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Low Energy-Consumption Industrial Production of Ultra-Fine Spherical Cobalt Powders

Chong-Hu Wu

Additional information is available at the end of the chapter

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1. Introduction

Cobalt powders have been used extensively in cemented carbides, high-temperature alloys, PCD and PCBN, and magnetic materials, etc., due to its excellent physical, chemical, and mechanical properties. The fabrication and final properties of the above materials are strongly affected by the quality (purity, phase, size, shape, dispersity, fluidity, etc.) of Co powders. In order to fabricate a homogeneous and densified microstructure without pores, Co-pool, Co-poor and Co-free zones, etc., ultra-fine spherical Co powders have been desired with the development of ultra-fine and even nano grain materials. However, it is very difficult to industrial fabricate ultra-fine spherical Co powders with good quality by the conventional decomposition and hydrogen-reduction technology. In this paper, a new low energy-consumption industrial production technology-a continuously dynamic-controlled combustion synthesis (CDCCS) technology has been proposed about investigating how to obtain ultra-fine spherical Co powders (the average particle size is smaller than $0.8\mu\text{m}$, and the length-diameter ratio is smaller than 2) with a lower impurity content.

2. Cobalt: Properties, minerals, extraction and applications

2.1. Properties

2.1.1. Physical properties

Cobalt does not occur naturally as a pure metal, but is a component of more than near a hundred naturally occurring minerals, including various sulfides, arsenides, sulfoarsenides, hydrates, and oxides. Pure cobalt can be produced by reductive smelting, and was firstly prepared by G. Brandt in 1735. Cobalt was confirmed as an element by T. Bergman in 1780. Cobalt is a metallic transition element, and its position in the Periodic Table is characterized:

Name, symbol, number: Cobalt, Co, 27

Element category: Transition metal

Group, period, block: 9(VIIIA), 4, d

Standard atomic weight: 58.933195

Electron configuration: 4s3d7

Electrons per shell: 2, 8, 15, 2

Co is a brittle, hard metal, resembling iron and nickel in appearance. Pure cobalt produced by reductive smelting is a hard, lustrous, silver-gray metal. Co has a relative permeability two thirds that of iron [1]. Its Curie temperature and magnetic moment are 1115°C [2] and 1.6~1.7 Bohr magnetons/atom [3], respectively. The basic physical properties are listed in Tab.1, and vapor pressure vs. temperature is shown in Fig.1. The transformation is sluggish and accounts in part for the wide variation in reported data on its physical properties. Metallic Co occurs as two crystallographic structures: a hexagonal closed-packed crystal structure (hcp) and a face-centered cubic crystal structure (fcc). During cooling, Co usually undergoes a polymorphous transformation from fcc to hcp. The temperature corresponding to the equilibrium between the high-temperature β (fcc) and low-temperature α (hcp) phases in Co is 417°C [4], but in fact, the energy difference is so small that random intergrowth of the two is common [5].

Physical properties	values
Color	Silver-gray
Density	8.9g/cm ³
Liquid density at melting point temperature	7.75g/cm ³
Melting point	1768K, 1495°C, 2723°F
Boiling point	3200K, 2927°C, 5301°F
Heat of fusion	16.06kJ/mol
Heat of vaporization	377kJ/mol
Molar heat capacity	24.81J/(mol·K)

Table 1. The basic physical properties of Co metal

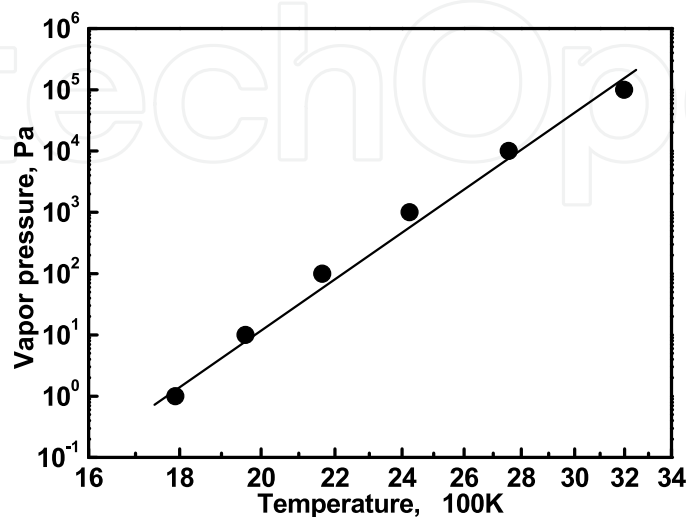


Figure 1. Vapor pressure of Co

2.1.2. Chemical properties

Pure Co does not dissolve in water and soil, and can stay for years at room temperature (RT). Co can stay in the air for a few days, and can be oxidized to CoO at about 300°C, and can be burnt to Co₃O₄ at high temperature. Fine Co powders prepared by the hydrogen-reduction technology are easily oxidized to cobalt oxide and even generate self-ignite in the air. So the fine Co powders must be carefully preserved in a vacuum or an inert gas container.

Co is a weakly reducing metal, and is easily attacked by halogens and sulfur, and is also rapidly dissolved by HCl, H₂SO₄ and HNO₃ acid solution, and is slowly eroded by HF, NH₄OH, NaOH solution.

Co can solid-dissolve many metal and nonmetal atoms to form many intermetallic compounds. Co can well infiltrate many ceramics (WC, TaC, TiC, ZrC, TiN, Al₂O₃, cBN, diamond, etc.), and the almost all wetting angles are lower than 50° [6], so it is often used as a binder in the above ceramic-metal composites.

2.1.3. Mechanical properties

Metallic Co occurs as two crystallographic structures: hcp- α and fcc- β . Strength and hardness of hcp- α should be higher than those of fcc- β , but inverse for their plasticity because there are more slipping systems in fcc- β than hcp- α . Some mechanical properties of Co are listed in Tab.2.

Mechanical properties	Crystal structures	
	hcp	fcc
Electrical resistivity ($\Omega\cdot\text{m}$)	6.24×10^{-8} at 20°C	-
Thermal conductivity (W/(m·K))	100	-
Thermal expansion (/K)	13.36×10^{-6} at 25°C	-
Young's modulus (GPa)	209	<hcp-Co
Shear modulus (GPa)	75	<hcp-Co
Bulk modulus (GPa)	180	<hcp-Co
Poisson ratio	0.31	-
Vickers hardness (MPa)	1043	<hcp-Co

Table 2. Some mechanical properties of Co

2.2. Co minerals and extraction

Co is not a typically rare metal since it ranks 33 in abundance. Content of Co in the earth's crust is about 0.035wt.%, and about 2.3 billion ton in the sea. Nearly, all Co is always found associated with metallic-lustered ores of other metals (for example, Cu, Ni, Fe, Pb, Zn, etc.), and Co minerals without other metals is very less except cobaltite in Morocco. So generally it is produced as a by-product of other metals mining. Near a hundred cobalt minerals have been already found in the nature, but about only 20 cobalt minerals are valuable and available, listed in Tab.3.

Based on the complexity of the Co minerals, the extraction processing is very complicated and efficiency of recovery is also very low. As usual, Co in the minerals is firstly concentrated or is transformed into the soluble states by the pyro-refining, and then Co in the calcine of pyro-refining is further enriched and extracted by the hydrometallurgy, the finally the cobalt compounds or pure cobalt are obtained. An extraction processing is shown in Fig.2 [7]. Section (the production of Co powders) in the dotted line scope in Fig.2 will be emphasized in the chapter.

Cobalt minerals	Chemical formula	Theory cobalt contents (wt.%)	Actual cobalt contents (wt.%)	Distribution
Arsenides	CoAs ₂	23.2	15~21	Canada, Morocco, USA
	(Co,Fe)As ₂	28.2	9~23	Morocco, Canada, Russian
	CoAs ₃			
	(Co,Ni)As ₃	20.8	16~20	Morocco, Canada, Russian
	(Co,Ni,Fe)As ₃			
Sulfides	CoAsS	35.5	29~35.3	China, Canada, Morocco, USA, Australia
	(Co,Fe)AsS		15~20	Morocco
	CuCo ₂ S ₄	38.7	27~42	Zaire, Zambia
	Co ₃ S ₄	48.7	36~53	Zaire, Zambia
	(Co,Ni) ₃ S ₄	26	4~10	USA, China
	CoS ₂			Zaire, China
Oxides	<i>m</i> (Co,Ni)O·MnO ₂ · <i>n</i> H ₂ O	<32	<30	Zaire, China, New Caledonia
	3CoO·As ₂ O ₃ ·8H ₂ O	29.5		Morocco, Canada
	CuO·2Co ₂ O ₃ ·6H ₂ O	57	45~47	China, Zaire
	CoCO ₃	49.6		Zaire, Zambia

Table 3. Cobalt minerals

2.3. Applications

Due to the excellent physical, chemical, and mechanical properties, it is widely used in fabricating various alloys (which are used as high-temperature and wear resistant components, dies, saws, cutting tools, etc.) by powder-metallurgy technology, such as super alloys, high speed steels, cemented carbides, PCD (polycrystalline diamond) and PCBN (polycrystalline cubic boron nitride), etc. Co in the above alloys is usually used as an additive, an alloying element or a binder.

An important use for Co is in the field of high-temperature alloys. Required in gas turbines, jet engines, and similar applications, such alloys retain their strength above 650°C; these alloys contain 5~65wt.% Co. Even higher operating temperatures in turbines have resulted in an increased use of cobalt-containing and cobalt-based alloys known generally as super alloys. These can withstand severe operating conditions and temperatures up to 1150°C. For example, Nimonic 90 is a nickel-based alloy containing 18wt.% Co, a similar amount of Cr, and some Ti, and Waspaloy is another alloy of this type.

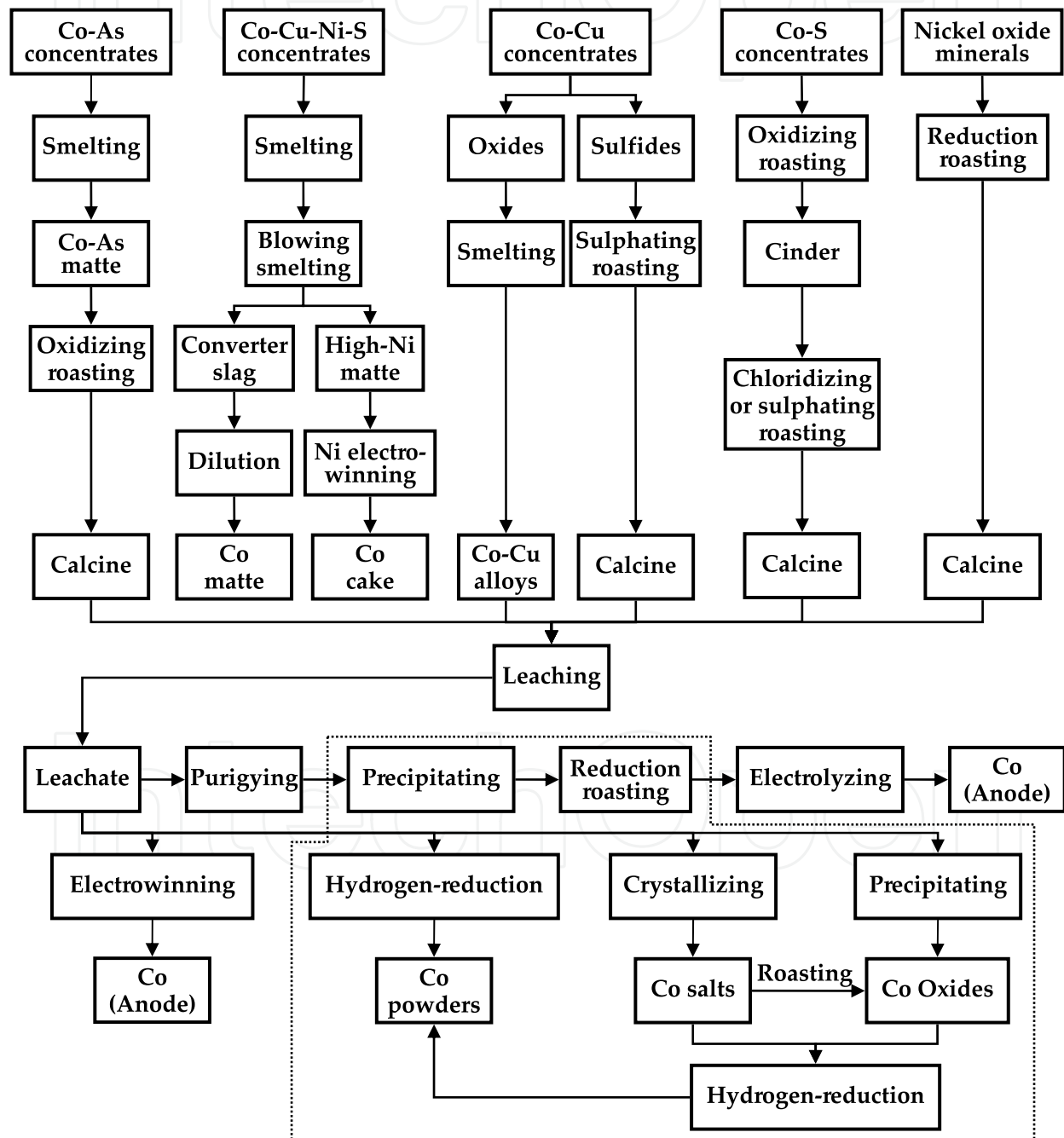


Figure 2. Cobalt extraction processing (the section in the dotted line scope will be emphasized in the chapter)

Cemented carbides, PCD and PCBN are used as cutting tools, wear-resistant components, dies, saws. In the production of a so-called cemented carbide, i.e. tungsten carbide composites, a briquetted mixture of tungsten carbide and soft cobalt powders is compacted and sintered at a temperature above the melting point of cobalt. The latter melts and binds the hard carbides, giving them the toughness and shock resistance needed to make carbides of practical value for cutting tools, drill bits, dies, and saws, etc. Co is the most satisfactory matrix metal for this purpose and may be adjusted in amounts from 3 to 25 percent by weight. A briquetted mixture of diamond or cBN and Co powders are sintered at high temperature and high pressure, and PCD and PCBN materials are obtained.

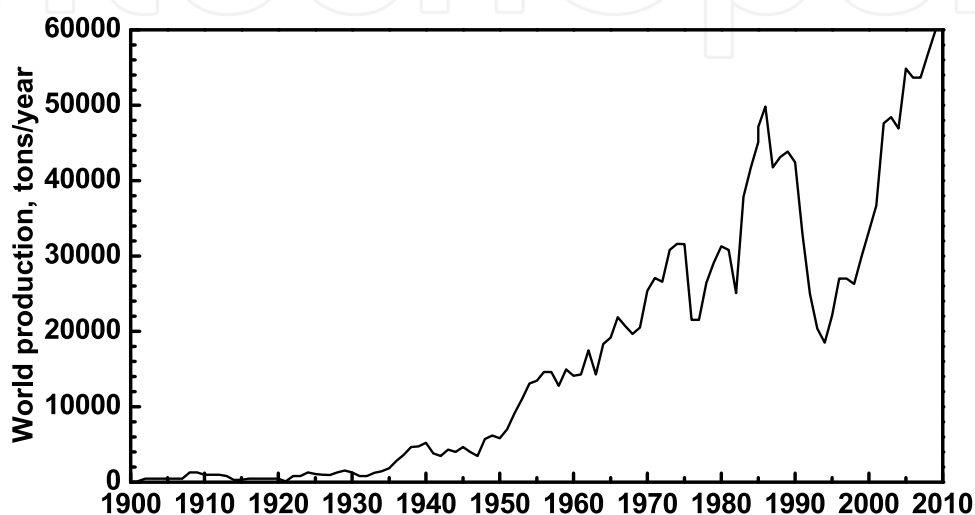


Figure 3. World production trend of cobalt

Very strong magnets are created when Co is alloyed with other metals. So Co is used in fabricating many advanced magnetic materials.

Cobalt's use in rechargeable batteries is the fastest growing use. Notably in 2007, the percentage of cobalt use for rechargeable batteries rose to 25% of total cobalt demand from 22% in 2006.

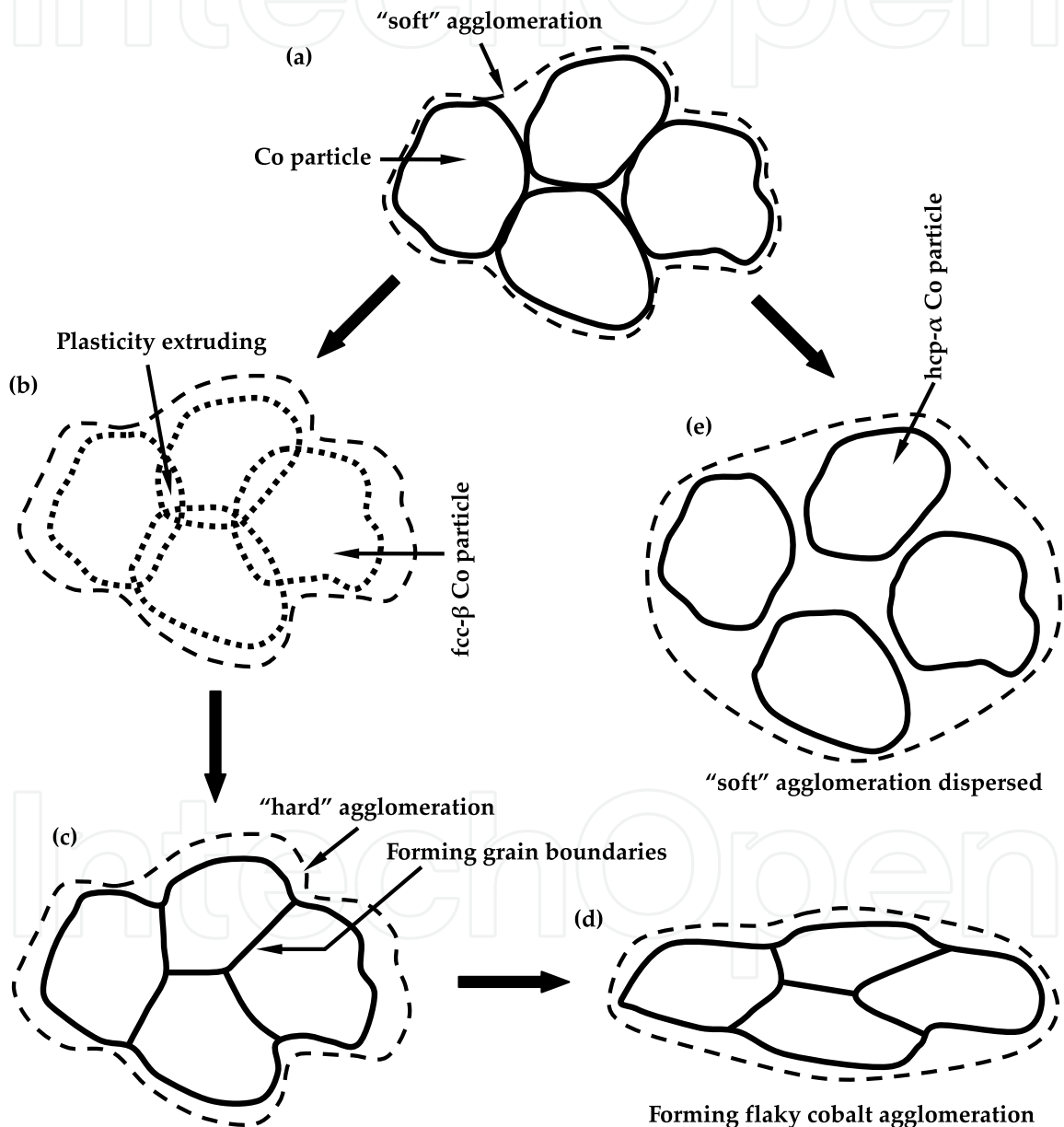
World production trend of cobalt is shown in Fig.3 [8,9]. The production of cobalt has been increasing steadily since 1996.

3. Expectation qualities of cobalt powders in powder metallurgy industry

Powder metallurgy materials (PMM) have been usually fabricated by mixing, pressing, and sintering processing. The quality (purity, phase, size, shape, dispersity, fluidity, etc.) of raw powders acts an important role in determining the fabrication and final properties of PMM. Especially with the rapid development of ultra-fine grain cutting tool materials (such as, WC/Co alloys, PCBN, PCD, etc.), ultra-fine spherical Co powders (the size is $\leq 0.8\mu\text{m}$ and the length-diameter ratio is smaller than 2) have been desired in order to fabricate a homogeneous and densified microstructure without pores, Co-pool, Co-poor and Co-free zones, etc.

Though hcp- α Co is a room temperature stable phase, fcc- β Co can also be steadily retained at RT by some especial techniques (for example, rapidly cooling). For metal alloys, the

strength and plasticity are generally contrary, so hcp- α and fcc- β structures must be alternative in applications. For cemented carbides (WC/Co alloys), hcp- α Co powders are desired because the cold welding among Co particles due to its higher brittleness can be decreased during ball-milling. The cold welding (seen as “hard” agglomerations, as shown in Fig.4) among Co particles can easily result in “Co-pool” which result in a rapidly decrease of mechanical properties of WC/Co alloys. However, fcc- β cobalt in the sintered WC/Co alloys is desired by rapidly cooling during sintering because its good plasticity can improve the toughness of WC/Co alloys.

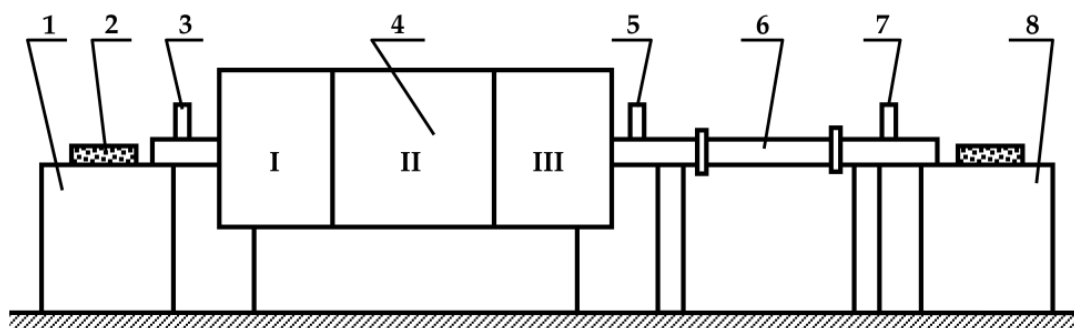


(a) Initial morphology ("soft" agglomeration) of Co particles; (b) Occurring cold welding among fcc- β Co particles due to each other extruding; (c) Forming grain boundaries at the cold welding positions, and forming a "hard" agglomeration; (d) Forming flaky Co agglomeration due to plastic deformation; (e) hcp- α Co particles well dispersed

Figure 4. Schematic representation of the evolution of hcp- α and fcc- β Co particle agglomerations during ball-milling

4. Decomposition-hydrogen-reduction to fabricate cobalt powders

Co powders in powder metallurgy industry are mainly fabricated by a decomposition-hydrogen-reduction technique using cobalt compounds of cobalt oxalate ($\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cobalt carbonate ($\text{CoCO}_3 \cdot x\text{H}_2\text{O}$), or cobalt oxide (Co_3O_4) powders as raw materials. Schematic representation of the device is shown in Fig.5. Raw powders are uniformly tilled in the boats, and then the boats are pushed into hydrogen-reduction furnace at regular intervals by a Feeder. The raw powders can also be continuously fed by a conveyor belt in some companies [10], but we consider that the conveyor belt should carry off a lot of heat, and resulting in an increase of energy-consumption and the complexity of the device is also increased. H_2 from an inverse direction enters the furnace. The raw powders are heated, decomposed, and reduced in the heating zone (in which there are usually not less than three different temperature zones). Obtained Co powders are cooled to RT in the long cooling zone, and collected into a Receiver, and protected by N_2 . In order to reduce energy-consumption and protect the environment, the residual H_2 including some other gases, such as CO , CO_2 , H_2O , etc., is purified by a Purifier, and then reused.



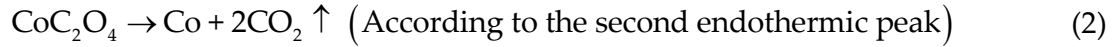
1. Feeder; 2. Boat; 3. H_2 exit to a Purifier; 4. Heating zone; 5. H_2 entrance; 6. Cooling zone; 7. N_2 Protecting; 8. Receiver

Figure 5. Schematic representation of the device used in fabricating Co powder

In order to well understand the decomposition mechanisms of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$, Co_3O_4 powders and further guide the production of Co powders, their thermal decomposition kinetics in an inert gas and air will be detailedly studied and discussed in the following sections. Effect of morphology, size and purity of three raw powders and technical parameters on the properties of Co powders is also discussed. Some beneficial methods are also summarized and proposed to improve the quality of Co powders.

4.1. Cobalt oxalate

The chemical formula of the commercial cobalt oxalate is $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Fig.6 shows TG and DTA curves of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in an inert gas (such as N_2 , Ar) and air, respectively. DTA curve in the inert gas exhibits two endothermic peaks, which are accompanied by the weight loss of $\sim 19.67\%$ and $\sim 48.09\%$ in the TG curve, respectively. The ranges of reactive temperatures at the peaks are in about $170\sim 225^\circ\text{C}$ and $350\sim 440^\circ\text{C}$, respectively, which will change a few with different testing conditions (such as changing heating rate). Such weight loss agrees with the value calculated for the following two transformations:



DTA curve in the air exhibits an endothermic peak and an exothermic peak, which are accompanied by the weight loss of ~19.67% and ~36.43% in the TG curve, respectively. The ranges of reactive temperatures at the peaks are in about 170~225°C and 270~320°C, respectively, which will also change a few with different testing conditions (such as changing heating rate). Such weight loss agrees with the value calculated for the following two transformations:

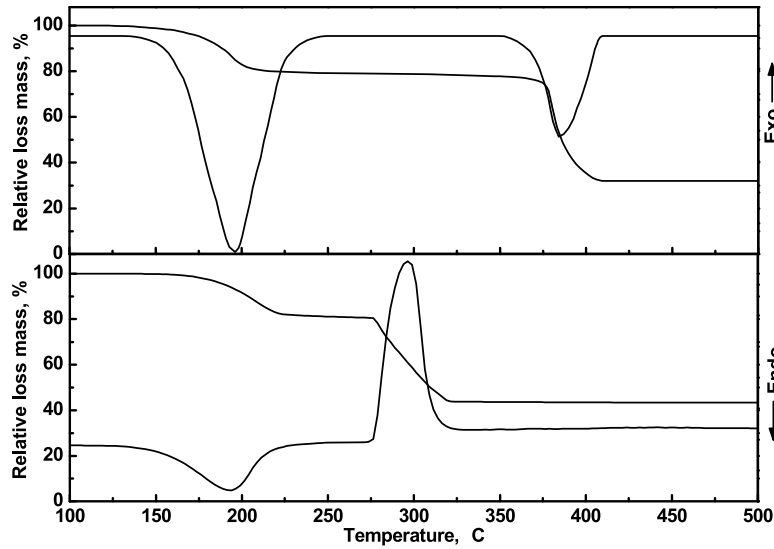
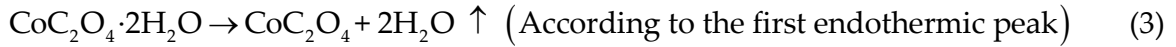


Figure 6. TG and DTA curves of $\text{CoC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in an inert gas (up) and air (down)

In actual industrial production of Co powders, the decomposition-hydrogen-reduction processing of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ occurs in a H_2 atmosphere in the device of Fig.5. Tikkanen *et al* [11] indicated that the decomposition-hydrogen-reduction processing of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was divided into a guide stage and a decomposition stage. The dehydration (see the reaction (1-1)) dominates during the guide stage. Huang *et al.* [12] indicated that high crystallinity CoC_2O_4 crystals with less defects can be obtained under a slow dehydration rate, and then further decomposition processing changes difficulty. Therefore, we easily surmise that it is disadvantageous to fabricate ultra-fine Co powders due to a decrease of the nucleation rate. In reverse, CoC_2O_4 crystals with many defects can be obtained under a rapid dehydration rate, and then the decomposition changes easy; resulting in an increase of the nucleation rate. So we propose to increase properly the feeding rate of boat and temperature during the guide stage. In actual industrial production, we can shorten properly the scope of the "I"

heating zone in Fig.5 and increase the dehydration temperature (usually higher 30~50°C than the result of DTA). On the other hand, the dehydration processing of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ can be incompletable because hcp- α Co powders are easily obtained during the decomposition of the CoC_2O_4 with a few H_2O .

Fig.7 shows the effect of decomposition temperature and time of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ on the specific surface area of Co powders [11]. There are two activation energies for the growth of Co powders, which implies two different growth mechanisms: the aggregating growth among Co crystalline nuclei at lower temperature and the second aggregating growth among Co particles. It is obvious that the second growth must be inhibited during decomposition. The temperature occurring the second growth is about ~450°C, which is similar to the results of DTA. Therefore, the temperature in the decomposition stage can not usually be higher than 450°C in order to obtain ultra-fine Co powders. In fact, it is very difficulty to completely inhibit the second growth due to the local overheating in the boat. The following methods are usually used to improve the temperature homogeneity in the boat: increasing the surface of the boat, decreasing the layer thickness of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders, and increasing the flow rate of H_2 .

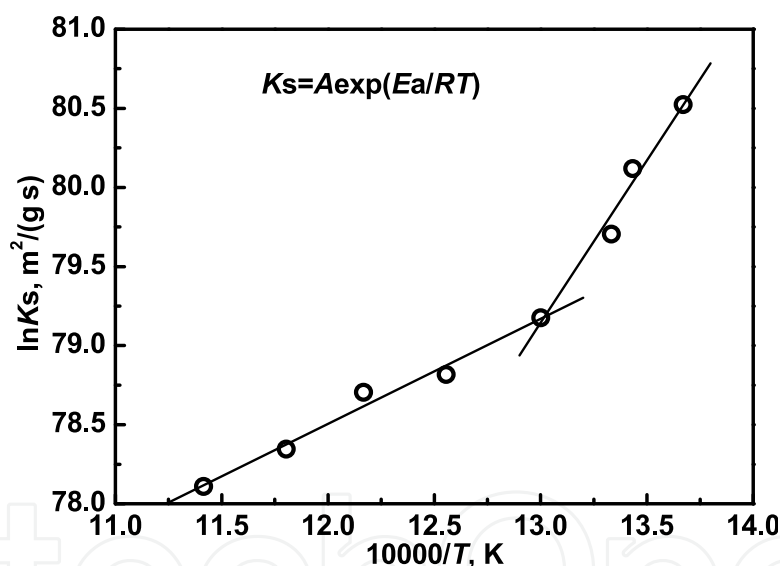


Figure 7. Effect of decomposition temperature and time of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ on the specific surface area of cobalt powders

Morphology of the commercial $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders is a short-fibrous structure with an average diameter of about 0.5~1 μm and an average length of about 4~10 μm , or a bunch (3~4 μm) of fibrous particles is formed when several short-fibrous cobalt oxalate particles are adhered or bonded together during crystallization, as shown in Fig.8(a). Because morphology of Co powders can easily inherit that of cobalt oxalate, it is very difficulty to obtain spherical Co powders by decomposing cobalt oxalate; usually replacing a short-string or dendritic structure, shown in Fig.8(b). Furthermore, the production practice shows that there is always 2~4% “hard” agglomeration (a size of 10~30 μm) in Co powders. The decomposition processing of cobalt oxalate is schematically shown in Fig.9. The short-

fibrous $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ particles stacked disorderly in the boat are decomposed and reduced *in situ* in the device of Fig.5. The Co nuclei are nucleating and growing to form a short-string structure along the short-fibrous of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ particle, and the short-string or dendritic structure, and even “hard” agglomerations are formed when several short-string Co particles grow or bond together.

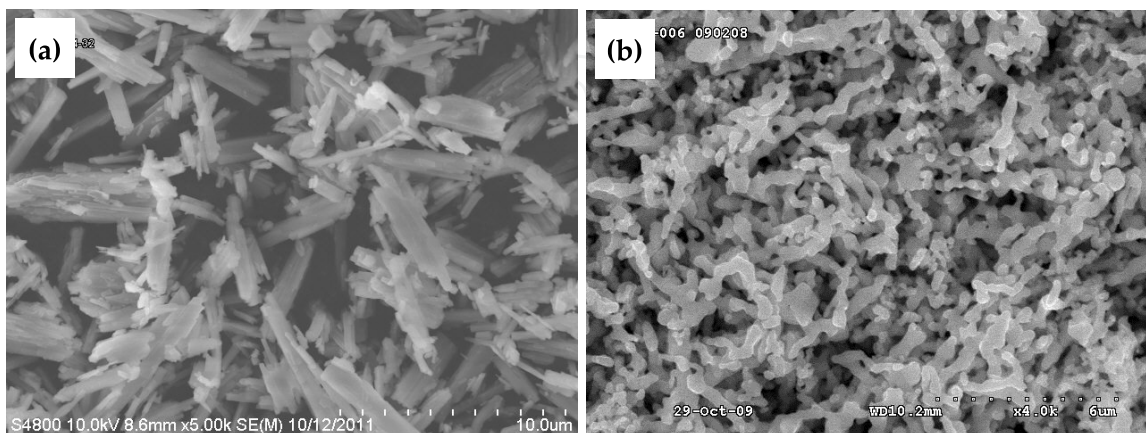
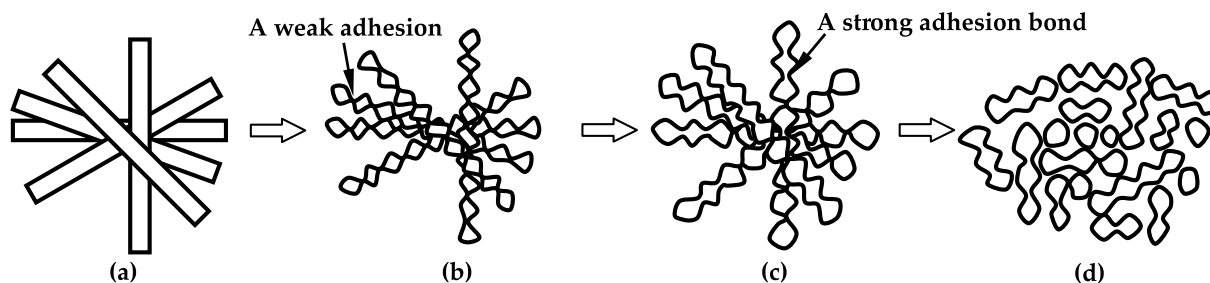


Figure 8. Morphology of the commercial cobalt oxalate powders and Co powders fabricated by decomposing cobalt oxalate: (a) short-fibrous cobalt oxalate powders and (b) short-string or dendritic cobalt powders



(a) Morphology of cobalt oxalate powders; (b) A short-string structure of Co particles along the short-fibrous after hydrogen-reduction, there is a weak adhesion between Co particles; (c) Co particles grow up, and a strong adhesion bond between Co particles is formed; (d) The short-string or dendritic structure of cobalt powders after sifting

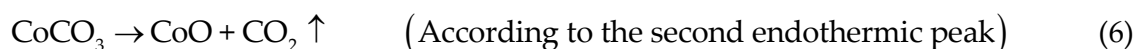
Figure 9. Schematic representation of *in situ* decomposition-hydrogen-reduction processing of cobalt oxalate

In order to obtain ultra-fine spherical cobalt powders, there are two methods: to obtain spherical cobalt oxalate powders and to impede or break the adhesion of cobalt nuclei during the decomposing processing of cobalt oxalate. Spherical cobalt oxalate powders can be crystallized by adding a few spheroidizer [13,14] into the cobalt salt leachate, but the spheroidizer can deteriorate the properties of the final sintered alloys. Du *et al.* [15] proposed that spherical cobalt oxalate powders can be crystallized by adding a pulsed magnetic field in the cobalt salt leachate, but the size of cobalt oxalate particles is up to $3.5\mu\text{m}$ which is disadvantageous to fabricate ultra-fine Co powders. Huang *et al.* [16] proposed to decrease the size of cobalt oxalate powders by an airflow dispersion method, but it is obvious to largely increase the production cost and to easily result in an increase of the content of impurity in cobalt oxalate powders. Li *et al.* [17] proposed to impede the

adhesion of cobalt nuclei by doping tungsten powders into cobalt oxalate powders, and then equiaxed or spherical-like Co powders are obtained and the size of Co particles decreases with increasing tungsten powders. But tungsten can promote to transform hcp-Co into fcc-Co, and the difficulty controlling the content of carbon in the final sintered WC/Co alloys is increased because the additional tungsten in Co powders must be completely reacted to form WC by adding carbon powders.

4.2. Cobalt carbonate

The chemical formula of the commercial cobalt carbonate is $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ (x is lower than 1.). Fig.10 shows TG and DTA curves of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ in an inert gas (such as N_2 , Ar) and air, respectively. DTA curve in the inert gas exhibits two endothermic peaks. The ranges of reactive temperatures at the peaks are in about $130\sim 220^\circ\text{C}$ and $320\sim 420^\circ\text{C}$, respectively. According to XRD results in Fig.11, there are the following two reactions:



DTA curve in the air also exhibits two obvious endothermic peaks. The ranges of reactive temperatures at the peaks are in about $130\sim 220^\circ\text{C}$ and $250\sim 320^\circ\text{C}$, respectively. According to XRD results in Fig.11, there are the following two reactions:

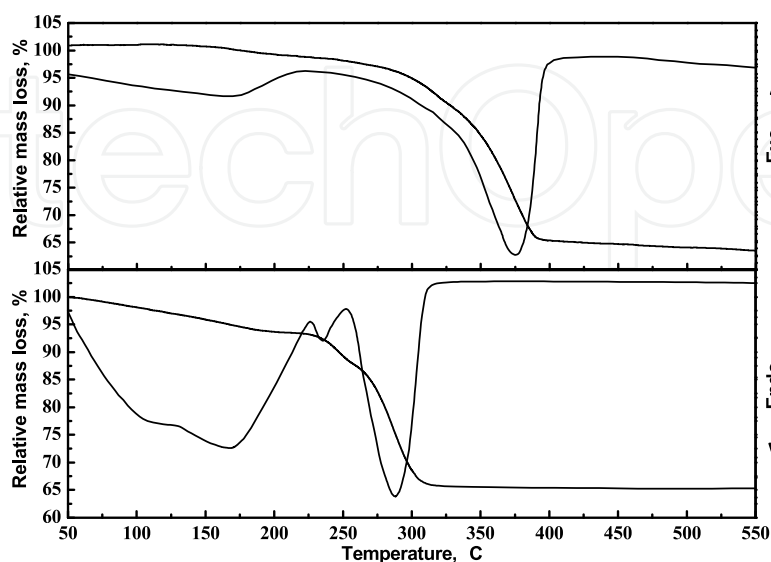


Figure 10. TG and DTA curves of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ in an inert gas (up) and air (down)

In addition, there seems a weak exothermic peak in about 220~270°C, in which the weight loss on the TG curve is a few slower than that in 270~320°C. According to XRD result at 220°C in the air, there also are the following two possible reactions:



A similar result was reported in Ref. [18], namely the decomposed products of $\text{Co}_5(\text{OH})_6(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ powders at a lower temperature are a mixture CoO and Co_3O_4 powders, and CoO is oxidized to form Co_3O_4 at a higher temperature.

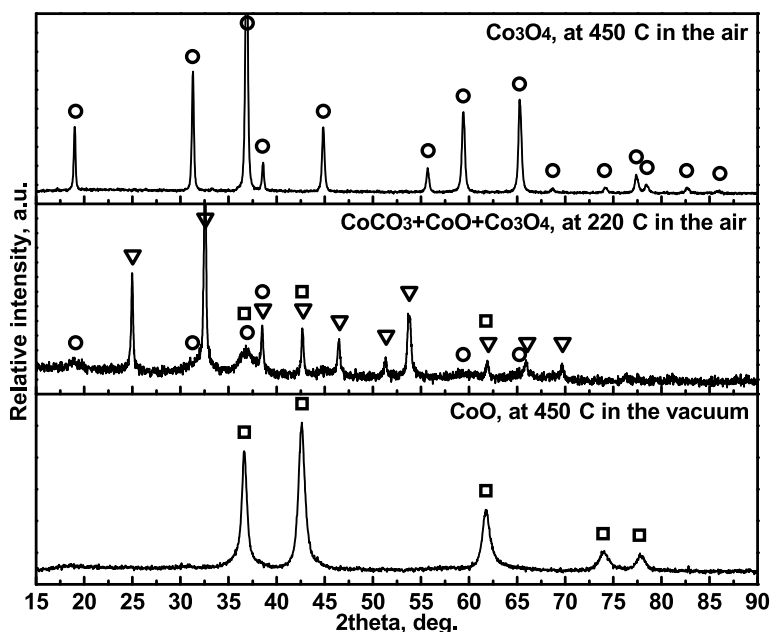


Figure 11. XRD patterns of the decomposed products of $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders at various conditions

Being different from the short-fibrous $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders, the production practice [19,20] indicates that the spherical Co powders can be easily obtained by decomposing a nearly spherical $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders (see Fig.12(a)). However, the minimum average size of Co powders obtained by decomposing $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders is only up to 0.8~0.9 μm (see Fig.12(b)), and Co powders also possess a wide particle size distribution. The content of fcc- Co in the powders is as high as 60%.

Another disadvantage is: the content of some impurities (such as S and Ca) in $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders are usually higher than those in $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders due to the different precipitation extraction processing. It is very difficulty to completely eliminate the impurities, which can be often retained into the final sintered WC/Co alloys. And then the properties of WC/Co alloys can be deteriorated by the impurities. Fig.13 shows that there is a higher content of S and Ca at a fracture origin in a sintered WC/Co alloy, and the raw Co powders are fabricated by decomposing and reducing cobalt carbonate powders. Although the impurities can be transformed into some non-deleterious compounds by adding a few

rare earth elements [21,22], the other questions are again introduced during fabricating WC/Co alloys.

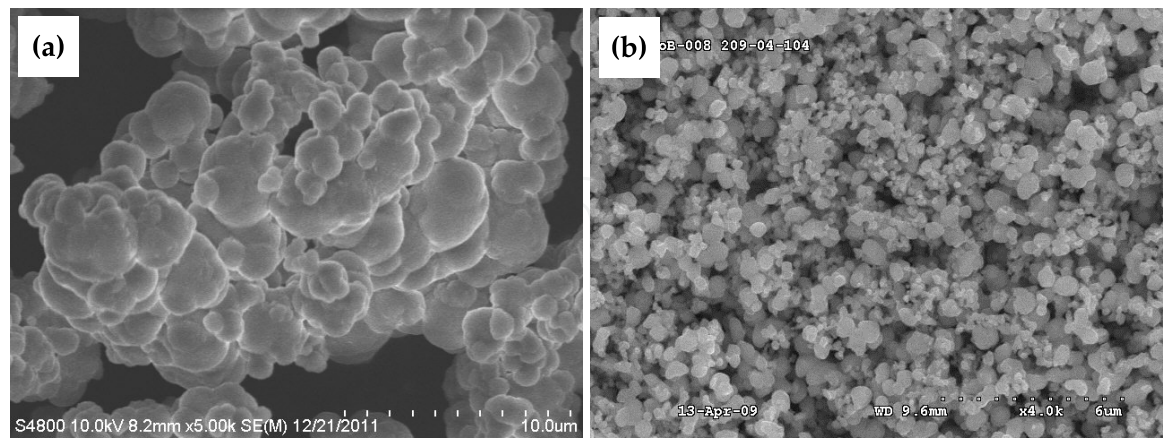


Figure 12. Morphology of (a) the commercial $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders and (b) Co powders fabricated by decomposing and reducing $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders

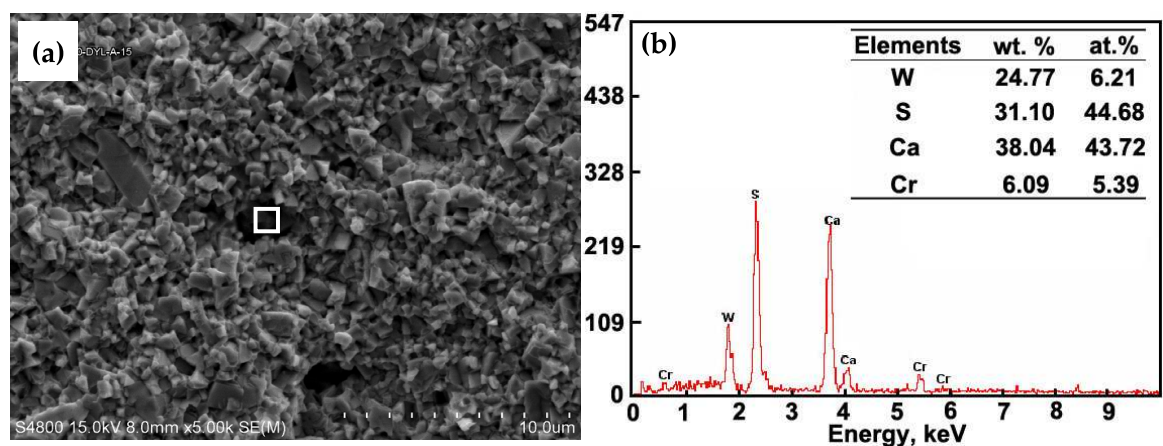


Figure 13. The failure of a sintered WC/Co alloy caused by the S and Ca impurities: (a) A fracture surface; (b) The EDS analysis at the fracture source (see the square region in (a))

4.3. Cobalt oxide

There are some advantages using Co_3O_4 powders to fabricate Co powders by hydrogen-reduction technology: (1) For $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders, Co powders easily grow if the decomposition and reduction processing (nucleation and growth processing) can not be completely separated. But for Co_3O_4 powders, there is only the reduction processing. So the technology processing is easily controlled. (2) The content of Co in Co_3O_4 is two times higher than those in $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$, as listed in Tab. 4. So the output of Co powders can be improved by double times at a same reduction condition. (3) The Co powders obtained by hydrogen-reducing Co_3O_4 powders are almost all hcp-Co. Therefore, ultra-fine spherical Co_3O_4 powders are the best raw material to fabricate ultra-fine spherical Co powders.

Compounds	$\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	$\text{CoCO}_3 \cdot x\text{H}_2\text{O}$	CoO	Co_2O_3	Co_3O_4
Cobalt contents (wt.%)	32.24	≤ 49.58	78.67	71.08	73.44

Table 4. Cobalt contents in various raw materials used to prepare cobalt powders

5. The continuous and controllable combustion synthesis

Basing on the above analysis, it is very difficulty to obtain the satisfied ultra-fine spherical Co powders by the conventional technique while using $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ as the raw materials. Ultra-fine spherical Co_3O_4 powders are the best raw material used to fabricate ultra-fine spherical Co powders. But the key question is how to obtain ultra-fine spherical Co_3O_4 powders by a low energy-consumption and low-cost method? And then a continuous and controllable combustion synthesis has been proposed.

5.1. Basic principles

5.1.1. Selecting the raw powders

As mentioned above, although spherical Co powders can be obtained by decomposing spherical $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ powders, there is the higher content of some impurities (such as S and Ca) and the size of Co powders is still larger. So $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders will be used as the raw materials to fabricate ultra-fine spherical Co_3O_4 powders, and then ultra-fine spherical Co powders can obtained by hydrogen-reduction technology in Fig.5. Using $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders to fabricate ultra-fine spherical Co_3O_4 powders, the following advantages can be utilized and some key technical difficulties must be resolved.

5.1.2. Utilizing the exothermal reaction of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ — Low energy-consumption

Selecting $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders as the raw material to fabricate ultra-fine Co_3O_4 powders, a main advantage is that the decomposition processing of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the air is an exothermal processing according to DTA. Seham *et al.* [23] showed that the total exothermal energy was 24.26kJ/mol during the decomposition of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the air, which is an enough energy to operate the following decomposition processing of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Therefore, after giving a starting energy, the decomposition once starts, and then further heating does not need, and the needful energy of the following decomposition can be provided by the released reaction energy of CoC_2O_4 converting into Co_3O_4 . So the decomposition processing of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the air is a spontaneous and continuous processing, and a lot of energy can be saved.

5.1.3. Utilizing airflow dispersion to in situ break the adhesion among Co_3O_4 particles

Morphology of Co_3O_4 powders can still inherit the short-fibrous structure of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders when the decomposition processing is carried out in a fixed bed, namely Co_3O_4 particles can easily grow together to form a short-fibrous structure (see Fig.14(a)) due to the exothermal reaction. But a short-fiber is composed of ultra-fine spherical Co_3O_4 particles

with a size of about $0.1\sim0.2\mu\text{m}$, see Fig.14(b). The Co_3O_4 particles arrange a short-string along to the fiber, and there is a weak adhesion between particles. The results further explain why the short-string or dendritic Co powders is easily obtained by decomposing and reducing $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ powders in a fixed bed. Ultra-fine Co_3O_4 powders with the size of $0.1\sim0.2\mu\text{m}$ can be obtained if the weak adhesion between them before forming a strong bond can be broken *in situ*. How to break the adhesion of Co_3O_4 particles? So a dynamic decomposing processing is proposed. If an airflow can be provided to $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ powders during decomposition, the released energy can be homogenized to avoid overheat in part and also impede the adhesion and grow among Co_3O_4 particles.

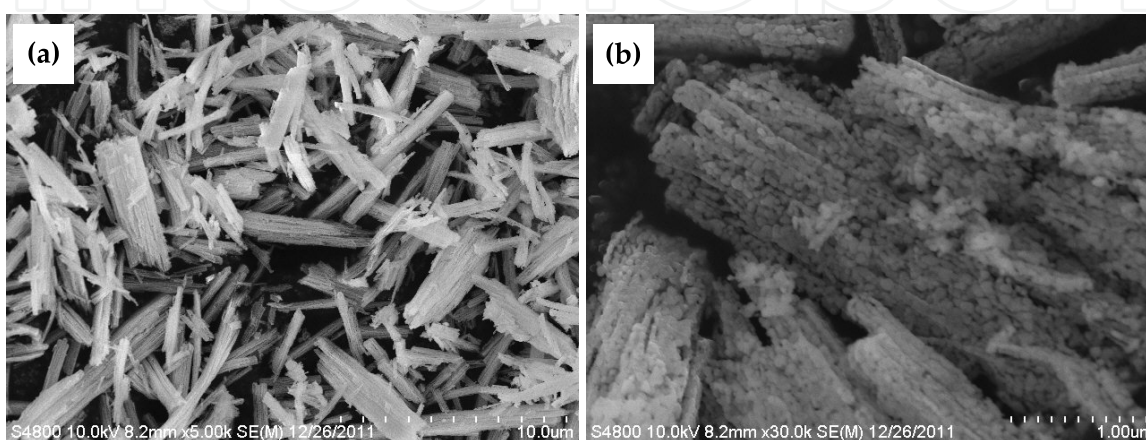


Figure 14. The short-fibrous structure of Co_3O_4 particles obtained by decomposing $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ powders in a fixed bed: (a) low multiple, the morphology with a short-fibrous structure is very similar to that of $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ powders; (b) Magnifying several fibrous particles, consisted of ultra-fine spherical Co_3O_4 particles with a size of about $0.1\sim0.2\mu\text{m}$

5.2. Production equipments

According to the above desires, a continuously dynamic-controlled combustion synthesis (CDCCS) process is proposed and the bottlenecks of continuous production and process controls of combustion synthesis (CS) have also been solved satisfactorily. The preparation of ultra-fine Co_3O_4 powders via CDCCS is carried out in a gas-solid fluidized bed unit (CS unit), as shown in Fig.15. The unit is patented equipment consisting of fluidized bed roaster, feeding systems, receiving systems, dust collection systems and air supply system [24,25].

There are reaction and cooling boiling (11 and 21) that formed by gas-solid fluidization on the upper and lower gas distribution plates (61 and 62), respectively. The raw material on the upper gas distribution plate (61) is fleetly penetrated by the gas from the upper gas pipeline (32). The boiling bed with the flowing property like liquid is formed when the superficial gas velocity reaches a critical value of 0.03m/s . In our experiments, the superficial gas velocity is $0.09\sim0.18\text{m/s}$. The height of boiling beds, locating between the gas distribution plates to the top of overflow gates, is about 500mm . And several thermocouples are installed on the CS unit' wall and the location is about at $2/3$ height of boiling beds.

When the boiling bed (11) containing $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders which are fed into by the screw feeder (51) is preheated to 380°C by the hot carrier gas, $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders will react with O_2 in the air. Co_3O_4 powders pour from the upper overflow pipe (35) under gravity and enter the cooling boiling bed (21), followed by collecting from the lower overflow pipe (34). The temperature of CS in reaction region can be perfectly controlled though the linkage of the upper thermocouple (71) and the upper gas pipeline (32).

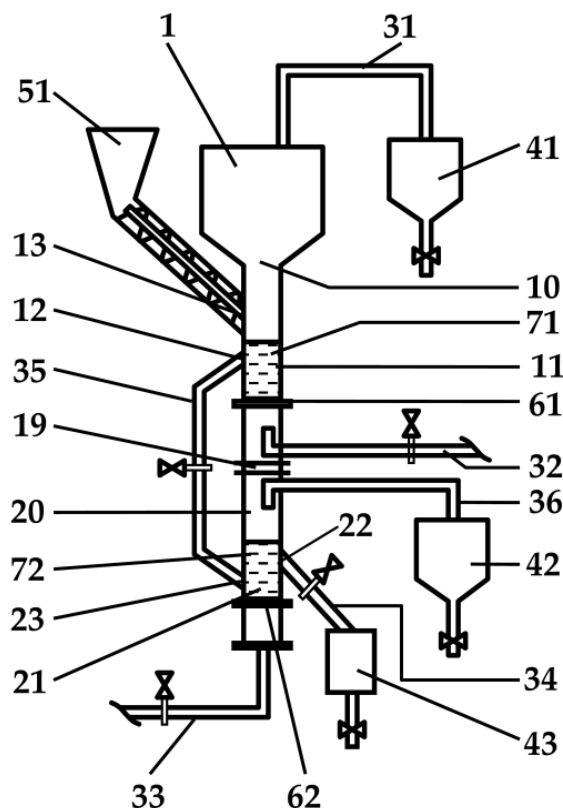


Figure 15. Schematic representation of CS unit, in which Co_3O_4 powders fabricated by CDCCS: 1. Fluidized bed roaster; 10. Upper chamber; 11. Reaction boiling bed; 12. Upper overflow gate; 13. Feed inlet; 19. Clapboard; 20. Lower chamber; 21. Cooling boiling bed; 22. lower overflow gate; 23. Overflow entry; 31. Upper exhaust pipe; 32. Upper gas pipeline; 33. Lower gas pipeline; 34. Lower overflow pipe; 35. Upper overflow pipe; 36. Lower exhaust pipe; 41. Upper dust catcher; 42. Lower dust catcher; 43. Product collection container; 51. Screw feeder with storage hopper; 61. Upper gas distributor; 62. Lower gas distributor; 71. Upper thermocouple; 72. Lower thermocouple

5.3. Process analysis of CDCCS to fabricate Co_3O_4 powders

When the reactant $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders are fed by the screw feeder (51) into the boiling bed, no self continuous reaction occurs. Only when $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders in the combustion zone are heated by hot carrier gas, and the continuous reaction is ignited. This means that once the combustion reaction between O_2 and $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders is ignited, the released heat by the combustion reaction can be used to ignite the following exothermic reaction and no external heat is needed, and then the hot carrier can be transformed into the cool carrier gas.

Fig.16 shows the effect of the feeding rate of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders and the superficial gas velocities in the boiling bed on the temperature of combustion wave [26]. Temperature of combustion wave decreases with increasing gas velocity at a given feeding rate. Therefore, the temperature of combustion wave can be adjusted and controlled dynamically by changing the feeding rate of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders and/or the superficial gas velocity. According to the thermal analysis of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the air, the CoC_2O_4 can be completely converted to Co_3O_4 at a temperature higher than 320°C . Therefore, in order to ensure the dehydration reaction of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and the oxidation reaction of CoC_2O_4 can be carried out rapidly and completely, and the combustion temperature is set at $380\sim 400^\circ\text{C}$.

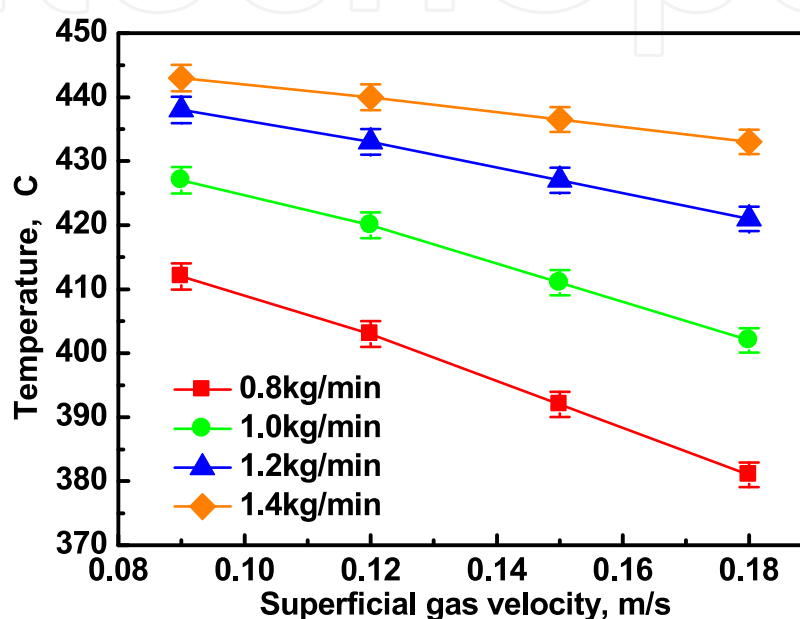


Figure 16. Effect of the feeding rate of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders and the superficial gas velocities in the boiling bed on the temperature of combustion wave

Being different from the conventional CS, the combustion wave here is almost full of the combustion zone in the middle of the boiling bed and the temperatures in whole space are homogeneous. The combustion wave is relatively suspended in the fluidized bed, and the temperature in the combustion zone can be dynamically controlled by adjusting the flow of carrier gas, as mentioned above. During the preparation, $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powders are continuously fed by the screw feeder into the upper area of reaction boiling bed and contacted with the combustion wave. The Co_3O_4 particles are dispersed by the carrier gas flow. After the CS, the dispersed Co_3O_4 powders fall down and leave the combustion wave in time through flowing out off the overflow gate on the wall of the unit continuously.

The CS unit in the paper is different from the conventional one reported in Ref. [27,28]. In the conventional unit, the reactants and products are nearly stationary while the combustion wave propagates from reactants to products. The advantages of the continuous fluidization technologies and the CS are well utilized and combined in our unit. The combustion wave is relatively stationary, but the reactants and products are continuous and mobile at a given speed.

5.4. Quality of products

Fig.17(a) shows the morphology of Co_3O_4 powders fabricated by the CDCCS. The adhesion among Co_3O_4 powders shown in Fig.14(b) is broken by the carrier gas flow. The particles exhibit a spherical or quasi-spherical shape, and the size of Co_3O_4 particles is about $0.1\sim 0.3\mu\text{m}$. In the gas-solid fluidized bed unit, the temperature of the whole boiling bed is nearly homogeneous, and almost each solid particle in the boiling bed has a similar surrounding, namely all $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ particles can be completely decomposed to form Co_3O_4 . The suspended solid particles collide and grind each other without aggregation by the action of airflow, which accelerates the formation of the spherical Co_3O_4 powders. The uneven distributions of particle size or hard aggregation appear scarcely due to the favorable diffusion condition and rapid transfer of heat and mass. The Co_3O_4 powders with a narrow particle size distribution, good dispersity and excellent fluidity are fabricated by the CDCCS.

As mentioned above, using the ultra-fine spherical Co_3O_4 powders fabricated by the CDCCS as raw materials, the ultra-fine spherical or quasi-spherical Co powders is easily obtained by hydrogen-reduction technology, as shown in Fig.17(b). The Co powders with an average size of $0.6\mu\text{m}$ possess a narrow particle size distribution, good dispersity, and excellent fluidity.

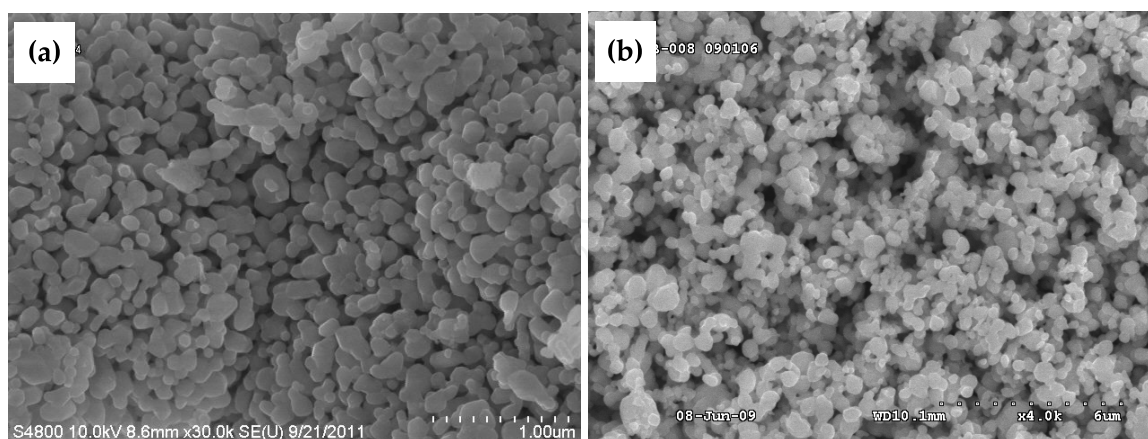


Figure 17. (a) Ultra-fine spherical Co_3O_4 powders fabricated by CDCCS; (b) Ultra-fine spherical Co powders fabricated by hydrogen-reduction technology using ultra-fine spherical Co_3O_4 powders as raw materials

5.5. Advantages of the CDCCS

The preparation of ultra-fine spherical Co_3O_4 powders (the size is smaller than $0.8\mu\text{m}$ and the length-diameter ratio is smaller than 2) by the CDCCS has been successfully applied in the industrialization production in Xiamen Golden Egret Special Alloy Co., Ltd [24,25]. The novel method has the following several advantages:

1. Comparison with the fixed bed, ultra-fine spherical Co_3O_4 powders are continuously produced in the fluidized bed unit and the production efficiency is improved.
2. No external heat is needed after the reaction is once ignited, and then the energy consumption is reduced.
3. The fabrication process is in a closed unit so that a clean operation environment is realized and a high pure product is fabricated.
4. The device operations are automated, except the transport of reactants and products, thus the labor intensity is largely decreased.
5. The most important advantage is that the properties of the products fabricated by CDCCS are more excellent than those fabricated by the conventional method.

6. Expectation

Ultra-fine spherical Co_3O_4 powders are firstly fabricated by CDCCS, and then ultra-fine spherical Co powders can be fabricated by hydrogen-reduction technology. Can ultra-fine spherical Co powders be directly fabricated by CDCCS if a hydrogen flow is blown into the CS unit? However, the hydrogen is a flammable and explosive gas. Therefore, our future work is how to directly fabricate ultra-fine spherical Co powders in the CS unit by solving the key technology difficulty of the hydrogen safety. Furthermore, the fabrication of many other metal powders (for example, W, Mo powders, etc.) can be applied in the CS unit.

Author details

Chong-Hu Wu
*China National R&D Center for Tungsten Technology,
 Xiamen Tungsten Co. Ltd. Technology Center, Xiamen, China;
 Xiamen Golden Egret Special Alloy Co. Ltd., Xiamen, China*

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