Advances in Gold Powder Technology

CLOSER CONTROL OF PARTICLE SIZE AND SHAPE

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The routes for the preparation of gold powders, required for many important industrial applications, are described in this article. Attention is drawn to the highlights of recent work designed to improve the reproducibility of particle size and shape of gold powders made by precipitation from aqueous solutions.

The use of gold in the form of powder has increased greatly during the last decade. Probably the largest growth is associated with those powders developed for the formation of films of gold on heat resistant, usually ceramic, substrates. The films form electrically conductive paths that form the "wiring", and the bonding areas for mounting active electronics components in microcircuitry. A long established use in decorating ceramic and glass table ware, in which the visual appearance of the gold surface is the most important parameter, has also taken advantage of the new developments in gold powders.

Now that controlled particle size distribution and shape characteristics, together with specific surface properties, can be achieved there has also been a growth in the use of gold in powder metallurgy. Mass production methods in die pressing and sintering can achieve reproducibility in dimensional and weight parameters because the necessary properties for metered flow of the powder and the packing characteristics required can be designed into the preparation of the powder.

The powders described are in the general size group of 0.1 μm to 100 μm and, apart from colloidal dispersions of gold particles, this range includes almost all the gold powders used.

The Importance of Reproducibility

Reproducibility is the key to all the applications for gold powder. The knowledge that has been developed during the last few years has made it possible to precipitate gold powders in a wide range of particle size distributions and shapes with a much improved degree of reproducibility. The properties of particle size and shape, together with free flow and ease of dispersion into liquids, are the limiting parameters in the three major areas of application that have been mentioned. Although they apply in powder applications with many materials other than gold, the ways in which they may be controlled have been researched and developed for gold powders following routes that are in many ways peculiar to gold.

Mechanical Methods

The major part of the development of gold powders in the last few years has been concerned with the precipitation of gold in aqueous systems. It would be wrong, however, to ignore the mechanical methods of producing gold powders, some of which are very old, because these are still used in a basically unchanged form to make some powders. A particularly interesting one is based upon the craft of the gold beater and his product—gold leaf. In this process sheets of gold or a malleable gold-rich alloy are reduced in thickness by rolling and beating. Rolling the gold produces a foil between 0.001 and 0.002 cm thick and this is beaten in a gold beaters "book" until the thickness is reduced to something in the order of 0.2 to 0.5 μm.

At this stage the edges of the leaf normally would be trimmed and the centre of the leaf packed between tissues. When the final product is to be a powder, the whole of the leaf including the thicker edges can be used. To make a powder the leaf is dispersed into a viscous, usually water soluble medium. Sugar and glucose syrups are often used. When the disperse is agitated or stirred the gold leaf is broken down into small particles. Very little welding occurs between the particles, and the powder produced in this way consists of pieces of fragmented leaf between 0.2 to 1.5 μm thick.

Figure 1 shows a scanning electron micrograph of a gold powder made from gold leaf. The particle size of the powder, in terms of the diameter of a circle of area equivalent to the mean projected area of the particles, can be varied by controlling the viscosity of the medium used and typically covers the range 3 to 50 μm. Where a highly viscous medium is used the particles are smaller. Dense films of gold

Fig. 1 This powder was made by breaking down gold leaf. The random shape of the flake-like particles is obvious, although there are also a few crystals present ×625

about 1 to 3 μm thick can be produced by firing a film of these particles on to a variety of heat resistant substrates.

Following a method of preparation that is based almost entirely on ancient craft, the next example bridges the gap in time and uses modern technology in the form of a mechanical method to modify the properties of a precipitated gold powder made by established methods. Gold powders have been produced by precipitation techniques that include reactions in aqueous systems and by the thermal decomposition of organic compounds of gold. There are problems associated with these methods that affected the quality of the products. Prior to the application of techniques that will be described later a severe degree of aggregation of the precipitated powder was often seen and little control could be exercised over particle shape. The same limitations apply to powders produced by the decomposition of organic gold compounds. In order to achieve powders with discrete particles—necessary for the development of flow characteristics for powder metallurgy and for dispersion into organic media for the preparation of electrically conductive paths for electronics applications—a mechanical milling process was often used as the final stage of preparation of the powder.

Standard ball mills were used, generally with an organic solvent as a milling vehicle in which surfactants could be dissolved or dispersed in order to reduce particle-to-particle welding. In this way a proportion of the aggregates formed in the precipitation, washing and drying processes used to produce the gold powder could be reduced to primary particles. In addition, the packing characteristics of the powder were often improved by "rounding off the corners" of gold particles that resulted from the movement of the mill balls. Two further effects were commonly seen. Despite the use of surfactants, some welding was inevitable when the aggregates were deformed by the motion of the mill balls. In addition, as very small particles were formed by detachment from the aggregates or as a result of attrition of other particles, there was a tendency for the gold to migrate from their new high energy surfaces to the surfaces of larger particles. The result was a gold powder relatively free from aggregates whose particles fitted into a narrower particle size range than the original powder before milling.

A final stage in the development, prior to the control of precipitation, also involved milling, but this time in a development of the conventional standard ball mill.

When the internal wall of a ball mill cylinder is equipped with flanges it is possible to rotate the mill and its charge at a speed that allows the charge to be lifted to the highest point and then dropped through the mill diameter to produce an impact on the lowest point.

If a gold powder with fairly closely controlled particle size is milled in this way, the impact when the balls and powder in the milling vehicle fall causes a deformation of the powder particles to take place and produces a flake-like powder. Flake powders made

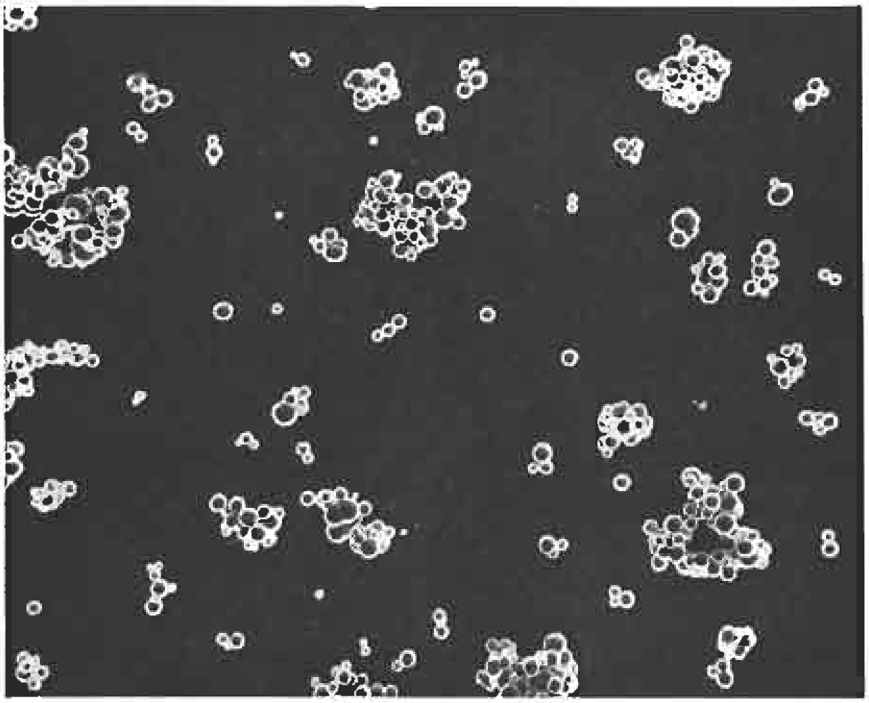

Fig. 2 The gold powder in this scanning electron micrograph illustrates the close particle size limits that can be achieved by precipitation. Virtually all the particles are between 0.6 and 1.0 μm in size ×1250

in this way played an important part in the development of applications for gold powder in electronics microcircuitry.

Advances in Chemical Methods

It is in the area of chemical reduction of gold in the form of powder from aqueous solutions that the major advances have been made in recent years. The need for such advances was presented by the growing requirements for specific properties of gold powders (1, 2, 3, 4). A summary of the ways in which the requirements have been met include the following:

The shape of gold particles can be determined by the conditions of precipitation—particularly by the type of chemical reductant used.

The use of colloidal materials during precipitation to inhibit particle to particle adhesion and growth provides control over the formation of aggregates.

Control of the nucleation stage followed by particle growth has made possible the precipitation of gold powders with closely controlled particle size ranges.

The formation of a discrete particle of gold in the size range 0.1 to 100 μm takes place in two stages. First the gold nucleus forms and then a period of growth follows during which quantities of gold are deposited on the nucleus. Exactly how a crystal nucleus is formed in a homogeneous liquid system is not known with certainty. In the preparation of gold powder the initiation of a gold nucleus is usually promoted by the use of a reducing agent. If an accurately controlled amount of reductant is dispersed very rapidly in the solution containing the gold, a reproducible number of gold nuclei will be formed. It is also possible to control the size of the

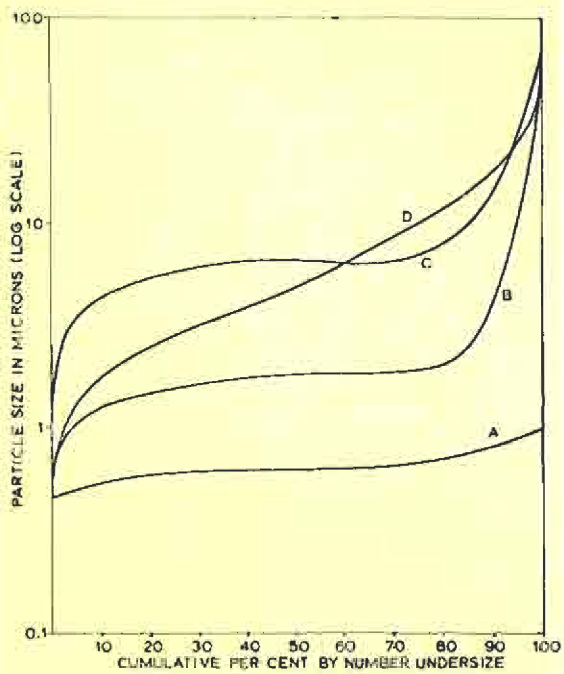

Fig. 3 Particle size distribution of four precipitated gold powders. Many variations in particle size distribution can be obtained by varying the number and the time of the nucleation steps

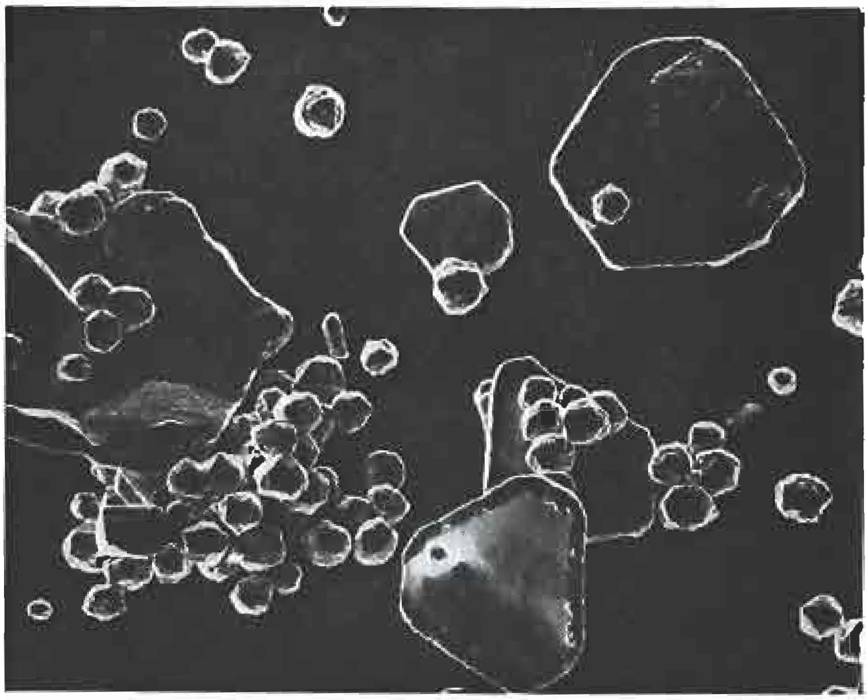

Fig. 4 The gold powder in this scanning electron micrograph contains crystalline particles some of which are roughly spherical. As more gold is deposited on these particles they will assume a shape similar to that of the larger particles ×1250

nuclei within some rather useful limits (5, 6, 7).

When it is then required to induce growth by further deposition of gold, it is necessary to prevent flocculation of the existing nuclei. If flocculation occurs, the sites upon which the further deposition of gold takes place will be of random size and shape and the size and shape characteristics of the product will reflect this starting point. The use of a lyophilic colloid will prevent both flocculation and the particle growth that is associated with the surface reaction phenomena that is characteristic of very small particles. Colloidal materials such as gelatin or gum arabic have been used to promote the stability of disperses of small particles. The availability of a large number of water soluble or dispersible polymeric materials has now reduced the dependence upon naturally occurring materials.

Following the preparation of a monodisperse of

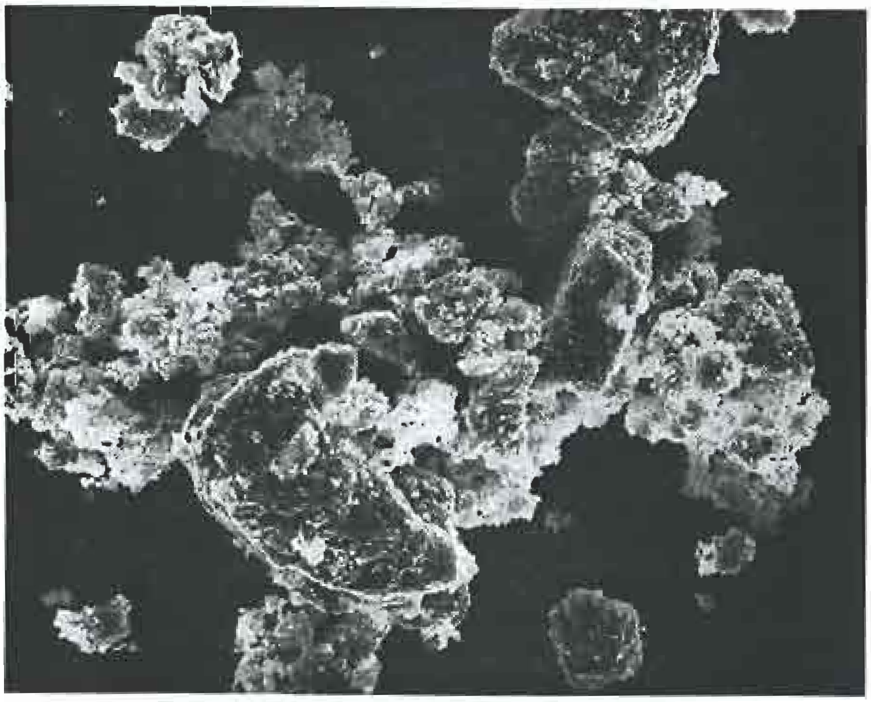

Fig. 5 This is a gold powder that consists of aggregates of small particles and shows little of the well formed shape characteristics of modern powders. It would be necessary to use a mechanical milling process before using the powder ×625

gold nuclei of the required character, the criteria being the size and number of nuclei, growth is induced by a reaction between the gold in solution and a reductant that does not easily initiate nucleation. The control parameters now include temperature and the concentration of gold in solution but two other factors have overriding influence. The first is the relationship between the number of nuclei present and the amount of available gold in solution. This determines the ultimate size of the gold particles. The second factor is the reductant used, and this can determine the shape and characteristics of the gold powder.

The relationship between the number of nuclei and the amount of gold available for subsequent deposition on the nuclei is simple. For a given quantity of gold the weight of each particle is proportional to the number of nuclei. The number of nuclei is reproducible by the control of temperature and concentration of reactants, and the rate of dispersion of the nucleating reductant. A typical result of the approach is shown in Figure 2, which is a scanning electron micrograph of a gold powder with a narrow particle size range similar to the plot A in Figure 3. In this powder virtually all the particles are between 0.6 and 1.0 μm.

If more than one nucleation stage is carried out, while the growth of particles on existing nuclei is continued, then a very powerful control over particle size characteristics is exercised. By changing the number of nucleation steps, and their times during the precipitation of the powder, many variations on particle size distribution are possible. Plot D is of a distribution similar to plot A, but with a much wider size range. Staggering the nucleation steps produces skewed distributions such as those of B and C. An example of a gold powder made by using more than one nucleation stage is shown in Figure 4. The scanning electron micrograph, Figure 5, shows a typical gold powder produced by a method in which nucleation and growth were not controlled.

The shape characteristics of gold powder fall into two categories. The gold powder particles can be almost entirely spherical. The reductants that produce spherical particles include sulphur dioxide, sulphites and related compounds.

Alternatively the gold powder has particles that show a well defined crystallinity. This situation arises from the use of reductants covering a wide range of chemical constitution (1, 2, 3, 4).

It is clear then that the technology, upon which the preparation of a number of styles of gold powder that are important in industrial applications rests, is now at a high stage of development. As a result it is a relatively simple matter to produce gold powders, in a reproducible manner, that span a wide range of particle size distributions and fit into the broad divisions formed by spherical particle habit and flat crystalline particles.

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Ultra-high Vacuum Seal for Stratospheric Sampler

COLD WELDED GOLD TUBE PROVIDES COMPLETE RELIABILITY

When the reliability of equipment is of paramount importance it is frequently found that the unique properties of gold result in it being utilised for the construction of the most critical components. An interesting application for gold tube, which makes full use of the corrosion resistance, ductility and weldability of the material has recently been reported by a group of workers at the Aeronomy Laboratory, NOAA Environmental Research Laboratories, Boulder, Colorado (*Rev. Sci. Instrum.*, 1976, **47**, (12), 1479).

In order to collect samples of the stratosphere for analysis of chlorocarbons and other minor constituents an all-metal sampling system, which is carried aloft by a balloon and recovered by parachute, has been developed. Prior to flight the spherical sampling containers are baked out and evacuated in the laboratory by an ultrahigh vacuum pumping unit before being sealed, which is done by pinching off a short length of high purity gold tubing with an external diameter of 6·35 mm and internal diameter 4·76 mm. Gold is an ideal material for this purpose being capable of withstanding both the high temperature required during the baking and evacuation stage in the laboratory and also the low temperature, about 200 K, encountered in the stratosphere. Even after such extremes the surface of the gold is still free from tarnish and oxidation and capable of being deformed and welded together by the modest forces available in such a lightweight system.

During the sampling and recovery stage of the flight, as the equipment descends by parachute, on-board electronic controls open the sampling container causing it to fill with air from a pre-selected altitude and then a sealing mechanism is activated. The sealing operation is again carried out on a section of gold tube which is closed off by an electrically fired explosive slug driving a wedge shaped bullet against one side of the tube while the other is constrained by a hardened anvil. As the inner surface of the gold tube is cold welded at the pinch-off a reliable seal is formed, and this is protected during the critical landing stage by the hardened tool steel bullet.