# Slag Systems in Copper Recycling from Cu-Mg Scraps

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## Abstract

Ever increasing metal consumptions starting with the industrial revolution, caused improper and irresponsible utilization of raw material sources. Initially, recycling concepts were purely based on economic motives. Today, however, it covers much broader concepts along with local economic views, such as globalization and environment. The rate of recycling from secondary raw materials is on the rise, and, therefore, not only the primary sources are conserved by the energy savings per unit ton of metal but also the secondary raw materials are rendered to be useful. For instance, the recycling ratio is more than 40% in terms of copper today. This study aims at determining a suitable slag system for the recycling of Cu-Mg scraps in order to obtain a slag with high fluidity. Oxygen and hydrogen absorption of these alloys, as well as the choice of refractories, represent major importance during the pyrometallurgical valorization of Cu and Cu alloys. The optimum experimental conditions for the valorization of Cu-Mg scraps (0.59% Mg) were found to be 1200°C; a slag composition of 16% CaO, 49% FeO, 35% $SiO_2$ + $B_2O_3$; chrome-corundum refractory brick with a ceramic-chemical bonding, and 30 minutes of reaction period. Characterization studies revealed that the slags produced did not contain free silicates [$(Fe,Mg)_2SiO_4$], that their soluble impurity content was below the limits, and that they displayed a glassy appearance.

## 1 Introduction

Copper is one of the oldest semi-precious metals discovered by mankind (7000 B.C.). The distinct color, that the metal and its alloys have, gives copper a special place among the rest of the metals, excluding gold. Moreover, the symbol of copper is the “Mirror of the Venus”, since it is historically the first tool that a woman wanted to see her reflection on. The mechanical properties of copper have been increased by the alloying processes, starting as early as 3000 B.C. (bronze age) in Anatolia, Greece, and India. Copper has been utilized as ornaments, handcrafts, and weapons through the ages, and the need for the metal amplified as the civilization advanced.

Copper plays an important role in today's modern industry owing to its various fields of use. Among the most important features that copper exhibits are its high electric and thermal conductivities, abrasion and corrosion resistance, and elastic limit and forgeability. The electric and electronic industries alone consume about 40% of the world copper production. Copper alloys, i.e. brass, bronze, etc. are also widely used for various purposes [1-4].

Alloying with magnesium increases the toughness of copper without sacrificing its good electric properties. The DIN 17666 standard describes two copper-magnesium alloys: 0.4% Mg and 0.7% Mg. Figure 1 shows the copper-magnesium phase diagram [5].

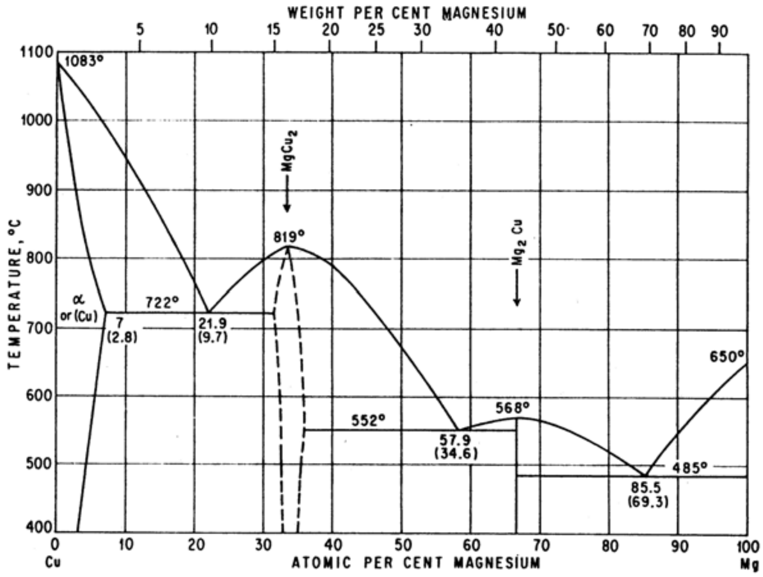



Figure 1: Copper-magnesium phase diagram [5].

As seen from the figure, copper magnesium alloys point to a homogeneous, α mixed-crystal structure below the 1% Mg range. Copper alloys, containing less than 5% alloying elements, are categorized by the DIN 17666 standard, and their special fields of use, lead by the electrotechnical industry are rising [6-8] (CuMg is suitable for electric connections, for connector pins and for overhead telephone lines. In recent years, this alloy has become more and more important as a material for contact wire and catenary cables for high-speed trains.). Magnesium is not only an alloying element in Cu-Mg alloys, but also a de-oxidation component in refining processes on account of its high oxygen affinity [5]. The strength of copper can be increased by adding magnesium, whilst the conductivity is only slightly reduced. By alloying Mg in the range of 0.1 to 0.8 %, the ratio of tensile strength and conductivity can be adjusted very precisely. The electric and mechanical properties of Cu-Mg alloys are given in Table 1.

Table 1: The electric and mechanical characteristics of Cu-Mg alloys [5, 7].

| Alloy Specification | Content (%) | Electric Conductivity ($\Omega^{-1}$ cm$^{-1}$) | Tensile Strength (N/mm$^2$) |
|---|---|---|---|
| CuMg0.4 | Mg 0.3-0.5 | < 48 | 400-600 |
| CuMg0.7 | Mg 0.5-0.8 | < 36 | 600-1000 |

In the year 2001, the world production of refined copper was 14.6 million tonnes, including the production starting from scraps. Today, the recovery from the scraps gained an important position, from the viewpoints of environment and conservation of energy resources [9].

The classical copper refining is based on the selective oxidation of impurities and assembling these oxides in a slag phase. However, the foremost difficulty in terms of copper and its alloys is that of their oxygen and hydrogen entrapment during the oxidation process. Furthermore, the selection of refractory is another important parameter. Processing period is about 24 hours for a typical charge containing complex copper scraps [10].

In the production processes, where scrap is the starting material, it is vitally important that the slags produced are silicate-based (FeO, $SiO_2$, and CaO being the major components), and metallurgically similar in character depending on the scrap utilized. The FeO content of the slags is lower in the plants where secondary production is carried out as compared to that of the primary production. It is quite the opposite in terms of CaO, the alkaline component [11].

# 2 Experimental

## 2.1. Raw material

Copper-magnesium alloy scraps (99.41 % Cu and 0.59 % Mg), kindly supplied by KM Europa Metal A.G., have been utilized in the experimental study. Graphite and corundum-based crucibles were used in the melting operations. The chemical composition and some physical properties of the corundum-based refractories are given in Table 2.

Table 2: Chemical composition (%) and physical properties of the corundum-based refractories.

| $Al_2O_3$ | $Fe_2O_3$ | $Cr_2O_3$ | $ZrO_2$ | porosity (%) | density (g/cm$^3$) | C.C.S.* |
|---|---|---|---|---|---|---|
| 85 | 0.3 | 5 | 2.5 | 12 | 3.3 | 150 |

C.C.S. : Cold Compression strength (N/mm$^2$)

The slag system chosen for refining was $CaO$-$FeO$-$SiO_2$ [16% CaO, 49% FeO and 35% $SiO_2$], which has always been considered in non-ferrous metal production.

## 2.2. Objectives

The $CaO$-$FeO$-$SiO_2$ ternary system (and some varying $B_2O_3$ additions) was selected as the basis to define a suitable slag composition for the refining of Cu-Mg alloy scraps, as described in the literature and as practised industrially.

FeO is one of the oxides that exists in the slag systems of non-ferrous metal production. As seen from Figure 2, the mixtures that melt at low temperatures exist in the mid sections of the $CaO$-$FeO$-$SiO_2$ ternary system. Thus, it can be concluded that the iron oxides and iron silicates are suitable melting agents for the calcium silicates that melt at high temperatures. The lowest melting point (1093°C) of the system is located in a $SiO_2$-rich region. The industrial slag compositions, that are utilized in Cu, Pb and Zn metallurgy, are shown in the dotted region of Figure 2 and can be characterized by their high FeO contents. Primary copper production slags contain 32% $SiO_2$, 52% FeO, 5% $Al_2O_3$ and 3% CaO, MgO [11, 12]. Industrial slags (i.e. Thomas Furnace slags, coming from secondary copper production), however, generally assay 13.9%CaO, 34.5% $SiO_2$ and MgO, FeO, $Al_2O_3$. The area is shown with a triangle.

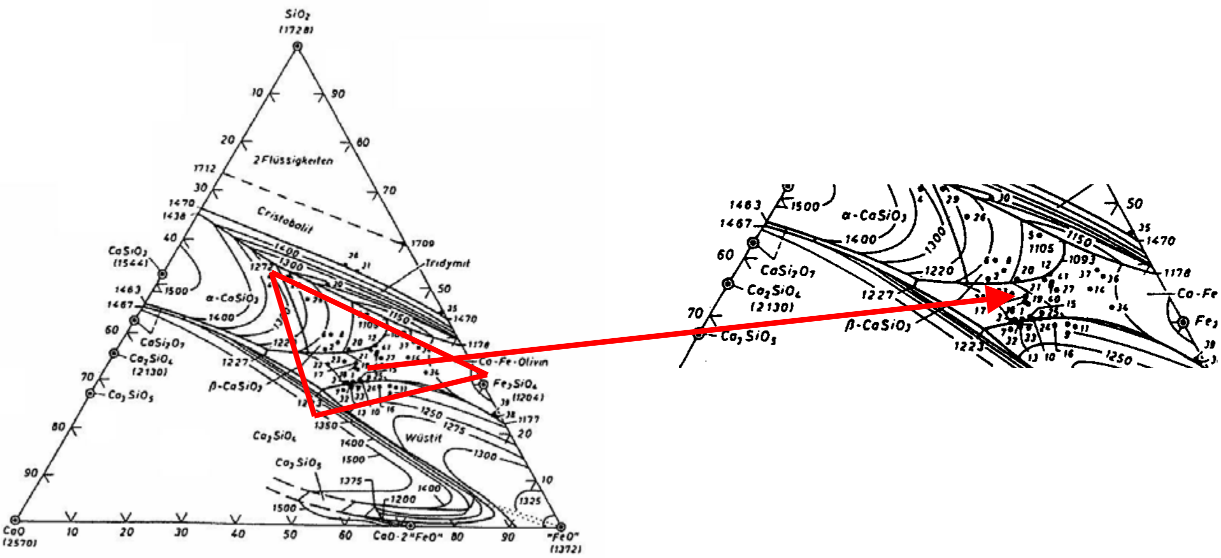



Figure 2: $CaO$-$FeO$-$SiO_2$ system [12].

Briefly, the **$CaO$-$FeO$-$SiO_2$ slag system,** 1200°C operating temperature and 30 minutes retention time were selected as the basis in this investigation to determine the suitable slag system.

## 2.3. Experimental procedure

Experimental work was carried out in two series. The melting operation was conducted in an Eurotherm-controlled Naber-Therm-Furnace and with graphite and chrome-corundum crucibles.

I. The synthetic slag composition, prepared by the help of ternary phase diagram (100 g, MgO-$Cu_2O$-CaO-FeO-$SiO_2$-$B_2O_3$) was melted at 1200°C in a chrome-corundum crucible for 30 minutes and cast into a copper die.
II. Approximately 200 g Cu-Mg alloy scrap was melted both in graphite and in chrome-corundum crucibles at 1200°C, and then the previously prepared 10 g slag mixture (49% FeO, 16% CaO, 35% $SiO_2$, and 10-50% $B_2O_3$) was added to the molten alloy. After about 30 minutes of waiting period, the blend was cast into a copper die.

Furthermore, the slag-refractory interaction was studied comparatively for both groups. Slag sample was ground in a vibrating mill after metallic copper was separated. XRD (Philips PW 3026), a scanning electron microscope (JEOL, JSM T330), AAS (Perkin Elmer 1100), and ICP (Spectro) instruments were utilized for the characterization of slag. The experimental flow sheet was given in Figure 3.

Preparation of the synthetic slag and alloy
↓
Charge of slag and/or alloy into the crucibles
↓
Melting, 1200°C
↓
Casting → Analysis
↓
Cutting crucibles into halves
↓
Calculation of the slag interaction region

Figure 3: Major steps of the experimental procedure.

# 3 Results and Discussion

In general, most slags can be defined as the oxide mixtures that form chemical compounds and eutectic combinations. Some chemical and physical changes occur during the slag formation from these oxides, which chemically react with each other and melt as a homogeneous liquid phase. Pyrometallurgical reduction processes usually involve slag formation. The major parameters that determine the success of a melting operation are viscosity, electric conductivity, and oxygen content of the slag. Viscosity primarily determines the flow characteristics of a slag and is a function of temperature and composition. Within the framework of this research, it is concluded that the synthetic slag composition, temperature and the crucible material affect the fluidity of molten copper and slag, both during the melting and the casting of molten metal and slag.

## 3.1. Effect of Slag Composition

Technical slags contain numerous components [FeO-CaO-$SiO_2$ (for non-ferrous metallurgy)]. Non-ferrous metals' slags usually exist within the fayalite composition "FeO-$SiO_2$" and in the CaFe-olivine region. Iron oxide, FeO, generally forms low melting point mixtures with CaO and $SiO_2$. As a result of the literature investigation, synthetic slag compositions were formed within the CaO-FeO-$SiO_2$ ternary [16% CaO, 49% FeO, and 35% $SiO_2$], which is the basic system for non-ferrous metal production systems. Synthetic slag compositions of the first group of experiments without additions of $B_2O_3$ and cast weights after the melting are given in Table 3. Additionally, a new synthetic slag was created by adding $B_2O_3$ (10-50% of the charge material) to this slag composition.

Table 3: Synthetic slag compositions (%) and cast weights (g) [1200°C, 30 min].

| MgO | $Cu_2O$ | CaO | FeO | $SiO_2$ | $B_2O_3$ | Σ % | Cast Weights |
|---|---|---|---|---|---|---|---|
| 3 | 50 | 7.5 | 23 | 16.5 | - | 100 | 78.7 |
| 5 | 50 | 7.2 | 22 | 15.8 | - | 100 | 90.9 |
| 7 | 50 | 6.9 | 21 | 15.1 | - | 100 | 87.0 |
| 9 | 50 | 6.6 | 20 | 14.4 | - | 100 | 73.6 |
| 11 | 50 | 6.3 | 19 | 13.7 | - | 100 | 70.4 |
| 13 | 50 | 5.9 | 18 | 13.0 | - | 100 | 27.9 |

Cast weight and slag fluidity decrease with increasing MgO content. Melting and casting operations were suitably conducted until 9% MgO content, but a crust formation on the liquid surface and decreased fluidity were observed for higher MgO contents; i.e. a slag sample with 13% MgO content was very viscous and not flowing easily. The change in cast weight depending on MgO content of the slag is illustrated in Figure 4. The low cast weight, observed at 3% MgO content is the result of the first experiment carried out with the refractory crucible. Boron oxide ($B_2O_3$) additions were made to improve the fluidity of the synthetic slag. The slag interaction and the fluidity were observed during the melting and casting operations. The change in cast weights with increasing $B_2O_3$ additions is given in Table 4. As seen, the fluidity improves and cast weights rise with escalating $B_2O_3$ additions. The necessary amount of $B_2O_3$ is about 20%, at the end of first group of experiments. Some slag-refractory interaction problems might be experienced for $B_2O_3$ ratios exceeding 20%.

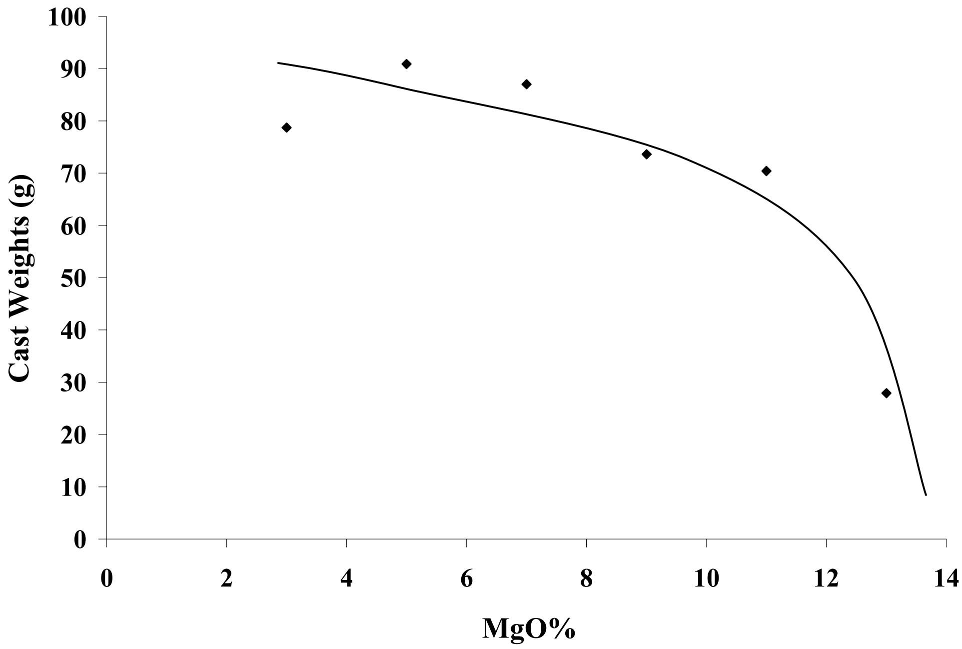



**Figure 4.** Cast weights *vs*. MgO content of the slag.

**Table 4.** Optimization of the $B_2O_3$ amount.

| MgO % | $Cu_2O$ % | CaO % | FeO % | $SiO_2$ % | $B_2O_3$ % | Σ % | Cast Weights (g) |
|---|---|---|---|---|---|---|---|
| 13 | 50 | 5.2 | 15.6 | 11.2 | 5 | 100 | 28.2 |
| 13 | 50 | 4.4 | 13.2 | 9.4 | 10 | 100 | 39.3 |
| 13 | 50 | 3.5 | 10.8 | 7.7 | 15 | 100 | 74.0 |
| 13 | 50 | 2.7 | 8.4 | 5.9 | 20 | 100 | 88.0 |

A Cu-Mg alloy scrap of 200 g was used in the second set of experiments, where both graphite and chrome-corundum crucibles were utilized. The fluidity of the slag obtained was very low for the melting operations where no $B_2O_3$ additions were made. On the contrary, casting operations were conducted flawlessly where $B_2O_3$ additions were made. The optimum range of $B_2O_3$ addition was chosen to be 10-30% in this set of experiments. Slag fluidity improves unnoticeably for $B_2O_3$ additions of less than 10%, while it increases remarkably for higher ratios. Thus, the effect of $B_2O_3$ additions on slag fluidity cannot be ignored.

## 3.2. Effect of Refractory Composition

Refractory materials are important part of the metallurgical industry, the maximum useful lives of which are attempted to be extended to the high temperature range and corrosive environment. The effect of reactions that take place between the refractories and gas, slag, and liquid metal can be perceived by the abrasion, melting, and fluidity behaviours. In metallurgical smelting processes, it is accepted that each slag component has a different corrosive effect. Therefore, for an extended service life of a furnace, high corrosion resistance is expected from the refractories, which eventually increases the efficiency and the product quality. The chemical and physical properties of the chrome-corundum refractory used in the experimental study are given in Table 2. According to the literature [13, 14], slag interaction increases with escalating temperature and fluidity. The effective parameters are: composition of the refractory material, temperature, viscosity, porosity, and the furnace atmosphere.

The crucibles were cut in half by the end of the experiment and the slag interaction regions were determined by the naked eye. Figure 5 displays the interaction observed in a ceramic-chemically bonded chrome-corundum crucible. As seen, the interaction region is small and there is deterioration on the crucible wall.

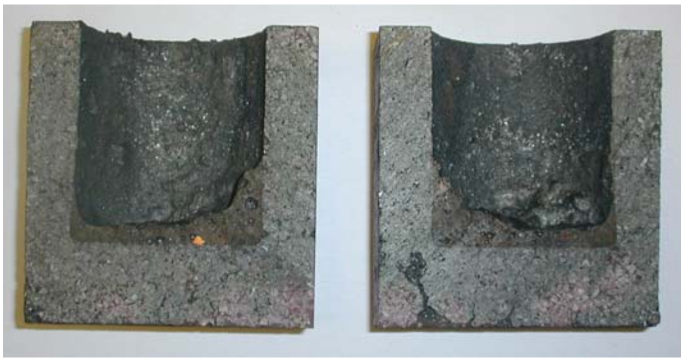
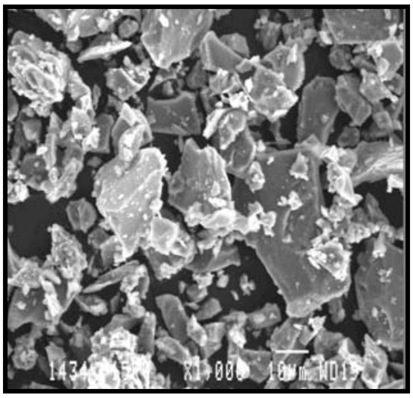


Figure 5: Slag-refractory interaction in chrome-corundum crucible.

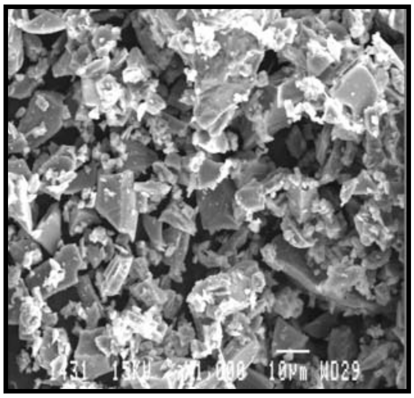
The low porosity value of the refractory is one of the determining factors of an insignificant interaction between the chrome-corundum refractory and the slag, since the slag cannot penetrate into the pores of the crucible.

## 3.3. Slag Characterization

Electron micrographs (Figure 6) of the ground slag samples, with and without $B_2O_3$ additions, both exhibit structures that contain glassy and sharp-edges grains.




**a-**with $B_2O_3$

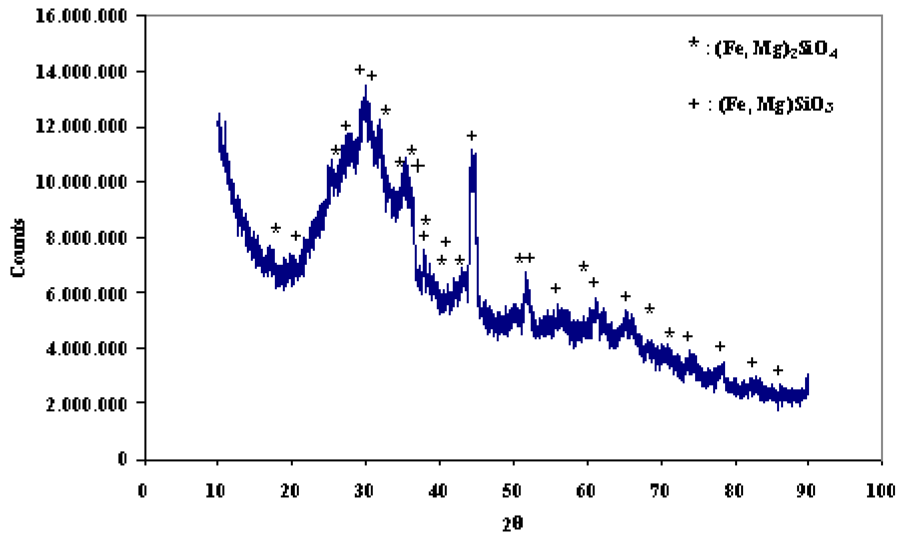



**b-**without $B_2O_3$

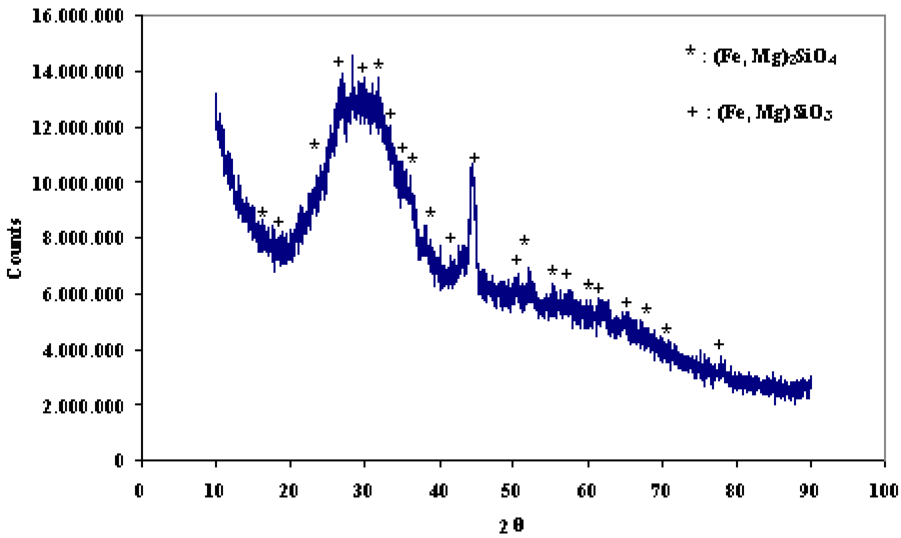
Figure 6: SEM micrograph of the slags (magnification: 1000X)

X-ray diffraction patterns of the ground slag samples without $B_2O_3$ and with $B_2O_3$ additions are displayed in Figure 7. The structure, determined by the x-ray diffraction, corresponds to

$$(Fe,Mg)_2SiO_4$$




**(a)**




**(b)**

Figure 7: X-ray diffraction patterns of the slag samples a) without $B_2O_3$, b) with $B_2O_3$.

X-ray analyses revealed no free $SiO_2$, indicating that it is bonded by Fe and Mg according to the formula given above. Thus, no "free $SiO_2$ problem" can be associated with these slags. Usually slags containing this high amount of Copper are treated in secondary Copper smelters. Due to the high valuable metal content there are not suitable for any other product (e. g. road construction, sandblasting).

# 4 Conclusion

1. Cu-Mg scraps were melted with a synthetically prepared slag [16% CaO, 49% FeO and 35% $SiO_2$ + 10-50% $B_2O_3$] at 1200°C.
2. Magnesium that existed in scrap moved 100% to the slag structure. Mg content of the cast metal was 0.001%.
3. Synthetically prepared slag [50 % $Cu_2O$, 5.9-7.5 % CaO, 18-23 % FeO, and 13-16.5 % $SiO_2$] has a theoretically low viscosity (5.2 P), alkalinity (0.83), and acidity (1.2). As indicated in the literature, viscosity values of non-ferrous metal slags are usually between 2 and 8 P (1200-1300°C).
4. Melting and casting operations were impeccably conducted until 9% MgO content, but a decreased fluidity was observed for higher MgO contents, resulting in a sticky and viscous slag, improper for casting. It is desired to keep the MgO content of slags as low as possible. Directly-bonded chrome-corundum refractory bricks showed an effective strength in this system.

5. For the best slag fluidity, 13% MgO ratio is optimized with 20% $B_2O_3$ addition.
6. The slag composition, as determined by the x-ray diffraction, corresponds to the $(Fe,Mg)_2SiO_4$ structure, and the most important of all, there is no free $SiO_2$.
7. Refractory crucible with ceramic-chemical bonding showed no slag interaction owing to its low porosity and bond structure.

In conclusion, the slag composition selected to melt the Cu-Mg alloy scraps was determined to be suitable by the experimental study conducted. The utilization of the slags obtained from the secondary operations can be decided by the market conditions. Usually the slags are treated in secondary Copper smelters.

# 5 Acknowledgments

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