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Deposition of Ultra Fine Particles Using a Gas Jet

Seiichiro KASHU, Eiji FUCHITA, Takeshi MANABE
and Chikara HAYASHI

Project of Hayashi, Ultra Fine Particles in Research and Development Corporation of Japan, 1-11-2 Kyobashi, Chuo-ku, Tokyo 101

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Use of a gas jet for the transfer and deposition of metal or ceramic UFP has been studied. Individual particles having a diameter of less than 0.1 μm, are produced by the so-called gas evaporation method. Deposition of the UFP can be made by preparing a colliding gas flow with UFP on a solid surface. Uniformly distributed deposition of different metals or ceramics, regardless of specific gravity, can also be made. A similar technique is also usable with frozen gas UFP (CO_2 for example). A CO_2 UFP blizzard can remove photoresist without contamination or damage to a substrate (thin film chromium coated on glass). The transfer and deposit technique could be a basic method for handling UFP for industrial application.

Utilization of individual particles of metal or ceramic ultra-fine powder (UFP) having a diameter of less than 0.1 μm, has been limited because of the difficulty of handling the powder. Such particles have an extremely large surface/volume ratio and are observable only under an electron microscope. Ordinary mechanical tools have not been adequate to explore the possible benefit of utilizing such UFP.

This paper presents a simple method for handling the UFP, transport, mixing, deposition, etc. Typical hardware arrangement for the method is illustrated in Figs. 1 and 2. Figure 1 represents a case for using UFP produced elsewhere, while Fig. 2 represents a case where very fresh and non-contaminated UFP are required for deposition.

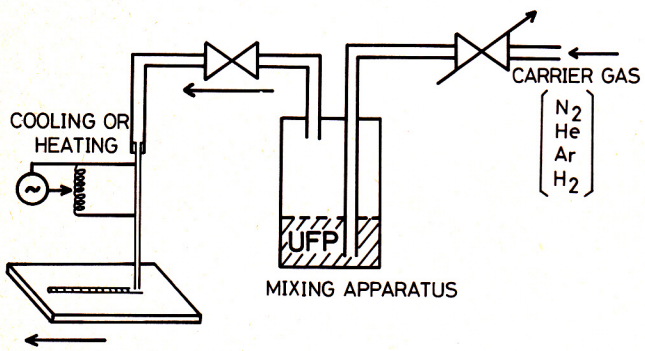

Fig. 1. Arrangement of the spray deposition for surface conditioned UFP (partial oxidation).

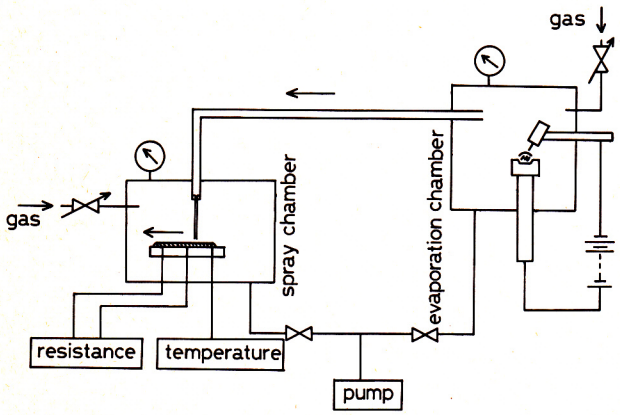

Fig. 2. Arrangement of the spray deposition for UFP as grown.

Although the method appears similar to the well-known powder spray method for plastics, etc., it should be considered as substantially different from conventional spray. Conventional spray deals with powders over several μm in diameter with a high pressure gas where the gas flow must be massive and the Knudsen number, the ratio of the length of mean free path of gas molecules to the diameter of an individual fine particle, must be very small.

In using the UFP, however, each particle is so small that it behaves like a large molecular component in a small molecular carrier gas, typically Ar, N_2, He or H_2. Even at an average gas pressure of 1 Torr ($\approx$133 Pa), where the gas flow must be considered as a free molecular flow against UFP, the UFP can be entrained practically instantly ($\sim 10^{-4}$ s); density or gravitation for conventional metals such as Fe or Ni has a practically negligible effect.

Thus such rarefied gas flow easily entrains UFP and gives a speed almost the same as the gas flow velocity. If such rather rarefied gas flow jet which has UFP as a component collides head on with a solid substrate, individual ultra fine particles hit the substrate and may stick to the surface, provided the flow velocity is sufficiently large, perhaps because of the sudden transfer of the relative momentum to surface vibration energy (heat). The major component of the carrier gas can be conventional permanent gases like Ar, N_2, H_2 that do not deposit unless the substrate temperature is below their condensation temperature. UFP of Ag, Fe, Ni, Al and TiN, having particle diameters in the range of 20 nm to 70 nm and entrained in an argon or hydrogen gas flow with calculated flow velocity around 30 m/s, have been deposited as illustrated in Figs. 1 and 2. Several nozzles with different inside diameters ranging from 0.2 mm to 1 mm have been tested. The chamber pressure, which is the intake pressure for the tubing was chosen at 860 Torr in the case of Fig. 1 and at 100 Torr of Fig. 2.

A very interesting feature of this deposition procedure is that one can probably get a variety of homogeneously mixed solid structures of any kind of UFP: Total internal energy of an individual ultra fine particle will be in

equilibrium with the temperature of the carrier gas, while the boundary surface temperature of such a particle around the contact point in a head on collision will be given by the gas flow velocity. In other words, individual particles can be sufficiently cold as a whole throughout the deposition while in the relatively small collision zone they can be joined together. Thus, the difference in specific density or solidification characteristics of the corresponding bulk metals, etc., will not be factors prohibiting a homogeneous structure. Figures 3 and 4 illustrate an example of a homogeneously mixed deposit of Fe–Ag obtained using simultaneous deposition of the two kinds of UFP. Both X-ray microanalysis and specific X-ray emission image have proven the homogeneity to the limit of the analytical instruments.

It is known that a homogeneously mixed thin layer can also be made by co-evaporation or co-sputtering in vacuum, provided such co-deposition is possible and the surface migration or rearrangement of the deposited atoms is negligible. A distinctively different feature of the proposed method as compared to a co-deposition in vacuum is that the former can be designed to produce an aggregate of microcrystalline UFP without adhesive. In vacuum deposition, however, the substrate temperature must be sufficiently high for recrystallization of the deposited layer, if a crystalline structure is required. Recrystallization temperature will normally be so high that it will be accompanied by segregation and rearrangement of the deposited layer, which will provide an adverse effect for obtaining homogeneity.

Another slightly different application of the proposed

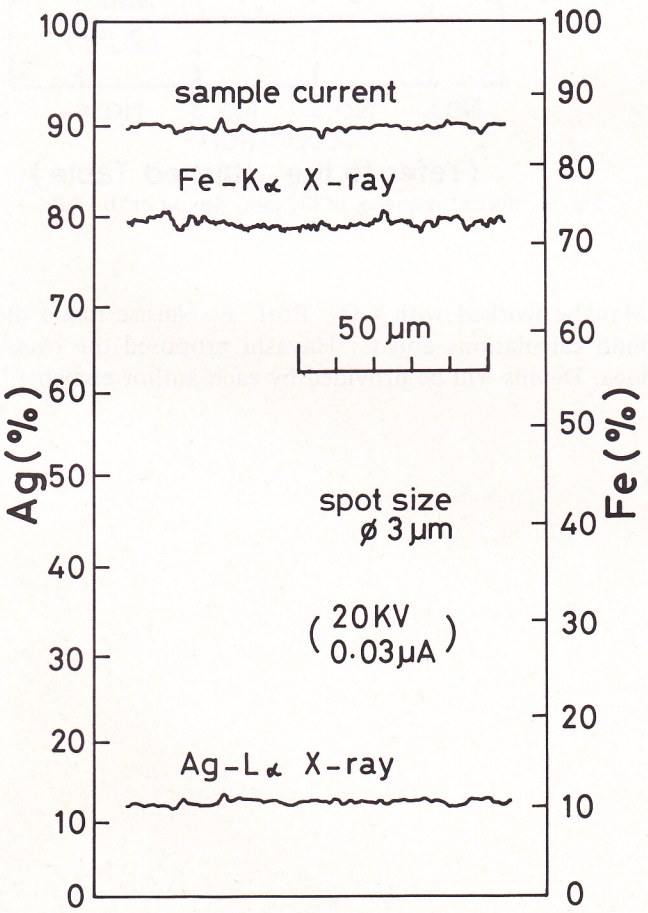

Fig. 3. X-ray microanalysis for the mixed deposit of Fe–Ag UFP.

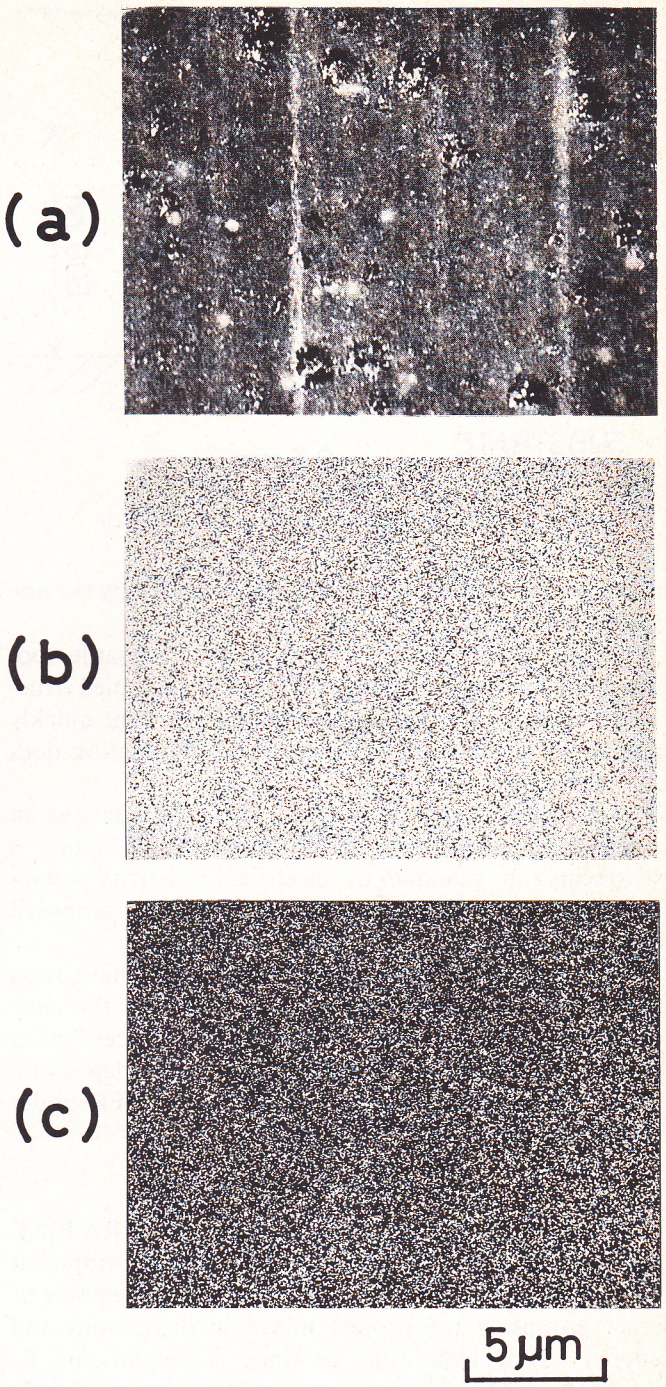

Fig. 4. Specific X-ray emission image for the mixed deposit of Fe–Ag UFP; secondary electron image (a), FeK_α X-ray image (b) and AgL_α X-ray image (c). Spot size is $\phi 3\ \mu m$. (20 KV, 0.03 μA)

method has been made with very small particles of frozen CO_2. The colliding CO_2 particles in this case sublime sooner or later from the substrate unless the temperature of the substrate is sufficiently low. A good application of the colliding CO_2 fine particles is to wipe off organic adhesive on glass, ceramics or metals. Photoresist Az-1350, as an example, can be removed to expose a chromium oxide layer on glass plate, that is, a blank mask plate for photolithography. The frozen CO_2 particle has apparently sufficient hardness to break the resist layer but it does no damage to the chromium oxide layer. The proposed method with frozen gas particles can be a clean, pollution-free procedure which may offer a new kind of surface treatment. Figure 5 illustrates a micro-

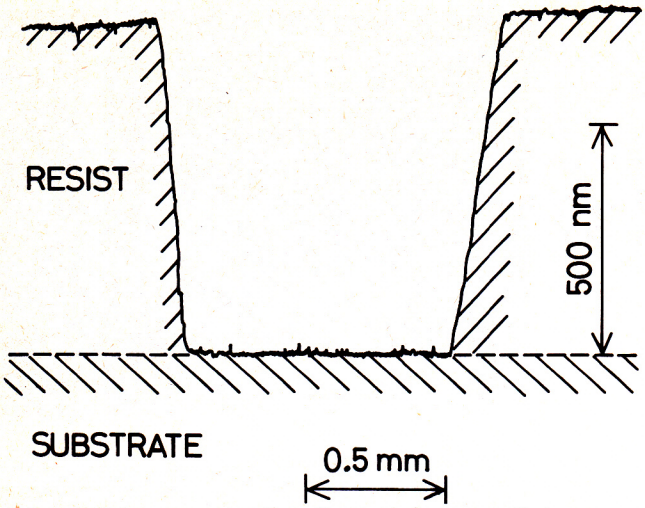

Fig. 5. Micro-depth profile scanned across a ditch.

depth profile scanned across a ditch generated by the fine gas jet with frozen CO_2 particles.

The proposed method can thus be a versatile tool which may produce materials of unusually designed structures; binding of different materials can be done quickly and at a low temperature where bulky liquidation does not play a role.

The proposed method is also a good candidate as an evaluation method for UFP themselves. Figure 6 represents an example of electrical resistivity values measured over deposits prepared by the proposed method.

Fair to good reproducibility of the values have been found with test samples prepared under nearly the same conditions. The electrical resistivity value often varies with hours and days from the time of the deposition which gives a reference for utilization of UFP under similar conditions.

(Table for Fig.6)

No.	character of U.F.P.	carrier gas	atmosphere at spray
1	surface conditioned (partial oxidation)	Ar	air
2		H_2 (heating)	
3	as grown	Ar	Ar
4			air

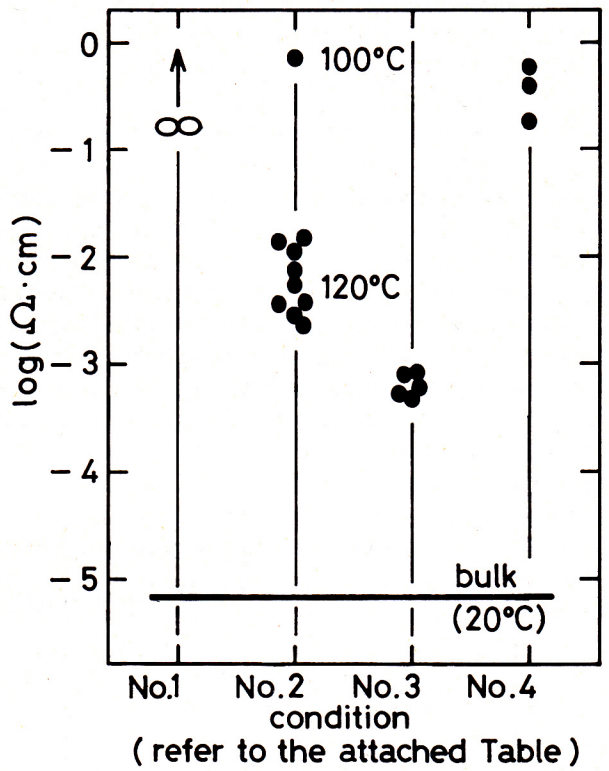

Fig. 6. Specific resistance of the spray deposit of Ni-UFP.

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