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THERMODYNAMIC CHARACTERIZATION OF AN AlCu5.5BiSn ALLOY WITH VARIOUS NEODYMIUM ADDITIONS

TERMODINAMIČNA KARAKTERIZACIJA ZLITINE AlCu5,5BiSn Z RAZLIČNIMI DODATKI NEODIMA

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The effect of a Nd addition on the AlCu5.5BiSn alloy was investigated using thermal analysis, calculations of thermodynamic equilibrium, differential scanning calorimetry (DSC), and optical and scanning electron microscopy (SEM) in order to identify the generated microstructures. The purpose of this study was to analyze the influence of the Nd addition on the AlCu5.5BiSn alloy from the thermodynamics point of view and, consequently, on its mechanical properties. The results show that the Nd addition caused an increase in the eutectic solidification temperature and solidus temperature, which led to a narrower solidification interval. It was also discovered that neodymium formed a binary eutectic (α_{Al} + $Al_2Cu(Nd)$).

Keywords: AlCu5.5BiSn alloy, Nd addition, thermodynamics

Preiskovan je bil vpliv dodatka neodima k zlitini AlCu5,5BiSn z enostavno termično analizo, izračuni termodinamičnih ravnotežij, diferenčno vrstično kalorimetrijo in z opazovanjem pod optičnim in elektronskim mikroskopom za identifikacijo nastalih mikrostruktur. Namen študije je bil termodinamična analiza vpliva dodatka Nd na zlitino AlCu5,5BiSn in posledično njene mehanske lastnosti. Rezultati kažejo, da je dodatek neodima povišal temperaturo strjevanja evtektika in solidusne temperature, kar privede do ožjega intervala strjevanja. Neodim skupaj z bakrom tvori evtektik (α_{Al} + $Al_2Cu(Nd)$).

Ključne besede: AlCu5,5BiSn, dodatek Nd, termodinamika

1 INTRODUCTION

Al-Cu alloys, which form 2xxx series with the main alloying element being copper, are primarily used in the automotive, aerospace and military industries for the production of forged and machined parts. These alloys usually contain the mass fraction of Cu up to 6 % that allows consolidation of the solid solution. In order to improve the processing properties, small quantities of alloying elements, such as lead and tin, are added.[1,2] When additional alloying elements are introduced to the 2xxx-series alloys, multi-phase equilibria with multi compounds will result in a complex course of solidification.[3]

During the cooling phase equilibria in the solid are also changing due to a limited solubility of certain alloying elements. A result of these changes is, for example, a precipitation hardening in the solid state via Al_2Cu precipitates. On the other hand, the Al_2Cu phase is also present within the binary eutectic, which is a result of an eutectic reaction at 547 °C and the mass fraction of Cu 33.2 %. During the cooling process the supersaturated α_{Al} matrix begins to decompose into α_{Al} (depleted with copper) and the intermetallic compound Al_2Cu.[3] This compound has a tetragonal unit cell with the parameters of $a = 6.066 \cdot 10^{-10}$ m, $c = 4.874 \cdot 10^{-10}$ m and a density of 4340 kg/m^3.[1] The presence of Al_2Cu precipitates will increase the strength and the hardness, which are strongly dependent on the shape and size of the precipitated Cu in the α_{Al} matrix.[3]

In order to improve the properties of the existing alloys or design new alloys, one has to introduce preselected alloying elements. The effect of the neodymium element has been studied on magnesium alloys and it has been proved that neodymium has a favorable effect on improving the mechanical properties, grain-size reduction and an increase in the temperature stability.[4–10] The precipitates in magnesium alloys in the form of an $Al_{11}Nd_3$ phase effectively prevent the movement of dislocations and grain-boundary sliding.[4] In the binary Al-Nd phase diagram six intermetallic phases are present: $AlNd_3$, $AlNd_2$, AlNd, Al_2Nd, Al_3Nd and $Al_{11}Nd_3$.[5,11,12] These alloys also contain small amounts of Fe that presents the most common impurity in the aluminium alloys that can, together with Si, form various intermetallic phases like α-$Al_x(Fe,Mn)_ySi_z$, $Al_{13}Fe_4$, β-Al_5FeSi, δ-Al_9FeSi_2, …[13] Elements Bi and Sn are added to these types of alloys with the purpose of forming the phases enabling a better processing of the latter.[14]

The purpose of neodymium additions was to improve the mechanical properties and to achieve a high-temperature existence of the AlCu5.5BiSn alloy.

2 EXPERIMENTAL WORK

The investigation was carried out on an industrial AA 2041 alloy marked as AlCu5.5BiSn. Different amounts of neodymium were added in the laboratory, **Table 1**. Neodymium was added as a pure element (99.99 % Nd).

Three pounds of each alloy were prepared having the following contents inmass fractions: (0, 0.1, 0.5, 1.0 and 5.0) % Nd. The base alloy was melted in an induction furnace using a graphite crucible. The alloy was then left for 20 min so that neodymium could fully dissolve and then poured into a measuring cell for a simple thermal analysis (ETA).[15] During the process of solidification the cooling curve was recorded and the characteristic solidification temperature was defined. The chemical composition was determined by a Spectrolab spectrometer. Using the Thermo-Calc software TCW5 and the COST507 database, all theoretically possible thermodynamic phases that could be expected in the microstructures of new alloys were calculated and the theoretical course of solidification was determined. Differential scanning calorimetry (DSC) was made using a STA 449c Jupiter, Netzsch apparatus and a corundum crucible. The measurements were performed in a protective atmosphere of argon. Samples were heated and cooled at a rate of 10 K/min.

The samples for examining the microstructures have been prepared with a conventional metallographic procedure and examined with an Olympus BX61 microscope and a DP70 camera. Identification of the phase present in an alloy was carried out using an EDS attached to the SEM (JEOL electron microscope). Brinell hardness was measured on a Zwick machine ZHU250.

3 RESULTS AND DISCUSSION

On the basis of the chemical compositions, the equilibrium, vertical cross-section phase diagrams were calculated to determine the solidification course. **Figure 1** shows the calculated phase diagram for 1.0 % Nd.

In the case of equilibrium solidification the AlCu5.5BiSn alloy should consist of the following phases: the primary crystals of α_{Al}, the secondary solidification of the intermetallic phases $Al_{11}Nd_3$ and $Al_{13}Fe_4$. Additionally, the last phase that solidifies should be α-AlFeSi. Neither bismuth nor tin was incorporated in the simulation of solidification.

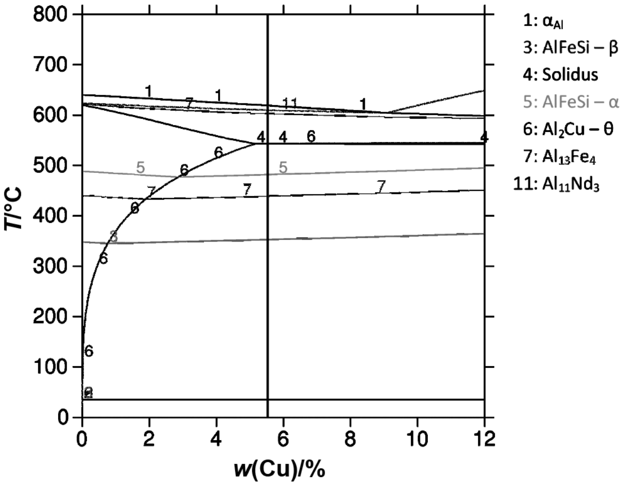

Figure 1: Equilibrium isopleth phase diagram of the AlCu5.5BiSn alloy with the mass fraction 1.0 % Nd

Slika 1: Ravnotežni izopletni fazni diagram zlitine AlCu5,5BiSn z masnim deležem 1 % Nd

Table 2: Characteristic solidification temperatures for AlCu5.5BiSn after ETA

Tabela 2: Značilne temperature strjevanja zlitine AlCu5,5BiSn po ETA

Specimen	T_L/°C	T_1/°C	T_E/°C	T_2/°C	T_S/°C
AlCu5.5BiSn	637.5	562.5	531		515.5
AlCu5.5BiSn + 0.1 % Nd	638	566.5	536	528.5	514.5
AlCu5.5BiSn + 0.5 % Nd	636.5	568	534.5	530	513
AlCu5.5BiSn + 1.0 % Nd	637	571	532	527.5	515
AlCu5.5BiSn + 5.0 % Nd	635	617	608.5	603	584

Figure 2 represents the cooling curves of a simple thermal analysis (ETA) of the alloys with different amounts of neodymium. The characteristic solidification temperatures were determined for all the specimens with different Nd additions (**Table 2**). T_L represents liquid temperatures; T_1 is the solidification temperature of the $Al_{13}Fe_4$ phase and, when Nd is added, also of the Nd-phases, T_E is the eutectic solidification temperature (α_{Al} + Al_2Cu), and T_2 is the solidification temperature of the AlFeSi phase. At T_S the solidification is completed. Temperature T_1 becomes higher after a Nd addition. T_E, the temperature of the eutectic solidification (α_{Al} + Al_2Cu), also becomes higher whereas the recalescence disappears even when a small amount of Nd is added.

Table 1: Chemical compositions of AlCu5.5BiSn alloys in mass fractions (w/%)

Tabela 1: Kemijska sestava zlitin AlCu5,5BiSn v masnih deležih (w/%)

Specimen mass fractions (w/%)	Cu	Fe	Zn	Si	Sn	Bi	Nd (nominal)	Nd (actual)	Al
AlCu5.5BiSn	5.45	0.217	0.023	0.096	0.549	0.555	0		bal.
AlCu5.5BiSn + 0.1 % Nd	5.69	0.233	0.024	0.096	0.565	0.061	0.1		bal.
AlCu5.5BiSn + 0.5 % Nd	5.70	0.234	0.026	0.099	0.552	0.582		0.47	bal.
AlCu5.5BiSn + 1.0 % Nd	5.43	0.213	0.027	0.100	0.555	0.500	1.0		bal.
AlCu5.5BiSn + 5.0 % Nd	5.63	0.197	0.041	0.101	0.541	0.645		4.97	bal.

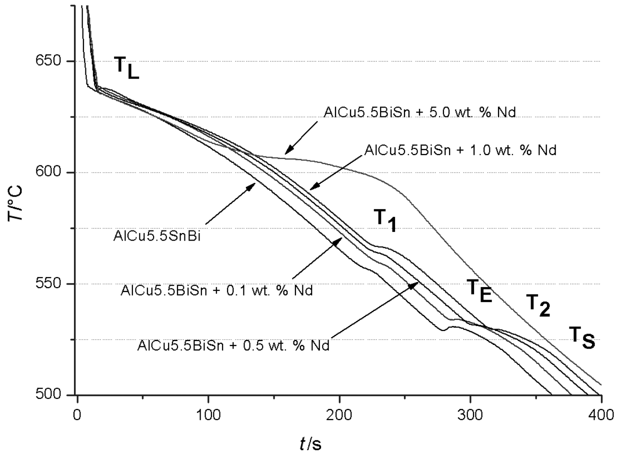

Figure 2: Effect of neodymium additions on the AlCu5.5BiSn alloy
Slika 2: Vpliv dodatka Nd na ohlajevalno krivuljo zlitine AlCu5,5BiSn

The solidification time interval is widened when the mass fraction 0.1–1 % Nd is added and narrowed when 5 % of Nd is added. The solidification of the specimen with the highest Nd content is completed at the temperature higher than the solidification temperatures of the specimens with lower Nd contents.

A simultaneous thermal analysis has been made on all the samples subject to the simple thermal analysis. **Figure 3** shows a comparison of DSC heating curves and **Figure 4** shows a comparison of the DSC cooling curves for the samples with mass fractions (0, 0.5 and 5.0) % Nd. All the characteristic temperatures have been noted and so were the heats released during the cooling or used during the heating.

The results of the simultaneous thermal analysis show that by increasing the proportion of neodymium we decreased the temperature of the liquids from 637.8 °C for an alloy without Nd to 631.1 °C for an alloy with w = 5.0 % Nd. A higher amount of neodymium narrowed the zone of solidification, which was also confirmed with the simple thermal analysis.

Microstructures of the alloys with different contents of neodymium are shown in **Figure 5** from a) to e). By

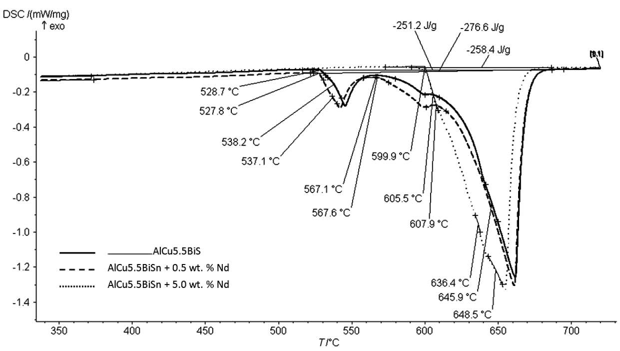

Figure 3: Heating DSC curves for the AlCu5.5BiSn alloy with different additions of neodymium
Slika 3: Ogrevalne DSC-krivulje zlitine AlCu5,5BiSn z različnimi dodatki neodima

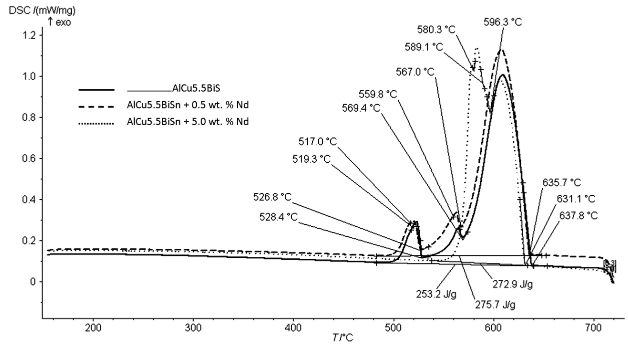

Figure 4: Cooling DSC curves for the AlCu5.5BiSn alloy with different additions of neodymium
Slika 4: Ohlajevalne DSC-krivulje zlitine AlCu5,5BiSn z različnimi dodatki neodima

increasing the amount of neodymium we increased the proportion of the dark-colored phase containing Nd. The needle phases disappeared from the microstructure as the content of Nd was raised.

Figures 6 and **7** show the microstructures of the alloy with 5.0 % Nd. **Figure 6** indicates that Nd is incorporated into the eutectic Al_2Cu phase forming a new phase. Nd also solidifies together with Bi forming a phase that could presumably be BiNd.[16] **Figure 7** shows that both Nd and Cu are contained in the last solidification area. Specified proportions of individual elements in the microstructure are given in **Table 3** and **Figure 8**.

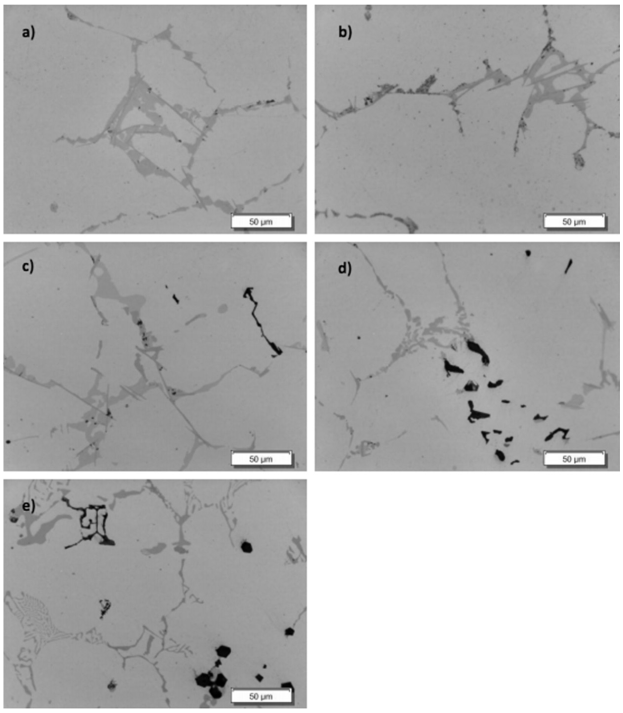

Figure 5: Influence of neodymium additions on the microstructure of the AlCu5.5BiSn alloy: a) pure alloy, b) 0.1 % Nd, c) 0.5 % Nd, d) 1.0 % Nd and e) 5.0 % Nd (mass fractions)
Slika 5: Vpliv dodatka neodima na mikrostrukturo zlitine AlCu5,5 BiSn: a) brez dodatka, b) z 0,1 % Nd, c) z 0,5 % Nd, d) z 1,0 % Nd in d) z 5,0 % Nd (masni deleži)

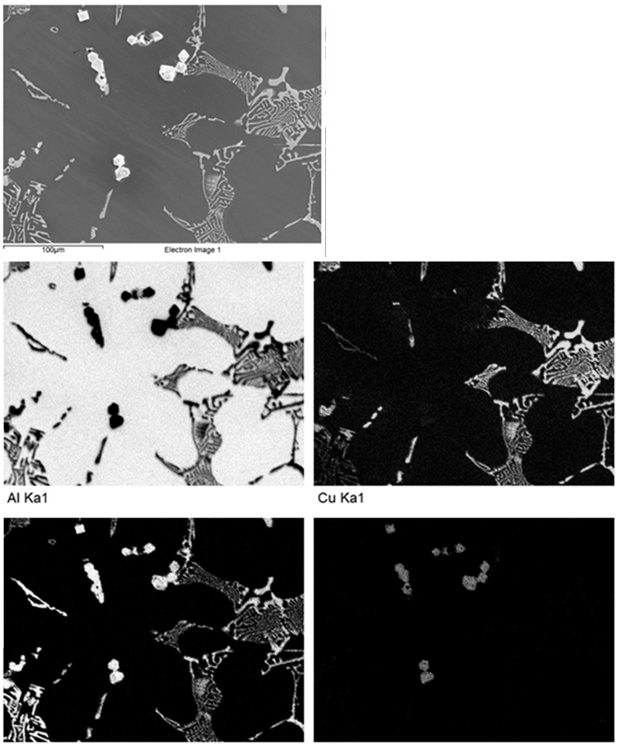

Figure 6: Mapping analysis of the AlCu5.5BiSn alloy with w = 5.0 % Nd

Slika 6: Analiza porazdelitve elementov v fazah zlitine AlCu5,5BiSn z w = 5,0 % Nd

By increasing the content of Nd, the amounts of the eutectic Al_2Cu phase and, consequently, the eutectic itself in the microstructure are increased. This was confirmed by the polygonal crystal precipitation along the crystal borders and the spaces between the dendrites as this phase adopts the form of the Chinese script.

The identification of microstructural components confirmed the course of solidification that was determined with equilibrium thermodynamic calculations (**Figure 1**) and a thermal analysis (**Figure 2**). Neodymium, which was added to the AlCu5.5BiSn alloy, solidified in the last solidification field as a $Al_2Cu(Nd)$ phase (**Figure 5**).

Implemented mechanical tests of hardness made at room temperature revealed no changes in the samples of the AlCu5.5BiSn alloy containing different amounts of neodymium (**Table 4**).

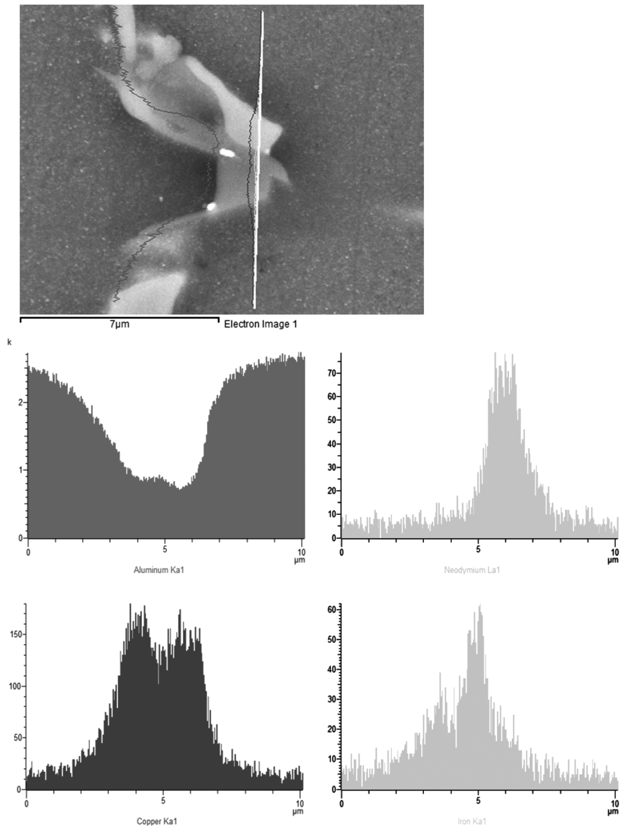

Figure 7: Line analysis of the Al_2Cu eutectic phase in the AlCu5.5BiSn alloy with w = 1.0 % Nd

Slika 7: Linijska analiza evtektične faze Al_2Cu v zlitini AlCu5,5BiSn z w = 1,0 % Nd

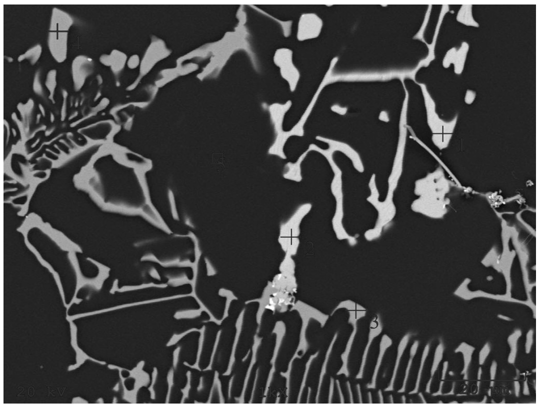

Figure 8: Microstructure (SEM) of AlCu5.5BiSn with w = 5.0 % Nd with the EDS analysis from **Table 3**

Slika 8: Mikrostruktura (SEM) zlitine AlCu5,5BiSn s 5,0 % Nd z EDS-analizo iz **tabele 3**

Table 3: EDS analysis of the phases in the investigated alloy (mole fractions, x/%)

Tabela 3: EDS-analiza faz v preiskovani zlitini (molski deleži, x/%)

phase	Al	Cu	Nd	Fe	Sn	Si	total
1	47.43	21.25	25.07		1.35	4.9	100
2	53.68	13.85	27.97		3.28	1.22	100
3	61.02	28.4	8.07	2.51			100
4	51.83	40.19	7.36	0.34	0.28		100
5	99.04	0.96					100

Table 4: Brinell hardness of the AlCu5.5BiSn alloy

Tabela 4: Trdota po Brinellu zlitine AlCu5,5BiSn

Specimen	HB
AlCu5.5BiSn	49.4
AlCu5.5BiSn + 0.1 % Nd	46.1
AlCu5.5BiSn + 0.5 % Nd	47.9
AlCu5.5BiSn + 1.0 % Nd	45.1
AlCu5.5BiSn + 5.0 % Nd	45.3

4 CONCLUSIONS

Effects of different neodymium additions to the wrought AlCu5.5BiSn alloy were investigated through a study of the solidification course and microstructures. Characteristic solidification temperatures of individual phases were identified. Temperatures T_1 ($Al_{13}Fe_4$ with a Nd-phase) and T_E (α_{Al} + Al_2Cu) increased with a Nd addition, whereas the T_E recalescence disappeared. The solidification interval was widened when 0.1–1 % Nd was added and narrowed when 5 % of Nd was added. The Al_2Cu phase became rich in neodymium and formed a new eutectic (α_{Al} + Al_2Cu(Nd)), which should be confirmed by an X-ray analysis.

In the microstructure of the AlCu5.5BiSn alloy with different additions of neodymium the neodymium phase Al_2Cu(Nd) was found, which solidifies in the last solidification area. The hardness of AlCu5.5BiSn alloys with an addition of neodymium does not change at ambient temperature, and further investigation of hardness at elevated temperatures is required.

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