Journal of the University of Chemical Technology and Metallurgy, 40, 3, 2005, 235-238

METHOD FOR OBTAINING OF COPPER-PHOSPHORUS ALLOYS

B. Lucheva, Ts. Tsonev and R. Petkov

University of Chemical Technology and Metallurgy
8 Kl.Ohridsky, 1756 Sofia
E-mail: plasma@uctm.edu

Received 01 July 2005
Accepted 31 August 2005

ABSTRACT

The main purpose of this work is to investigate the synthesis of Cu-P alloys by a carbothermal reduction of copper phosphate. In order to realize this aim copper phosphate is synthesized via the reaction of copper (II) oxide and phosphoric acid. The mechanism of the carbothermal reduction of the copper phosphate with charcoal was examined using DTA/TG and XRD. The reduction is carried in two stages – in the first stage copper oxide is reduced to metallic copper at 350 - 400^o C and the second stage is reduction of P_2O_5 to elementary phosphorus and its solution in copper at temperature above 650^o C. To avoid phosphorus losses a predetermined quantity of copper and/or copper oxide is added into the initial copper phosphate. The obtained results are used to develop a technology for producing Cu-P alloys. The phosphorus content in these alloys may be of the order of 7 to 12,5 % and they can be successfully applied in the non-ferrous metallurgy for copper alloys deoxidation and aluminum alloys modification.

Keywords: Carbothermal reduction, copper-phosphorus alloy, copper phosphates.

INTRODUCTION

Copper-phosphorus alloys containing 7 to 12 % phosphorus have wide application in the non-ferrous metallurgy mainly for deoxidation of copper alloys, for modification of aluminum alloys, for production of phosphorus bronze and for brazing.

There are several methods for producing of copper-phosphorus alloys, which can be divided into three groups:

- By reaction directly between red elementary phosphorus and molten copper at raised temperature [1];
- By reaction between phosphine and copper oxides or halogens at 700-900^{o}C [2];
- By reduction of phosphorus from its oxygen compound, melting of copper and phosphorus dissolving in it. Hydrogen [3], aluminum, magnesium or calcium as a reducer can be used. As oxygen compound of phosphorus P_2O_5, apatite or phosphorite concentrate can be used [4, 5]. Disadvantages of the existing methods for Cu-P alloys production are - using of deficit, expensive, toxic and ecologically dangerous red phosphorus, necessity of hermetic equipment providing, potentially high ecological risk of white phosphorus emission, high energy consumption.

Phosphorus is not produced in Bulgaria, and there is no import in the last years as well. This is the reason to search for a new method for Cu-P alloys production, meeting the needs of the Bulgarian market as the main purpose of this work.

EXPERIMENTAL

Copper phosphate synthesis

In order to realize the aim, the obtaining of Cu-P alloys by carbothermal reduction of copper phosphate was investigated.

Copper phosphate is not produced in Bulgaria, because of this it has to be synthesized. The following Cu^{2+} -ion containing phosphates have been described in the literature: $Cu_2(PO_3)_4$, $Cu_2P_2O_7$, $Cu_3(PO_4)_2$, $Cu_4P_2O_9$ and $Cu_5P_2O_{10}$, as well as Cu^+ - ion - $CuPO_3$ and one phase that contains the Cu^+ and Cu^{2+} - Cu_2PO_4. In general, these compounds have been prepared by using one of two methods [6]:

- reaction of a solid copper compound, such as $CuCO_3$, CuO, $CuCO_3.Cu(OH)_2.H_2O$ or $CuCl_2$ with $(NH_3)_2HPO_4$, $NH_3H_2PO_4$, BPO_4 or H_3PO_4. This type of reaction has been used to synthesize $Cu_2(PO_3)_4$, $Cu_2P_2O_7$, $Cu_3(PO_4)_2$, $Cu_4P_2O_9$ and $Cu_5P_2O_{10}$.
- precipitation from solution, followed by dehydration and calcinations in air. This type of reaction has been used to synthesize $Cu_2P_2O_7$, $Cu_3(PO_4)_2$.

In this work the synthesis of copper phosphate was performed via reaction of copper (II) oxide and 75% phosphoric acid:

$$3CuO + 2H_3PO_4 \longrightarrow Cu_3(PO_4)_2 + 3H_2O \qquad (1)$$

The obtained product was dried at 105° C for a period of 2 hours. XRD analysis (Fig. 1,a) shows the presence of two compounds - $Cu_8(PO_3OH)_2(PO_4)_4.7H_2O$ and $Cu_3(PO_4)_2.H_2O$. The behavior of this phosphate (mixture of phosphates) at elevated temperatures was examined with DTA/TG (Fig. 2) by heating a specimen in air at a rate of 10° C/min over a temperature range of 20-1000°C.

Samples of initial copper phosphates were calcinated in a corundum crucible for 1 hour at 300, 450, 650 and 800°C and were analyzed by XRD for identification of the resultant phases (Fig. 1).

The DTA/TG curve had three endothermic peaks at about 240, 357 and 620° C and one exothermic at about 680° C. The first endothermic peak at 240°C was considered to be due to dehydration. The mass loss at this temperature is 5,75 %. The second peak at 357°C is considered to be due to thermal decomposition of $8CuO.3P_2O_5$ according to the reaction:

$$8CuO.3P_2O_5 \xrightarrow{300-400^o C} 2Cu_3(PO_4)_2 + Cu_2P_2O_7 \qquad (2)$$

XRD analysis confirmed that at 300°C $Cu_3(PO_4)_2$ and $Cu_2P_2O_7$ (Fig. 1,b) exist. Copper pyrophosphate probably decomposes above 400°C, because at temperature in a range of 450-800°C only $Cu_3(PO_4)_2$ exists according to the XRD analysis (Fig. 1, c, d, e). The exothermal peak at 680° C is likely connected with the appearance of an amorphous copper phosphate.

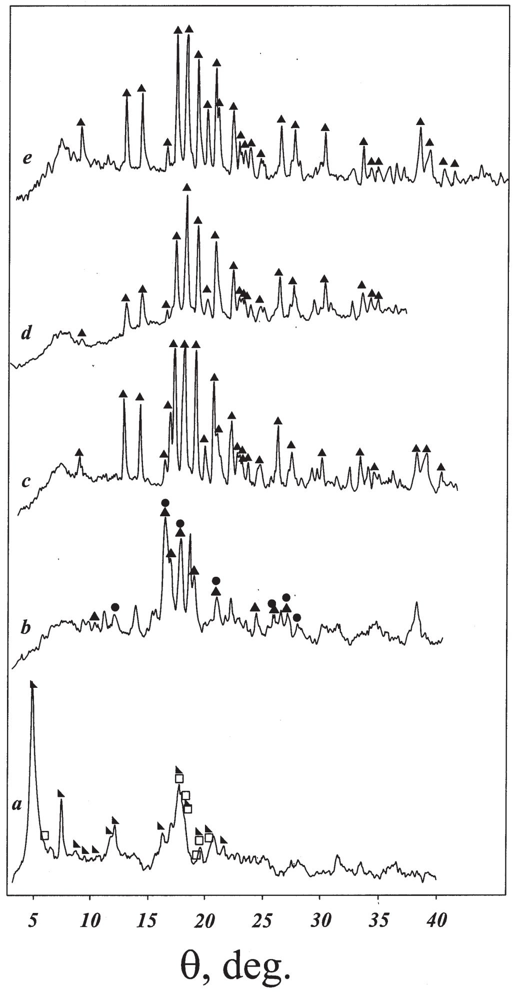

Fig. 1. XRD of copper phosphate.
a– 105° C; b – 300° C; c – 450° C; d – 650° C; e – 800° C
▲ - $Cu_3(PO_4)_2$; ● - $Cu_2P_2O_7$; □ - $Cu_3(PO_4)_2.H_2O$; ◣ - - $Cu_8(PO_3OH)_2(PO_4)_4.7H_2O$

Carbothermal reduction of copper phosphate with charcoal

The copper phosphates described above is mixed with charcoal (-0,25 mm) by milling.

Samples of this mixture were analyzed by DTA/TG (Fig. 4) in order to investigate the reduction mechanism. Other samples were heated at 300, 450, 650 and 800°C in a graphite crucible and analyzed by XRD (Fig. 3).

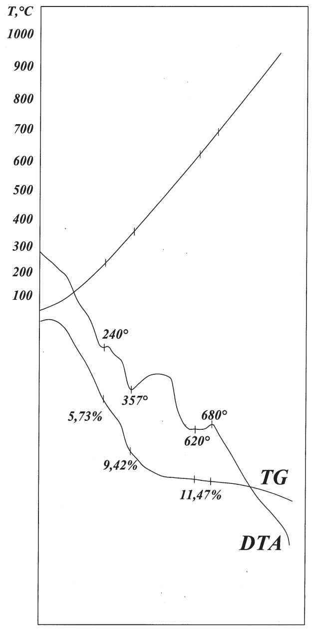

Fig. 2. DTA of copper phosphate.

XRD analysis of copper phosphate as well as copper phosphate with charcoal (Fig. 1b and Fig. 3b) at 300°C are identical, thus a carbothermal reduction does not begin.

Cu° and Cu_2O appeared at 450°C according to XRD. The three most intense peaks of $CuPO_3$ are very similar to the three most intensive peaks of Cu° which suggest that $CuPO_3$ may exist. These crystalline phases are dispersed in a glass phase which exists also at 650°C. Only copper as a crystalline phase was identified at 650°C. The sharp exothermic effect at 540°C (Fig. 4) is due to copper oxide reduction to metallic copper, and carbon oxidation.

Copper-phosphorus equilibrium diagram shows that the eutectic temperature is 714° C and phosphorus content is 8,4 mass %, so the endothermic effect at 714°C (Fig. 4) is due to eutectic formation.

The above mentioned results assume that the first stage of carbothermal reduction – reduction of copper oxide to metallic copper is carried out at a temperature in the range of 450-650°C. The second stage is reduction of P_2O_5 to elementary phosphorus and its solution in copper at temperature above 650°C. XRD data shows that copper phosphide exist at 800°C (Fig. 3, d). The XRD of copper phosphide, obtained by carbothermal reduction is represented in Fig. 3, e.

The synthesis of copper phosphide may be described by means of the following reactions:

$$2Cu_3(PO_4)_2 + 3C \longrightarrow 3Cu_2O + 2P_2O_5 + 3CO \quad (3)$$

$$Cu_2O + C \longrightarrow 2Cu + CO \quad (4)$$

$$P_2O_5 + 5C \longrightarrow 2P + 5CO \quad (5)$$

$$3Cu + P \longrightarrow Cu_3P \quad (6)$$

Thus, the overall reaction can be written as:

$$Cu_3(PO_4)_2 + 8C \longrightarrow Cu_3P + P + 8CO \quad (7)$$

Experiments on carbothermal reduction of copper phosphate based on reaction (7) were carried out at 1100°C depending on the holding time. The chemical analyses of the obtained Cu-P alloys are presented in Table 1.

The elementary phosphorus is produced in reaction (7) whereas it is in a gaseous state at process conditions. To avoid phosphorus losses to the charge CuO and/or Cu should be added. Thus reaction can be expressed as follows:

$$3CuO + Cu_3(PO_4)_2 + 11C \longrightarrow 2Cu_3P + 11CO \quad (8)$$

The carried out experiments were based on the stoichiometry of reaction (8) - in order to realize the carbothermal reduction for every 100 g copper contained in the charge, 35 g carbon or 40g charcoal (80% carbon in charcoal) were necessary.

The mixture, containing 58 mass % CuO; 24 % H_3PO_4 and 18 % charcoal was treated in an induction

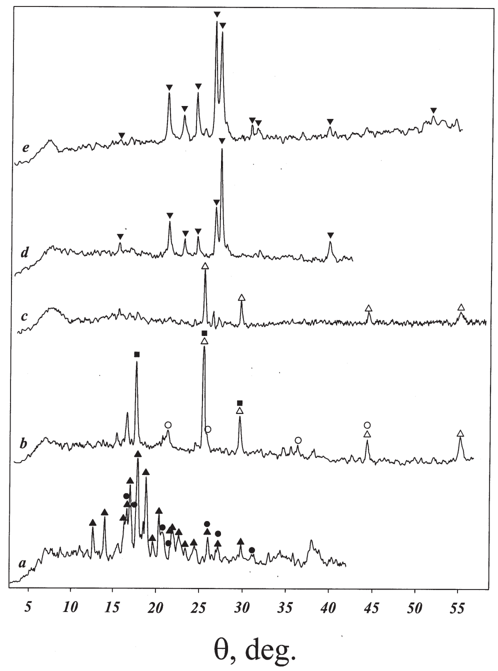

Fig. 3. XRD of copper phosphate with charcoal.
a – 300°C; b – 450°C; c – 650°C; d – 800°C; e – 1100°C
▲ - $Cu_3(PO_4)_2$; ● - $Cu_2P_2O_7$; △ - Cu; ▼- Cu_3P; O – Cu_2O;
■ - $CuPO_3$

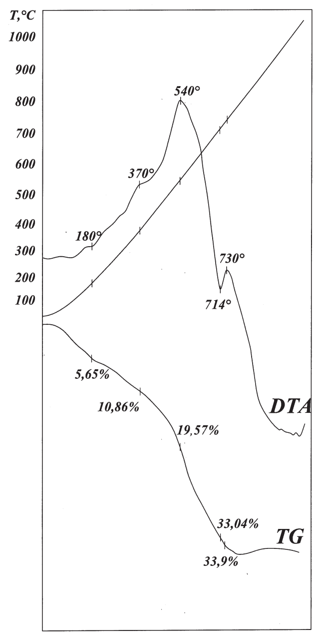

Fig. 4. DTA of copper phosphate with charcoal.

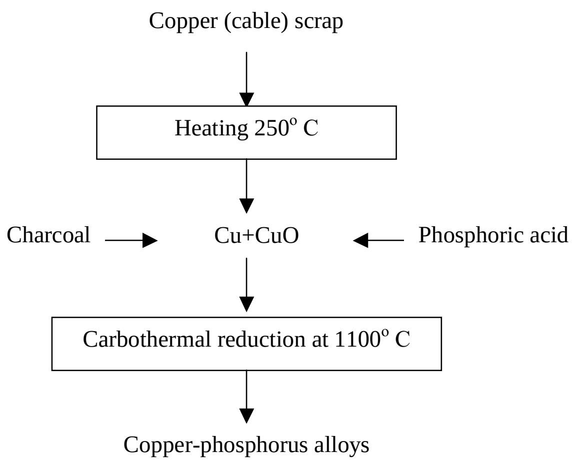

Fig. 5. Technological scheme for Cu-P alloys production.

furnace in a graphite crucible at a temperature of 1100°C for 1 hour. The resulting copper-phosphorus alloy has 12,6 % phosphorus.

The mixture, containing 38 % Cu, 16 % CuO; 26 % H_3PO_4 and 20 % charcoal was also treated in an induction furnace in graphite crucible at a temperature of 1100°C for 1 hour. The resulting copper-phosphorus alloy has 11,3 % phosphorus.

The described results were used to develop the technology for Cu-P alloys production. A simplified scheme of the technology is shown in Fig. 5.

Table 1. Chemical analyses of Cu-P alloys.

Holding time at 1100° C, hours	Mass of the charge, g	Mass of the Cu-P alloys, g	P, %	Cu, %
1	25	10,7	10,9	89,1
2	25	10,8	10,6	89,4
3	25	9,7	9,6	90,4

Phosphorus content in these alloys may be of 7 up to 12,5 % depending on the metallic copper excess in respect to the stoichiometric quantity for reaction (8) and they can be successfully applied in non-ferrous metallurgy for copper alloys deoxidation and aluminum alloys modification.

CONCLUSIONS

• Carbothermal reduction of copper phosphate with charcoal was studied using DTA/TG and XRD. Reduction is carried in two stages – in the first stage copper oxide is reduced to metallic copper at 350-400° C and the second stage is reduction of P_2O_5 to elementary phosphorus and its solution in copper at temperature above 650°C.

• A technology for Cu-P alloys production is developed. The technology is simple, economical and ecological, and allows for utilization of cheap copper scrap.

REFERENCES

1. O. Peterenko, Method of preparing copper phosphides, RU 2108965, 1998, (in Russian).
2. H. Buckholtz, G.Miller, Method of making eutectic mixture of copper and tricopper phosphide, US 5019157, 1991.
3. I. Kolesnikova, V. Serba, Poluchenie splavov Cu-P metodom vodorodnovo vosstanovlenie fosfatov medi, Metalli, 1999, 6, p.22-25, (in Russian).
4. V. Serba, Method for producing phosphorus-containing alloy, RU 2080405, 1997, (in Russian).
5. I. Kolesnikova, V. Serba, Poluchenie splava Cu-P s izpolzuvaniem apatitova koncentrata, Metali, 1999, 1, p.7-10, (in Russian).
6. B. Carlos, E. Specht, L. Anovitz, Crystalline Copper Phosphates: Syntesis and Thermal Stability, J. Am. Soc., **80**, 12, 1997, p.3133-3138.