

THE CHARACTERIZATION OF PHASE TRANSFORMATIONS IN RAPIDLY SOLIDIFIED Al-Fe AND Cu-Fe ALLOYS THROUGH MEASUREMENTS OF THE ELECTRICAL RESISTANCE AND DSC

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For the characterization of the phase transformations in the alloys during the heat treatment the various methods of the thermal analyses are available. Thermogravimetry, differential thermal analysis (DTA) and the differential scanning calorimetry (DSC) are the most frequently used methods. The phase transformations proceed in two stages, i.e. nucleation and the growth of the new phase. Both processes are closely linked with the movement of the atoms. Rapidly solidified alloys often contain the elements with the low diffusivity. During the transition from the unstable to the stable state the energy changes are small, therefore the characterization of the changes by DTA, DSC is very difficult and could not be measured. During the heat treatment the phase transformations of the rapidly solidified alloys of Al-Fe and Cu-Fe were successfully detected by the simultaneous measurements of the electrical resistance, and were compared by the DSC method. By determination of the temperature regions of the phase transitions or temperatures, where the dynamics of the changes is maximal, the samples were heat treated and analysed by the scanning and transmission electron microscopy respectively.

Key words: *rapidly solidified Al-Fe and Cu-Fe alloys, transformations, electrical resistance, differential scanning calorimetry*

Karakterizacija faznih transformacija brzo skrutnutih Al-Fe i Cu-Fe slitina pomoću mjerenja električne otpornosti i diferencijalno skenirajuće kalorimetrije. Za karakterizaciju faznih transformacija slitina tijekom toplinske obrade koriste se različite metode toplinske analize (DTA). Najčešće korištene metode su termogravimetrija, diferencijalno toplinska analiza i diferencijalna skenirajuća kalorimetrija (DSK). Fazne se transformacije odvijaju u dva stadija, tj. nukleacija i rast nove faze. Oba su procesa usko povezana s gibanjem atoma. Brzo skrutnute slitine često sadrže elemente niske difuznosti. Tijekom prijelaza iz nestabilnog u stabilno stanje energetske su promjene male i zato je karakterizacija promjena pomoću DTA i DSK veoma teška i ne mjerljiva. Za vrijeme toplinske obrade mikrostrukturne transformacije brzo skrutnutih Al-Fe i Cu-Fe slitina uspješno su detektirane istodobnim mjerenjem električnog otpora. Određivanjem temperaturnih područja faznih prijelaza ili temperatura, gdje su dinamičke promjene maksimalne, uzorci su toplinski obrađeni i analizirani pomoću skener i transmisivne elektronske mikroskopije.

Ključne riječi: *brzo skrutnute Al-Fe i Cu-Fe slitine, transformacije, električna otpornost, diferencijalna skenirajuća kalorimetrija*

INTRODUCTION

Many methods exist for the analysis and for the characterization of the phase transformations of the rapidly solidified alloys, which are also described in the literature [1 - 3]. Frequently used methods are the scanning electron microscopy (SEM), transmission electron microscopy

(TEM), and the diffraction of the X - rays (XRD). All the results should be in mutual agreement. For determination of the phase transformations of the samples during the heat treatment the different methods of the thermal analysis are available, by which the physical properties of the substances and the reaction products are examined as the function of the temperature. Among those the thermography (TM), DTA and DSC are the most frequently used methods. At the most analytical procedures the phase transformations at the constant temperature are examined, and less frequently after the given involved program. The results of the measurements of

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the heat excited processes are the heating and cooling curves as the function of the temperature. The kinetics parameters established by the measurements are detailed in the book of Chena and Kirsha [4].

The phase transformations are possible only, if the free energy change of the system is lowered. While the possible phase transformations are established by thermodynamics, their progress to form the microstructure depends by the kinetics. The phase transformations proceed in two stages, i.e. nucleation and the growth of the new phase. Both processes are closely linked with the movement of the atoms. The parallel development of the powder metallurgy and the procedures of the rapidly solidification enable the manufacture of the new alloys [5]. Rapidly solidified alloys often contain the elements, which have the small diffusivity, so that the changes of the reaction energies for the transition from unstable into the stable state are low. These phenomena intensify difficulties to investigate the alloys by DSC and DTA.

EXPERIMENTAL WORK

Making of the rapidly solidified ribbons

Alloys of Al-Fe (4,7 mas. % Fe) and Cu-Fe (4,4 mas. % Fe) were remelted in the vacuum induction furnace, and then cast into the metal mould of the diameter of 45 mm. Thus made alloys were inserted into the graphite crucible. The component parts of the graphite crucible are shown in Figure 1.a. The rapidly solidified ribbons were made in the pilot plant shown in Figure 1.b [6, 7].

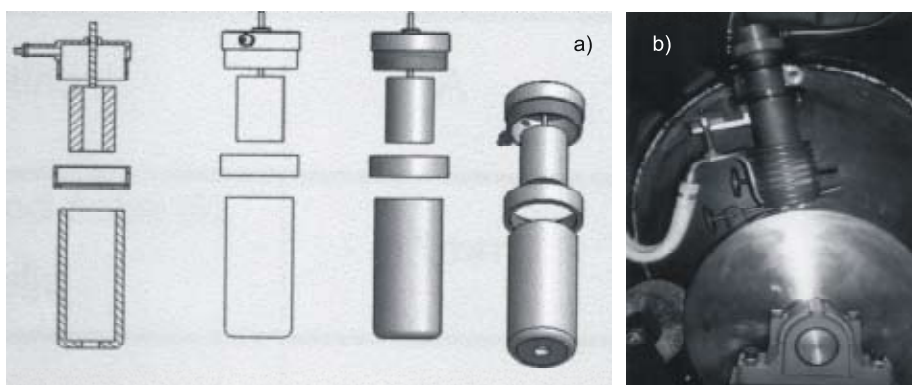


Figure 1. The scheme of the preparation of the crucible with the constituents (a) and the pilot plant for the rapid solidification - Melt Spinner (b)

Slika 1. Shematski prikaz lonca s konstituentima (a) i pilot postrojenje za brzo skrućivanje - Melt spinner (b)

Both alloys were inductively remelted in argon at the pressure of 350 mbar. Under the argon overpressure in the graphite crucible the molten alloy was sprayed through the nozzle on the rotating disc of the copper alloy. The heel was formed at the contact of the melt with the roll as the origin of

the formation of the continuously rapidly solidified ribbons. The chemical compositions and the dimensions of ribbons are presented in Table 1.

Table 1. Chemical composition and dimensions of the rapidly solidified ribbons of Al-Fe and Cu-Fe alloys

Tablica 1. Kemijski sastav i dimenzije brzo skrutnutih vrpci Al-Fe i Cu-Fe slitina

Alloy	Dimensions of ribbons		Chemical composition / mas. %		
	Thickness / μm	Width / mm	Fe	Al	Cu
Al - Fe	37 – 62	2,2	4,7	95,289	-
Cu - Fe	43 – 71	2,9	4,41	-	95,576

Differential scanning calorimetry

Microstructural transformations of the rapidly solidified alloys were examined by DSC at the constant heating rate of 5 °C/min. The differences of the thermoelectric voltages between the investigated and the reference samples were measured. The results of measurements were presented on the heating curve, which introduce the dependence between the consumed and the liberated energy regarding to the temperature. The tests were performed on the STA 449 device of the Netsch firm, which enable precise investigation of the physical and chemical processes. The results of the DSC were compared with the results obtained by measurements of the electrical resistance of ribbons of the rapidly solidified alloy.

Measurement of the electrical resistance

For the simultaneous measurement of the electrical resistance the four-probe D.C. method was used [8 - 10]. It was applied on ribbons of 200 to 250 mm length, which was coiled up on the 50 mm long ceramic tube. Reliability and repeatability of measurements were assured by the special girder construction for the samples with the tungsten and platinum lines (Figure 2.). During the heat treatment of the samples the electrical resistance was measured in the tube furnace

and the temperature by the thermocouple of Pt - Pt 10 % Rh, which was attached to the sample respectively. The temperature heating program of the furnace was controlled by the Eurotherm control system. The thermocouple with the reverse loop and thyristor were regulating that system.

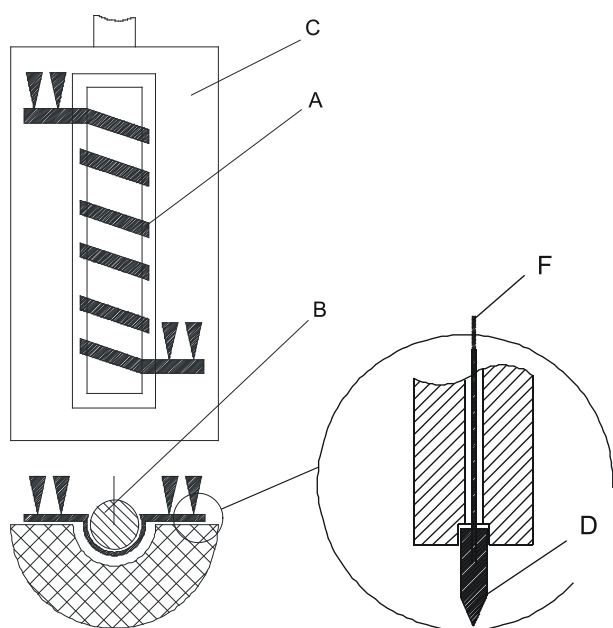


Figure 2. Schematic representation of the sample on the girder: sample (A), core (B), ceramic base (C), contacts (D), Pt-lines (F)

Slika 2. Shematski prikaz uzorka na nosaču: uzorak (A), jezgra (B), keramička osnova (C), kontakti (D), Pt-linije (F)

The voltage drop on the sample, which was heated by the constant rate, was measured at the constant electric current by the amplifier with the closed loop (Figure 3.).

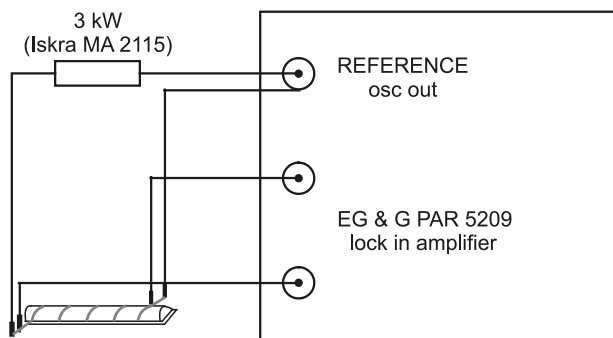


Figure 3. The circuit for the measurement of the electrical resistance by the amplifier with the phase closed loop

Slika 3. Električni krug za mjerenje električne otpornosti uz pojačalo s fazno zatvorenom petljom

The computer collected the temperature data through the rectifier and the voltage drops through the GPIB intermediate every 5 seconds. The electrical resistance was simultaneously calculated at known electric current through the sample and measured voltage drop. After the completed measurement of the electrical resistance at the heating rate of 5 °C the samples were quenched to preserve the microstructure. By establishing the temperature regions

of the phase transformations the samples were suitable heat treated and analysed by SEM and TEM.

RESULTS AND DISCUSSION

Microstructure of rapidly solidified Al-Fe 4,7 mas. % alloy

Rapidly solidified ribbons of the aluminium alloys with various iron content have different microstructure through the thickness. Two zones named zone A and B after H. Jones are characteristic for the microstructure [11, 12]. Zone A with the nano-cell is in contact to the disc, and the zone B is extending to the upper free surface (Figure 4.a).

Primary α_{Al} phase of the observed region is forming the interior of the cells, and the excess iron quantity is precipitating on their walls. In zone B the precipitates of the high-temperature phase are seen, which are located in the middle of the oblong cells (Figure 4.b and 4.c).

Microstructure of rapidly solidified Cu-Fe 4,4 mas. % alloy

In the lateral section the microstructure of rapidly solidified ribbons of Cu-Fe alloy is constituted of more zones (Figure 5.a). At the contact disc surface the zone of fine globular grains appeared, which proceed to the zone of columnar - crystal in the middle of the ribbon. The zone of the coarse globular grains is in the upper part of the ribbon and is enriched with the iron. In Figure 5.b the zone of fine globular grains is shown.

As is seen in Figure 5.b, the microstructure is homogeneous and the precipitated particles are not observed on the grain boundary or within the grains respectively. By TEM investigation the zone with columnar crystals was observed in the middle of the ribbon. The spot on the crystal boundary with the numerous dislocations and fine precipitates of the size of some nanometres is shown in Figure 5.c.

Phase transformations and the results of the thermal analysis

Phase transformations of the rapidly solidified ribbons of Al-Fe in Cu-Fe alloys in dependence of the temperature with the heating rate of 5 °C were followed by DSC and measurements of the electrical resistance. In Figure 6. two DSC thermograms without endothermic and exothermic peaks are seen. Therefore there is no sign of the precipitation from the supersaturated solid solution or the transitions of the intermetallic compounds from the unstable into the stable state respectively.

The electrical resistance changes depending on the temperature are shown in Figure 7. Due to the phase transformations the temperature dependence of the elec-

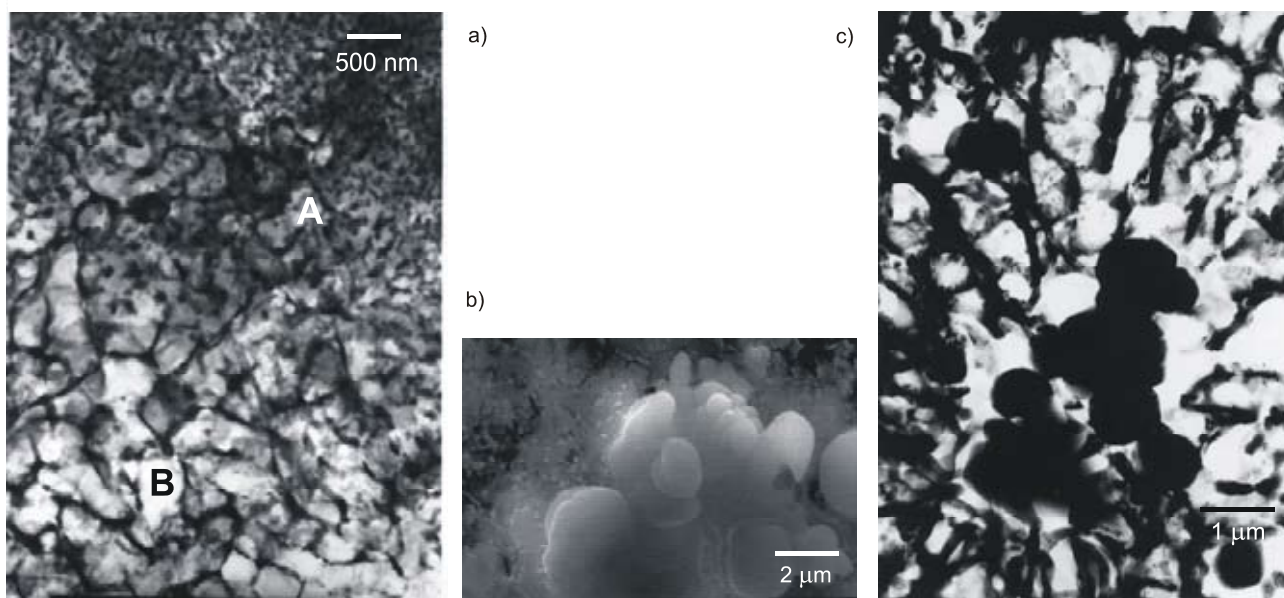


Figure 4. Microstructure of the rapidly solidified ribbons of the Al - Fe 4,7 mas. % alloy: (a) transition region from zone A to zone B, (b) high-temperature phase (SE) and (c) high-temperature phase in the middle of the oblong cells (TE)

Slika 4. Mikrostruktura brzo skrutnu-te Al-Fe 4,7 mas. % slitine: (a) prijelazno područje od zone A do zone B, (b) visoko-temperaturna faza (SE) i (c) visoko-temperaturna faza u sredini duguljastih ćelija (TE)

trical resistance is changing too. Linear parts of the curve represent the resistance change regarding to the increasing temperature. At fixed temperature the deviations of the linearity are observed. With higher temperature the electrical resistance is temporarily decreasing and then it is increasing again. The deviations of the linearity are well visible.

and the second one is between 515 and 570 °C. In Figure 7.b the result of the simultaneous measurement of the electrical resistance of the rapidly solidified Cu-Fe alloy is presented. The electrical resistance change is lower before the iron precipitation from the supersaturated solid solution of copper than after that. Therefore the

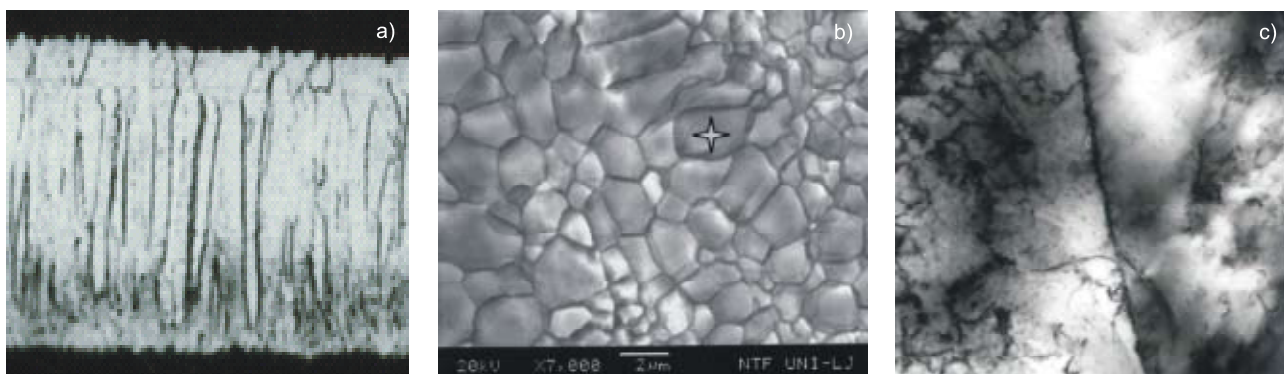


Figure 5. Microstructure of rapidly solidified Cu - Fe 4,4 mas. % alloy: (a) lateral section (OM), (b) on the contact disc surface (SEM) and (c) in the middle of the ribbon (TEM)

Slika 5. Mikrostruktura brzo skrutnite Cu-Fe 4,4 mas. % slitine: (a) bočni poprečni presjek (OM), (b) na kontaknoj površini diska (SEM) i (c) u sredini vrpce (TEM)

The temperatures, at which those deviations of linearity were appeared, are more visible on the curves of the first differential of the electrical resistance with respect to the temperature (Figure 7.a). On these curves two temperature intervals of changes are seen. The first one is between 315 and 480 °C with the minimum of 428 °C,

temperature coefficient of the electrical resistance is lower for the supersaturated solid solution of copper than for the precipitated iron. From the temperature depending diagram of the electrical resistance both temperatures of the interval changes were directly read and are between 318 °C and 660 °C.

Phase transformations of the Al-Fe alloy, that correspond to the first temperature interval of the electrical resistance changes, are the decompositions of the cell microstructure linked with the transformation of the unstable intermetallic phases formed during the rapid solidification into the stable ones and the iron precipitation from the supersaturated solid solution of α_{Al} . After the decompo-

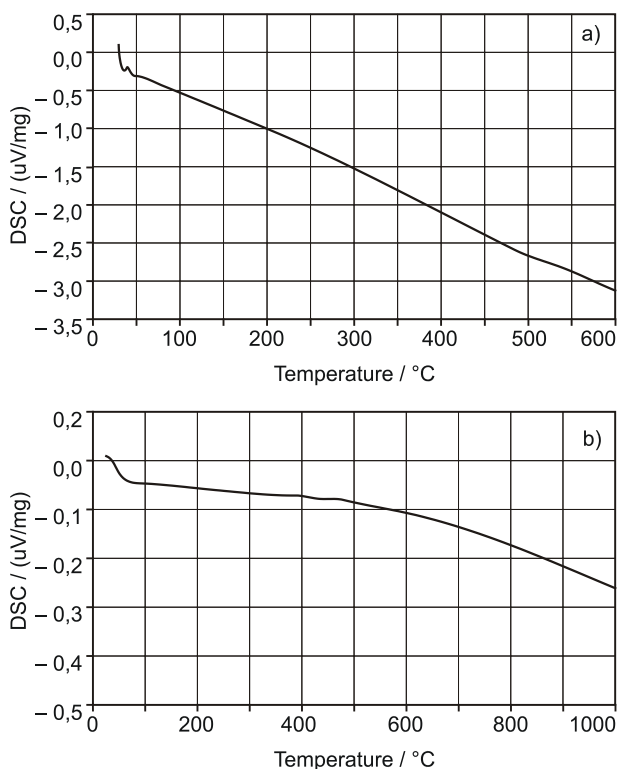


Figure 6. Thermograms of rapidly solidified alloys of (a) Al-Fe and (b) Cu-Fe

Slika 6. Termogrami brzo skrutnutih slitina: (a) Al-Fe i (b) Cu-Fe

sition of the cell microstructure the globular, oblong and acicular particles are present in the matrix (Figure 8.a). The changes formed after the second temperature interval are linked with the transformation of the needles into the

Table 2. Microstructure of the Al-Fe alloy after the rapid solidification and heat treatment

Tablica 2. Mikrostruktura Al-Fe slitine nakon brzog skrućivanja i toplinske obrade

Alloy	Microstructure of the Al - Fe alloy		
	After rapid solidification	After the first temperature interval	After the second temperature interval
Al - Fe	cell micro-structure: α_{Al} wall: AlFe particles: Al_6Fe	cell micro-structure: α_{Al} particles: globular Al_6Fe needles $Al_{13}Fe_4$	cell micro-structure: α_{Al} particles: globular and oblong $Al_{13}Fe_4$

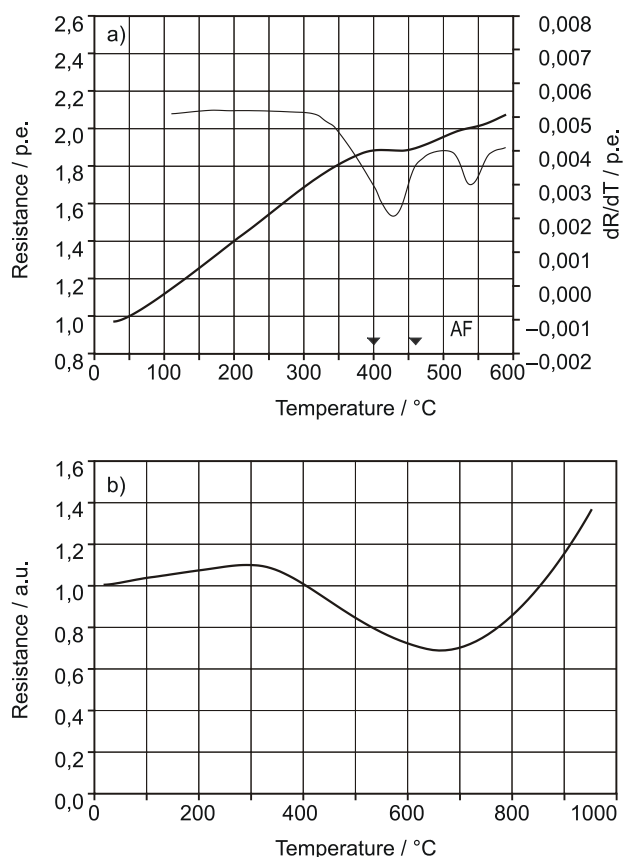


Figure 7. Thermographs of rapidly solidified alloys of (a) Al-Fe and (b) Cu-Fe

Slika 7. Termogrami brzo skrutnutih slitina: (a) Al-Fe i (b) Cu-Fe

oblong or globular particles and of the metastable phases into the stable ones respectively (Figure 8.b). The most significant reaction of the first interval of the electrical resistance changes is the iron precipitation from the supersaturated solid solution. But the transition of the unstable into the final stable state is indicated by both temperature intervals of changes. The results of the analysis of the phase transformations are shown in Table 2.

The characteristic of the phase transformations of rapidly solidified Cu-Fe alloy is the decomposition of the α_{Cu} solid solution. The microstructure of the ribbon which was in contact with the cooling disc after the heating over the temperature interval of the phase transformations is presented in Figure 9.a. That difference is shown before and after the heat treatment.

During the heating over the temperature interval of the phase transformations the iron-enriched particles start to precipitate. It was established by TEM (Figure 9.b), where essentially greater magnifications are possible as by SEM, that within the matrix the large number of the precipitated particles of the size of 5 to 20 nm are mainly presented. Particles of the size of 50 to 100 nm are observed also on the grain boundaries (Figure 9.a).

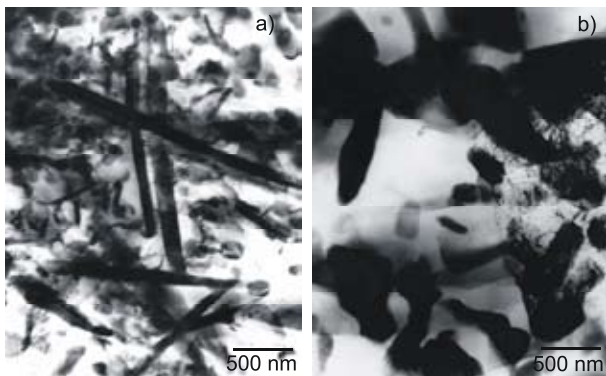


Figure 8. Microstructure of the rapidly solidified Al-Fe alloy (a) after heating over the first temperature interval and (b) after heating over the second temperature interval
 Slika 8. Mikrostruktura brzo skrutnute Al-Fe slitine: (a) nakon zagrijavanja kroz prvi temperaturni interval i (b) nakon zagrijavanja kroz drugi temperaturni interval

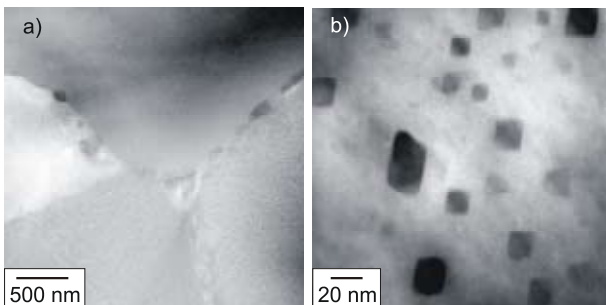


Figure 9. Microstructure of rapidly solidified Cu-Fe alloy after the heating up to 700 °C; (a) precipitated particles along the grain boundaries and (b) within the grain (TEM)
 Slika 9. Mikrostruktura brzo skrutnute Cu-Fe slitine nakon zagrijavanja do 700 °C; (a) precipitirane čestice duž granica zrna i (b) unutar zrna (TEM)

CONCLUSIONS

Phase transformations in the ribbons of rapidly solidified alloys of Al-Fe and Cu-Fe during the heating were

successfully investigated by measurements of the electrical resistance.

It was established that the electrical resistance is effective sensitive method for sensing of the phase transformations by elements of the low diffusivity in the alloys, where the changes on DSC were not perceived.

The most significant reactions during the heating of the ribbons over the first interval change is the iron precipitation from the supersaturated solid solution of α_{Al} and α_{Cu} . The transformation process of unstable phases into the stable ones was simultaneously taking place beside the iron precipitation. At transition over the changes of the second interval the transformation of the metastable phases of aluminium with iron into the stable phase of $Al_{13}Fe_4$ and acicular structure into the globular one were taking place respectively.

REFERENCES

- [1] C. D. Lien, M. A. Nicolet, *Journal Vacuum Science Technology B* 2 (1984), 783.
- [2] K. N. Tu, G. Ottaviani, U. Goesele, H. Foel, *Journal of Applied Physics* 54 (1983) 4, 758.
- [3] X. W. Wendlandt: *Thermal analysis, 3rd*, J. Wiley&Sons, New York, 1986.
- [4] X. R. Chen, Y. Kirsh: *Analysis of Thermally Stimulated Processes*, Pergamon Press, Oxford, (1981).
- [5] I. Mamuzić, *Metalurgija* 43 (2004) 1, 3 - 12.
- [6] B. Kosec, *Euroteh* 3 (2004) 5, 32 - 33.
- [7] G. Lojen, I. Anžel, A. C. Kneissl, A. Križman, E. Unterweger, B. Kosec, M. Bizjak, *Journal of Materials Processing Technology* 162 - 163 (2005), 220 - 229.
- [8] M. Ohring: *The Materials Science of Thin Films*, Academic Press, San Diego, (1992).
- [9] L. B. Valdes, *Proceedings of the IRE* 42, (1954).
- [10] G. Riontino, C. Antonione, L. Battezzati, A. Zanada, *Material Science Engineering A* 123 (1991), 1166 - 1169.
- [11] H. Jones, *Materials Science and Engineering* 5 (1969/70) 1, 1 - 18.
- [12] M. H. Jacobs, A. G. Doggett, M. J. Stowell, *Journal of Materials Science* 9 (1974), 1631 - 1643.