

## STUDY OF THE SILVER IONS CEMENTATION AFTER MECHANICAL ACTIVATION OF CEMENTATOR

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### Abstract

Thiosulphate leaching of silver is a proposed alternative to cyanide or thiourea leaching for certain types of refractory silver ores and secondary resources. Traditional method for the recovery of rare metals from various sources by hydrometallurgy is leaching followed by cementation onto zinc powder and electrowinning. Silver cementation is an inexpensive and simple way to deposit thin metal films. Cementation of silver onto zinc powder, treated by mechanical activation, from thiosulphate solutions was studied by measuring  $\text{Ag}^+$  ions concentration in the solution. The high energy attrition and planetary ball milling in methanol was applied for the mechanical activation of zinc powder. The changes in the particle size distribution and surface area of cementator, occurring during mechanical treatment have been registered. The observed changes in the physicochemical properties illustrate the possibility of applying activation to modify the surface and/or volume properties of zinc powder and its further application in well-known hydrometallurgical process of cementation. The study was also focused on the changes in the concentration of zinc and pH as a function of reaction time. The morphology of cementation products on zinc powder was also investigated.

### Introduction

Silver is a precious metal well known for its singular beauty as well as for its utilization in electronic technology, photography and medical applications. The most popular electrolytes for rare metals plating are the cyanide – based rare metals plating baths. Besides that, the cyanide leaching processes have also been used by the mining industry for over 100 years in the extraction of rare metals [1]. The current use of cyanidation techniques to leach rare metals from its various sources is undesirable from an environmental point of view. In recent years, cyanide leaching has been banned in many regions due to environmental concerns [2]. This is due predominantly to the acute toxicity of cyanide, effectively demonstrated by various disasters: Baia Mare, Romania in 2000; Tolukuma, Papua New Guinea in 2000; Placer, Philipines in 1999; Los Frailes, Spain in 1998; Homestake, South Dakota, USA in 1998; Zortman, Montana, USA in 1998; Gold Quarry, Nevada, USA in 1997; Omai, Guyana in 1995; Harmony, South, Africa in 1994; Brewer, South Carolina, USA in 1992; Summitville, Colorado, USA in 1992 and Carson Hill, California, USA in 1989.

Thiosulphate leaching of rare metals is a proposed alternative to cyanide or thiourea leaching for certain types of refractory silver ores and secondary sources [3-7]. Traditional methods for the recovery of rare metals from various sources by hydrometallurgy are leaching followed activated carbon adsorption, cementation onto zinc powder and electrowinning. One of the potential problems of the thiosulphate systems is that the gold thiosulphate complex, unlike gold cyanide, does not adsorb onto carbon directly [8] or it is frequently combined with the electrolysis following adsorption on carbon and elution [9].

Silver cementation is an inexpensive and simple way to deposit thin films with a thickness usually not more than 0.1–0.3  $\mu\text{m}$ . This process has been applied in metallurgy, to the greater or lesser extend, since the Roman times until today [10]. Some of cementation reactions were noticed by alchemists, when an alchemist during apparent transmutation of metals dipped a piece of iron into a solution of blue vitriol, i.e., copper sulphate, the iron was immediately covered by a layer of metallic copper. The name of the process is probably derived from Spanish “cementación” meaning precipitation [11]. The advantages of this method are low concentration and good stability of solutions, simple composition, and the opportunity to deposit films with a uniform thickness on complex-shaped parts without a special installation. According to the electrochemical theory of cementation, the reaction:



takes place through the galvanic cell:



The most popular cementators are iron, copper and zinc. Due to this phenomenon many authors studied the cementation of rare metals from cyanide [12-15], thiourea [16,17], sulphate [18,19] and thiosulphate solutions [20-23].

Several scientists have tried to verify metals cementation by various techniques. One of the most common studied phenomena was the effect of surface-active substances or surfactants on the process of cementation [24-26]. Other improvements in cementation process have been introduced by using vibrating reactor [27] and combination of cementation with liquid membrane permeation [28].

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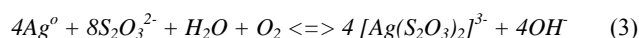
Mechanical activation belongs to innovative processes, that improve technological methods by creating of new surfaces and structural defects of solid state, which plays an important role in the process of cementation [29].

It is the aim of this study to verify the possibilities of mechanical activation to influence the silver cementation from sodium thiosulphate solutions by mechanically activated zinc powder.

## Experimental

### Materials

A stock solution was prepared using 99.27 g of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), sodium hydroxide (for pH adjustment) and 145 mg of silver sulphate ( $\text{Ag}_2\text{SO}_4$ ). The sodium thiosulphate was dissolved in distilled water to produce a 0.4 M solution in slightly less than 1000 ml volume. The pH was adjusted to 9.5 by sodium hydroxide. Distilled water was added to bring the final volume of 1000 ml. The mentioned amount of silver was dissolved in this solution by the following reaction:



Atomic absorption spectroscopy indicated that the silver concentration was 100  $\mu\text{g}/\text{ml}$  in the final stock solution.

### Mechanical Activation

Mechanical activation of zinc powder was performed in two different types of mills: a planetary ball mill, PULVERISETTE 6 (Fritsch, Germany) equipped with a tungsten carbide grinding chamber; and a stirring ball mill (attritor), Molinex PE 075 (Netzsch, Germany) equipped with a steel grinding chamber. The milling the planetary mill was carried out under the following conditions: volume of grinding and chamber = 250 ml; weight of sample = 5 g; tungsten carbide balls (360 g of 10 mm diameter) as grinding means, grinding medium = 50 ml methanol, grinding time = 30, 60 and 120 min; revolutions of the mill =  $500 \text{ min}^{-1}$ , ambient temperature. The milling in the attritor was carried out under the following conditions: volume of grinding chamber = 500ml; weight of sample = 50g; steel balls (2000g of 2 mm diameter) as grinding means; grinding medium = 200 ml methanol; grinding time = 30, 60 and 120 min; revolutions of grinding shaft =  $1000 \text{ min}^{-1}$ , ambient temperature.

### Cementation

The cementation tests for silver from sodium thiosulphate solution were carried out in a reaction vessel maintained at constant temperature ( $25^\circ\text{C}$ ) and equipped with a stirring motor. First, 450 ml of the pregnant solution was placed in the enclosed vessel maintaining the stirring speed constant (200 revolutions per minute) and a pre-determined amount of zinc powder (0.45 g) was added to the solution.

During the runs,  $5 \text{ cm}^3$  of each sample was taken for the determination of metal content at convenient time intervals.

## Physicochemical Characterization

The specific surface area ( $S_A$ ) of zinc powder was determined by the BET technique using low temperature nitrogen adsorption in a Gemini 2360 sorption apparatus (Micromeritics, USA). The particle size distribution of the zinc powder was measured by a laser beam scattering in a Helos and Rodos granulometer (Sympatec, Germany). The determination of silver and zinc content in the solution was carried out by the atomic absorption spectrometry using Spectra AA 240 FS (Varian, Australia) and the pH was measured by pH meter (WTW, Germany). The FTIR spectra were recorded on Avatar 330 spectrophotometer (Thermo – Nicolet, USA). The scanning electron microscopy (SEM) of zinc particles was carried out by BS 340 (TESLA Brno, Czech Republic) and SEM–EDAX analysis on the JSM 6400 (JEOL, Japan). XRD patterns were collected using a Philips PW 1820 (Netherlands) diffractometer with  $\text{CuK}_\alpha$  radiation under the following conditions of measurement:  $2\theta$  - range: 3 - 70, step:  $0.05^\circ$ , measuring time: 10 s. XRD data were analyzed using the STOE (utilizing the JCPDS PDF database) software.

## Results and Discussion

### Physicochemical Changes of Mechanically Activated Zinc Powder

Mechanical activation has induced significant changes of the surface as well as the bulk structure of zinc powder. The dependence of surface area and average particles size of mechanically activated zinc on the time of milling is depicted in Fig. 1A. It is visible, that mechanical activation performed in planetary mill has an favourable effect on the increase in surface area of zinc powder. After one hour of milling the increase in the average particles size has been observed.

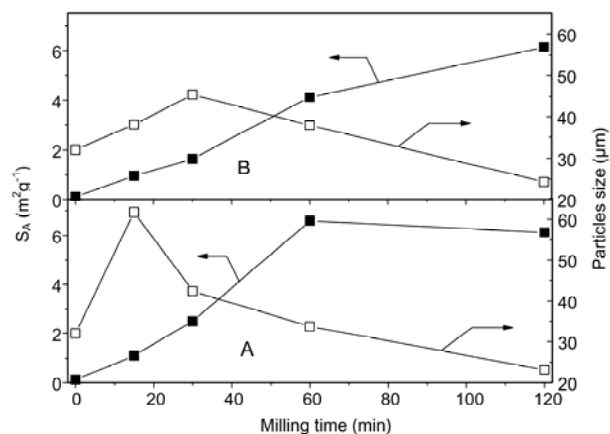


Figure 1. The specific surface area ( $S_A$ ) and particle size as a result of mechanical activation, A – for planetary mill, B – for attrition mill

For the attrition milling the same effect of decrease in particles size and increase surface of zinc powder has been observed (Fig.1B).

The interesting phenomenon has been observed by comparison of particle size distribution for zinc powder treated by attrition and planetary milling. Zinc particles treated by planetary milling have the highest value of particles size after 0.5 hour of milling. This is probably involved by the plasticity and/or agglomeration of zinc powder. The longer time of mechanical treatment leads to separation of zinc particles what is accompanied by the increase in the specific surface value  $S_A$ . In the case of attrition milling the similar process in minor scale has been observed.

### Cementation

The influence of mechanical activation of zinc powder on the cementation of silver from thiosulphate solution is depicted in Fig. 2. Analogous to planetary milling, which is mostly used only in laboratory applications, the effect of attrition milling, very often used in industrial applications, on the cementation process was investigated. The effect of mechanical activation of zinc powder in planetary as well as in attrition mill on the process of cementation is clearly demonstrated.

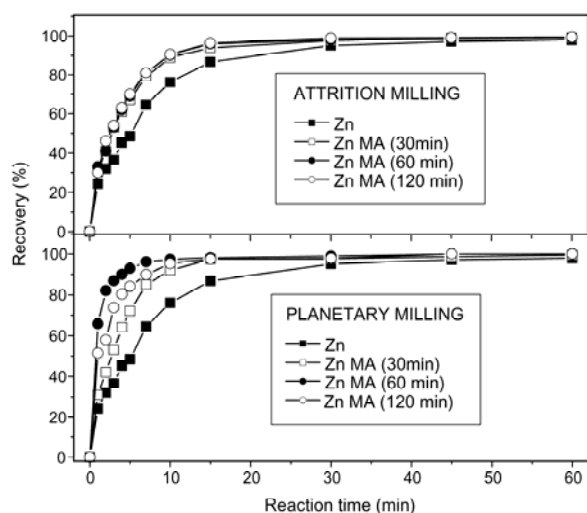


Figure 2. Cementation of silver after mechanical activation of zinc powder [Aqueous phase (450 ml):  $100 \mu\text{g/ml Ag}^+$  (0.93 mM  $\text{Ag}^+$ ),  $0.4 \text{ M } (\text{S}_2\text{O}_3)^{2-}$ , Cementation agent:  $0.45 \text{ g Zn}$  (6.9mM Zn); temperature:  $25^\circ\text{C}$ ]

Whereas the recovery of reaction is moreover 100 % in all cases, the high recovery of silver in shorter period of cementation has been considerably influenced by mechanical activation in planetary mill. The value of specific surface area and particles size distribution indicates the behaviour of the process. The highest recovery of silver has been achieved by zinc powder mechanically treated for one hour. The longer time of mechanical activation leads to decreasing of value of specific surface area. This is probably the reason of lower recovery of cementation process. The silver recovery after cementation by zinc treated for half an hour in planetary mill confirms the theory of influence of induced changes in specific surface area and the structure of cementator on the cementation process.

In the case of attrition milling the similar behaviour of cementation has been noticed. The process runs very fast and due

to attrition milling of zinc powder it is possible to reach almost 100 % recovery of silver in a shorter period. The behaviour of cementation in time confirms the influence of the generated defects of cementator on the described process.

The cementation kinetics behaviour, depicted on Fig. 3, was best fitted to the kinetics equation:

$$-\ln(1-X) = k t_c \quad (4)$$

where  $X$  is recovery of silver from cemented solution,  $k$  is the rate constant ( $\text{s}^{-1}$ ) and  $t_c$  is time of cementation (s). The silver cementation on untreated zinc powder and zinc powder mechanically activated in planetary (and attrition) mill for 0.5; 1 and 2 hours respectively is graphed as a function of the cementation time.

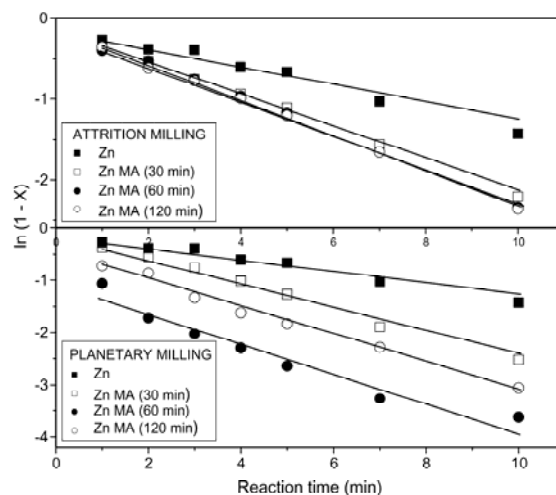


Figure 3.  $\ln(1-X)$  vs. time of cementation with zinc powder activated in planetary and attrition mill

Whereas the recovery of cementation after 60 minutes was rather high, the shortened time period of the cementation (up to 10 min) has been included into the calculations. It is visible, that the kinetics of the reaction is dramatically influenced by the mechanical activation of zinc powder. It is noted, that by the mechanical modification of cementator the silver cementation kinetics increases. Whereas mechanical activation of zinc powder has an favourable effect on the reaction kinetics, it should be highlighted, that the time of mechanical treatment influences the recovery of reaction in minimum scale.

Fig. 4 shows the change in pH and zinc concentration during cementation reaction by using of zinc powder with and without mechanical treatment. It is noted, that in the all cases the zinc concentration has an increasing tendency on the beginning of the cementation process. When the silver recovery is up to 90 % the zinc concentration has a decreasing tendency. Rather different behaviours of curves are visible in the case of solution pH.

This can be accounted by the reduction of water occurring during process of cementation:



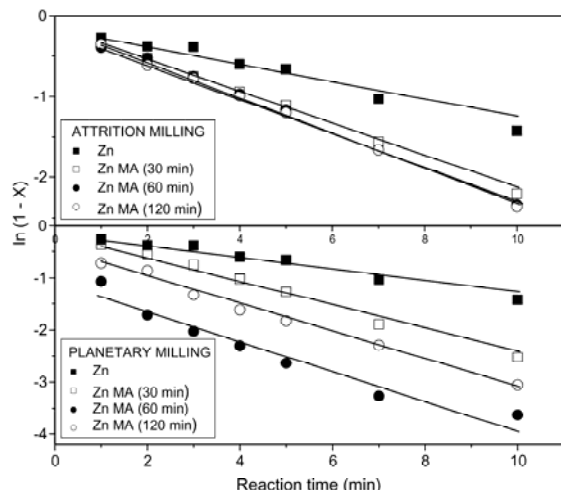


Figure 4. Zinc concentration and pH of solution as a result of reaction time

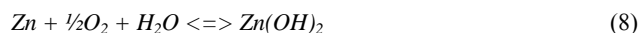
The high growth of solution pH is visible when almost all silver is cemented by zinc powder mechanically activated by planetary milling. The growth in pH at the beginning of the process is probably inhibited by cementation reaction. This increase in pH of solution explains the visible decrease in zinc ions concentration in the solution. According Younesi *et al* [30] the zinc ions reacts with hydroxyl groups according equation:



In addition the zinc ions in the solution can react with air oxygen according equation:



and/or



The  $\text{Zn(OH)}_2$  is precipitated back on the surface of zinc powder [31]. The lower value of dissolved zinc in solution cemented by zinc powder mechanically activated in planetary mill is probably caused by back precipitation of  $\text{Zn(OH)}_2$  on the surface of zinc powder at the beginning of process immediately. In the case of attrition milling the similar behaviour of the zinc concentration and solution pH have been observed.

Fig. 5 shows FTIR spectra characterized the species formatted on the surface of cementator after its mechanical treatment in planetary and attrition mill as well as the species formatted on the surface of pure zinc powder.

For zinc hydroxide films on the surface of zinc powder small metal – hydroxide and metal- oxide adsorption peaks exist as broad peaks at 540 – 555, 670, 890 – 900, 944 – 976  $\text{cm}^{-1}$ . The strong peaks in the region 1635, 1150, 1012 and 665  $\text{cm}^{-1}$  corresponds to present of  $\text{SO}_4^{2-}$ . Thus, the decomposition reactions of thiosulphate [32]:

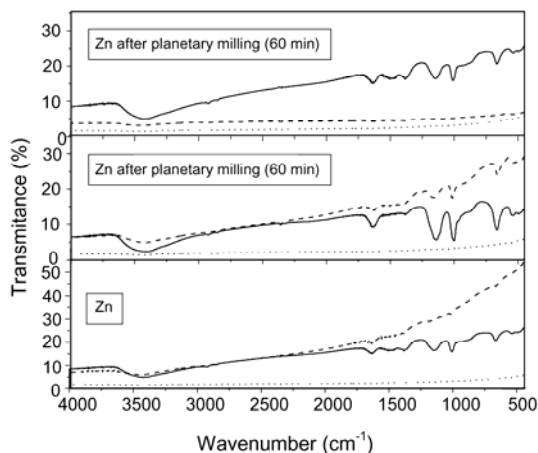
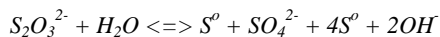


Figure 5. FT – IR spectra of zinc powder after cementation, dot line – before cementation, dash line – after 15 min of cementation, solid line – after 60 min of cementation

(9)



can takes place and the precipitated sulphur decreases the effective area over which silver precipitation occurs [33]. We

assumed, that formed  $\text{SO}_4^{2-}$  can be precipitated back on the surface of cementator as  $\text{ZnSO}_4$ . Back precipitation could be formed as the special kind of corrosion of the zinc powder as was described by Muster and Cole [34]. This behaviour can partially explain the increase of the solution pH in the cementation process on mechanically activated zinc powder.

#### Morphology of Cementation Product

SEM was used to examine cementation reaction products obtained in the presence or absence of mechanical activation in planetary and attrition mill for 60 minutes. All experiments proceeded at 25°C and 200 rpm, time of the cementation was 15 minutes, when the recovery of reaction was up to 85 % for untreated zinc powder and almost 100 % for zinc powder activated in planetary and attrition mill respectively.

The morphology of pure zinc powder is presented in Fig. 6A, while the product of cementation is shown in Fig. 6B. The effect of the mechanical activation in planetary mill, which induces the increase in the specific surface area of zinc powder is depicted in Fig. 6C. The presence of cementation products on activated zinc powder can easily be seen in Fig. 6D. The morphology of deposit seems to be more porous, distributed uniformly and covering most of the entire surface. Fig. 6E shows, that the effect of attrition milling has the same effect on the morphology of zinc powder as well as effect of the planetary milling. The morphology of deposit on the surface of zinc powder mechanically activated in attrition mill (Fig. 6F) is similar to the products on the zinc powder treated in planetary mill. In fact, the EDAX analysis (Fig. 7) of the cementation product shown in the same figure provides evidence of the presence of sulphur in the precipitate. Thus it is visible, that the silver can be precipitated in its typically morphology (ring C) as well as in a forms together with sulphur species (ring B).

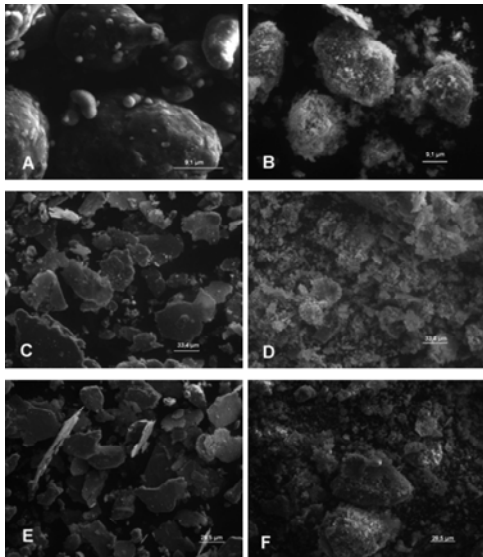


Figure 6. SEM zinc powder surface micrographs :

- A. zinc powder without cementation
- B. zinc powder after 15 min cementation at initial Ag = 100 µg/ml
- C. zinc powder after mechanical activation in planetary mill ( $t_M = 60$  min)
- D. mechanically activated zinc powder in planetary mill after 15 min cementation at initial Ag = 100 µg/ml;
- E. zinc powder after mechanical activation in attrition mill ( $t_M = 60$  min)
- F. mechanically activated zinc powder in attrition mill after 15 min cementation at initial Ag = 100 µg/ml

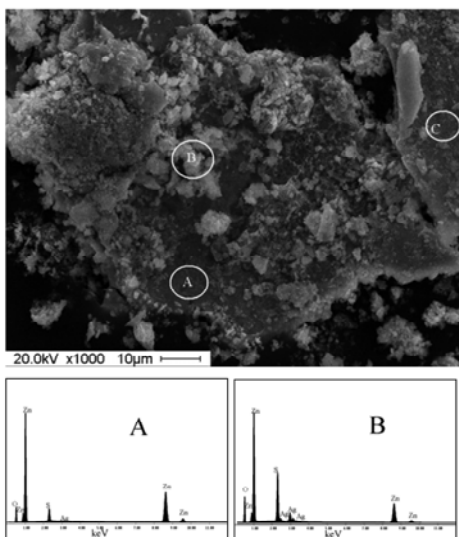


Figure 7. SEM top view image of the zinc surface (mechanically activated for 60 min in planetary mill) with cemented silver and products of the side reactions after 15 min of cementation with EDAX analysis of selected areas

The presence of the crystal form of cemented silver on the cementator surface has been also declared by X-ray diffraction (XRD) analysis. Fig. 8 shows the present of the cemented silver in the crystal form. It is seen (inset), that in the case of cementation onto zinc powder (JCPDS PDF 4-831) mechanically activated in the planetary mill the intensity of the main peak for silver ((111) reflection) (JCPDS PDF 4-783) is higher in the comparison with silver precipitated onto zinc powder without mechanical treatment. Also the present of ZnO (JCPDS PDF 36-1451) species precipitated on the cementator surface as a result of side reaction are presented in crystal form.

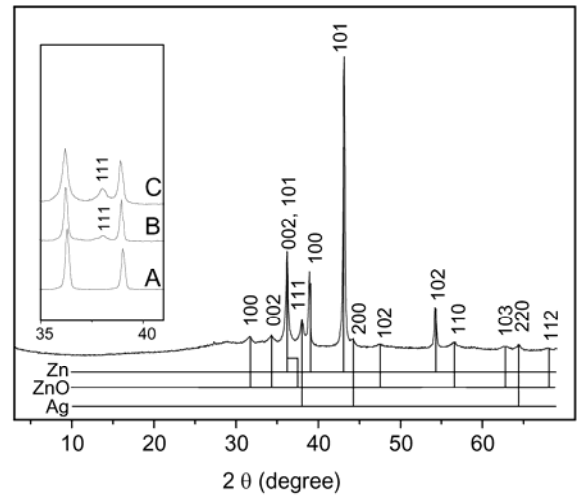


Fig. 8 XRD pattern of zinc surface mechanically activated in planetary mill after 60 min of cementation (Inset: A – unmilled zinc powder before cementation, B – the (111) XRD reflection of silver after cementation on unmilled zinc powder, C – the (111) XRD reflection of silver after cementation on zinc powder after 60 min of planetary milling)

While the EDAX analysis and FTIR spectra measurements clearly demonstrated the presence of sulphur and sulphate species, the XRD analysis shows only the characteristic reflections for the presence of zinc powder, precipitated silver and zinc oxide, no sulphate or sulphur form have been detected. It can be explain by the presence of these species on the surface of cementator in the amorphous form.

## Conclusions

The results obtained from this investigation show the potential of cementation of silver by zinc powder as a method of silver recovery from thiosulphate solutions. The mechanical activation in planetary or attrition mill influences the mechanical properties of cementator. The favourable effect on the kinetics and recovery of silver cementation has been observed. SEM investigation confirms the changes induced by milling of zinc powder as well as soft changes in morphology of deposited layer of precipitated silver and the products of the side reactions after cementation. The formation of crystal silver as well as the products of side reactions during the cementation have been declared by FTIR, SEM-EDAX and XRD analysis.

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