

THE SASAKI LABORATORY

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On the Formation of Powder

For last several years our laboratory carried out research of the morphological changes of substances caused by chemical and physical treatments. We studied chiefly wolframic oxide and metallic wolfram powder by employing optical and electron microscopes, X-ray diffraction, a quartz-fibre spring-balance as well as using the BET adsorption method.

1. Precipitated Wolframic Acids

Wolframic acids or wolframic oxide hydrates made by decomposing aqueous solutions of wolframate with mineral acid are known in three different colors, yellow, white, and green, probably due to different contents and different modes of combination of water.

Electron microscopic observations were made with wolframic acid crystals obtained by the decomposition of a sodium wolframate solution with hydrochloric acid under different conditions. The decomposition at 25°C yields a white precipitate consisting of 1-2 μ thin crystals of various shapes, such as a disc, halfmoon, boat, and polygon. The decomposition at a higher temperature (80°C) gives a yellow precipitate consisting of ca. 0.05 μ thin, generally angular crystals, which, though finer than the white one, precipitates faster than the latter. The part of the white precipitate which resists centrifugal precipitation, consisted of ca. 0.1 μ needles and ca. 0.2 μ particle of indefinite shape, which grow slowly to a network and strings of beads of different lengths, respectively. The dehydration-temperature curve obtained by means of a quartz-fibre spring-balance shows, with the white precipitate, a monotonously falling curve ending in the composition of WO_3 at ca. 300°C, while, with the yellow precipitate, the curve has a horizontal part extending from 85 to 185°C, which corresponds to the composition of $WO_3 \cdot H_2O$. This fact indicates the differences in the state of the combination of water of hydration. WO_3 particles obtained by dehydration are roughly of the same size (ca. 0.02 μ), independent of the condition of the formation of wolframic acids, their shape and size, and the manner of dehydration.

2. Decrease in the Surface Area of Wolframic Oxide Powder by Heating

Wolframic oxide powder is generally made by the dehydration of wolframic acid, which is complete at about 300°C. The fine powder thus obtained grows in size on heating at higher temperatures. The change in the total surface area of various powders when heated in air and in vacuum at 500-900°C was measured by the BET method with especial regard to the effect of the doping materials (K_2SiO_3 , Al_2O_3 , and KCl) added to the powders. The decrease in the surface area is greater, when the heating temperature is higher, for instance, with pure WO_3

powder the decreases effected by heating in air for five hours at 500°C and 900°C are 15 and 45 per cent respectively. The doping materials retard the surface decrease, and the effect increases with the amount added, for instance, the decreases by heating in the air for five hours at 800°C of WO_3 with 0.0, 0.1 and 0.3 per cent of K_2SiO_3 added are 40, 33, and 25 per cent respectively.

Doped WO_3 shows greater chemical adsorbing power for carbon dioxide, and a smaller volatility, when exposed to strong electron beams, these facts suggesting the doping materials can cover the surface of the oxide particles. The covering seems to be favored by the elevation of heating temperature and by the elongation of heating time, for the CO_2 adsorption is then increased. The doping materials seemingly suppress the surface mobility and the evaporation of WO_3 molecules, and consequently retard the process of surface decrease.

3. Reduction of WO_3 with Hydrogen

(i) Wolfram Powder

Inspection with an optical microscope reveals that wolfram powder obtained by reduction with hydrogen from WO_3 ultimately consists of single crystals (let us call them primary particles) of the dimension of ca. 0.5μ . If a comparatively large needle crystal of WO_3 made by sublimation is layed flat on a silica plate and reduced with hydrogen, there are formed wolfram single crystals about 0.5μ in diameter (primary particles) scattered in a row along the full length of the needle which has disappeared. If an oxide needle projecting into a free space with its one end clinging to a supporter is reduced, the primary particles formed are found clinging together to form a slightly curved string of beads whose length is slightly shorter than the original straight needle. If a larger oxide crystal or a heap of crystals is reduced, a number of primary particles formed are found clinging together to form a more or less uniform agglomerate (let us call it a secondary particle), which in its turn forms with other secondary particles a more loosely bound tertiary particle and so on.

(ii) Powder

The idea of primary, secondary, and higher order particles may be applied to numerous other cases of powder formation by chemical processes. Metallurgists, especially in wolfram metallurgy, seem to be much concerned with the particle shape, size, and size distribution without any definite idea about particles as elaborated above. In practice it is a matter yet to be determined whether the shape and size of the primary particles are more essential than those of the secondary and the higher order particles. The strength of the binding between primary particles inside a secondary particle, the porosity of higher order particles, or more generally the mode of agglomeration may also be of importance.

The shape and size of the primary particles may best be estimated by the optical or electron microscope. The BET method gives the total surface area of a definite quantity of powder which may conventionally be related to the mean size of the primary particle, if they are assumed to be all of a definite simple form.

If Stokes' law is taken to determine the particle size we must take among others into consideration firstly the fact that the density of each of the secondary and the higher order particles are smaller by an unknown amount than that of the bulk substance, and secondly the fact that the secondary and the higher order particles are liable to destruction by the process of preparing specimens for observation and measurement, while they are apt to form temporary agglomerates, when they come into contact with a certain kind of liquid.

(iii) Change in the Total Surface Area in the Course of Reduction

Pure and doped wolframite oxide was reduced with hydrogen at 800°C, and the total surface area was measured at intervals with the BET method. The results are shown in Fig. 1. The

surface area first increases, and, when about fifty per cent reduction has been reached, it begins to decrease, provided that the BET method can give correct values with such highly indefinite substance as has just been suffering vigorous reduction. This intermediate substance contains, as X-ray investigations show, various amounts of WO_3 , W_4O_{11} , WO_2 , and W.

After the completion of reduction the surface area remains constant for a time, and then begins to shift slowly to a slightly smaller constant value, but it decreases rapidly by 50 per cent, if the temperature is elevated to 900°C. Thus the change in the surface area occurs almost exclusively during the reduction, but some metallic particles melt together in hydrogen or in the vacuum at a slightly higher temperature which is still very much lower than the sintering temperature actually used in industry (2900°C). On some electron-micrographs we often find two primary particles with a rounded contour line apparently in an earlier stage of mutual fusion.

The dotted horizontal line in the figure indicated the surface area the metallic powder may assume, if each oxide particle be reduced to a metallic particle of the form similar to that of the oxide particle. If the initial oxide powder is very fine, the surface area of the resulting metallic powder comes much further below the dotted line. If they are very coarse, the metallic powder can have a surface area even larger than that of oxide powder.

With doped oxides the velocity of reduction and the amount of increase of the surface area are smaller, while the time interval for constant surface area and the final surface area are larger. The doping materials seemingly suppress both the formation of the initial primary particles and the final sintering of these particles.

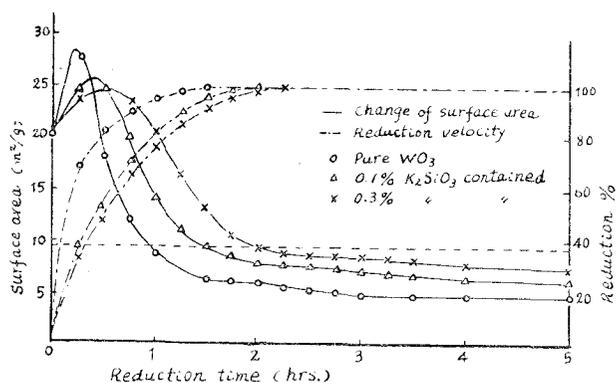


Fig. 1.

(iv) **Velocity of the Reduction of Wolframic Oxide and the Reoxidation of Wolfram Powder Freshly Reduced**

By means of a quartz-fibre spring-balance the velocity of reduction of pure WO_3 in a stream of hydrogen and the velocity of reoxidation in air were measured. Fine oxide powder (ca. 0.02μ) can be reduced to metal even at 480°C in three hours, while, a coarser one (ca. $2-3\mu$) requires three hours at 500°C for forty per cent reduction.

Metallic powders obtained at a temperature below 700°C are easily reoxidized in air, and those obtained below 610°C are even pyrophoric.

As stated above electron microscopic observations indicated that the freshly reduced metallic surface is changed by mere exposure to air. The BET method has confirmed that a fresh powder with the surface area of $2.63\text{m}^2/g$ increased its surface to $3.14\text{m}^2/g$, when exposed to air. Oxidation roughens the surface.

Occasional observations in the electron microscope of formation of needles radiating from metallic wolfram particles may be ascribed to heating by electron bombardment and consequent rearrangement of the surface oxide films already formed around the particles.

(v) **Electron Microscopic Observation of the Reduction Process**

An adaptor for the electron microscope has been devised by us, and by means of it we can observe one and the same part of a specimen before and after a certain chemical treatment without exposing the freshly treated specimen to air which may injure the new surface.

Using this adaptor, we followed individual crystals of WO_3 and MoO_3 in the course of reduction, and observed the formation of the primary particles from oxide crystals. With finer metallic crystals formed from MoO_3 we could ascertain that their contours uniformly expanded by about $10-70\text{m}\mu$, when exposed to air. The expansion is enormous, when heated in air. The expanded contours remain almost unchanged, when reduced again. In oxidation metallic atoms seem to wander outward to meet oxygen molecules.

4. The Mechanism of the Formation of Wolfram Powder

If a piece of WO_3 crystal is exposed at a high temperature, for instance 800°C , to a stream of hydrogen, there will at once be formed W atoms on the surface, though the average composition may correspond to a lower oxide. These metallic atoms initially separated by oxygen atoms must come into contact with each other as further oxygen atoms are removed by hydrogen, and form a nucleus of crystal. The nucleus will grow by coming in contact with other W atoms as the reduction proceeds. The addition of W atoms may also occur, if a freshly reduced atom can move along the surface to the nucleus by its own thermal energy, (though the negative heat of reduction can not contribute to it), or if a WO_3 or a lower oxide molecule which is easy to volatilize migrates along the surface to the nucleus to be reduced there with a smaller amount of heat of activation to a W atom which just fits into a place of the minimum energy of the growing lattice. Such a process may be called an atomic sintering. But the growth of a nucleus may not be limited

to atomic sintering. It may come, sooner or later as oxygen atoms are removed, into contact with another nucleus to form a single crystal (a primary particle) which in turn again fuses with another into a larger primary particle and so on, as the reduction progresses. The mutual fusion or the sintering of primary particles seems to be limited by the temperature, so that in a metallic powder obtained at a lower temperature of reduction the final primary particles are generally smaller.

The mutual fusion can occur between primary particles which have evolved from different oxide crystals, so that in one instance a single primary particle in the final reduction product was calculated to have assimilated all primary particles originating from several hundreds of oxide crystals of the finest size.

Since we have observed X-ray patterns corresponding to W_4O_{11} and WO_2 in a specimen incompletely reduced, we may assume the existence of W_4O_{11} and WO_2 primary particles, about which the same may be said as about metallic primary particles with the difference that lower oxide particles ultimately disappear altogether.