P. SCHLAFKA, A. W. BYDAŁEK, M. HOLTZER, W. WOŁCZYŃSKI

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# THE INFLUENCE OF THE IONIC REACTIONS ON THE REFINING SECONDARY RAW MATERIALS

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The article presents the concept of refining with the use of slag activated with carbide coating. It pointed out the important role of stimulators of ionic reactions. The results of research from the melting of the CuAl10Fe4Ni4 alloy obtained from recycled materials in metallurgical conditions were shown. The changes in the structure of the alloy depending on the nature of the used simulators were indicated. Chemical reagents used and the stimulants in the form of haloids helped to improve the molding sand exchange process. The use of chemical regent in the form of calcium carbide and stimulants has also contributed to the formation of a protective atmosphere in the furnace bottom.

*Key words:* secondary metallurgy, slags, aluminum bronze, copper, structure

## INTRODUCTION

In refining interactions during aluminum bronzes melting the main role is played by oxygen, whose balance in atmosphere, slag, and in liquid metal is determined by the size of electric charges on the border of contacting phases [1 - 5]. In Figure 1 [6] a diagram of physicochemical phenomena occurring on the border of metal, slag and melting atmosphere has been shown in a simplified way.

The slag technique of copper alloys refining reflects the process with the deliberate use of slag layer of extractive influence in relation to metallic and non-metallic inclusions coming from a metal bath. Except for the extractive role the products of a reaction in slag influence the structure of alloys [7 - 9]. Because of the physicochemical phenomena complexity, these layers are also the reason of defects appearing in casts as well as toxic substances emission in the melting process [10 - 13].

Substances that initiate changes occurring on the border of atmosphere X – slag S – refined metal M cause acceleration of the phenomena occurring in these areas and therefore have been called reaction stimulators [10 - 12]. Stimulators inserted into a slag layer may influence both the casting structure and the process of liquid metal slag refining. It is of significant importance in secondary raw materials processing.

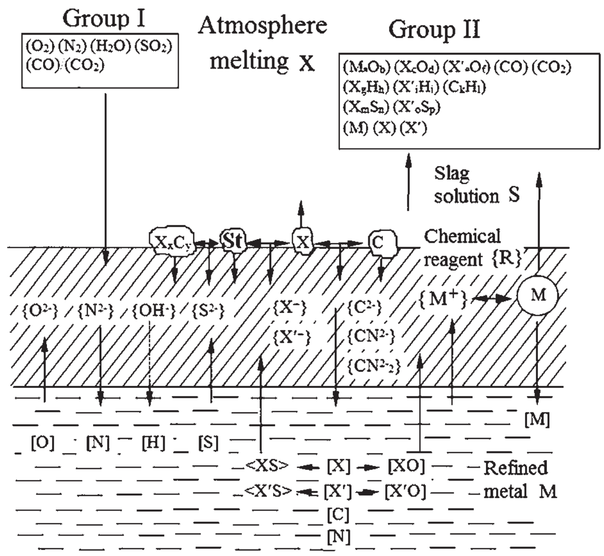



**Figure 1** The melting process: diagram of the refining process for the actual fusion atmosphere system - carbo - nitro - oxygen slag - liquid metal, where: { }- substance dissolved in liquid slag, ( ) - gas substance, [ ] - substance dissolved in liquid metal, < > - solid substance, $X^-$, X' - metallic ingredients of the chemical slag reagent, St - reaction stimulator in slag, M - refined metal, $\{M^+\}$ - ion of the refined metal dissolved in liquid slag, M - drop of liquid metal in liquid slag [6]

## RESEARCH AND DISCUSSION

The researched material was aluminum bronze CuAl10Fe4Ni4 (Table 1).

The melting process has been carried out in an induction coreless furnace Radyne 1 500.

The charge for the induction coreless furnace was scrap metal in the form of copper and aluminum shavings as well as nickel and iron scrap in the form of pipes,

P. Schlafka, University of Zielona Góra, Faculty of Mechanical Engineering, Poland
A. W. Bydałek, AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Krakow, Poland
M. Holtzer, AGH University of Science and Technology, Faculty of Foundry Engineering, Krakow, Poland
W. Wołczyński, Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Krakow, Poland

Table 1 **Chemical composition of CuAl10Fe4Ni4 / wt. %**

| Al | Fe | Ni | Zn | Sn |
|---|---|---|---|---|
| 10,04 | 4,98 | 3,59 | 0,07 | 0,001 |
| Pb | Mn | Si | P | Sb |
| 0,02 | 0,21 | 0,21 | 0,01 | 0,01 |
| Bi | As | Mg | S | |
| 0,001 | 0,006 | 0,005 | 0,005 | |

wires and ropes. The charge was the subject of preselection with the use of portable spectrometers. Shavings and other materials coming from machining were initially dried. Copper feedstock including in its composition cooling-lubricating liquid, which was delivered directly from mechanical processing, was also initially dried. The size of a single charge, was 1 200 kg.

To carry out smelting in industrial conditions chemical compositions of refiners on the basis of $Al_2O_3$, $SiO_2$, $B_2O_3$, additionally involving carbide chemical reagent involving technical calcium carbide were marked for research. The choice of refining mixtures composition was carried out with the use of Slag-Prop software [6]. Slag composition is presented in Table 2.

Table 2 **Slag composition A**

| Base slag B | Chemical reagent R | Stimulant |
|---|---|---|
| 70 % borate glass<br>30 % soda | 15 % R ($CaC_2$) | 5 % $B_2O_3$ |

Slag B consists of slag A complemented with stimulating substances in the form of chlorides and fluorides given in Table 3.

It was a technological recommendation to remove ash and dross created earlier before inserting the last furnace charge of solid feedstock, subsequently insert the scrap feedstock into the furnace and drift upon it the ‘A’ part’. The procedure results from gathering a considerable amount of ashes and dross in technology of smelting alloys from shavings. In order to make the active reagents R work properly, the ‘B’ part should be put on the surface of melted slag of the ‘A’ part with the use of the furnace cover. The stages and plans of smelting have been presented in Table 3.

Table 3 **Stages and plan of heats**

| Refining means | | The number of heat | | | | | |
|---|---|---|---|---|---|---|---|
| | | I | | II | | III | |
| Slag A | | x | 1 - 1 | x | 2 - 1 | x | 4 - 1 |
| Black lead | | | | x | 2 - 2 | | |
| Slag B | | | | | | | |
| Stimulate substance | 10 % NaCl | x | 1 - 2 | | | | |
| | 10 % NaF | | | x | 2 - 3 | | |
| Modifier | | | | | | | |
| Cu-Ti | | x | 1 - 3 | x | 2 - 4 | x | 4 - 2 |

During each heat monitoring measurements with the use of differential thermal analysis (DTA) were used along with chemical composition analysis (Table 4). A microprocessor-based temperature recorder WMPT-1 was used. Differential Thermal Analysis (DTA) researches in each of the smelting stages were carried out according to the plan presented in Table 3.

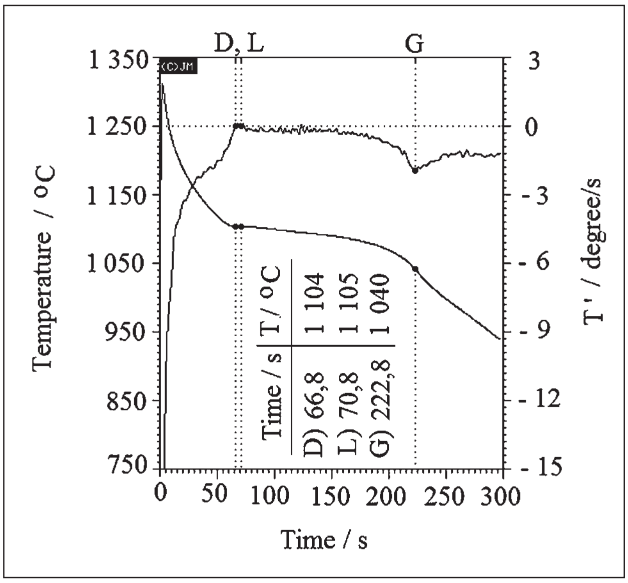



**Figure 2** The DTA graph of aluminum bronze˝CuAl10Fe4Ni4, heat no. 2-4

In Figure 2 an exemplary result of the Differential Thermal Analysis (DTA) research (2 - 4) has been presented. Characteristic points were marked with letters:

L – the temperature of the beginning of liquidus reaction,

D – the temperature of liquidus line overcooling,

G – the end of solidification process.

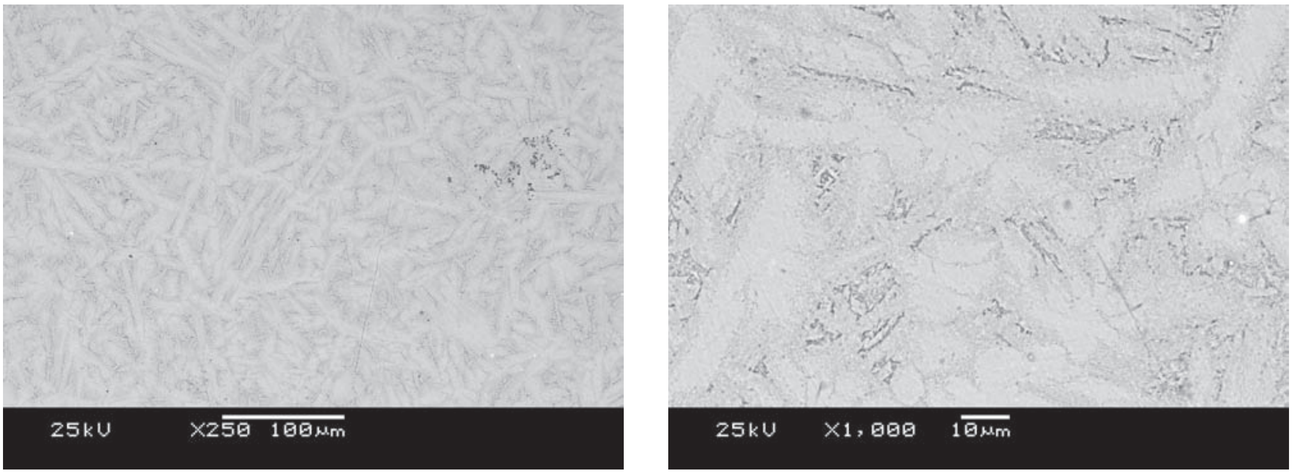
In Table 4 the results of the DTA analyses were gathered taking into consideration such characteristic points as: the highest temperature noted down ($T_A$), the temperature of the liquidus line overcooling ($T_D$), the beginning of the liquidus reaction ($T_L$) and the end of solidification ($T_G$).

In Figure 3 of aluminum bronze microstructure from the last stage of heat no. 1 have been presented.

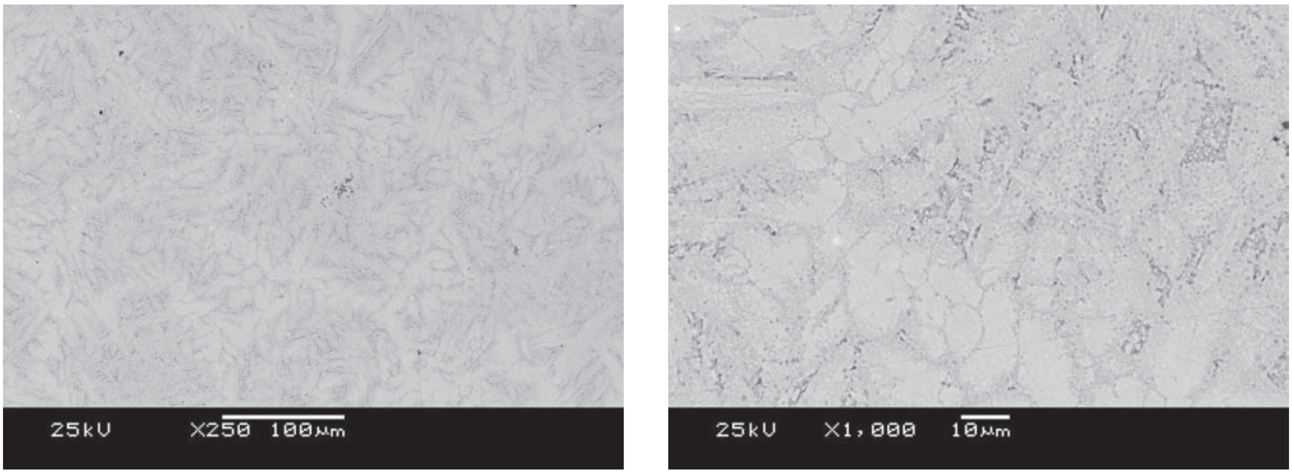
Table 4 **The results of the carried out DTA research and noted down characteristic points for particular heats**

| Smelting stage / sample no | Temperature / °C | | | |
|---|---|---|---|---|
| | The highest noted down ($T_A$) | The liquidus line overcooling ($T_D$) | The beginning of liquidus reaction ($T_L$) | The end of solidification process ($T_G$) |
| 1-1 | 1 301 | 1 101 | 1 102 | 1 037 |
| 1-2* | 1 307 | 1 103 | 1 103 | 1 038 |
| 1-3 | 1 308 | 1 103 | 1 104 | 1 039 |
| 2-1 | 1 302 | 1 101 | 1 102 | 1 038 |
| 2-2 | 1 299 | 1 102 | 1 103 | 1 038 |
| 2-3* | 1 313 | 1 105 | 1 105 | 1 039 |
| 2-4 | 1 315 | 1 104 | 1 105 | 1 040 |
| 4-1 | 1 298 | 1 100 | 1 101 | 1 037 |
| 4-2 | 1 317 | 1 103 | 1 103 | 1 038 |

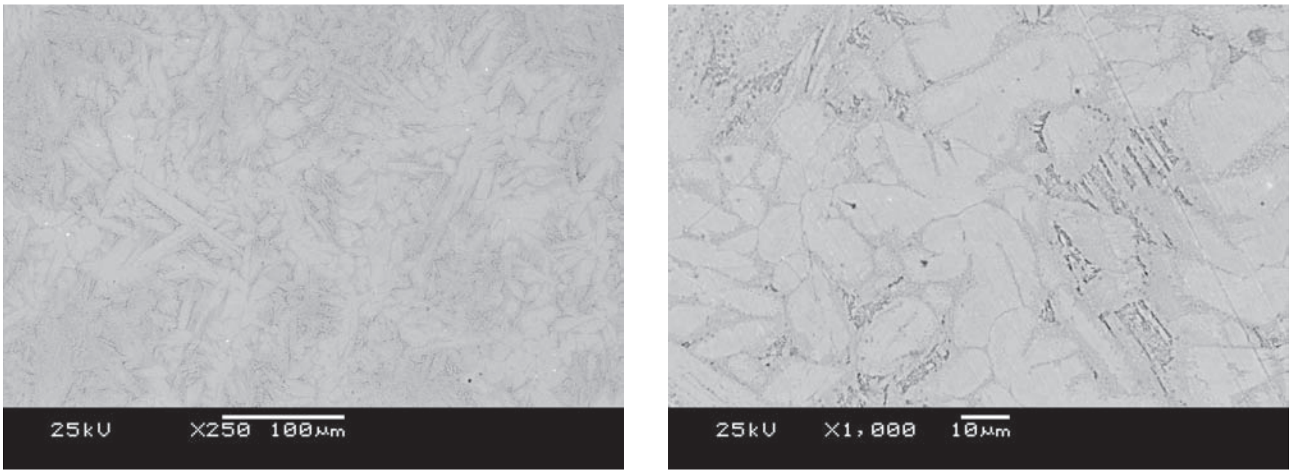
* smelting stage in which along with B slag a stimulating substance was inserted, where 1-2 – 10 % NaCl, 2-3 – 10 % NaF




**a)**




**b)**




**c)**

**Figure 3** Microstructure of aluminum bronze CuAl10Fe4Ni4 refined with the RA1 refiner, heat no. 1-3, for the place: a) the top of the sample, b) ½ of the sample section, c) the core of the sample. Enlargement x 250 and x 1 000

Metallographic researches were carried out with the use of a JEOL JSM - 5 600LV scanning microscope interfaced with an EDS 2 000 x - ray microanalyser – model 500 by IXRF SYSTEMS.

## SUMMARY AND CONCLUSIONS

The results of the researches that have been presented confirmed the possibility of using chemical reagent in the form of calcium carbide and stimulating substances in the process of aluminum bronzes refining. In the samples numerous extractions of iron phase could have been observed. The microstructure after the process of refining with refiners consists of $\alpha$ phase solution and $\alpha + \gamma_2$ eutectoid. There appear extractions of iron phase and $\beta_2$ phase (AlNi). In heats I - III an even distribution of $\alpha$ solution and $\alpha + \gamma_2$ eutectoid can be noticed. The use of stimulating substances in the form of fluorides additionally contributes to remission of the extraction size of iron phase. The use of a chemical reagent contributes to improvement of the mass exchange process, and the use of stimulating substances in the form of haloids intensifies the exchange process. The use of the chemical reagent in the form of calcium carbide and stimulating substances contributes to shaping a protective atmosphere in the basin of the furnace. The received results attest that the selection of new slag mixtures from the point of view of the used stimulators of physicochemical reactions is possible. In heat no. III gas porosity in the core of the sample has been seen. In the samples taken in heats no. I and II while the metallographic researches were carried out no gas porosity has been observed. It might be thought that insertion of stimulating substances in the form of 10 % NaCl i 10 % NaF together with B slag contributed to the porosity remission.The use of refining slag containing calcium carbide and stimulating substance in the form of haloids (NaCl and NaF) for aluminum bronzes refining contributes to the improvement of the alloy quality.

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**Note:** The responsible translator for English language ANGOS, Krakow, Poland