Determination of precipitation sequence in Al-alloys using DSC method

Določitev sekvence izločanja v Al-zlitinah z DSC-metodo

Maja Vončina[1,] *, Anton Smolej[1], Jožef Medved[1], Primož Mrvar[1] & Rok Barbič[2]

[1]University of Ljubljana, Faculty of Material Science and Engineering, Department of Materials and Metallurgy, Aškerčeva 12, 1000 Ljubljana, Slovenia
[2]Sistemska tehnika, d. d., Koroška cesta 14, 2390 Ravne na Koroškem, Slovenia

*Corresponding author. E-mail: maja.voncina@ntf.uni-lj.si

Received: January 19, 2010 **Accepted:** February 18, 2010

Abstract: The precipitation hardening of Al-5 % Cu based alloy was studied using the differential scanning calorimetry (DSC). Different transition phases were gained by the suitable temperature program. The microstructure was investigated using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The type of the precipitated phases was determined. The distribution, shape and size of investigated precipitates were determined.
The goal of this paper was to present how the DSC method can help to pursue the precipitation in to already known alloys or even to determine if the precipitation occurs in unknown alloys.

Izvleček: Izločevalno utrjevanje zlitine Al-5 % Cu je bilo preiskovano z diferenčno vrstično kalorimetrijo (DSC). Prehodne faze so bile v mikrostrukturi dosežene z uporabo ustreznega temperaturnega programa. Mikrostruktura je bila določena z uporabo vrstične elektronske mikroskopije (SEM) ter presevne elektronske mikroskopije (TEM). Tip, porazdelitev, oblika in velikost preiskovanih izločkov/prehodnih faz so bili tudi določeni.
Namen raziskav je bil predstaviti uporabnost DSC-metode pri spremljanju izločanja v poznanih ter nepoznanih zlitinah.

Key words: Al-Cu alloy, differential scanning calorimetry (DSC), precipi-

Original scientific paper

tation, precipitation kinetics, Scanning electron microscope (SEM), Transmission electron microscope (TEM)
Ključne besede: zlitina Al-Cu, diferenčna vrstična kalorimetrija (DSC), izločanje, kinetika izločanja, vrstična elektronska mikroskopija (SEM), presevni elektronski mikroskop (TEM)

INTRODUCTION

The formation and the distribution of various precipitates from supersaturated solid solution have a significant meaning of strengthening of many engineering alloys. The strength of the precipitation hardening alloy depends on the distribution, size and shape of the precipitated intermetallic phases. Regarding the type of the precipitates the corresponding hardness, tensile strength and ultimate tensile strength of the alloy is expected. [2]

Al-Cu alloys are widely known and discussed in many works. When the alloy of composition

Al-5 % Cu is heated to the temperature of about 530 °C the copper is dissolved in solid solution, and by quenching the alloy rapidly into water there is no time for any transformation to occur. The solid solution is then supersaturated with Cu and there is a driving force for precipitation of the equilibrium θ-phase, Al_2Cu.

The total precipitation process appears in followed sequence:

$$\alpha_0 \rightarrow \alpha_1 + \text{GP zone} \rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \theta$$

where 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 θ'' phase, α_3 the composition in equilibrium with θ' phase and α_4 the composition in equilibrium with θ-Al_2Cu phase. [1, 2, 3, 4, 5, 10]

The total sequence of GP zones and transition phases takes place only if the alloy is aged under the solvus temperature of GP zones. For example, if ageing is carried out at temperature above the θ'' solvus but below θ' solvus, the first precipitate will be θ', heterogeneously nucleated on dislocations. If ageing is carried out above the θ' solvus, the only precipitate that is possible is θ which nucleates and grows at grain boundaries. Also, if an alloy containing GP zones is heated to above the GP zone solvus the zones will dissolve. [6, 7, 8]

Differential scanning calorimetry (DSC) is a popular technique which is often used to study the thermodynamics and kinetics of phase changes in materials. It is particularly useful for precipitation reactions in light alloys used for structural applications, where successive solid-state reactions of precipitation and dissolution can be analysed at increasing temperatures. [15, 16] In this study the application of this method is presented.

Experimental

The Al-5 % Cu alloy with composition presented in Table 1 was prepared and melted in the induction furnace from aluminium (99.8 %) and refined copper (99.9 %). The alloy was cast into grey cast iron mould of a cylindrical shape of internal diameter 15 mm and length 123 mm. Furthermore the as-cast specimens were homogenized at temperature 520 °C for 8 h and then quenched in water to room temperature. The specimens for DSC analysis were turned to disks of 5 mm diameter and 3 mm high. The DSC analysis was performed in atmosphere of argon by the different temperature programs to reach different precipitates:

A. Heating up to 100 °C for 10 min with heating rate of 10 °C/min and cooling rate of 20 °C/min
B. Heating up to 200 °C for 10 min with heating rate of 10 °C/min and cooling rate of 20 °C/min
C. Heating up to 360 °C for 10 min with heating rate of 10 °C/min and cooling rate of 20 °C/min
D. Heating up to 500 °C for 10 min with heating rate of 10 °C/min and cooling rate of 20 °C/min

Whole experimental process is presented in Figure1.

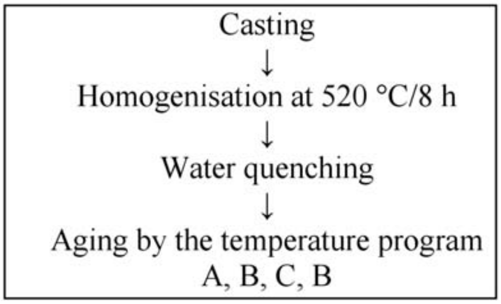

Figure 1. Schematically presentation of experimental process

The DSC instrument (Jupiter 449c of NETZSCH) was previously calibrated and the basic curves for individual temperature program were recorded. Furthermore DSC curves were plotted, temperatures of the precipitation were marked and the energies of a various precipitates were determined. In addition the specimens were observed with the scanning electron microscope (SEM) SIRIUM 400nc of a Fey Company equipped with the EDS analyzer INCA 350 and with transmission electron microscope JEM-2000FX. The shape, sizes and distribution of the precipitates were determined.

Table 1. Chemical composition of investigated alloy Al-5 % Cu

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al
mass fraction (*w*/%)	0.028	0.043	4.730	0.0012	0.004	0.001	0.003	Rest

Table 2. Temperature of the precipitation of different precipitates at two heating rates

Precipitate/transition phase	Heating rate 10 °C/min	Heating rate 20 °C/min
GP zone	58.0 °C	60.5 °C
Θ″	87.6 °C	106.8 °C
Θ’	210 °C	219.4 °C
Θ-Al_2Cu	419.1 °C	421.7 °C

Results and discussion

The first experiment was made to compare the influence of the heating/cooling rate on the precipitation intensity (temperature and precipitation energy/enthalpy). DSC curves are presented in Figures 2 and 3. Regarding the cooling rate it can be observed that with the increasing heating rate the starting temperature for the precipitation of various precipitates (precipitation sequence) increases (Table 2) as it was described by Gaber A. et. al. [13,14]

After the temperature and the precipitation energy of transition phases and Al_2Cu precipitates were determined, the purpose was also to prove which transition phase (precipitate) actually occurred. The DSC experiment was carried out with a suitable temperature program (A, B, C and D) to reach the desired precipitates in the microstructure.

Peak A on Figure 4 belongs to the formation of GP zones. The activation energy for the formation of GP zones at heating rate 10 °C/min was 0.392 J/g. At peak B the transformation from GP zone to the θ″ zone took place. This peak is an endothermic peak where enthalpy of –5.126 J/g is used. Precipitate θ’ usually nucleate at dislocations, [2, 3] what takes course in section C with the enthalpy of 13.97 J/g. Incoherent equilibrium θ phase of a approximate composition Al_2Cu precipitates in section D presented on Figure 4. For this transformation 4.029 J/g energy was relaxed.

The gained specimens were analysed using Scanning electron microscope and Transmission electron microscope (Figures 5–8). On Figure 5 bright-field TEM micrographs of specimen analysed by temperature program A is presented. Regarding the final heating temperature it can be expected, that these are GP zones that precipitated from supersatu-

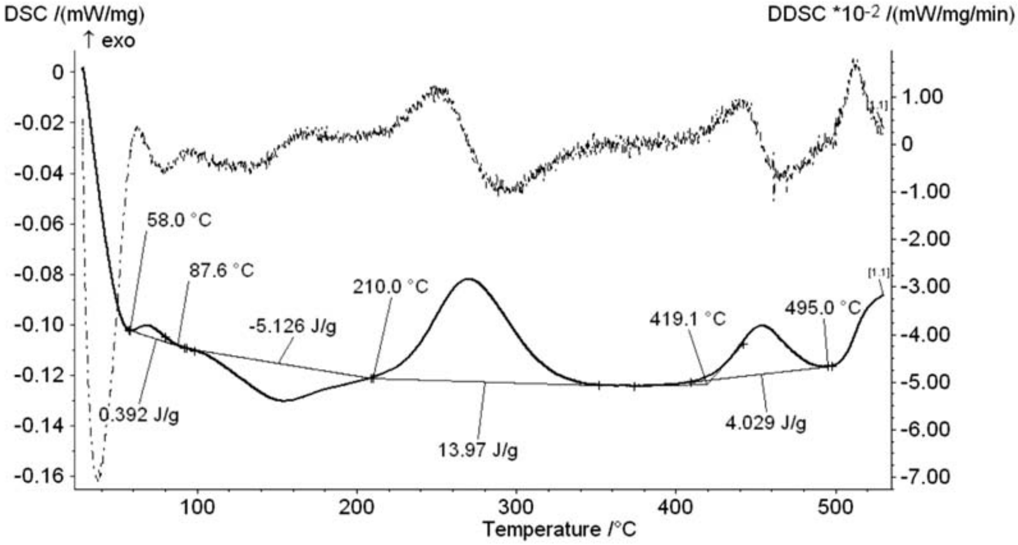

Figure 2. DSC curve obtained at heating and cooling rate 10 °C/min up to 530 °C for casted and homogenized Al-5 % Cu alloy

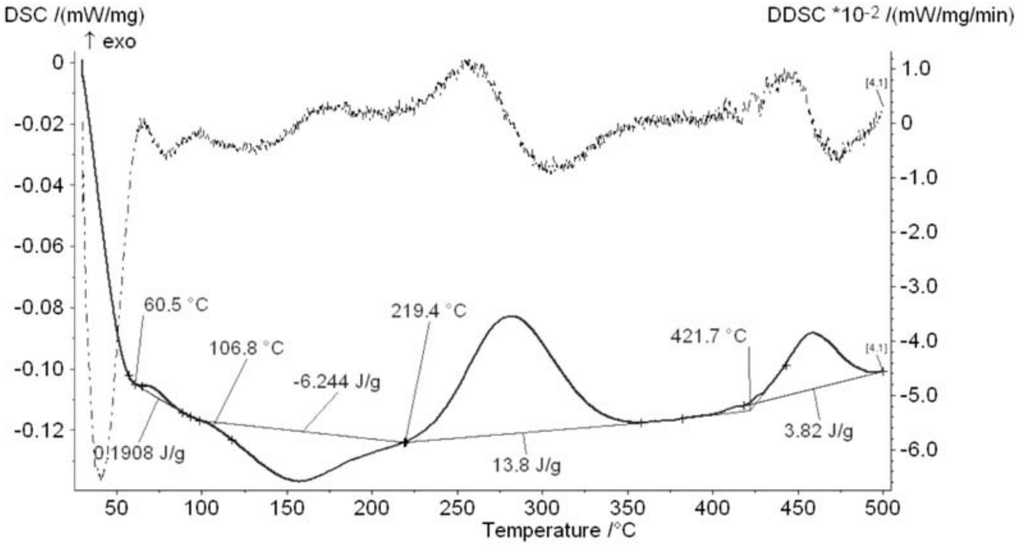

Figure 3. DSC curve obtained at heating and cooling rate 20 °C/min up to 500 °C for casted and homogenized Al-5 % Cu alloy

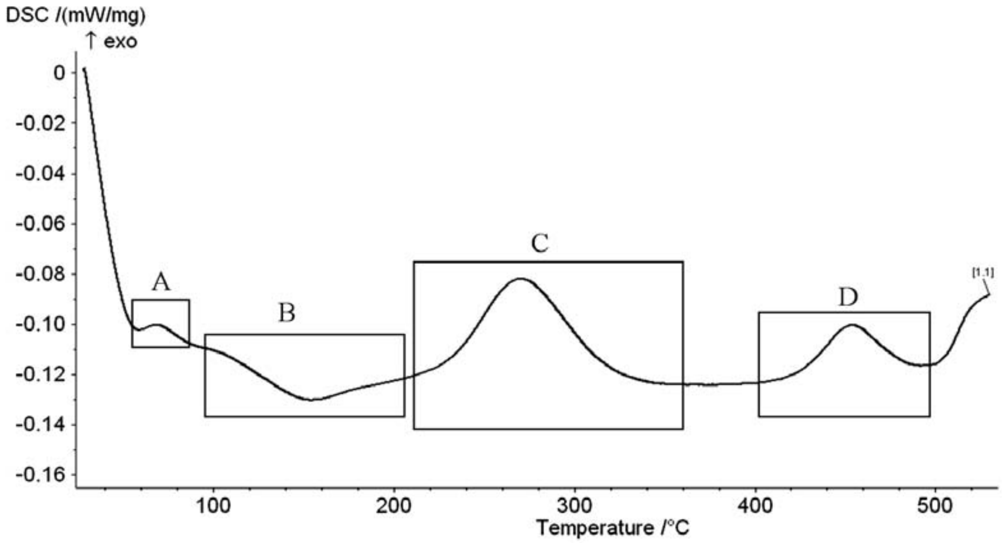

Figure 4. DSC curve analysed by the temperature program that provides desirable precipitate in the microstructure.

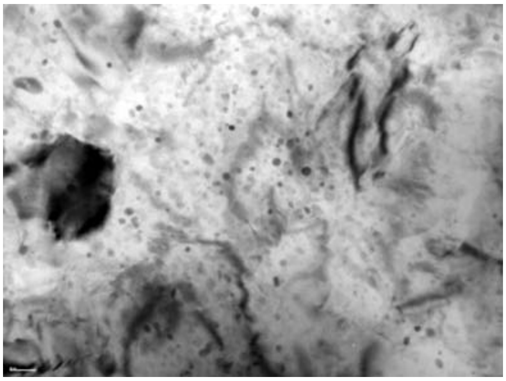

Figure 5. TEM micrographs of Al-5 % Cu specimen prepared by temperature program A (GP zone).

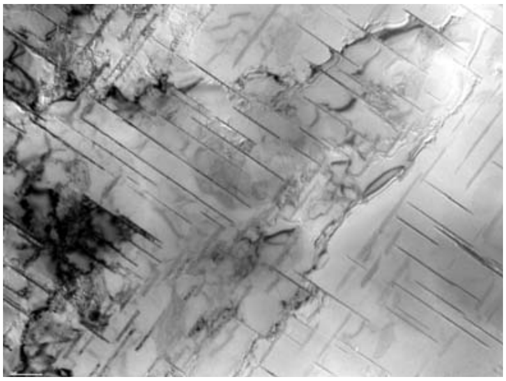

Figure 6. TEM micrographs of Al-5 % Cu specimen prepared by temperature program B (θ″ precipitates)

rated solid solution. Phases could not be analysed with EDS because the electron beam is too wide and the phases are too small (the error would be too large).

Figure 6 presents microstructure of a specimen analysed by DSC temperature program B. At heating to temperature 200 °C at most fully and semi-coherent

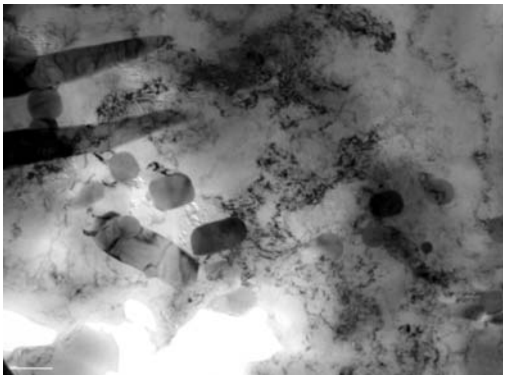

Figure 7. TEM micrograph of Al-5 % Cu specimen prepared by temperature program C (θ' precipitates)

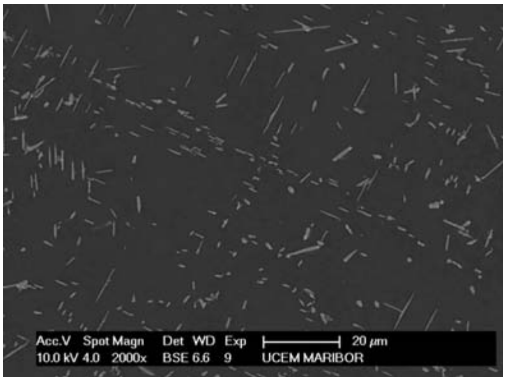

Figure 8. SEM microstructure of Al-5 % Cu specimen prepared by temperature program D (θ-Al_2Cu precipitates)

plate-like θ″ precipitates precipitate in the matrix beside GP zone. These precipitates also could not be analysed with EDS because of their small size however the length was measured and was 500–1500 μm and the tightness was 30–35 nm. TEM analysis confirmed two variants of precipitates, first θ″ precipitate which plane (001) is parallel to plane (100) of aluminium and second θ' precipitate which plane (100) is parallel with (100) plane of aluminium (Figure 6). The orientation of the specimens is also evident from Figure 6.

With heating to temperature 360 °C with heating rate of 10 °C/min and cooling rate of 20 °C/min (C) the specimen presented in Figure 7 was tested. Here θ' precipitates can be observed that grew bigger. It was found that they had approximate composition of stable Al_2Cu. On Figure 8 microstructure of specimen analysed by temperature program D is presented. Regarding the final heating temperature it can be expected to find equilibrium θ-Al_2Cu phase. EDS analyzer showed that it was combine from mole fractions 35–40 % of copper and 60–65 % of aluminium what corresponds to a composition of Al_2Cu phase. [7, 9, 10]

Conclusion

In this study the temperature of precipitation sequence and the precipitation energy was investigated. It can be seen that the DSC method is very useful when the precipitation or even the course of the precipitation in the alloy is to determine.

In this case the temperature of formation of transition phases and the influence of heating rate ware determined with the DSC analysis. It was shown that the precipitation temperature shift to a higher temperature when heating rate increases. At higher heating rate 20 °C/min the precipitation energies are a little smaller than at heating rate of 10 °C/min because of a shorter precipitation time. For the formation of GP zones, Θ' and Θ-Al_2Cu the exothermic peak occurs on heating DSC curve. However for the formation Θ″ precipitate the endothermic peak appears on the heating DSC curve. The aim was also to prove which transition phase or precipitate precipitated from supersaturated solid solution at defined temperature. TEM micrographs and convergent beam electron diffraction confirmed the sequence of the precipitation.

Differential scanning calorimetry (DSC) is a popular technique which is often used to study the thermodynamics and kinetics of phase changes in materials. It is particularly useful for precipitation reactions in light alloys, where successive solid-state reactions of precipitation and dissolution can be analysed at increasing temperatures.

Acknowledgements

The authors would like to thank to dr. Franc Zupanič, University of Maribor, Faculty of Mechanical Engineering and dr. Goran Dražić, Jožef Stefan Institute, Ljubljana, for technical assistance.

References

[1] TEIXEIRA, J., DA COSTA, CRAM, D. G., BOURGEOIS, L., BASTOW, T. J., HILL, A. J., HUTCHINSON, C. R. (2008): On the strengthening of aluminum alloys containing shear-resistant plate-shaped precipitates. *Acta Materialia*, Vol. 56, 6109–6122.

[2] PORTER, D. A. (1992): Phase Transformation in Metals and Alloys; Chapman & Hall, 1992.

[3] MONDOLFO, L. F. (1976): Aluminium Alloys: Structure and Properties; Butter worths, 1976, London.

[4] ANDO, Y., MIHAMA, K., TAKAHASHI, T., KOJIMA, Y. (1974): Growth of Guinier-Preston Zones and the θ''-phase in Al-4% Cu Alloys. *Journal o Crystal Groeth*, Vol. 24–25, 581–584.

[5] ALTENPOHL, D. (1965): Aluminium und Alminiumlegierungen, Reine und angewandte Metallkunde in Einzeldarstellungen, Springer-Verlag, Berlin/Göttingen/Heidelberg/New York, 1965.

[6] Karlik, M., Bigot, A., Jouffrey, B., Auger, P., Belliot, S., Hrem (2004): FIN and tomographic atom probe investigation of Guinier-Preston zones in an Al-1.54 at.% Cu alloy., *Ultramicroscopy*, Vol. 98, 219–230.

[7] MAIO, W. F., LAUGHLIN, D. E. (1999):

Precipitation Hardening in Aluminium Alloy 6022. *Scripta Materialia*, Vol. 40/7, 873–878.

[8] GUPTA, A. K., LLOYD, D. J., COURT, S. A. (2001): Precipitation hardening in Al-Mg-Si alloys with and without excess Si. *Material Science and Engineering*, A316, 11–17.

[9] OVONO, D., GUILLOT, I., MASSINON, D. (2006): The microstructure and precipitation kinetics of a cast aluminium alloy. *Scripta Materialia*, Vol. 55, 259–262.

[10] WANG, S. Q., SCHNEIDER, M., YE, H. Q., GOTTSTEIN, G. (2004): First-priciples study of the formation of Guinier-Preston zones in Al-Cu alloys. *Scripta Materialia*, Vol. 51, 665–669.

[11] BOYD, J. D., NICHOLSON, R. B. (1971): The Coarsening Behaviour of θ'' and θ' Precipitates in Two Al-Cu Alloys. *Acta Metallurgica*, Vol. 19, 1379–1391.

[12] HAN, J. (2005): Processing, microstructure evolution and properties of nanoscale aluminium alloys. Doctors dissertation, University of Cincinnati, July 2005.

[13] GABER, A., MOSSAD ALI, A., MATSUDA, K., KAWABATA, T., YAMAZAKI, T., IKENO, S. (2007): Study of the developed precipitates in Al–0.63Mg–0.37Si–0.5Cu (wt.%) alloy by using DSC and TEM techniques. *Journal of Alloys and Compounds*, Vol. 432, 149–155.

[14] STARINK, M. J. & ZAHRA, A. M. (1998): β' AND β PRECIPITATION IN AN Al-Mg ALLOY STUDIED BY DSC AND TEM. *Acta mater*, Vol. 46/10, 3381–3397.

[15] HERSENT, E., DRIVER, J. H., PIOT, D. (2009): Modelling differential scanning calorimetry curves of precipitation in Al–Cu–Mg, S*cripta Materialia*.

[16] SON, S. K., TAKEDA, M., MITOME, M., BANDO, Y., ENDO, T. (2005): Precipitation behavior of an Al–Cu alloy during isothermal aging at low temperatures. *Materials Letters*, Vol. 59, 629–632.