

## **4 METAL POWDER TREATMENT**

### **4.1 Annealing**

It is customary that the powder producer delivers the powder to the fabricator ready for mixing. The aims of annealing are:

- 1) to soften the powder
- 2) to reduce the residual amount of oxygen, carbon and/or nitrogen from the powder.

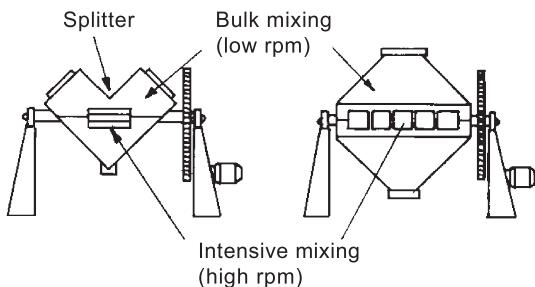
The annealing operation may be done in an atmosphere furnace or a vacuum furnace. The former may be of batch or continuous type. The furnace construction is similar to that given in Chapter 6, which deals with sintering technology. Annealing temperatures are kept as low as possible to minimize sintering.

### **4.2 Powder Mixing**

The term ‘blending’ is strictly applied to a one component operation, whereas mixing involves more than one type of powder, e.g. mixing of solid lubricant with a metal powder or powders of several other metals. Sometimes the additive acts as lubricant as well as alloying addition, e.g. graphite in iron powder.

Various variables in the powder mixing process have been highlighted by Hausner.<sup>1</sup> They are:

1. Type of mixer
2. Volume of the mixer
3. Geometry of the mixer
4. Inner surface area of the mixer
5. Constructional material and surface finish of the mixer
6. Volume of the powder in the mixer before mixing
7. Volume of the powder in the mixer after mixing
8. Volume ratio of component powders
9. Volume ratio of mixer to powder
10. Characteristics of component powders
11. Type, location and number of loading and emptying devices
12. Rotational speed of mixer
13. Mixing time
14. Mixing temperature
15. Mixing medium (gaseous or liquid)
16. Humidity, when mixing in air.



**Fig. 4.1** V-type and double cone mixers.

Mixing efficiency is best when the powder volume is about 50% to 60% of the mixer volume. Optimum mixing time may be from between 5 to 30 minutes but this can be determined only by experience with a given mixture in a particular mixer. The aim is to mix the powders only as long as necessary to achieve a thorough mix and to fix a uniform apparent density of the mix from batch to batch. The apparent density of the mix tends to increase with mixing time.

#### Types of Mixers

Among various types of mixers available, the following are most common for metal powders (Fig.4.1):

**Double Cone Mixer:** This consists of vertical cylinders with conical ends, which rotate about a horizontal axis. This rotation imparts a continuous rolling motion which spreads and folds the powders as they move in and out of the conical area. This action thoroughly mixes the powders with little or no change in the size and shape of the individual particles. Figure 4.2 shows the double cone mixer flow pattern.

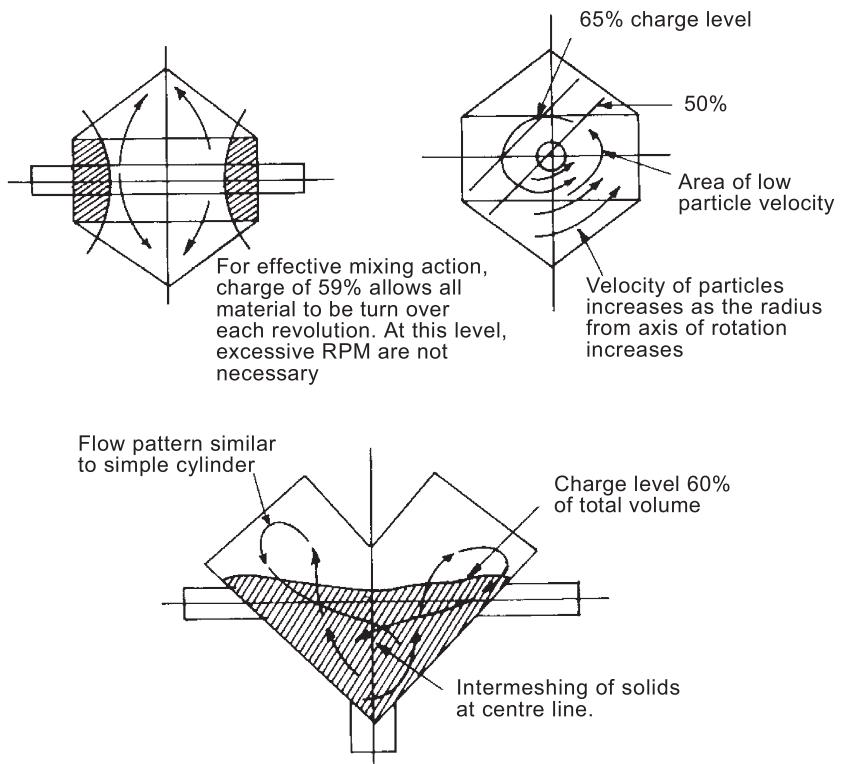
**V-Mixer:** This is constructed by joining two cylinders of equal length into a 'V'. As the 'V' rotates about its horizontal axis, the powder charge splits and refolds. Figure 4.2 illustrates the V-mixer flow pattern.

#### 4.3 Particle Size Reduction

Suitable size reduction processes normally produce an increase in the surface area (as a result of decreasing the average particle size) with narrow particle size distribution (i.e. small deviation of particle sizes from a mean value). This results in increased homogeneity of nonuniform mixtures, increased chemical reaction rates, to mention but a few examples of applications. The actual requirements of a suitable size reduction process are extremely varied and depend on several parameters.

Before selecting an equipment for size reduction, the following aspects may be looked into:

(a) **Type of Material:** What are the physical and chemical properties of the material? Is the size reduction process affected by, for example, hardness or toughness or by chemical reactions?



**Fig. 4.2** Flow pattern in (a) double cone and (b) V-type mixers.

**(b) Final Size:** To what particle size the metal be reduced? Should as narrow particle size distribution as possible be achieved?

**(c) Abrasion:** Which impurities caused by abrasion of the grinding elements must be avoided? What quantity of impurities is still permissible in other cases?

**(d) Versatility:** If necessary, should wet size reduction be possible? Should the size reduction be carried out in an inert atmosphere or in a vacuum?

Various methods for size reduction can be classified as:

(i) **Crushing:** The major equipments are mortar and pestle, heavy drop hammer, and jaw crushers. In jaw crushing the crushing chamber is formed by one fixed jaw and one movable jaw between stationary side support walls. The movable jaw is mounted eccentrically at the top and is driven by a motor via a flywheel. During the crushing process, the material is drawn down into the tapered crushing chamber as a result of the eccentric jaw motion and is reduced in size by compression and frictional forces. In addition, the angle between the jaws can be altered to give optimum adjustment to the crushing of the material. The final crushed product particle size can be adjusted to values between 15 and 1 mm by adjusting the gap at the base of the jaws. The standards jaws and side walls are manufac-

tured from hardened steel. If the feed material is very abrasive or particular impurities are to be avoided, these components are also available in stainless steel or hard tungsten carbide. If the fixed jaw is removed, access is given to the crushing chamber and the equipment can be cleared easily. In addition, the connection of an exhaust device allows work to be carried out in dust free conditions.

(ii) **Ball Milling:** The ball mills can be divided into two types: centrifugal and planetary mills. In a centrifugal ball mill, a single bowl fastener is merely horizontally and eccentrically driven while not rotating itself. In spite of this, the velocity of the grinding balls in this case is still six times that of the grinding balls in the gravity ball mills.

In planetary ball mills two or four bowl fasteners, each of which accommodates one grinding bowl, are attached to a supporting disc. During grinding, the grinding bowls and supporting disc rotate in opposite directions, so that two different centrifugal forces act on the bowl contents. The grinding material is reduced in size as a result of both attrition and impact. The grinding balls have a velocity which is twelve times that of the grinding balls in a grinding ball mill. Each grinding medium influences the grinding process via the specific weight of balls. For example, if a grinding medium of agate (specific weight 2.6 g/cm<sup>3</sup>) is used, the corresponding balls have a smaller impact energy than those of tungsten carbide (specific weight 14.75 g/cm<sup>3</sup>). The more mixing grinding process is intended, the smaller is the ball size selected. The grinding time in case of centrifugal ball mill is increased because of smaller ball acceleration.

(iii) **Disc Grinder:** The disc grinders are suited for processing hard brittle materials. A wet grinding in a closed grinding vessel which is driven horizontally and eccentrically and which contains grinding elements (disc or ring) is used to reduce the material to give a final particle size of a few micrometers. Impact and friction between the grinding elements and the grinding vessel cause such grinding energy that the process is generally concluded within a few minutes.

Table 4.1 gives the details of various grinding elements. The chemical composition qualitatively determines the type of contamination which can occur, whilst the abrasion behaviour determines the quantity thereof. Other details like specific weight (ball weight in ball mills), Mohs hardness, compression and breaking strength (in the crushers) and chemical resistance should also be considered.

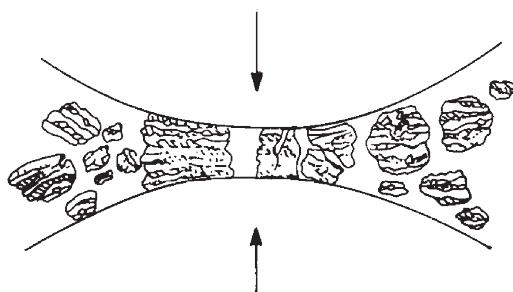
(iv) **Attritor Milling:** Attritor milling or mechanical alloying is achieved by high energy ball milling under conditions such that powders are not only fragmented but also rewelded together. In this case, the ball charge is stirred vigorously with rotating paddles. The first commercial production used attritors able to process up to 34 kg of powder per charge but nowadays, up to 1 t of powder is milled in a 2 m diameter mill containing more than a million balls which weigh a total of 10 t. The charge is a blend of elemental and prealloyed powders at least one of which is

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**Table 4.1** Some grinding element materials

Material	Abrasion behaviour	Specific weight g/cm <sup>3</sup>	Mohs hardness	No chemical resistance in
Agate ( $\text{SiO}_2$ )	Very abrasion-proof approx. 200 times more resistant than hard porcelain	2.65	7	Hydrofluoric acid (HF)
Zirconium oxide ( $\text{ZrO}_2$ )	Very abrasion-proof approx. 10 times more resistant than sintered corundum	5.7	8.5	Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) Hydrofluoric acid (HF)
Alumina ( $\text{Al}_2\text{O}_3$ )	Good abrasion resistance	4.0	9	conc. Acids
Hard porcelain	Sufficiently abrasion proof	3.1	8	conc. Acids
Hardened chromium steel 2080	Good abrasion resistance better than CrNi-steel	7.9		Acids
Hardened steel CK45	Good abrasion resistance	7.9		Acid
Stainless steel 4301	Average abrasion resistance	7.9		Acids
Hard metal tungsten carbide	Extremely abrasion proof approx. 200 times more resistant than agate	14.75	8.5	Nitric acid ( $\text{HNO}_3$ ) Hydrochloric acid (HCl)

a ductile material. To provide a dispersed phase in superalloys, fine inert oxides can be included in the charge, usually  $\text{Y}_2\text{O}_3$ . Mechanical alloying process was first invented by J.S. Benjamin at INCO, N.Y., in early seventies.



**Fig. 4.3** Effect of single collision between two balls on trapped powder.

Figure 4.3 illustrates the effect of a single high energy collision between two balls or powder trapped between them. The ductile elemental metal powders are flattened, and where they overlap, the atomically clean surfaces just created weld together, building up layers of composite powder, between which are trapped fragments of the brittle powder and the dispersoid. At the same time, work hardened elemental or composite powders fracture. These competing processes of cold welding and fracture occur repeatedly throughout the milling, gradually kneading the composites so that their structure is continually refined and homogenized.

Mechanical alloying is not simply mixing on a fine scale: true alloying occurs. The progress of alloying can be monitored by x-ray diffraction studies.

#### **4.4 Granulation**

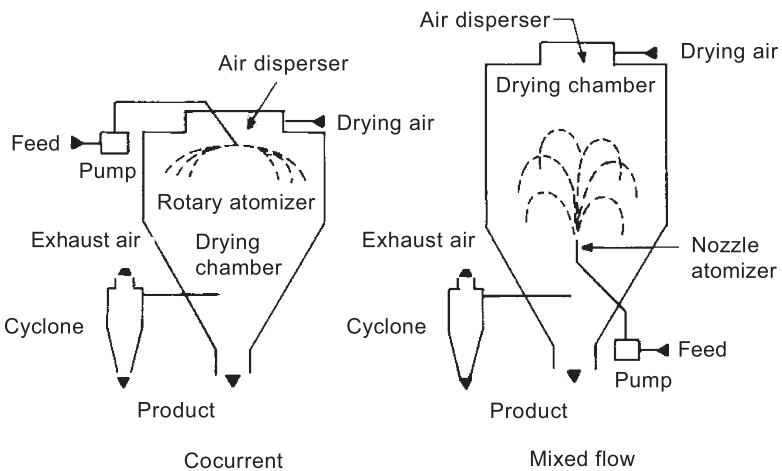
Fine hard particles such as tungsten, molybdenum and WC–Co are non-freeflowing and are difficult to press. Moreover the handling of such fine particles is also difficult. Consequently, large agglomerates are formed by granulation method. In this case, the continuous stirring of powder-organic slurry is used, while the volatile agent is removed by heating. The process is better suited for small batch sizes.

One of the better form of processing the slurry is known as spray drying. The slurry is sprayed into a heated free-fall chamber where surface tension forms spherical agglomerates. Heating of the agglomerate during free fall causes vaporization of the volatile agent, giving a hard dense packed agglomerate.

Three standard techniques are used to atomize slurry for spray drying: 1. single-fluid nozzle atomization; 2. centrifugal (rotating disc) atomization, and 3) two-fluid nozzle atomization. The largest agglomerate sizes (600  $\mu\text{m}$ ) are achieved by the single-fluid nozzle. The centrifugal atomizer yields agglomerate sizes up to 300  $\mu\text{m}$ , and the two-fluid nozzle produces agglomerates only up to about 200  $\mu\text{m}$  in size.

Suitable binder materials must be homogeneously dispersable (preferably soluble) in the liquid used to form the slurry. Plasticizers, e.g. ethylene glycol, may be used with binding materials that are hard or brittle and that tend to crack during drying. Suspending agents, e.g. sodium carboxymethyl cellulose, may be needed to prevent solids from settling within the slurry. Deflocculating agents, e.g. sodium hexametaphosphate, aids in the formation of slurry by preventing the agglomeration of fine particles. Wetting agents, e.g. synthetic detergents, also may be used to maintain solids in suspension.

Figure 4.4 illustrates schematics of centrifugal and single-fluid nozzle atomizers. In the former, the atomizer and the inlet for the drying air are positioned at the top of the dryer. The atomized slurry is of maximum liquid content when it encounters the laminar flow of hot incoming air. The maximum product temperature is relatively low and the evaporation time is relatively short. However, the product exists with moist air, and the exit



**Fig. 4.4** Spray dryers: (left) cocurrent spray-dryer with centrifugal atomizer and (right) mixer flow spray-dryer with a nozzle atomizer.

temperature must be relatively high to obtain a dry product. In the nozzle atomizer, the slurry and drying air inlet are at opposite ends of the drying chamber. Partially dried droplets encounter the incoming hot air, and the product heating is greater. In the two-fluid nozzle atomization, the residence time of the spray is increased and it provides a means for reducing the size of the chamber needed for drying.

The majority of the spray dried product is discharged through a rotary valve into interchangeable containers attached at the base. Product fines entrained in the exhaust air are separated using a cyclone or bag filters. Product fines may be used in some pressing operations, but are often recycled into the feed slurry. Periodic cleaning of the dryer using a liquid spray is required to remove the granulate crust. Abnormal large granules and flakes of granulate crust from the wall of the dryer are undesirable and are commonly removed by screening.

Air bubbles present in the feed slurry or occluded during atomization using a two-fluid nozzle may persist as relatively large pores in the granule. Granules with a large crater are often noticed in industrial spray dried material. The tendency for these shapes is higher when the inlet temperature is relatively high, the binder content or molecular weight is relatively high and the solids loading in the slurry is relatively low. Rapid surface drying and the formation of the surface of low permeability cause bursting of the granule due to gas pressure.

A major precaution in spray drying is the fact that the granules should not be so strong that it does not lose its identity during compaction. The popularity of spray drying as a means of using fine powder sizes in high productivity forming equipment is increasing. A disadvantage is that the organic binder must be removed in the sintering cycle.

#### **4.5 Coating on Metal Powders**

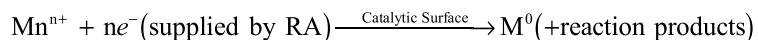
In number of cases, the base metal powders may be coated by another chemical species. The purpose may be to produce a homogeneous mixing, e.g. W–Cu, a hard surface or deposition of soft low melting point metals on ceramics to impart better compressibility during compaction. One of the simplest method may be the mechanical method, say ball milling of WC–Co. However, the uniformity of coating in such case is questionable. Some of the more common methods are described below:

(i) **Electroplating:** In this method, a second dispersed phase of controlled particle size may be introduced into a plating solution. This is referred to as dispersion, inclusion, occlusion, composite or electrophoretic plating, deposition or coating. The requisites are:

- The particles must be insoluble (or only slightly soluble) in the solution;
- The particles must be compatible with the solution, i.e. not produce any detrimental effect;
- The particle must be dispersed either naturally (as colloid size particles) or mechanically (stirring, agitation) in order to contact physically the surface being coated.

Electrophoretic coating produces a coating on a conducting substrate from a dispersion of colloidal particles. The powder to be coated is immersed in an aqueous dispersion which dissociates into negatively charged colloidal particles and positive cations. An electric field is applied with the powder mass as anode; the colloidal particles are transported to the anode, where they are discharged and form a film. The coating is air dried and baked to remove the solvent medium. The coating is nonadherent and must be processed faster by compaction and sintering. The coating thicknesses can be varied by controlling voltage, electrode spacing, suspension concentration and time.

(ii) **Electroless Deposition:** Electroless plating processes differ from electroplating processes in that no external current source is required. Metal coatings are produced by chemical reduction with the necessary electrons supplied by a reducing agent present in the solution (RA):



The significance of the process is that the reaction is catalysed by certain metals immersed in the solution and proceeds in a controlled manner on the substrates surface.

The deposit itself continues to catalyze the reduction reaction so that the deposition process becomes self-sustaining or autocatalytic. These features permit the deposition process of relatively thick deposits. This process is different from other types of chemical reduction by (a) simple immersion or displacement reactions in which deposition ceases when equilibrium between the coating and the solution is established (e.g. copper immersion on steel

from copper sulphate solution) and (b) homogeneous reduction where deposition occurs over all surfaces in contact with the solution. The reducing agents most widely used are sodium hypophosphate (for Ni, Co), sodium borohydride (for Ni, Au), dimethyl amine boron (for Ni, Co, Au, Cu, Ag), hydrazine (for Ni, Au, Pd) and formaldehyde (for Cu). To ensure spontaneous reduction other chemicals are added. These are generally organic complexing agents and buffering agents. Other additives provide special functions as in electroplating solutions: additional stabilizers, brighteners, stress relievers.

The following are the advantages of electroless plating over electroplating:

1. Internal surfaces are evenly coated. The uniformity is limited only by the ability of the solution to contact the surface and be replenished at the surface.
2. Deposits are less porous.
3. Almost any metallic, nonmetallic, non-conducting surfaces, including polymers, ceramics, glasses can be plated. Those materials which are not catalytic can be made catalytic by suitable sensitizing and nucleation treatments.
4. Electrical contacts are not required.
5. The deposits may have unique chemical, mechanical, physical and magnetic properties.

However, there are some disadvantages too as compared to electroplating:

- Solution instability
- More expensive
- Slower deposition rates
- Frequent replacement of tanks or liners
- Greater and more frequent control for reproducible deposits.

(iii) **Coating by Hydrometallurgical Process:** The details of the hydrometallurgical process for production of metal powders have been described earlier in Chapter 2. A great number of metals, metalloids, non metals, metal alloys, oxide natural minerals, hard metal compounds and plastic powders can be coated with one or more metals selected from Ni, Co, Mo, Cu or Ag to form new materials, called composite powders.

In developing composite powders, the cores must conform to certain requirements: (a) they must be nonreactive in the system selected for metal deposition; (b) they must be catalytically active with respect to the deposited metal, and (c) they should be in such a physical form as to be able to remain suspended in solution in the agitated autoclave. Many metals, metal alloys carbides, nitrides and some nonmetals such as graphite and phosphorus are catalytically active and are readily coated without special treatment of the core but some cores have to be activated. The most effective way of activating is to wash with a stannous chloride solution followed by treatment with palladium chloride. During this treatment, palladium chloride is adsorbed on the surface and is reduced in the autoclave by hydrogen to the metallic form, thus forming catalytically active sites on which the metal precipi-

**Table 4.2** Molybdenum coated composite powders prepared by precipitation of molybdenum from the aqueous ammonical–ammonium sulphate solution by hydrogen and subsequent heat treatment under H<sub>2</sub> atmosphere at 950°C<sup>2</sup>

Composition	Conditions			Core	PdCl <sub>2</sub> treatment	Product		Mo left in reduced solution, g/l
	Temperature, °C	P <sub>H<sub>2</sub></sub> , kg/cm <sup>2</sup>	Time, min			Mo	Core	
Mo/Ni	160	36	30	22 g/l	Ni powder, 10 µm	no	69.4	29.1
Mo/Fe	190	36	30	12 g/l	Fe, RZ365	no	n/a	n/a
Mo/Fe	160	25	120	21 g/l	Fe, RZ365	yes	70.0	28.8
Mo/Al	190	25	120	12 g/l	Al, type 40	no	n/a	39.7
Mo/Al	160	34	60	21 g/l	Al, spherical	yes	59.4	39.7
Mo/W	160	36	45	21 g/l	W, 7–9 µm	yes	58.0	41.4
Mo/Si	180	35	15	11 g/l	Si, -325 mesh	yes	64.0	32.5
Mo/C	190	25	60	22 g/l	Graphite, 38	no	69.9	27.5
Mo/Al <sub>2</sub> O <sub>3</sub>	160	38	30	21 g/l	Al <sub>2</sub> O <sub>3</sub>	yes	68.8	30.9
Mo/ZrO <sub>2</sub>	190	26	35	21 g/l	ZrO <sub>2</sub>	yes	51.3	43.7
Mo/TiO <sub>2</sub>	160	36	35	21 g/l	TiO <sub>2</sub> , Micria	yes	60.0	39.6
Mo/TiC	160	40	20	21 g/l	TiC, 3 µm	yes	60.6	38.2
Mo/Cr <sub>3</sub> C <sub>2</sub>	160	39	45	21 g/l	Cr <sub>2</sub> C <sub>3</sub> , -325 mesh	yes	70.4	26.0
Mo/SiC	160	35	40	21 g/l	SiC, 11 µm	yes	63.5	35.5
Mo/WC	160	40	90	21 g/l	WC, 200/325 mesh	yes	51.4	48.5
Mo/Glass	160	39	70	21 g/l	Glass, -400 mesh	yes	63.5	35.8
Mo/Si <sub>3</sub> N <sub>4</sub>	160	35	15	21 g/l	Si <sub>3</sub> N <sub>4</sub> , Un. Carb.	yes	63.5	35.7
Mo/Asbestos	160	38	20	6 g/l	Asbestos, Merck	yes	66.6	32.7

### *Metal Powder Treatment*

tates preferentially. The metal most easy to coat with is nickel. Coating with cobalt is much more difficult and only the very active cores, such as carbides can be coated completely. The deposition of Cu or Ag can be achieved, but without catalyst forms spotty coating.

There are no restriction on the composition of composite powders and powders containing 1 to 99 % of the coating metal have been prepared. However, in order to ensure complete coating of the core a 2–3  $\mu\text{m}$  layer of the coating metal is considered to be a minimum requirement.

When complete coating is desirable, the specific gravity of the components, and the particle size and shape should be taken into consideration for the calculation of the percent coating.

Table 4.2 illustrates a list of molybdenum coated powders, which is precipitated from aqueous ammonium sulphate–ammonia system as a lower molybdenum oxide containing 4–5%  $\text{NH}_3$ . The reduction takes place in the presence of a catalyst and it was established that palladium chloride and molybdenum powder itself can catalyze the reaction. The molybdenum oxide precipitated on the cores in converted to the metallic form by treatment with hydrogen at 950°C.<sup>2</sup>

Composite powders produced by such method have found commercial applications in flame and plasma spraying. Such powders are useful in preparation of alloys, dispersion-strengthened materials, porous materials, low friction materials and hardfacing coatings.

### **References**

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2. W. Kunda, New Developments in the Preparation of Composite Powders, in: Proceedings of 7th Plansee Seminar, 21–25 June, 1971, Vol.IV, Metallwerk Plansee, Reutte.