The development of preparation technology of molybdenum powder

With the increasingly development of automobile, electronics, aviation, spaceflight and other industries, it has put forward higher and higher requirements on the quality of molybdenum powder metallurgy products. Therefore, it is required that molybdenum powder should have better performance in chemical composition, physical morphology, average particle size, particle size distribution, apparent density, mobility and other aspects. Molybdenum powder will develop towards high purity, superfine, adjustable composition and other directions, thus it will have higher requirements on preparation theory and preparation technology.

Research on the reduction theory of molybdenum powder

The preparation process of molybdenum powder mainly includes three independent chemical reactions: ammonium molybdate will be reduced into MoO3, MoO will be reduced into MoO2 and MoO2 will be reduced into molybdenum powder. It is a very complex physical and chemical process that will have a series of complex phase change processes and will be related with
morphology, size, structure, performance and many other factors of ammonium molybdate as well as MoO3, MoO2, molybdenum blue and other intermediate molybdenum oxidation products.

Currently, the dynamic mechanics of reducing MoO3 into Mo has basically become clear, which means that the reaction process will be similar with nuclear dissociation when MoO3 is reduced into MoO2, while the reaction process will be similar with nuclear shrinkage when MoO2 is reduced into Mo. There are two processes when reducing MoO2 into Mo: under low dew point, they will be changed in the form of pseudomorph; under high dew point, they will be migrated by chemical gas phase. However, people still have different opinions on the reactive mode when reducing MoO3 into MoO2. Sloczynski thought that the reaction of reducing MoO3 into MoO2 is in fact a kind of continuous reaction that uses Mo4O11 as intermediate products. Ressler and other people thought that in the reduction process, MoO3 will absorb hydrogen atom and will generate HxMoO3, afterwards, HxMoO3 will release hydrogen atom and will change to MoO3 and MoO2. As the temperature rises, MoO2 will continuously grow up, while the intermediate state MoO3 will be further reduced into Mo4O11, which will be further reduced into MoO2.

Research on the preparation technology of superfine/nano molybdenum powder

Currently, the preparation method of superfine molybdenum powder mainly includes evaporative state molybdenum trioxide reduction method, activation reduction method and ammonium dodecamolybdate hydrogen reduction method. The preparation method of nano molybdenum powder mainly includes microwave plasma method, electric pulse discharge and so on.

Evaporative state molybdenum trioxide reduction method

By using evaporative state molybdenum trioxide reduction
method, **MoO3 powder** (the purity is 99.9 percent) will be filled in the molybdenum boat, which will be replaced in the preheating furnace at 1,300-1,500 degrees Celsius and will be evaporated into gas state. After being carried by H2-N2 under 150 ml/min flow and H2 under 400 ml/min flow, MoO3 vapor will enter the reaction zone and will be reduced into superfine molybdenum powder. This method can obtain uniform and spherical molybdenum powder that has the particle size of 40~70nm, but it will be difficult to control the technological parameter. Among them, the mixing temperature of MoO3-N2 and H2-N2 as well as the composition of MoO3 will have large influence on the particle size of powders.

**Activation reduction method**

In activation reduction method, hexaammonium molybdate (APM) will be used as raw material, which will be used in making superfine molybdenum powder through the reduction process under the catalytic action of NH4Cl. In the reduction process, NH4Cl will fully volatilize. The reduction process mainly includes four stages: ammonium chloride will be heated and decomposed, APM will be decomposed into molybdenum oxide, MoO3 will react with HCl and will generate MoO2Cl2 as well as MoO2Cl2 will be reduced into superfine molybdenum powder by hydrogen. Compared with traditional method, the reduction temperature has reduced about 200-300 degrees Celsius by using this method. Besides, it only has one time reduction process and has simple technological process. Molybdenum powder that produced by this method, of which the average particle size can reach 0.1μm, besides, powders will have good sintering character.

**Ammonium dodecamolybdate hydrogen reduction method**

By using ammonium dodecamolybdate hydrogen reduction method, ammonium dodecamolybdate will be filled in nickel alloy boat, which will be placed in tube furnace and will be reduced by hydrogen at 530 degrees Celsius. Afterwards, it will be
reduced by hydrogen again at 900 degrees Celsius, thus molybdenum powder that has the specific area of larger than 3.0m2/g and the particle size of 900nm can be obtained. However, as this method only has technological process description and is still lack of analysis on the process mechanism, its feasibility is waiting to be observed.

Hydroxy thermal decomposition method

In hydroxy thermal decomposition method, hydroxyl molybdenum will be used as raw material, which will have thermal decomposition by vapor under normal pressure, 350-1,000 degrees Celsius and under N2 atmosphere. As hydroxyl compound will finish nucleation, crystallization and crystal nucleus growth after being decomposed, molybdenum powder will have fine particles as well as the average particle size will be 1-2μm. Molybdenum powder that produced by carbonyl method will have high chemical purity and good sinterability.

Microwave plasma method

Microwave plasma method is used in producing molybdenum powder by using the principle of carbonyl thermal decomposition. In this method, microwave plasma device will be used in the breakdown of N2 and other gases by high frequency electromagnetic oscillation microwave, thus it will generate high temperature microwave plasma, furthermore, Mo(CO)6 will have thermal decomposition under N2 plasma atmosphere and will generate nano molybdenum powder that has uniform particle size. By using this kind of device, CO that generated in this process can be removed immediately, besides, Mo will be rapidly condensed and will be sent into gathering unit. Therefore, by using this method, it can obtain nano molybdenum powder that has smaller particle size (the average particle size will be smaller than 50nm) than carbonyl thermal decomposition method, the single particle will have near-spherical shape as well as will have high stability under normal temperature. As a result, this kind of molybdenum
powder can be widely used.

**Plasma hydrogen reduction method**

The principle of plasma hydrogen reduction method is as follows: high pressure direct current arc will be ejected to high frequency plasma airflow by hybrid plasma reaction unit, thus it will generate hybrid plasma airflow, which will be reduced by plasma vapor and will be made into superfine molybdenum powder. Afterwards, the superfine molybdenum powder will be injected in the direct current arc ejector and will immediately cool down under the effect of cooling water and will generate superfine particles. Molybdenum powder that produced by this method will have the average particle size of 30-50nm as well as can be used in the spherical powder of thermal spraying. This method can also be used in producing other superfine powders of refractory metals, such as tungsten powder, tantalum powder and niobium powder. Although molybdenum powders that produced by microwave plasma method and plasma hydrogen reduction method will have high purity and good morphology, the production cost will be very high.