Obtaining of Copper Metallic Powders from Worn-Out Catalysts Using the Iron Cementation Procedure

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For obtaining copper powders out of worn-out catalysts by iron cementation, a series of factors that influence their obtaining of acid solutions, both quantitavely and qualitatively, were studied, with a view to their utilization as alternative solutions to the copper powders obtained by mechanical procedures.

Keywords: copper, metallic powders, cementation, iron

The powder metallurgy has been utilized since ancient times starting with China and Egypt where, even in 5000 BC, iron powder was obtained in order to manufacture high temperature pressing products. Copper powder was found in the grave of Tutankhamon, while the American Incas used to manufacture platinum jewels, probably resorting to powders, before the Spanish conquest.

The technical and economic progress has lead to the development of the powder metallurgy, especially due to the advantages offered to products and materials (price, quality, precision class).

The powder obtaining methods can be classified as mechanical, physical-chemical, chemical and physical-chemical methods, as they are strongly related to their utilization in fields such as physics and chemistry, thus having an interdisciplinary character.

The cementation procedure requires an acid solubilization of the metallic copper from worn-out catalysts, using H_2SO_4, and the powdery metal is then extracted from the final solution. The capitalization of worn-out catalyst materials as metallic powders is related to the modern technical trends regarding the reducing of the environmental impact caused by wastes and of storing costs [1-5].

Experimental part

In order to obtain copper powder from acid solutions, was studied the cementation procedure using iron as cementation metal.

As far as the cementation is concerned, we resorted to a plant made up of a round-bottomed flask endowed with four weeks, a stirrer, heating-cooling possibilities (temperature control), a back-flow condenser and possibilities regarding the temperature measurement.

The copper sulphate solution was introduced into the flask and then the amount of cementation metal corresponding to the α metal excess was added.

The temperature could be maintained within the imposed limits by controlling the flask temperature. After the cementation period expires, the flask cools off, the powder is washed and then dried inside an oven.The *p*H correction was possible due to the use of HCl conc. The copper powder was washed directly on the filter in order to remove the metallic sulphates and the free acid retained by powders as mother solution.

The quality of the washing influences not only the purity of the powder, but also its stability regarding the air oxidation.

The copper powder was dried at a temperature of 60-80°C, in a nitrogen flow in order to avoid oxidation.

Copper powders characterized by humidities of 0.1-0.2% and even lower were obtained.

The results regarding the influence of several factors on the cementation of copper from acid solution by resorting to iron are presented in the following paragraphs.

The influence of the experiment period

The experiments took place at temperatures that varied between 25 and 50°C. The optimum temperature is of 30-35°C as the reaction is exothermal, then the temperature of the reaction mode rises up to 35-40 °C and at this point the cementation takes place under good conditions. A higher temperature is not recommendable, as it encourages the oxidation of the metallic copper – Cu_2O.

The influence of the average reaction pH

During the experiments a $CuSO_4$ 2N solution was used, the excess of the cementation metal was α = 1.1 and the cementation period was of seven hours [6].

Table 1 presents the variation of the copper cementation efficiency depending on the *p*H.

The influence of the cementation metal excess, α

The excess of the reduction agent has a specific temperature when a superior quality for the copper powder is required.

The results of the experiments regarding the efficiency variation depending on α are presented in table 2.

The influence of the concentration of the initial solution in copper.

This concentration have no significant influence on the cementation efficiency, as the experiments are made using solutions with the following concentrations: 0.1, 0.2 and 2N.

The influence of the powder washing procedure

The indicators of the powder washing procedure depends on the properties of the powder, on the water temperature and consumption.

A dispersed fine powder makes its own processing more difficult to achieve. While the water temperature rises, its consumption decreases, as well as the impurity content, which makes the process faster.

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Table 1
VARIATION OF THE COPPER CEMENTATION EFFICIENCY DEPENDING ON *p*H

Current No.	The solution pH	ml HCl conc. added to 100 mL $CuSO_4$	The concentration efficiency
1	2.1	0.1	19.92
2	2.0	0.2	20.41
3	1.9	0.4	28.24
4	1.8	0.7	58.23
5	1.7	1.0	83.90
6	1.6	1.3	89.35
7	1.4	1.5	91.58
8	1.4	1.7	90.21

Table 2
VARIATION REGARDING THE EFFICIENCY OF THE COPPER CEMENTATION USING IRON, DEPENDING ON α

Current No.	The Normal Situation the $CuSO_4$ solution / (mL. sol.)	Cementation metal excess, α	The process duration, [h]	Cementation efficiency η, [%]	
				Iron splinter	Iron plate
1	1N/500	0,90	7	90,83	84,14
2	1N/500	0,95	7	91,65	85,33
3	1N/500	1,00	7	92,34	86,09
4	1N/500	1,05	7	93,28	87,54
5	1N/500	1,10	7	97,00	89,65
6	1N/500	1,15	7	97,70	90,22
7	1N/500	1,20	7	98,11	90,83
8	1N/500	1,25	7	98,20	91,65

Table 3
IMPURITY CONCENTRATIONS IN THE WASHED POWDER SAMPLES

Current No.	The Cl^- concentration, [%]	The SO_4^{2-} Concentration, [%]
1	0.023	-
2	0.033	-
3	0.060	-
4	0.0294	-

A full washing is achieved at a consumption of 5-9 water volume for one powder mass unit; however, after the first three cycles, more than 90% of sulphate was washed.

The powder washing took place when the consumption was 3-5 times higher than the powder mass, at a temperature of 40-50°C; under these conditions the process proved to be highly qualitative.

Table 3 presents the impurity concentrations obtained when hot water (40-50°C) was used for the washing procedure – ratio: L/S=10/1.

Results and discussions

The obtaining of the copper powder by iron cementation was performed out of copper sulphate acid solutions obtained from worn-out catalyst, with an average cementation of 63.1% Cu^{2+}.

The results of the study concerning the influence of several factors on the cementation related to these solutions were presented in table 1-3.

Table 1 slightly emphasizes the fact that the highest cementation degree – 99.58% was achieved when the solution *p*H was 1.5; when this value is surpassed, the cementation efficiency decreases, which indicates a redissolution of the case-hardened copper.

The disadvantage of the copper precipitation from a solution with a *p*H = 1.5 is that it requires an advanced washing of the powder after filtering it in order to remove the Cl^+ ion, the ratio being L/S=10-15/l, which leads to a decrease of the efficiency caused by the losses that takes place during the washing-filtration operations.

Table 2 indicates that the efficiency of the copper cementation when the iron is used as case-hardener has a rising tendency, depending on the metal excess and reaches high values with the small smoothing iron due to the larger surface.

A reduction agent excess α higher than 1.2 improves the powder quality and it can be found as impurity in the copper powder (fig. 1).

The period required by the process depends on the type of the reducing metal surface and it proves to reach the optimum level when the small smoothing iron is used.

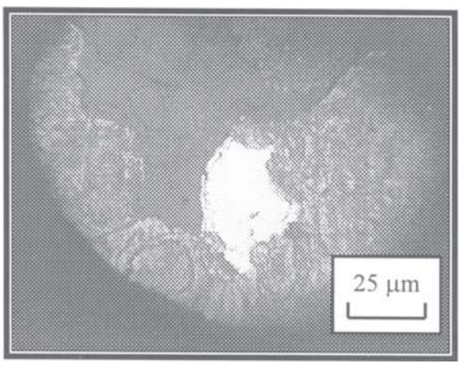

Fig. 1. Copper Powder particle containing an iron "core"

Even if the concentration of the initial copper solution has not a significant influence, as the copper limit is established by the $CuSO_4$ solubility in water at 20°C, we still have to take into account the fact that high copper concentrations make cementation faster; however, the product is dense and difficult to remove from the metal that it fell down on.

The inferior limit of the concentration can be low enough, however, this situation requires large solution volumes that are difficult to work with.

A complete washing is achieved when there is a consumption of 5-9 water volumes for one mass unit, however, after the first three cycles more than 90% of the sulphate was washed.

Conclusions

The copper from the acid technological solutions obtained from worn-out catalysts can be efficiently recovered as metallic powders by direct processing.

The studies regarding the extraction of copper from solutions as metallic powder by resorting to the iron cementation establishes the way a series of factors influences the cementation degree (temperature, the nature of the environment, concentration, contact surface, the process duration etc.).

These powders can be directly utilized in the Powder Metallurgy in order to obtain products related to the machine manufacturing industry, as they can successfully replace the coppers powders obtained by traditional procedures.

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