Mg4 (0.25%Ti)	0.15	0.15	0.246	5.030	0.063	4.235	0.004	0.002	0.010
AlCu15Mg2 (0.25%Ti)	0.15	0.16	0.289	14.970	0.097	2.691	0.000	0.002	0.013
AlCu15Mg4 (0.25%Ti)	0.20	0.11	0.261	16.060	0.082	4.967	0.002	0.005	0.014

Table 2: Transition enthalpies calculated from DSC curves
Tabela 2: Tranzicijske entalpije, izračunane iz DSC-krivulj

Type of sample	I Peak		II Peak	
	T / °C	$-\Delta H$ / (J/g)	T / °C	$-\Delta H$ / (J/g)
AlCu5Mg2 (0.25%Ti)	515.3	10.44	641.5	88.97
AlCu5Mg4 (0.25%Ti)	519.5	21.67	627.3	78.52
AlCu15Mg2 (0.25%Ti)	512.4	45.98	602.5	52.75
AlCu15Mg4 (0.25%Ti)	522.2	72.07	581.6	33.53

calorimeter type Shimadzu DSC-50 in protective argon atmosphere and at a scanning rate of 10 °C/min up to the maximum temperature of 725 °C. Differential scanning calorimetry was carried out for aluminium-copper-magnesium alloys samples: AlCu5Mg2(0,25%Ti), AlCu5Mg4(0,25%Ti), AlCu15Mg2(0,25%Ti) and AlCu15Mg4(0,25%Ti).

The DSC tests produced curves which were used for the calculation of the transition enthalpy (the activation energy of the transformations responsible for the thermal effects). The results are reported in **Table 2** show that the addition of copper and magnesium induces a modification of the microstructure. If the result is a better dispersion of insoluble components, porosity and nonmetal inclusions, the mechanical properties will be improved.

The X-ray diffraction analysis was performed on the aluminium-copper-magnesium alloys using wide range of angles (2θ) from 5° to 100° with a step of 0.02° and a holding time of 0.50 s at each step. A diffractometer with a graphite monochromator and a constant divergence slit (D) of 1mm was used. The current and the voltage of the X-ray tube during the analysis were 30 mA and 40 kV, respectively. The width of the receiving slit (*R*) was 0,1mm, corresponding to fine focused X-ray tubes. The radiation was the Cu $K\alpha_1/\alpha_2$, doublet ($\lambda\alpha_1 = 0.154060$ nm and $\lambda\alpha_2 = 0.154438$ nm).

Compression strength of the samples of cast alloys was tested on a universal electronic tensile testing machine of 10 t. The results are shown in **Table 3**.

Table 3: Results of hardness and compression tests
Tabela 3: Rezultati preizkusov trdote in tlačenja

Type of sample	HB	$\sigma_{0,2p}$ / (N/mm^2)	σ_{mp} / (N/mm^2)
AlCu5Mg2 (0.25%Ti)	94.4	181.5	628.0
AlCu5Mg4 (0.25%Ti)	99.9	191.2	665.8
AlCu15Mg2 (0.25%Ti)	153.6	283.3	678.9
AlCu15Mg4 (0,25%Ti)	160.8	369.1	698.6

3 RESULTS AND DISCUSSION

The copper content in the standard alloys ranges up to around 5 %, since the maximum solubility of copper in solid state, at the eutectic temperature (548 °C) is of w = 5,65 %. Alloys containing copper up to mass fraction 15 % have been also tested and, accordingly, a considerable share of eutectic was found in the microstructure. With standard alloys the primary α-solid solution solidifies in dendritic form. With higher copper contents, the eutectic appears in interdendritic spaces and between grains, as shown in **Figures 3** and **4**.

The content of copper and magnesium in the white phase is low. X-ray analysis showed magnesium in the eutectic gray phase, while copper is found in the bright phase. Titanium is present in white platelets in some eutectic areas. Isolated particles containing titanium are found also dispersed in the interior of matrix grains.

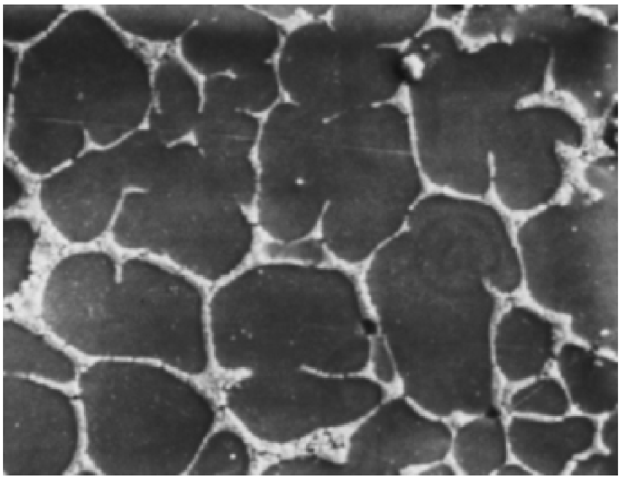

Figure 3: Microstructure of the alloy AlCu5Mg4 (0.25%Ti) x600
Slika 3: Mikrostruktura zlitine AlCu5Mg4 (0,25Ti). Povečava 600-kratna

Magnesium increases[3] the strength and hardness of the alloys, and especially in castings, it decreases the ductility and impact resistance. Titanium is added as grain refiner and it is very effective in reducing the grain size. Grain size controls the distribution[4] of the porosity and of the constituents of the microstructure. For this reason, the properties of the low-copper alloys are very sensitive to grain size. Grain size, dendrite and eutectic morphology depend on technological parameters[5], first of all on melt temperature and solidification rate and determine the mechanical properties of the alloy.

With X-ray powder diffraction in the alloys AlCu15Mg2 the tetragonal intermetallic compound Al_2Cu with the lattice parameters: a = 0.6074 nm, c = 0.4869 nm and V = 0.17971 nm^3 was found, while in the alloys AlCu5Mg2, AlCu5Mg4 and AlCu15Mg4 the orthorhombic intermetallic compound Al_2CuMg was found with the lattice parameters for the alloy AlCu5Mg2 a = 0.3993 nm, b = 0.9209 nm, c = 0.7128 nm

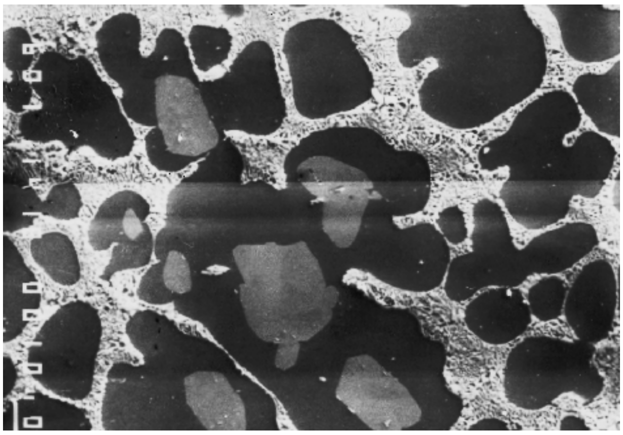

Figure 4: Microstructure of the alloy AlCu15Mg4 (0.25%Ti) x600
Slika 4: Mikrostruktura zlitine AlCu15Mg4 (0,25Ti). Povečava 600-kratna

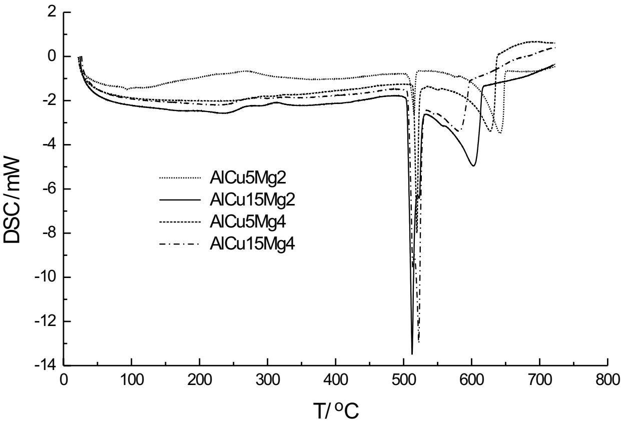

Figure 5: DSC traces for the alloys AlCu5Mg2, AlCu5Mg4, AlCu15Mg2 and AlCu15Mg4 for the heating rate of 10 °C/min
Slika 5: DSC-krivulje za zlitine AlCu5Mg2, AlCu5Mg4, AlCu15Mg2 in AlCu15Mg4 pri hitrosti segrevanja 10 °C/min

and V = 0.26216 nm^3, for the alloy AlCu5Mg4 a = 0.4011 nm, b = 0.9290 nm, c = 0.7116 nm and V = 0.2652 nm^3 and for the alloy AlCu15Mg4 a = 0.4010 nm, b = 0.9251 nm, c = 0.7107 nm and V = 0.26371 nm^3. The obtained lattice parameters for both intermetallic phases agree with published data.

DSC traces obtained at the heating rate of 10 °C/min are shown in **Figure 5**. Thermograms can be briefly described as follows: a) a "low temperature" interval ranging between room temperature and 500 °C where several endo- and exothermal effects occurr (up to this temperature in the alloys the α solid solution is in equilibrium with the intermetallic compounds Al_2Cu and Al_2CuMg); b) an "intermediate temperature" range between 500 °C and 540 °C, where only endothermal effects were detected, c) a "high temperature" range between 540 °C and 700 °C where a broad endothermic effect is present.

In the thermograms in **Figure 5** with two endothermal signals the first effect is detected at the temperature of about 515 °C. It refers to a phase transition with the reaction enthalpy of –10.44 J/g for alloy AlCu5Mg2, –21.67 J/g for alloy AlCu5Mg4, –45.98 J/g for alloy AlCu15Mg2 and –72.07 J/g for alloy AlCu15Mg4. These results show that the first peak is due to the localized melting with the formation of a melt rich in copper and magnesium in presence of the α solid solution and the compounds Al_2Cu and Al_2CuMg. In the alloys with the copper : magnesium ratio above 8:1 the main hardening agent is Al_2Cu; while in the alloys with the Cu/Mg ratio in the range 8:1 to 4:1 both Al_2Cu and Al_2CuMg are present. By lower Cu/Mg ratio between 4:1 and 1,5:1 the compound Al_2CuMg determines the properties.

In the thermograms in **Figure 5** the second thermal effect is a high temperature endothermal peak. It refers to a phase transition with the reaction enthalpy of –88.97 J/g for alloy AlCu5Mg2, –78.52 J/g for alloy AlCu5Mg4, –52.75 J/g for alloy AlCu15Mg2 and –33.53 J/g for alloy AlCu15Mg4. From these results it is concluded that for the alloys: AlCu5Mg2, AlCu5Mg4 and AlCu15Mg4 the second peak is due to the melting of the intermetallic compound Al_2CuMg and for the alloy AlCu15Mg2 to the melting of the intermetallic compound Al_2Cu. Further, it is concluded that with the increased copper and magnesium content in the alloy, the heat of transition is increased (see **Table 2**) and the temperature of the second peak is decreased from 641.59 °C for the alloy AlCu5Mg2 to 581.69 °C for the alloy AlCu15Mg4 (see also **Table 2**).

4 CONCLUSIONS

Different parameters obtained with DSC analysis on the aluminium-copper-magnesium alloys make it possible to explain the influence of copper contents on the mode of solidification and the microstructure of the investigated alloys. On the base of the obtained data the following conclusions are proposed:

- For all alloys the first peak is due to the localized melting of a probably ternary eutectic, producing a high copper and magnesium melt in presence of the α solid solution and the intermetallic compounds Al_2Cu and Al_2CuMg.
- With the increased copper content in the alloy for the first peak, the transition enthalpy is decreased.
- With increased magnesium content in the same basic chemical composition of the aluminium-copper alloy the value of transition enthalpy for the first peak is decreased.
- For the alloys AlCu5Mg2, AlCu5Mg4 and AlCu15Mg4 the second peak is due to the melting of intermetallic compound Al_2CuMg and for the alloy AlCu15Mg2 to the melting of the intermetallic compound Al_2Cu.
- Compression strength and hardness of the aluminium-copper-magnesium alloys increase with the copper and magnesium content.

5 REFERENCES

[1] I.J. Polmear, *Light Alloys*, London: Arnold, 1995

[2] P. Ratchev, B. Verlinden, P. De Smet, and P. Van Houtte, Mater Trans JIM, 40 (**1999**), 34

[3] L.F. Mondolfo, *Aluminium Alloys: Structure and Properties*, Butterworth and Co (Publishers) Ltd, London 1976, 245

[4] X. Yang, J.D. Hunt and D.V. Edmonds, *A quantitative study of grain structures in twin-roll cast aluminium alloys*, part II: AA 3004, Aluminium, 69 (**1993**) 2, 158-162

[5] B. Radonjic, *Directionality of Cast Aluminium Structure*, Aluminium, 58 (**1982**) 11, 646-649