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THE INFLUENCE OF NITRIDE ON THE MELTING Cu-Al ALLOYS CONDUCTIONS

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In some copper alloys can be not exept influence of nitrogen sevant as a refining gas on the character of structure and on other properties cannot be expected. Taking into account high stimina requirements placed aluminium bronzes, except rafination, is necessary the modification of structure. Because in both cases (the refining and modification) the nitrogen can have the essential influence on the structure and properties of copper alloys. It was decided to conduct the analysis of phenomenon proceeded during the refining with modification.

Key words: *gas refining, nitrogen, modification, Cu-Al bronzes*

Utjecaj nitrida na provođenje taljenja slitina Cu-Al. Različite bakarne slitine se ne mogu izuzeti od utjecaja dušika, kao rafinirajućeg plina na karakter strukture i na druga svojstva. Uzimajući u obzir visoke zahtjeve koji se postavljaju za aluminijsku broncu, osim rafiniranja potrebno je i modificiranje strukture. Zbog oba ova slučaja (rafinacije i modificiranja) dušik može imati odlučujući utjecaj na strukturu i svojstva bakarnih slitina. Odlučeno je da se provede analiza tih fenomena tijekom rafiniranja modificiranjem.

Ključne riječi: *rafinirajući plin, dušik, modificiranje, bronca Cu-Al*

INTRODUCTION

One of widely applied techniques for castings structure refining is the process of passing gases through liquid alloys. Process with composition modification, i.e. additon of Ti or Zr, leads to castings with particularly good properties. Copper alloys modified or not, are mainly refined by nitrogen which seems to be inert in the casting temperature range [1 - 5]. The various nitrides TiN, ZrN or AlN, sometimes observed in the alloys after casting, were treated as impurites which cause degradation of endurance strength friction as well as other properties. However if the formation of nitrides is a consequence of passing nitrogen through liquid alloy, the understanding of this process may help to avoid their homogeneous distribution.

It proves that there is a big discrepancy in the opinions of the structure and the basic features of slag as well as the essence of their interaction with refined metal and the atmosphere of melting. There are three methods of slag refining in the copper alloys melting conditions: the oxidising [6 - 8], the neutral and the alternative method of melting copper and its alloys in conditions of reduction with an activator introduced into the slag [4, 9 - 13]. On the basis of the analysis of the problem and the results of the author's research [4, 10, 11, 13] it is stated that the most promising ones are the reducing conditions of refining.

The aim of the paper was to influence the nitrogen refining in the reducing melting conditions. Here are used commercialy Cu9wt%Al casting bronzes and then verified their mechanical properties and the microstructure.

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THERMODYNAMIC ANALYSIS

In the binary metal-nitrogen system nitrogen with copper, aluminium and zirconium form one type of simple nitrides i.e. CuN, AlN and ZrN. Only titanium may form Ti_2N and Ti_3N. Analysis of the M-N systems, type nitrides [1 - 3, 5], which are common to all investigated systems, reveals that the interreaction between metal and nitrogen can be represented by the following reaction: 2M + N = 2MN.

In the case of Cu-Al and Cu-Ti or Cu-Zr systems regular solution parameter "*b*" was evaluated using experimental data published by Kleppa, Kleppert, and Hultgren [1 - 3]. For the Al-Ti and Al.-Zr system parameter "*b*" was calculated using Miedema approximation. The modified Krupkowski method [14] was also used for interpretation of the binary solution.

The nitrogen equilibrium pressure p_N for formation of TiN and ZrN nitrides calculated for the Cu-Al-Ti and Cu-

Al-Zr system is shown in Figures l. and 2. respectively. The isobaric lines are drown for 1370K as solid lines and for 1500K as dashed lines. In the range of commercially used bronzes denoted by dashes, the equlibrium p_N pressure for TiN nitride is the lowest one. As the values of ln p_N for AlN, are higher than –0,8, its formation in this temperature range is rather impossible. However, the ln p_N for TiN or for ZrN being less than –6,5 (for ZrN to – 12) is lower than the equilibrium pressure for Cu-nitrogen and Al-N equilibrium.

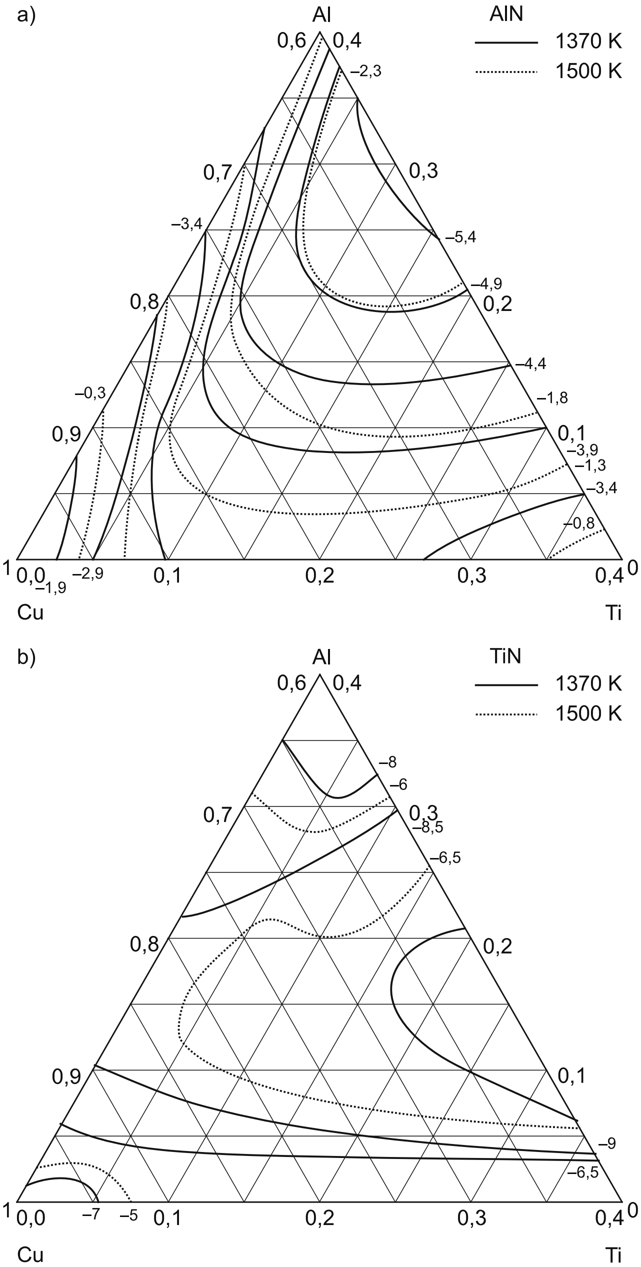

Figure l. **Nitrogen equilibrium pressure for AlN a), TiN b) nitrides formation in the Cu-Al-Ti alloy**

Slika 1. **Ravnoteža tlaka dušika za AlN a), TiN b) nastajanje nitrida u slitini Cu-Al-Ti**

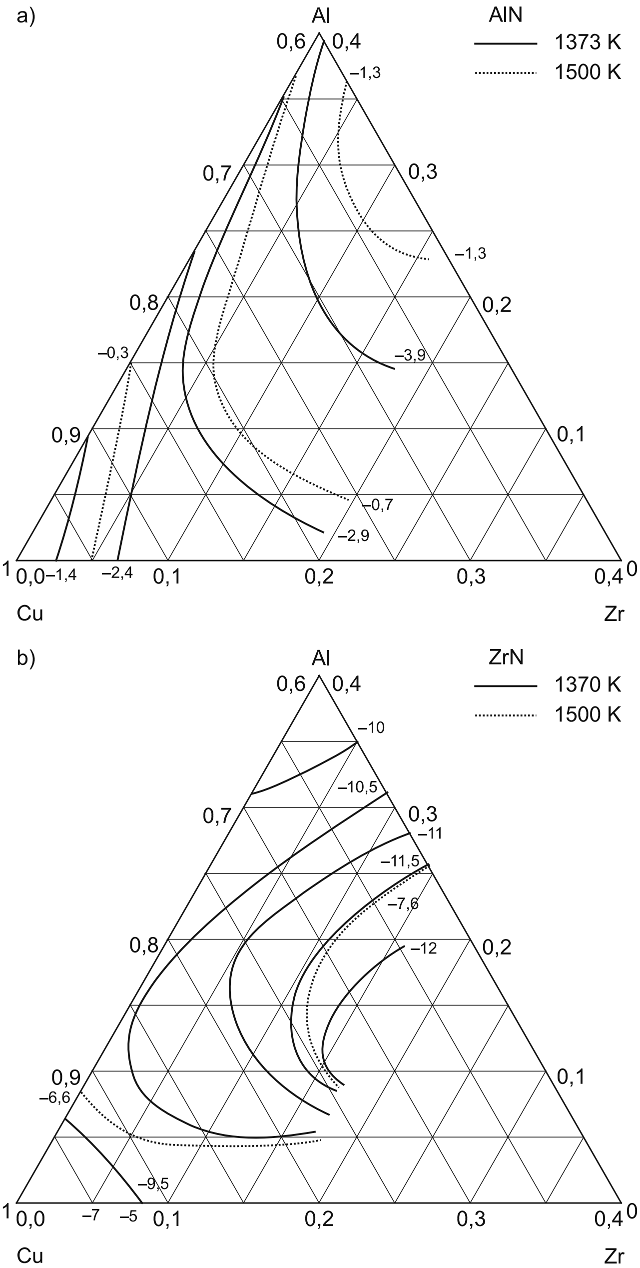

Figure 2. **Nitrogen equilibrium pressure for AlN a) and ZrN b) nitrides formation in the Cu-Al-Ti alloy**

Slika 2. **Ravnoteža tlaka dušika za AlN a) i ZrN b) nastajanje nitrida u slitini Cu-Al-Zr**

Experimental procedure and results

The Cu-Al-Ti alloy was prepared from pure copper and aluminium 4N in the induction furnace. Titanium and zyrconium were introduced in the Cu-Al mother alloy (in 0,1 % wt). Subsequently, molten alloy was saturated with argon or nitrogen (Table 1.). Metal is refining during 5 minutes with argon or nitrogen.

Table 1. **The plane and results of the investigation**
Tablica 1. **Plan i rezultati istraživanja**

L. p.	Used elements			Trybological properties		Endurance properties	
	Ar	N_2	others	R_{PW}/(m/g)	$\mu \times 10^{-5}$	R_m/MPa	A_5/%
1.1	+	---	---	790	200	410	20
1.2	---	+	---	1480	120	450	35
2.1	+	---	Ti	820	105	470	15
2.2	---	+	Ti	2080	130	585	20
3.1	+	---	Zr	1850	125	505	20
3.2	---	+	Zr	2380	140	610	25
Note: R_{PW} trybological resistance, μ - friction coefficient							

Thin foils for transmission electron microscope observation were prepared using a disc polishing method in the electrolyte containing 33% HNO and 67% CH_3OH. Figure 3.

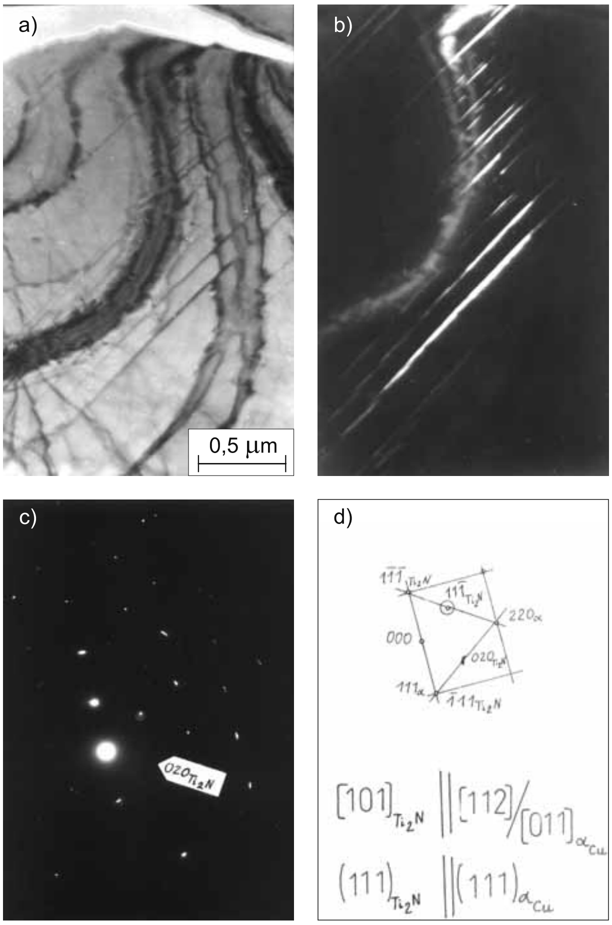

Figure 3. **Transmission electron micro-graph probe 2.2 with group Ti_2N nitride plate a), dark field image b), diffraction pattern c), indexing schema of diffraction pattern d)**
Slika 3. **Transmisijska elektronska mikroskopija (TEM) probe 2.2 s grupom nitridne pločice Ti_2N a), polje tamne slike b), difrakcijska slika c), indeksna shema difrakcijske slike d)**

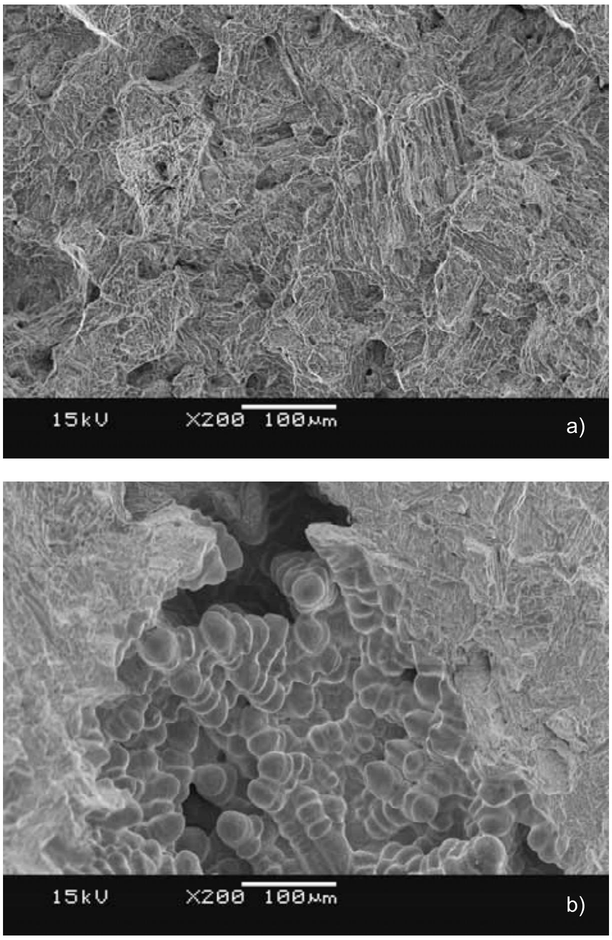

Figure 4. **The break-through scanning-structure of the probe 1.1 a) and probe 1.2 b)**
Slika 4. **Skenirana struktura (SEM) prijeloma probe 1.1 a) i probe 1.2 b)**

shows transmission electron micrograph with band extinction contoures and thin plates of a secend phase. The position of two sets of diffraction spots agrees with [112] *a*-phase and [101] Ti_2N orientations tetragonal a = 0,495 nm, c = 0,303 nm, with parallel (111) type planes as shown in Figure 3.d. The crystallographic correspondense according to solution of diffraction shown in Figure 3.d is as follows:

$[013]_{alfaCu}$ II $[111]_{TiN}$
$(100)_{alfa\ Cu}$ II $(110)_{TiN}$

The crystallographic correspondence according to solution of diffraction for ZrN is as follows:

$[112]_{alfa\ Cu}$ II $[011]_{ZrN}$
$(110)_{alfa\ Cu}$ II $(011)_{ZrN}$

The analysis of the break-through structure, past the endurance investigations, made on the scaning microscop is shown in the Figures 4.-6.

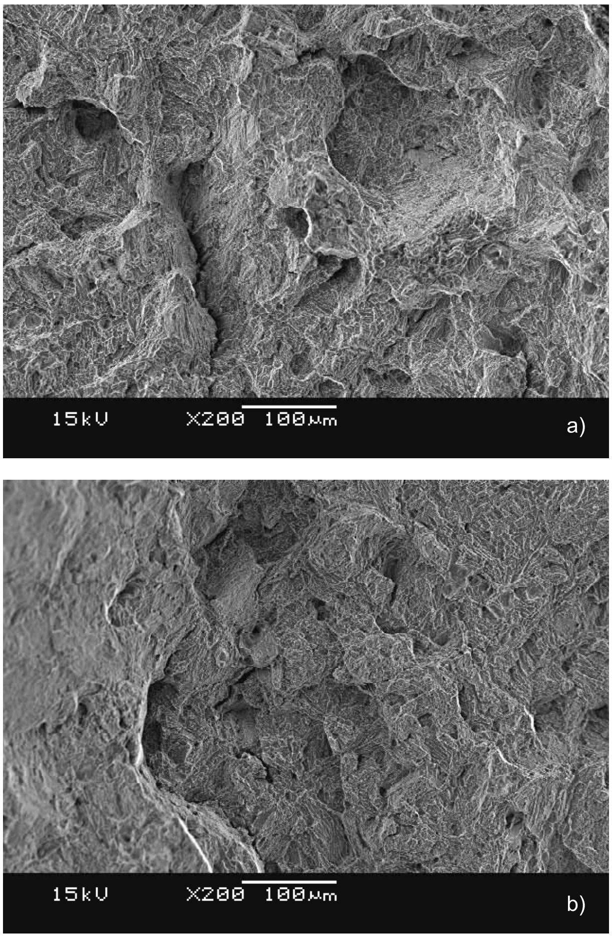

Figure 5. **The break-through scanning-structure of the probe 2.1 (a) and probe 3.1 (b)**
Slika 5. **Skenirana struktura (SEM) prijeloma probe 2.1 a) i probe 3.1 b)**

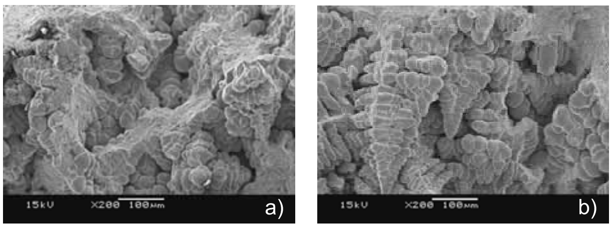

Figure 6. **The break-through scanning-structure of the probe 2.2 a) and probe 3.2 b)**
Slika 6. **Skenirana struktura (SEM) prijeloma probe 2.2 a) i uzorka 3.2 b)**

CONCLUSION

The thermodynamic study has shown that nitrogen pass through the liquid Cu-Al-Ti alloy causes the formation of titanium nitrides (Ti_2N) or circonium nitrides (ZrN). The laboratory investigation of the trybological and strange properties has shown that the influences of nitrogen refining are very different ones. The best ones are when Cu-Al alloys are with Ti or Zr.

A considerable intensifying of the refining processes has very great influence on the structure, specialy when the probe is compared with Ti or Zr before nitrogen rafining (Figure 5.) and after nitrogen refining proces (Figure 6.). The chemical analysis has shown that in the Cu-Al-Ti or Zr, after nitrogen refining proces are always the same parts of Ti or Zr elements as without refining. The fibrous structure after nitrogen refinings proceses (Figure 4.b and 6.) interpreted the very good mechanical properties, specialy a good lenght of the probe with Ti or Zr.

The results have shown that:

1. Nitrides formation may be possible during nitrogen refining in the Cu-Al-Ti or Zr alloys.
2. There has been described that during Cu-Al (with additions of modification elements as Ti or Zr) bronze metling process, the most important flow on the structure and tendency of the mechanical properties the art of the art of the gas refining were.
3. The results of the macrostructure investigations presented in this work have confirmed the argument on low reducing effectiveness of nitrogen refining in the Cu-Al alloys with Ti or Zr additions.
4. This nitride being product of reaction during casting the process of nitride formation in these alloys may be controlled by the change of parameters, i.e. nitrogen pressure or titanium or zirkonium addition.

REFERENCES

[1] H. Mulfinger, Journal of American ceramics Soc., 49 (1966), 462 - 471.
[2] E. Brunchuber, Schmelz und Leghierungs-technik, Verlag Schiele una Schon, Berlin 1968.
[3] A. Fuwa, Y. Shimizu, T. Ohisi, Metall. Rev. Of MMIJ, 6 (1989) 1, 62 - 66.
[4] A. W. Bydałek, J. Król, Inżynieria Materiałowa, 1 (993) 1, 14 - 18.
[5] R. Inoue, H. Suito, Metall. Trans. B, 25 (1994), 235 - 238.
[6] R. K. Mysik, J. P. Porucznikow, S. M. Cuchlew, Cwet. Metałły, 11 (1989), 88 - 92.
[7] T. Nakumara, F. Noguchi, Y. Neda, Metall, Review of M.M.I.J., 3 (1986) 2, 102 - 108.
[8] S. Rzadkosz, R. Wodecki, Acta Metall. Slovaca, 5 (1999), 422 - 430.
[9] A. Bydałek, Chem. Process, (1971) 10, 27 - 31.
[10] M. Czyż, A. W. Bydałek, Conference Transcom 95, TU Žilina 1995, s. 311 - 314.
[11] A. W. Bydałek, Acta Metallurgica Slovaca, 5 (1999) 2, 465 - 468.
[12] E. Krasicka-Cydzik, Journal of Applied Electrochemistry, 31 (2001), 1155 - 1161.
[13] A. W. Bydałek, A. Bydałek, Conference Modern Trends in Manufacturing, Center for Advanceed Manufacturing Technologies - Wrocław, TU Wrocław 2003, 20 - 25.
[14] A. Krupkowski, Podstawowe zagadnienia teorii procesów metalurgicznych, Wydaw. PWN, Kraków 1974.