*Association of Metallurgical Engineers of Serbia* *Scientific paper*
*AMES* *UDC:669.35-153.881-412.2=20*

# RAPIDLY SOLIDIFIED COPPER ALLOYS RIBBONS

M. ŠULER[1], L. KOSEC[1], A. C. KNEISSL[2], M. BIZJAK[1],
K. RAIĆ[3], M. BRUNČKO[2,4], B. KOSEC[1], I. ANŽEL[4]

*[1] University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva c. 12, Ljubljana, Slovenia, [2] University of Leoben, Franz-Josef Straße 18, Leoben, Austria, [3] University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia, [4] University of Maribor, Faculty of Mechanical Engineering, Smetanova ul. 17, Maribor, Slovenia*

ABSTRACT

In the following article, the synthesis and analysis of rapidly solidified ribbons of copper alloys are presented. Binary copper alloys, with a maximum iron content of 4.41wt.% and similar alloys with a maximum carbon content of 0.014wt.% were produced by rapid-solidification on a rotating wheel (melt-spinning). In both groups of alloys, highly supersaturated solid solutions were achieved.

Rapidly quenched ribbons were examined both prior to and after heat treatment using optical and scanning electron microscopy in order to determine microstructural characteristics along the thickness of the ribbons. Thickness of the ribbons and the concentration of alloyed elements had the highest effect on microstructural changes after heat treatment. Analysis by X-ray diffraction and transmission electron microscopy were carried out to evaluate the resulting crystallography and changes in the face centered cubic cell which were controlled by the concentration of the alloyed elements.

To evaluate the decomposition of supersaturated solid solutions during heat treatment, which is controlled mostly by the concentration of copper in the alloy, in-situ electric resistance measurements were also carried out.

**Key words:** rapid solidification, copper alloys, heat treatment, lattice parameter

## 1. INTRODUCTION

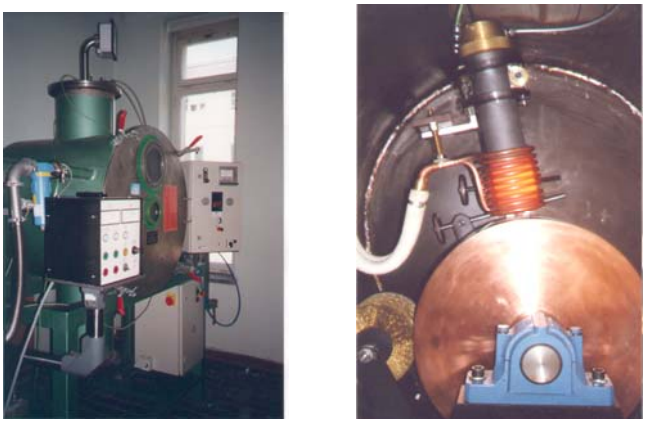
Rapidly solidified alloys can be produced by various methods. The most applicable in industrial environment are production of metal powder by atomization and production of thin ribbons by melt spinning on a rotating wheel.

With rapid solidification techniques higher solubility of alloyed elements in solid solutions can be achieved, what is especially important with a production of alloys with elements that have a small solubility in equilibrium state [1,2]. After rapid solidification the microstructure is unstable and is transformed into more stable during heat treatment [3,4]. On cross sections of rapidly solidified ribbons are areas of characteristic microstructures, which can be seen in the size and shape of crystal grains [5,6]. The present work includes synthesis and characterization of rapidly solidified copper-iron and copper-iron-carbon alloys.

Maximal solubility in solid state copper is only 4.1 wt.% at 1096 °C and is rapidly decreasing with a lower temperature and is already around zero at 600 °C. With slow cooling there are iron rich precipitates in the microstructure with a minimal iron content but with rapid solidification techniques supersaturated solid solutions can be achieved with iron content higher than 4.1 wt.%. Maximal solubility of carbon is only 0.008 wt.% at 1100 °C and is also decreasing rapidly with a falling temperature [7].

Despite incredibly small solubility of iron and carbon in copper we manage to maintain a large share of both alloyed elements in copper matrix.

Figure 1a shows a device (melt spinner) for production of rapidly solidified ribbons and figure 1b the interior of a chamber [8]. For alloys characterization following research methods were used: optical (OLYMPUS BX61) and scanning electron microscopy (JEOL JSM – 5610), simultaneous thermal analysis (NETZSCH STA 449), X-ray diffraction analysis (Philips PW 3710, $Cu_{K\alpha}$), transmission electron microscopy (JEM 2000 FX) and in-situ electric resistance measurements (IRT) during heat treatment.



*a)* *b)*

*Figure 1. Melt spinning device (a) and the interior of a chamber (b).*

## 2. EXPERIMENTAL WORK

Chemical composition of in the frame of our investigation analyzed alloys is presented in Table 1.

*Table 1. Chemical composition of the alloys*

| Alloy | Fe[wt.%] | Cu[wt.%] | C[wt.%] | S[wt.%] |
|---|---|---|---|---|
| A | 3.00 | 96.986 | | 0.014 |
| B | 4.41 | 95.576 | | 0.014 |
| C | 2.99 | 96.984 | 0.012 | 0.014 |
| D | 3.92 | 96.052 | 0.014 | 0.014 |

Figure 2 shows microstructures of slowly cooled alloys which were later cast with melt-spinner into ribbons. Crystal grains are relatively large and are getting smaller with a content of alloying elements (in alloys B and D are much smaller as in alloys A and C).

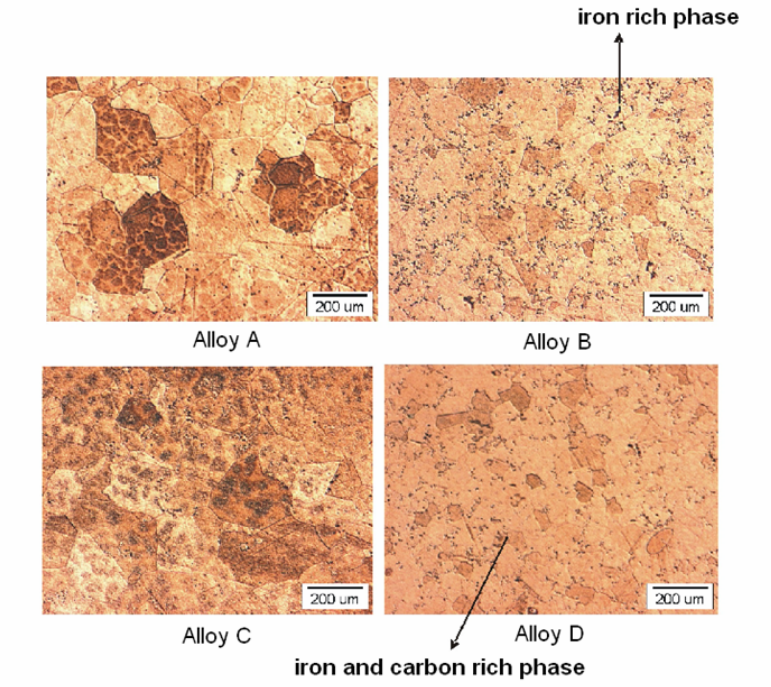



*Figure 2. Microstructure of classicaly casted alloys*

Longitudinal cross-sections of rapidly solidified ribbons show typical micro structural changes across the profile. Curved crystal grains indicate the course of solidification (Figure 3).

At the contact surface of the ribbons are in spots undersized crystal grains, which pass over in large transcrystal grains with banded substructure. There are also places where transcrystal grains grow already from the contact surface of the ribbon, which does not follow exactly the theory that describe the kinetics of rapid solidification.

Observations under SEM at magnifications approximately 10000x microstructure appears to be homogenous. Ribbons of all rapidly solidified alloys were annealed at 715 °C for 5, 10, 15, 30 and 60 minutes. To determine the amount of segregated iron from solid solution after one hour, the quantitative chemical analysis within the grains were carried out by EDS prior to and after heat treatment. Canges of iron contcentration within the crystal grains during isothermal annealing are shown in Table 2 and microstructural changes in Figure 4.

*Table 2. Changes of iron contcentration within the crystal grains after annealing for one hour at 715°C*

| ALLOY | Iron concentration changes [wt. %] |
|---|---|
| A | 0.16 |
| B | 1.17 |
| C | 0.27 |
| D | 1.08 |

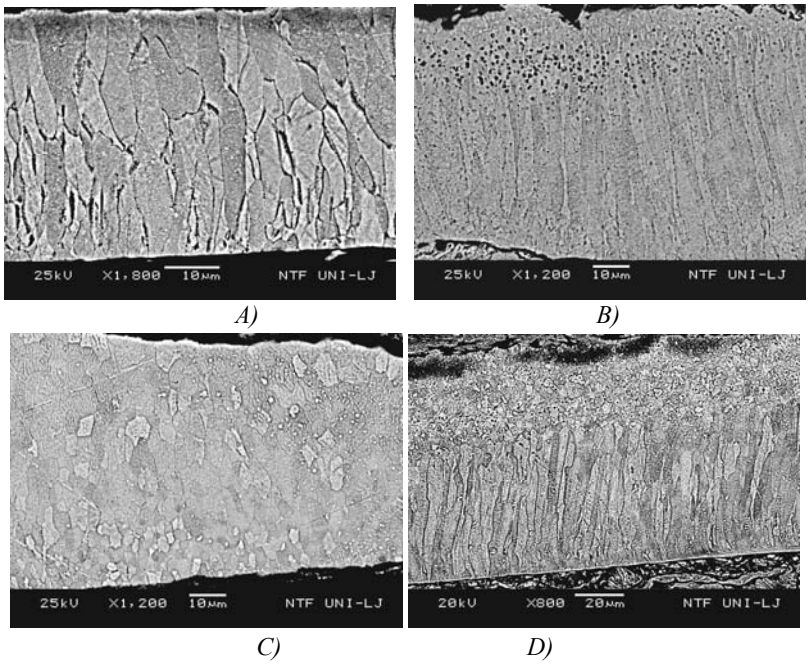



*Figure 3. Microstructure on crosssections of rapidly solidified ribbons*

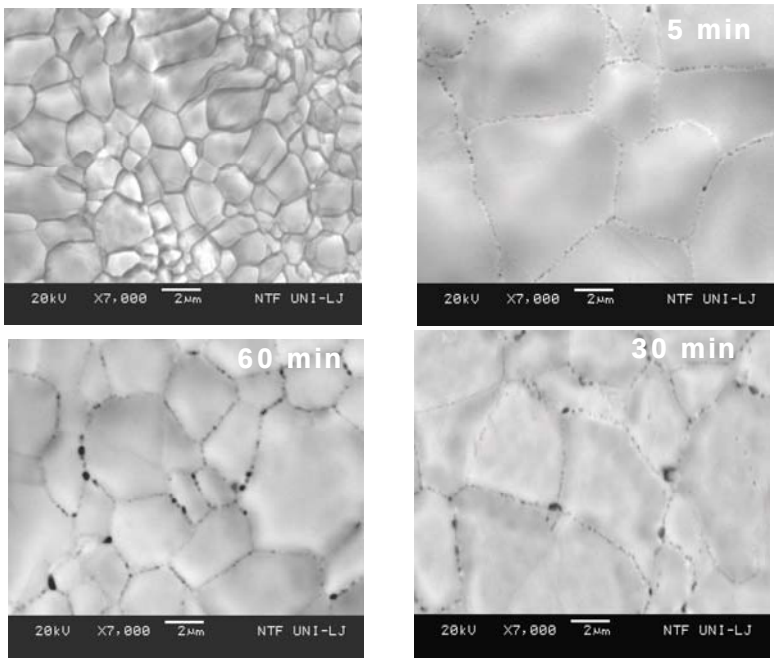



*Figure 4. Microstructural changes during isothermal annealing at 715 °C*

Because differential scanning calorimetry did not indicate decomposition of supersaturated solid solutions that should appear at lower temperatures, in-situ electric resistance measurements during slow heating were carried out what proved very successful to determine temperature and time intervals of decomposition [11 - 13].

In Figure 5 are presented the results of in-situ electric resistance measurements during heat treatment of rapidly solidified alloys. For each analyzed alloy the temperature and time intervals of solid solution decomposition can be obtained (Table 3) [14].

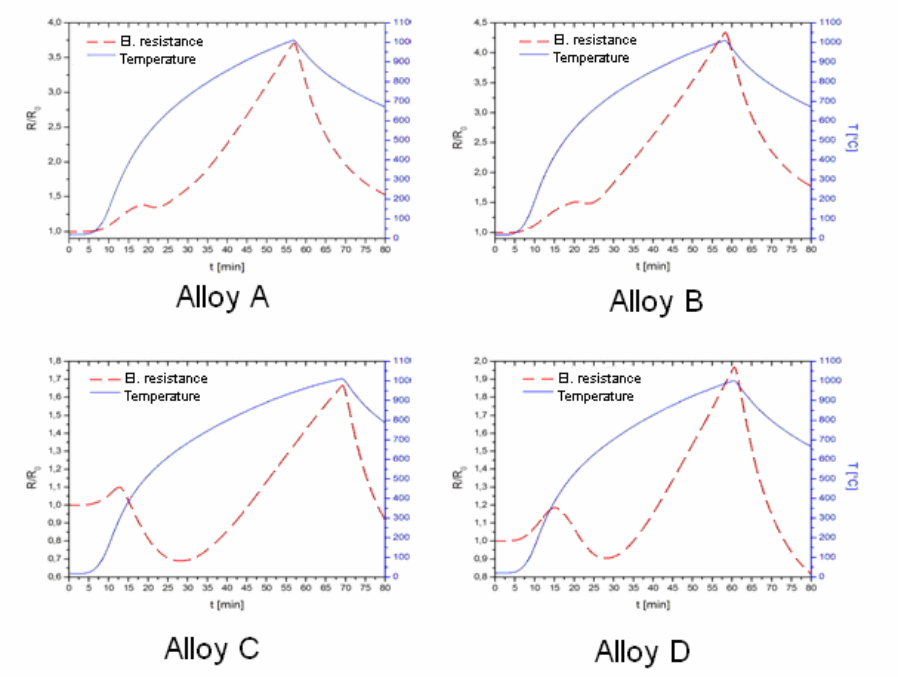



*Figure 5. In-situ electrical resistance measurements*

Transformations in copper-iron-carbon alloys (C and D) begin at lower temperatures and they are finished at much higher temperatures in comparative with binary non-carbon alloys. During transformation period the electrical resistance decreases despite increasing temperature. This phenomenon is much more explicit in alloys with carbon. Because of drastic changes in relative resistance in iron-carbon alloys during transformations distinctive deviations were expected also at the end of heat treatment but as seen in Table 3 the final increase is almost twice as higher in non-carbon alloys.

With X-ray diffraction analysis no precipitates were detected in CuFe (B) and CuFeC (D) alloys (roentgenograms correspond to pure copper) because of their insufficient volume fraction in the alloys. There was noticed a movement of peaks toward smaller angles with higher saturation (Figure 6). That movement reflects in the size of copper crystal cell (Table 4). Insignificant changes in lattice parameter of rapidly

solidified and annealed copper point out no influence of solidification velocity in crystal cell size.

*Table 3. Temperature and time intervals of decomposition of supersaturated solid solutions in investigated alloys*

| Alloy | A | B | C | D |
|---|---|---|---|---|
| Temperature interval of transformation [ °C] | 500 °C to 563 °C ΔT=63°C | 564 °C to 629 °C ΔT=65°C | 388.5 °C to 660 °C ΔT=271.5°C | 379 °C to 675.5 °C ΔT=296.5°C |
| Elapsed transformation time [min] | 2.65 | 3.1 | 12.9 | 15.4 |
| Relative resistance changes during transformation | -0.04 | -0.05 | -0.41 | -0.28 |
| Relative resistance changes during heat treatment (25-1020 °C) | 3.71 | 4.35 | 1.66 | 1.96 |

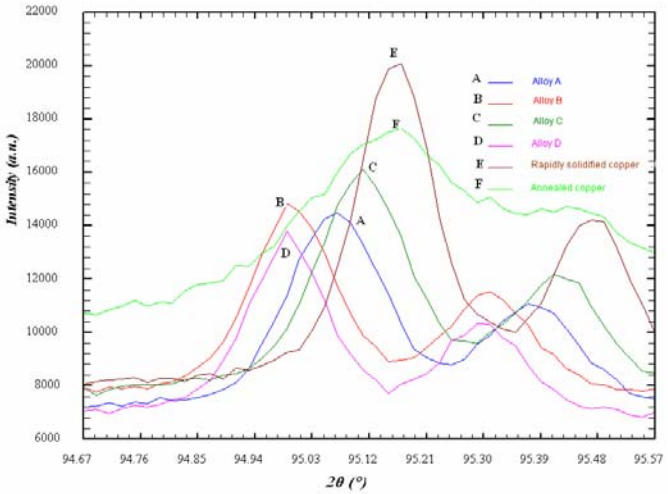
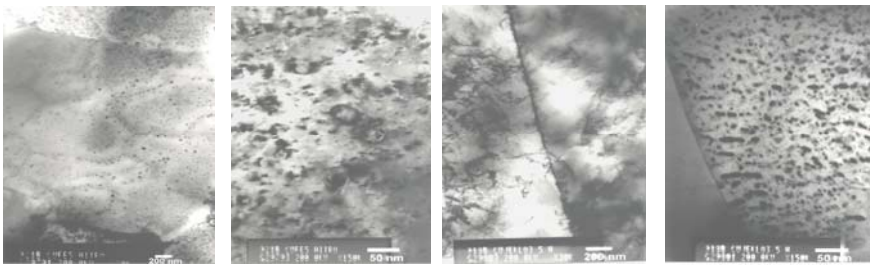



*Figure 6. X-ray diffraction analysis results of A, B, C, D alloys, rapidly solidified and annealed technical pure copper*

*Table 4. Lattice parameter changes in alloys*

| **Alloy** | **Lattice space distance d[nm]** | | **Basic unit edge[nm]** |
|---|---|---|---|
| | **(111)** | **(200)** | |
| A | 0.2085 | 0.1809 | 0.3612 |
| B | 0.2093 | 0.1813 | 0.3625 |
| C | 0.2085 | 0.1809 | 0.3612 |
| D | 0.2091 | 0.1811 | 0.3621 |
| Rapidly solidified copper | 0.2084 | 0.1806 | 0.3611 |
| Annealed copper | 0.20835 | 0.1805 | 0.3610 |

At magnification approximately 20000x there were found dispersive nanoprecipitates within the crystal grains in alloy B. With higher magnifications we found out there are two different sizes of precipitates within copper matrix. Larger measure between 20 and 30 nm in diameter, while smaller are only a few nanometers. Although the precipitates are spherical, there can be seen a tension field around them as a result of differences in the size of crystal unit of matrix and precipitate. Microstructures taken by TEM of alloy B and C are in Figure 7. There is a high density of dislocations in alloy C and a large number of very small precipitates that were detected with magnifications over 100000x.



a) b)

*Figure 7. Microstructure of alloy B (a) and alloy C (b), TEM*

Electron submission results of copper matrix lattice parameter were identical with XRD-analysis. For precipitates that were not detected with XRD we found out that they have as same as copper a cubic face centered cell with lattice parameter 0.41 nm. Measured crystallographic parameters indicate toward iron oxide FeO, but there is a very small possibility for a FeO to be found in the alloy.

## 3.CONCLUSIONS

Microstructure on cross sections of rapidly solidified ribbons is made of undersized crystal grains at contact surface, which pass over in large transcrystal grains toward free surface.

At free surface of rapidly solidified ribbons a banded substructure can be detected. After isothermal annealing at 715 °C, the growth of crystal grains is minimal. Their growth is blocked by small precipitates on grain boundaries.

In-situ electric resistance the measurements during heat treatment is more accurate method for detecting micro structural changes than methods of thermal analysis.

Decomposition of solid solutions in CuFeC (C, D) alloys starts at lower temperatures and last approximately five times longer as in CuFe (A, B) alloys. With super saturation the lattice parameters also changes. Rapidly solidified alloy C does not represent a homogeneous solid solution what was determined by TEM analysis.

In rapidly solidified alloys often appear constituents with chemical composition different as already known equilibrium and non equilibrium phases that are crystalographicaly identified.

## REFERENCES

[1] M. Bizjak: Temperature stability of rapidly solidified multi component aluminuim alloys, Doctoral thesis, University of Ljubljana, 1999.

[2] L. A. Jacobson, J. McKittrick: Rapid solidification processing, Materials Science and Engineering, 98, 1988, 1-12.

[3] W. Kurz, R. Triverdi: Rapid solidification processing and microstructure formation, Material Science and Enginering, A179/A180, 1994, 46-51

[4] H. Jones: The critical concentration for formation of segregation-free solid by solute trapping during rapid solidification from the melt, Materials Letters, vol. 6, No. 5, 1987

[5] I. Anžel: Internal oxidation of rapidly solidified copper alloys, Doctoral thesis, University of Maribor, 1996.

[6] J. W. Martin, R. D. Doherty and B. Cantor: Stability of microstructure in metallic systems, 2nd edition, Cambridge University Press, 1997.

[7] Alloy Phase Diagrams, ASM International Handbook, Vol. 3, Materials Park, Ohio, 1992.

[8] B. Kosec: Device for rapid solidification of metal alloys, Euroteh, 5, 2004, 32-33.

[9] W. Kurz, R. Triverdi: Solidification microstructures: Recent developments and future directions; Acta Metallurgica Materialia., vol. 38, No. 1, 1-17, 1990

[10] M. Šuler: Synthesis of rapidly solidified copper alloys, Diploma work, University of Ljubljana, 2005.

[11] G. Lojen, I. Anžel, A. C. Kneissl, A. Križman, U. Unterweger, B. Kosec, M. Bizjak: Microstructure of Rapid Solidified Cu-Al-Ni Shape Memory Alloy Ribbons, Journal of Materials Processing Technology, Vol. 162, No. 15, 220-229, 2005.

[12] L. A. Dobrzanski: Technical and Economical Issues of Materials Selection, Silesian Technical University, Gliwice, 1997.

[13] M. Šuler, L. Kosec, I. Anžel, M. Bizjak, B. Kosec, A.C. Kneissl, J. A. Amangual: Synthesis of Rapidly Solidified Ribbons of Copper Alloys, Metalurgija, Vol. 45, No. 3, 230, 2006.

[14] M. Šuler, M. Bizjak., L Kosec, B. Kosec, A.C. Kneissl, I. Anžel: Sinteza in analiza hitro strjenih trakov iz bakrovih zlitin, RMZ – Rudarsko-Metalurški Zbornik, Vol. 53, No. 2, 193 – 202, 2006.