Recovery of Nano-Sized Cobalt Powder from Cemented Carbide Scrap

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Abstract

A process is developed to recover nano-sized cobalt from cemented carbide scrap (WC-Co) by nitric acid leaching and finally obtaining a nano-sized spherical pure cobalt powder by ultrasonic spray pyrolysis (USP). The optimization of the leaching and preparation of cobalt powders by USP are conducted within the framework of an environment-friendly and economical process, enabling reduced waste streams. According to the results obtained, it is possible to dissolve cobalt with high efficiencies (91.5%) via HNO_3 leaching of cemented carbide scrap. The optimum leaching conditions were 90 μm, 25 °C, 2 h, 0.5 M HNO_3, 900 rpm, and 1/10 solid/liquid ratio. The leach residue (WC-TiC) has a BET specific surface area of 1.08 m^2/g and finds has a wide range of applications in key technologies, varying from mechanical to chemical industries. After leaching, nano-sized cobalt powder (300-700 nm) can be produced from $Co(NO_3)_2$ by ultrasonic spray pyrolysis with hydrogen reduction. The nano-sized powders can be used for the production of new nano-structured thermoelectric materials, nanomagnets, nanosensors and nano-structured tungsten carbide-cobalt powders.

Key words: Recovery, Hydrometallurgy, Ultrasonic spray pyrolysis, Nano-sized cobalt powder

Introduction

Nano-sized metallic powders with high purity offer new physical and mechanical properties. The growing interest in the specific properties of nanocrystalline materials is supported by a strong tendency towards the miniaturization of high-technology materials. Magnetic metal nanoparticles (such as Co, Fe and Ni) have applications such as high-density magnetic data storage, magnetic toners in xerography, magnetic inks and ferrofluids (Xicheng et al., 2003). The increasing demand for metals worldwide has required intensive studies for the extraction of metals from low-grade ores and/or secondary resources. Cobalt can be extracted from secondary resources like chemicals (for rechargeable batteries), super alloys, cemented carbides, and magnets. Most scrap materials are richer in cobalt than even ore concentrates. "Cemented carbides", often called "Hard Metals", are a range of very hard, refractory, wear-resistant materials produced by powder metallurgy techniques (i.e. sintering). These materials have found a wide range of applications as cutting tool inserts (about 50-60%), dies, nozzles and valve components, etc., where severe wear and high temperature properties are required. The majority of cemented carbides are based on WC and Co (Kang et al., 2000; Ullmann, 1963; Enqvist and Uhrenius, 2003; Andren, 2001; Lin et al., 1996; Brookes, 1998). When the tools and components are scrapped, they are collected with the purpose of recovering the tungsten and cobalt in the light of their strategic importance. The $ 2 billion worldwide cemented carbide industry generates large quantities of scrap due to parts rejected at various stages of production and worn out cutting tools. Numerous recycling pro-

cesses have been developed that can be classified into different categories. The "Zinc melt" and the "Cold-Stream" processes are also popular methods to recycle cemented carbide (Ullmann, 1963; Lin et al., 1996; Brookes, 1998; ASM Handbook, 1998; Lin et al., 1995). Regarding the "Zinc melt" process, the binding metal (cobalt) reacts with high purity zinc (99.995%) during the cemented carbide recovery operation. The energy consumption is therefore high; about 4000 to 6000 kWh is required for 1 t of tungsten carbide scrap. The cycle time of the complete zinc process is 24 h. The "Cold-Stream" process is a mechanical method where cemented carbide scrap is transported by a high velocity air stream (>1000 km/h) to hit a cemented tungsten carbide plate. Nitric acid is used to dissolve the binding medium (anodic dissolution of cobalt) at a current density of 2-10 A kg^{-1} of the scrap (an electrochemical process) (Lin et al., 1995; Lin et al., 1996; Latha et al., 1989). Cobalt leaching from cemented carbide scrap is a hydrometallurgical method for cobalt recovery and offers the potential of environment-friendly management. Selective leaching is a potential alternative in view of its lower energy consumption and environmental impact.

Ultrasonic spray pyrolysis (USP) is a useful tool for the large or small scale production of particles with controlled particle size and has been used to prepare nano-sized powders of metallic and intermetallic compounds, and ceramic materials. USP has advantages such as simplicity, safety and low cost of the apparatus and raw materials (Messing, 1993; Kim et al., 2003; Tsai, 2004). Spherical nano-sized cobalt powders were obtained by the USP of aqueous cobalt nitrate solutions followed by thermal decomposition of the aerosols generated in hydrogen atmosphere.

In this study, a novel process was developed for the recycling of cobalt from cemented scrap carbides. Finally, cobalt is recovered in the form of spherical nano-sized cobalt powder (by USP), which is the most important product today, for the production of new nano-structured thermoelectric materials and nano-structured tungsten carbide cobalt powders.

Experimental

Materials

Experiments were carried out with powderized cemented carbide scrap. The chemical composition and X-ray diffraction analysis of the cemented tungsten carbide scrap powder are given in Table 1 and Figure 1.

Table 1. Chemical composition (wt%) of the cemented tungsten carbide scrap powder used in the experiments (particle size -90 μm).

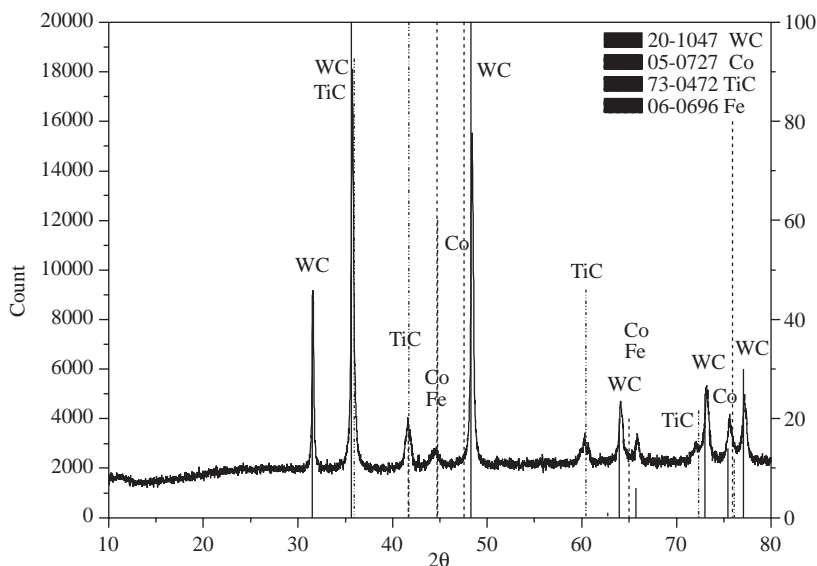| W	Co	C	Ti	Fe	Nb	Ni
75.86	8.14	6.07	4.18	3.40	1.35	1.00

Figure 1. X-ray diffraction analysis of cemented carbide scrap powder (-90 μm).

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By the X-ray diffraction analysis, it was found that the structure of cemented carbide scrap is WC, TiC, and Co.

Experimental procedure

Cemented tungsten carbide scrap was ground in a vibrating mill for 15 min. Screening of the ground material was conducted in a Retzsch brand sieve. Leaching experiments were carried out in a 3-neck glass reactor with 0.25 l capacity, heated by a thermostatically controlled heater (Heraeus). The mixture was stirred from the top with a teflon-plated propeller, which was hooked onto a mixer (Ika-Werk RW-20) with adjustable speed and stirring direction. A spiral condenser was also utilized to return evaporation losses to the system. The ground cemented carbide scrap powder was added to the agitated nitric acid solution at the required temperature. Samples of the solution were taken at 30 min intervals. All the samples were filtered and analyzed by ICP (Spectroflame Modula EOP). The carbon content of the cemented carbide scrap was determined using a Leco-CS 400 analyzer. The surface area of WC-TiC (mixed powder) was measured by BET equipment (Flow Sorb II 2300). An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (Zeiss DSM 982 Gemini) were utilized for the characterization of the material and product. All the chemicals used in the experiments were analytical grade (Merck). Generally, the experiments were conducted under the following conditions: a solid/liquid ratio of 1:10, 20 g sample and -90 μm particle size. A purified leach solution from cobalt extraction experiments from cemented tungsten carbide scrap using nitric acid was used as the starting material for the USP experiments. The final concentration of cobalt was 0.08 Mol Co/l. A spray pyrolysis system was used in this study, consisting of an ultrasonic atomizer, a quartz tube reactor, a furnace and collection units. Very fine droplets of the aerosol were obtained in an ultrasonic atomizer Pyrosol 7901 (R.B.I. with a frequency of 800 KHz). The aerosol was transported with reducing gas into the quartz tube (0.7 m length and 0.02 m diameter) placed in the furnace (Ströhlein, Germany) with a temperature control $\pm$ 1 °C. Hydrogen atmosphere was used for cobalt production. Nitrogen with a flow rate of 1 l/min was used for the air removal prior to the reduction process. Under spray pyrolysis conditions in hydrogen atmosphere and at a flow rate of 1 l/min, the dynamic reduction took place in the quartz tube reactor. Figure 2 shows the schematics of the apparatus.

Results and /iscussion

Leaching

Effect of leaching temperature: The temperature effect was examined in the range 25-70 °C under the standard conditions of -90 μm particle size, 0.5 M HNO_3, 2 h, 900 rpm, and 1/10 solid/liquid ratio. Figure 3 shows the effect of temperature on the dissolution of cobalt in the HNO_3 and H_2O system. Cobalt solubility decreased from 91.5% to 78.2% between 25 and 70 °C.
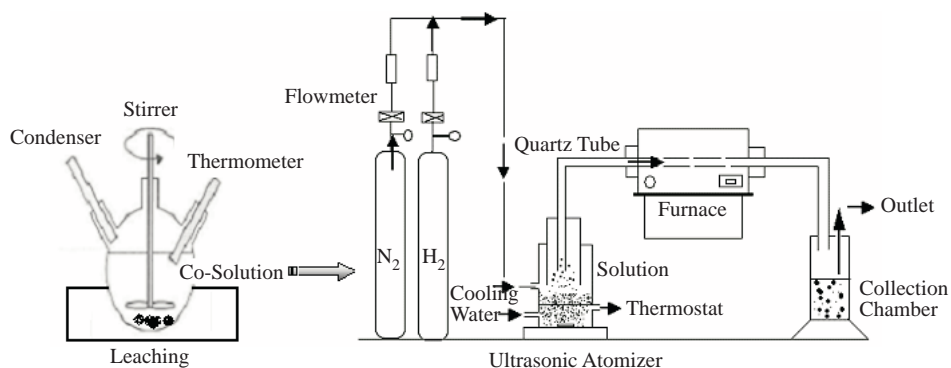

Figure 2. Schematics of the experimental apparatus for the synthesis of cobalt nanoparticles.
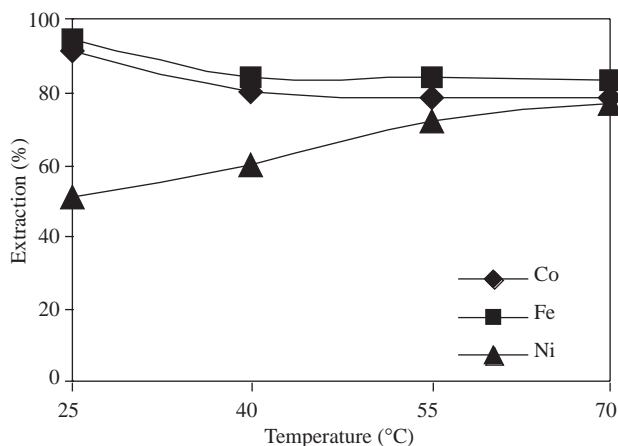
Figure 3. Effect of temperature on the dissolution of cobalt and associated elements [-90 μm, 2 h, 0.5 M HNO$_3$, 900 rpm, and S/L: 1/10].

The results shown in Figure 3 indicate that rising temperature has no advantageous effect on the leaching rate, and cobalt should be extracted at room temperature. The leach residue was washed with distilled water. X-ray diffraction analysis of the leach residue (for the optimum leaching conditions) is given in Figure 4. While the main structure shows typical WC and TiC characteristics, some cobalt peaks observed in the X-ray analysis indicate that additional grinding might be necessary in order to liberate all the cobalt present in the scrap. The characterization studies, conducted on WC-TiC

leach residue to determine the re-utilization possibilities in the Hard Metal Industry (or Powder Metallurgy), revealed that it has a density of 11.9 g/cm^3, a BET value of 1.08 m^2/g and a grain size of -90 μm.

Effect of reaction time: The highest cobalt efficiency (91.5%) was obtained after a leaching period of 2 h (Figure 5). Iron, on the other hand, dissolves within the first hour of leaching with 90% efficiency and shows a dissolution trend similar to that of cobalt for the rest of the leaching. This shows that the reaction period and rate depend on the liberation rate of the particles in ground cemented carbide scrap. In contrast to the fact that cobalt gives a very fast dissolution reaction, nickel shows a slow reaction with HNO$_3$ and acts as the rate-determining factor on total efficiency.

In practice, 120 min of leaching was optimum. Extended leaching periods (over 120 min) seem to increase the efficiency for cobalt, iron, and nickel only insignificantly.

Effect of initial acid concentration: Figure 6 displays the effect of acid concentration on the dissolution of cobalt at 25 °C. Various experiments were carried out by changing the HNO$_3$ concentration from 0.5 M to 1.5 M. At 0.5 M HNO$_3$ concentration, 91.5% cobalt extraction was obtained in 120 min, whereas at 1.0-1.5 M HNO$_3$ concentration cobalt extraction of approximately 90.5-89.9% was achieved within 120 min, as shown in Figure 6. Increasing the acid concentration from 0.5 M to 1.5 M caused the dissolution efficiency of iron to decrease from 94.5%
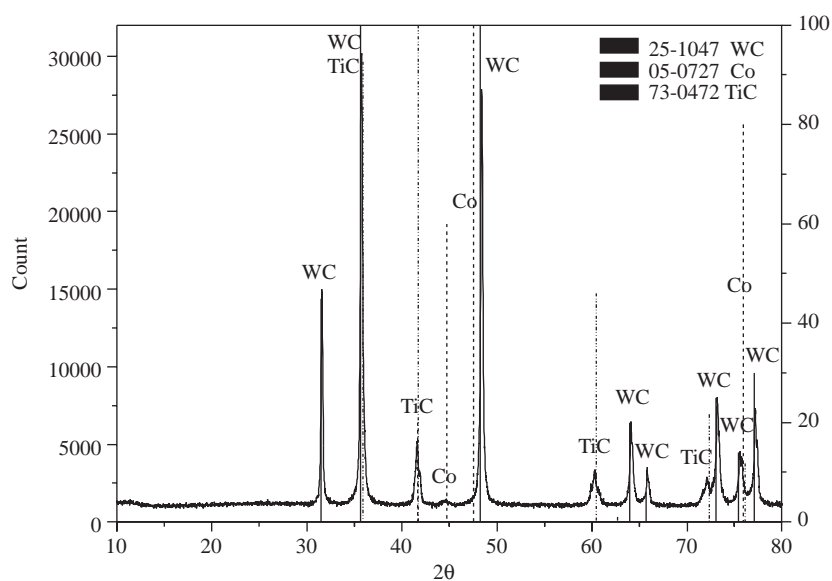

Figure 4. X-ray diffraction analysis of the leach residue (the optimum leaching conditions).

to 90.0%. On the other hand, nickel extraction increased with increasing HNO_3 concentration. The viscosity of the solution increased as a result of high acid concentration. This leads to a reduction of the diffusion rate of the ions. The reaction rate remained constant for higher acid concentrations, indicating stabilized iron dissolution. The main determining factor for the rate of leaching, as mentioned earlier, is the continuing reaction of cobalt particles that are entrapped in WC particles.
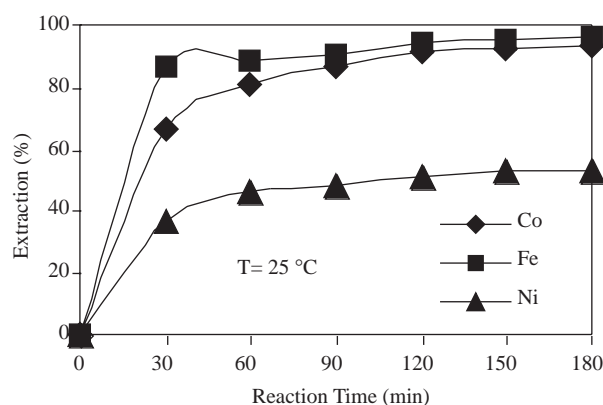

Figure 5. Effect of leaching time on the dissolution of cobalt and associated elements [-90 μm, 25 °C, 0.5 M HNO_3, 900 rpm, and S/L: 1/10].
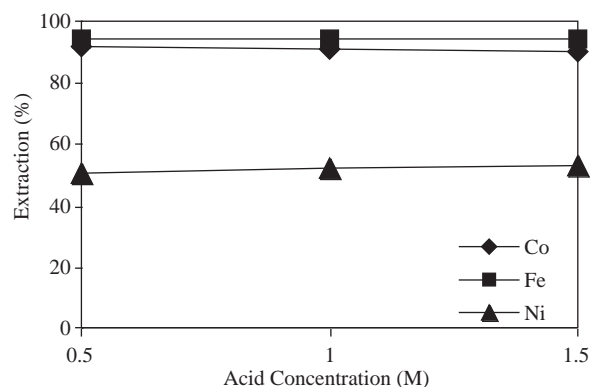

Figure 6. The effect of acid concentration on the dissolution of cobalt and associated elements [-90 μm, 25 °C, 2 h, 900 rpm, and S/L: 1/10].

Effect of stirring speed: The effect of the stirring speed was studied under the conditions of -90 μm particle size, 25 °C, 0.5 M HNO_3, 2 h, and 1/10 solid/liquid ratio. The results show that the leaching rate of the cobalt increases quickly when the stirring speed is amplified from 700 to 900 rpm. Extraction percentages of Co, Fe, and Ni in relation to the in-

creasing stirring speed are given in Figure 7. The highest extraction appeared to be at 900 rpm.
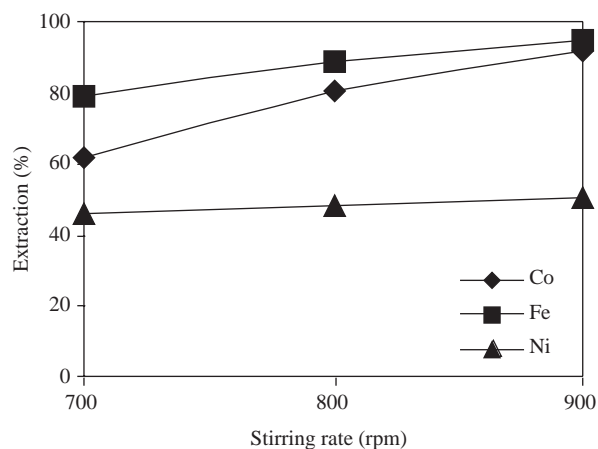

Figure 7. The effect of stirring speed on the dissolution of cobalt and associated elements [-90 μm, 25 °C, 2 h, 0.5 M HNO_3, and S/L: 1/10].

It is known that higher stirring rates often result in an increased dissolution rate. In diffusion-controlled processes, the rate of dissolution can be expressed as a function of stirring speed. In this case, the process is diffusion controlled and the boundary layer thickness decreases with increased speed of stirring.

Effect of particle size: The effect of particle size was studied using 2 ground size fractions of -90 μm and
-250 + 90 μm at 25 °C, 2 h, 0.5 M HNO_3, 900 rpm, and 1/10 solid/liquid ratio. Smaller particle sizes result in a more efficient leaching of cobalt. As seen from Table 2, leaching efficiencies are lower than those obtained with a particle size of –90 μm, which shows the effect of particle size.

Table 2. Effect of particle size on the dissolution of cobalt and associated elements [25 °C, 2 h, 0.5 M HNO_3, 900 rpm and S/L: 1/10].

Particle size	Co %	Fe %	Ni %
-90 μmm	91.5	94.5	50.7
-250 + 90 μmm	68.5	49.1	54.1

Effect of solid/liquid ratio: Figure 8 gives the cobalt recovery during leaching, as a function of the S/L ratio. According to these experimental cobalt extraction increases with decreasing S/L ratio and at ratios higher than 1:10 there is no significant increase in cobalt recovery.
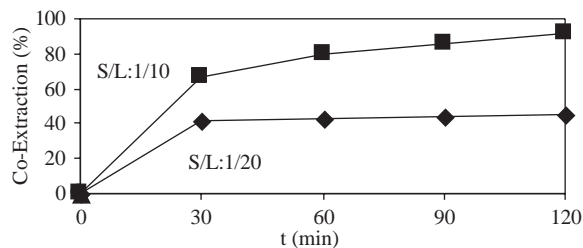
Figure 8. The effect of S/L ratio on the dissolution of cobalt [-90 μm, 25 °C, 0.5 M HNO$_3$, and 900 rpm].

Synthesis of nano-sized spherical cobalt powder by USP

The composition of the homogenized leach solution for the USP experiments (analyzed by ICP Spectroflame Modula EOP) is shown in Table 3, which indicates that Fe and Ni are two 2 impurities. The cobalt is the major component to be recovered.

Table 3. Chemical composition of leach solution.

Initial solution	Co	Fe	Ni
mg/l	5000	10	8

Cobalt powder can be produced by a number of methods, but those of industrial importance involve the thermal hydrogen reduction of oxides, the pyrolysis of carboxylates, and the reduction of cobalt ions in aqueous solution with hydrogen under pressure. USP is a powerful tool for preparing powders and films, because of the easy control of the target composition, the excellent availability of the precursors, and the high quality of the products. In the preparation of a powder by USP, a solution is atomized into a hot reactor, where the aerosol droplets undergo drying, droplet shrinkage, solute precipitation, thermolysis, and sintering to form the final particles. Metals, metal oxides, and non-oxides can be readily produced by spray pyrolysis. Figure 9 shows the X-ray diffraction pattern of the USP cobalt powder. The X-ray diffraction analysis of the powder, produced at 800 °C from Co(NO$_3$)$_2$ solution in H$_2$ atmosphere by USP, indicated the formation of pure cobalt powder.

A typical SEM micrograph of the cobalt powder obtained from cobalt solution (5 g/l) under dynamic conditions at 800 °C is shown in Figure 10. As seen, the particle size of the powder varies between 388.0 and 490.7 nm, although larger particles (about 700 nm) are also observed.

Ideally, spherical non-agglomerated cobalt powders are produced by USP. This powder could be suitable for Powder Metallurgy and Hard Metal Industry applications. In this study, a novel process was developed for the recycling of fine, spherical and nano-sized cobalt powder from cemented carbide scrap by leaching and USP.
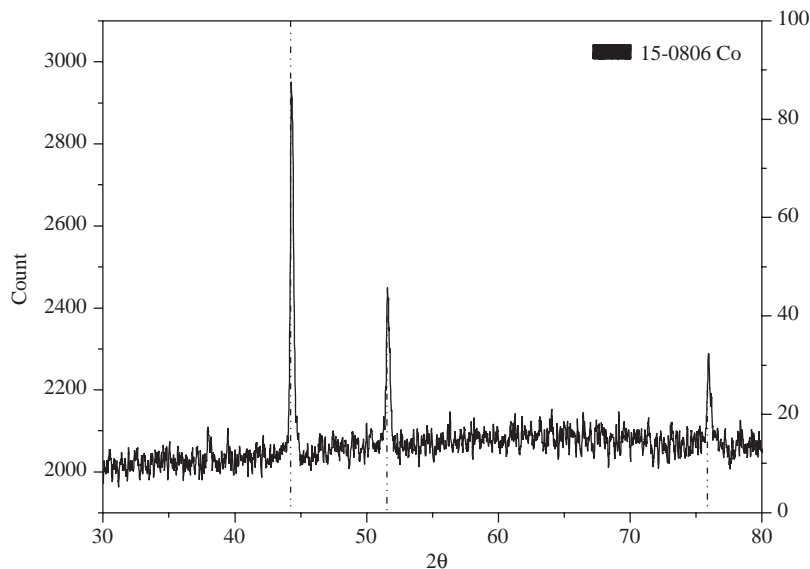

Figure 9. X-ray diffraction analysis of the USP cobalt powder [reduction periods: 2 h, flow rate of H$_2$: 1 l/min].
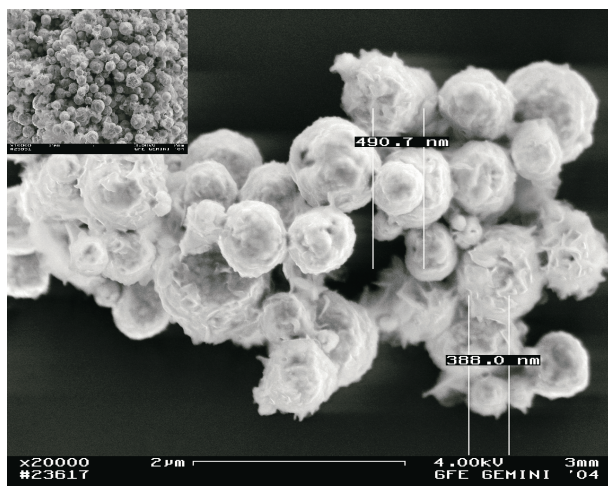
Figure 10. SEM micrograph of the cobalt powder obtained under dynamic conditions at 800 °C [2 h, 1 l/min H_2].

2 h of leaching, 0.5 M HNO_3, 900 rpm, and S/L ratio of 1/10. Cobalt can be more efficiently dissolved when fractions of –90 μm particle size are used. The particle size of the cemented carbide scrap can easily be decreased below 90 μm through classical grinding processes. The highest leaching efficiency was attained at 25 °C and temperature does not seem to affect the leaching efficiency of cobalt. Stirring speed, however, has a determining role in leaching. The obtained leach residue (WC-TiC) has a density of 11.8 g/cm^3, BET specific surface area of 1.08 m^2/g and grain size of -90 μm. Nano-sized cobalt powder (300-700 nm) can be produced from $Co(NO_3)_2$ by ultrasonic spray pyrolysis with hydrogen reduction. A total of 2 h reduction periods are required for cobalt powder. Hydrogen gas plays a significant role in a pyrolysis reactor as carrier and reducing gas. No liquid waste (neither acidic nor alkaline) is generated in this process, since $Co(NO_3)_2$ solution is recycled back to the USP step.

Conclusions

The recycling of cemented carbide scrap is becoming increasingly attractive. For this purpose, the suggested method, combining, leaching and USP, represents an alternative to the classical recycling techniques. The optimum leaching conditions -90 μm, 25 °C,

Acknowledgments

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