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XIII. An experimental study of gas borne suspensions of thermionic emitters as m.h.d. working fluids

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The use of gaseous suspensions of thermionically emitting particles as alternatives to alkali metal seeded gases for use as m.h.d. working fluids is discussed briefly. Theoretical relations proposed by Sodha & Bendor (1964) are used to show that suspensions of barium oxide in argon can have significantly higher electrical conductivities than thermally ionized caesium–argon mixtures at temperatures below about 2000 °K. This advantage is emphasized at pressures above atmospheric pressure.

Experimental studies to check the theoretically predicted conductivities are described. A technique has been developed for the preparation of submicron suspensions of barium oxide and other alkali earth oxides in inert gases. A suspension of barium oxide particles in argon has been shown to have a conductivity of 0·1 mho/m at atmospheric pressure and 1600 °K. This value is low, because of the relatively large average particle size, 0·3 μm diameter, but is of the same order as the theoretical conductivity for the experimental conditions.

1. Introduction

Most experimental work on m.h.d. power generation has relied on a working fluid made electrically conducting by the thermal ionization of an alkali metal seed. An interesting alternative is to use a finely divided suspension of thermionic emitting particles in an inert gas as the working fluid. Theoretical predictions on the application of such suspensions to m.h.d. generators were made by several workers (Dennery 1964; Sodha, Kaw & Srivastava 1965; Halasz, Szendy & Kovacs 1964) at the Symposium on m.h.d. power generation held in Paris in 1964. The predictions of Sodha & Bendor were encouraging, but of necessity contained several assumptions; principally that the work function as measured for thermionic valve cathodes applies also to submicron particles in atmospheres containing trace impurities and that uniform suspensions of charged submicron oxide particles can exist under conditions of m.h.d. interaction. Accordingly, a series of experiments are being carried out to discover whether or not stable suspensions of submicron thermionic emitting particles can be made and whether they are as electrically conducting as predicted theoretically.

2. Calculated conductivity comparison of emitter suspensions with alkali metal seeded gas

The most promising system involving thermionically emitting particles is a closed cycle loop containing a working fluid of barium oxide particles or a mixed oxide of barium, strontium and calcium suspended in a noble gas such as argon. These alkali metal oxides have low work functions provided they remain uncontaminated and therefore their application in open cycle combustion driven systems appears unlikely.

The main theoretical advantage of an emitter suspension over an alkali metal seeded gas is its higher conductivity at temperatures up to about 2000 °K especially at the pressures of 10 atm and above preferred for gas cooled nuclear reactors. Theoretically the conductivity of a suspension should vary (Sodha & Bendor 1964) as about $P^{-0.13}$ rather than $P^{-\frac{1}{2}}$ for thermal ionization of alkali metal seeded gases and P^{-4} (Lindley, McNab & Dunn, this volume, p. 368 above) for non-equilibrium ionization of alkali metal seeded gases.

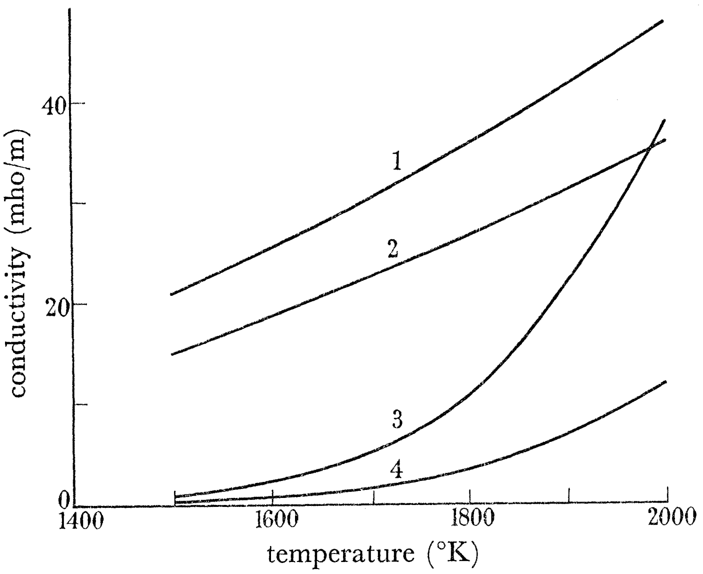

FIGURE 1. Variation of conductivity with temperature and pressure for barium oxide/argon suspension and caesium seeded argon. Curve 1, barium oxide/argon, theoretical (1 atm); curve 2, barium oxide/argon, theoretical (10 atm); 3, caesium/argon, experiment Harris (1963) (1 atm); 4, caesium/argon (10 atm) (extrapolated from 1 atm). Barium oxide/argon suspension conditions: spherical barium oxide particles; particle diameter = 0·05 μm; barium oxide/argon weight ratio = 1 at both pressures; particle work function = 1·7 eV; caesium concentration = 0·132* at. % (found by Harris (1963) to give highest conductivities).

Figure 1 shows the conductivities of some barium oxide suspensions in argon calculated from the theoretical relationships of Sodha *et al.* (1965). Experimental values for caesium–argon as measured at one atmosphere by Harris (1963) are also shown. These latter values have been extrapolated to 10 atm by taking conductivity as proportional to $p^{-\frac{1}{2}}$. The suspension conductivities were put on the same basis as the caesium/argon conductivities by taking the electron/argon collision cross-section at 1750 °K as 0.4×10^{-16} cm^2, the value calculated by Harris (1963), from his experimental conductivity values. Cross-section values at other temperatures, 0.37×10^{-16} cm^2 at 2000 °K, and 0.43×10^{-16} cm^2 at 1500 °K were obtained by extrapolation from the value at 1750 °K using the general shape of the cross section/temperature curves plotted by Shkarofsky, Bachynski & Johnston (1961).

Theoretical calculations of the non-equilibrium conductivities of alkali metal seeded noble gases near atmospheric pressure yield conductivities much higher than those shown in figure 1. For example, Talaat (1963) calculates values up to 5000 mho/m for helium seeded with 1 at.% of caesium at 1973 °K and 0·75 atm absolute pressure with an applied magnetic field of 5 Wb/m^2. However, if non-equilibrium conductivity is taken as approximately proportional to P^{-4} as proposed by Lindley *et al.* (1965) then the barium oxide–argon suspension would appear to offer higher conductivities at pressures of 10 atm and above, the range in which gas cooled nuclear reactors operate most efficiently. The detrimental affect of increased pressure on the specific power output of a non-equilibrium m.h.d. generator is also shown by Lindley *et al.* (p. 387 above).

In calculating the conductivities of the suspensions, several assumptions have been made. For example, a stable suspension of spherical barium oxide particles of uniform diameter 0·05 μm is assumed possible, also, the particle work function is taken as 1·7 eV, a value attained in thermionic valves operating under vacuum but which may be difficult to attain under the relatively impure conditions existing in an m.h.d. duct. Clearly, the calculated conductivity values must be checked experimentally before suspensions of thermionic emitters can be further considered.

3. Experimental work

The first objective was to prepare stable suspensions of pure submicron particles of alkali earth oxides in argon at atmospheric pressure and to measure the electrical conductivities of the suspensions.

(*a*) *Preparation of submicron particle suspensions*

Particles of barium oxide can be obtained by precipitating barium carbonate from a solution of barium nitrate and heating the carbonate to form the oxide. Particles of barium carbonate with diameters of about 0·3 μm have been prepared in this way but agglomeration tended to take place on converting to the oxide and the method was abandoned.

A method has now been developed in which oxygen is injected into a stream of argon carrying vapour of the appropriate alkali earth metal. Small oxide particles are thus formed *in situ*. A diagram of the apparatus is shown in figure 2.

The central vessel is made of recrystallized alumina (99·7 % pure) as are the connecting tubes which are jointed to the vessel with alumina cement. Before use the vessel is heated at 1400 °C for 24 h while purging with argon (99·999 % pure—Air Products Ltd) dried to less than 0·1 p/M water. Barium metal chips (purity better than 99·5 %), prepared under oil to prevent oxidation, washed with carbon tetrachloride, and dried with argon, are inserted into the vessel under argon. The temperature of the vessel is regulated to keep the molten barium (m.p. 860 °C) at a temperature, generally in the range 1000 to 1400 °C chosen to give the desired vapour concentration in the argon stream.

The argon plus barium vapour in the exit tube meet oxygen added at a controlled rate through a concentric inner tube and barium oxide particles leaves via a T piece outside the furnace enclosure. By regulating the vessel temperature and argon and oxygen flow rates the particle loading of the suspension can be varied. Particle loadings were measured by collecting particles on a cellulose membrane filter and weighing this at intervals.

Samples of particles prepared in this way have been collected on electron microscope grids coated with Formvar. Figure 3 shows an electron micrograph of one of these samples with particles ranging from about 0·03 to 1·0 μm in diameter. The particles are essentially spherical and there are few examples of agglomeration. The cause of the irregular outlines

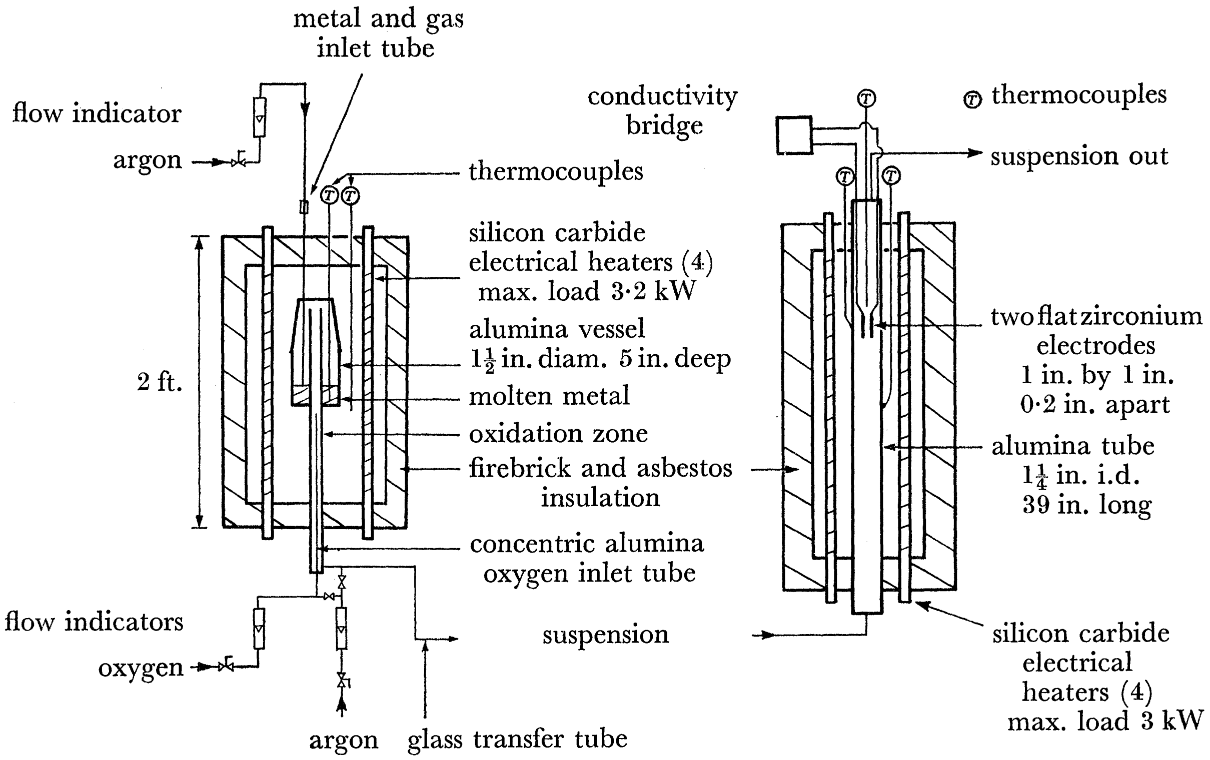

Figure 2. Apparatus for preparation of suspensions of barium oxide in argon and measurement of their electrical conductivities. (Not to scale.)

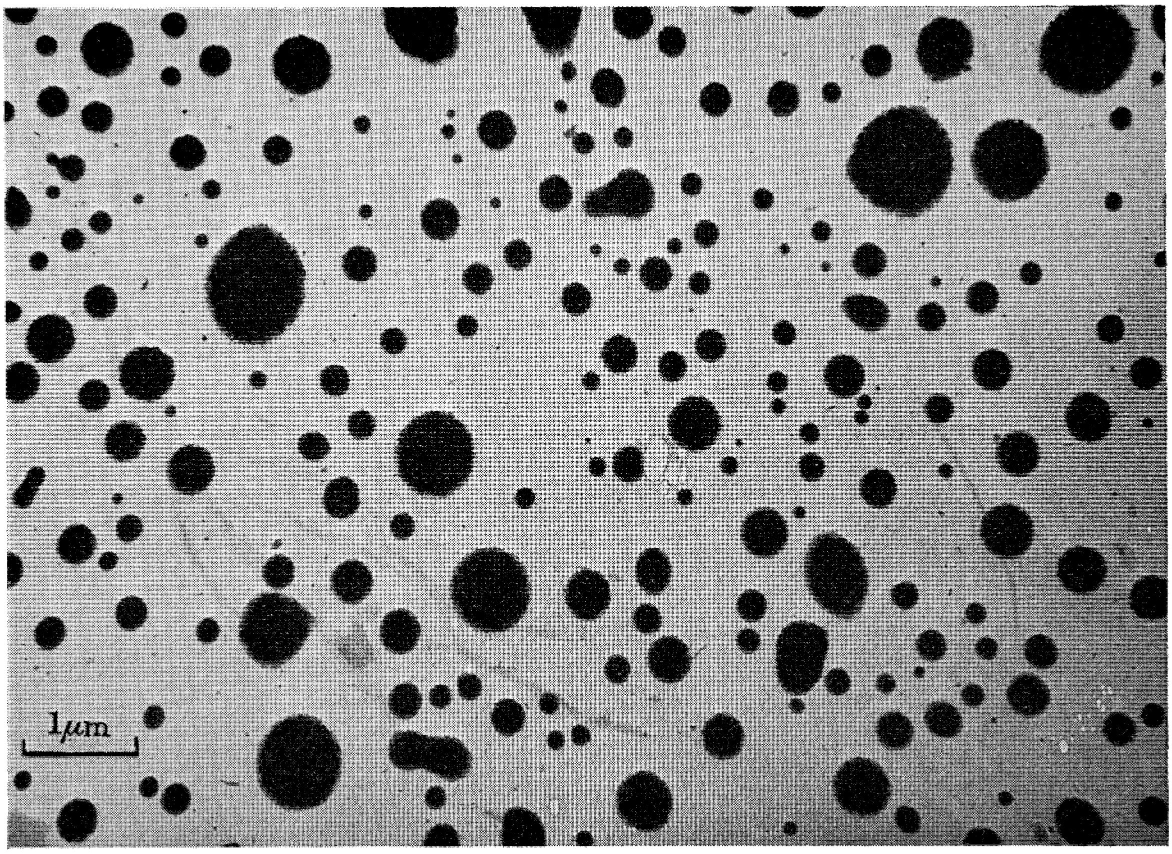

Figure 3. Electron micrograph of barium oxide.

of the larger particles is under investigation. Two possible explanations are that the larger particles are droplets of barium being oxidized at their surfaces, or, that they are massive agglomerates of very small particles. For this investigation another reactor system is being made in which the metal vapour–argon mixture passes through a superheating zone before the oxidation zone so that any liquid droplets are vaporized before reaching the oxidation zone.

(*b*) *Conductivity measurement*

An initial conductivity measurement has been carried out on a barium oxide–argon suspension prepared in the reactor shown in figure 2. The suspension was passed through a heated alumina tube containing a pair of 1 in. × 1 in. zirconium electrodes (see figure 2). The suspension flow rate of 260 ml./min of argon (s.t.p.) was such that the suspension attained the tube wall temperature before passing between the electrodes. An a.c. conductivity bridge (applied potential at balance 30 mV (r.m.s.)) connected to the electrodes indicated the conductance of the suspension.

The suspension was found to be electrically conducting, the conductivity reading could be made to fluctuate by altering the argon and oxygen flow rates. The highest conductivity measured was 0·1 mho/m, at 1600 °K for a barium oxide–argon suspension with a barium oxide/argon weight ratio of approximately 0·2 and an average particle size of 0·3 μm. Some particles were deposited in the cold transfer line after the reactor so that the barium oxide/argon weight ratio is not known exactly but would be somewhat less than 0·2, the value measured at the reactor exit earlier in the run. The theoretical conductivity values for a weight ratio of 0·2 and with 0·3 μm particles are 0·50, 0·30 and 0·12 mho/m for values of the work function taken as 1·7, 2·2 and 2·7 eV respectively.

DISCUSSION

The data reported here are from preliminary experiments but are encouraging in that suspension of essentially spherical particles of barium oxide having diameters as low as 0·03 μm have been made. Further, a suspension of these particles in argon has been found to have an electrical conductivity within an order of magnitude of the theoretical value.

The precise nature of the particles is not known yet and is under investigation. Efforts are being made to eliminate the formation of the larger particles and so obtain a more uniform size distribution with smaller average particle diameters than the 0·3 μm value reported here. Average particle diameters of about 0·05 μm or lower are needed to obtain the theoretical conductivities shown in figure 1. The formation of some particles as small as 0·03 μm in our preliminary experiments suggests that this average size of 0·05 μm may be possible in future experiments.

The experimental electrical conductivity value of 0·1 mho/m cannot be compared precisely with theoretical values because of the uncertainty in the effective work function and to a lesser extent the uncertainty in the value of the barium oxide/argon weight ratio. However, making reasonable assumptions for the values of these variables, it is found that the experimental value is of the same order of magnitude as the theoretical value. To assess the effect of work function on conductivity future experiments will be made with barium oxide, strontium oxide, and calcium oxide and mixtures of these oxides, so that the theoretical work function can be varied over a range of about 1 eV. Studies of the effect of partial oxidation of the metals will also be made as a slight excess of metal in the oxides favours lower work functions.

Change in the composition of the suspensions between the reactor and the conductivity measuring zone will be minimized in future experiments by measuring suspension conductivity in the reactor outlet tube whose temperature will be controlled by a secondary electrical heater. Particle/electrode interaction will be studied in these experiments by applying a d.c. field across the electrodes thus simulating more closely conditions in an m.h.d. generator duct.

Conclusions

(*a*) A method for preparing suspensions of submicron particles of barium oxide in argon has been developed.

(*b*) The electrical conductivity of a suspension of barium oxide particles in argon with a solids/gas weight ratio of 0·2 and average particle diameter 0·3 μm has been measured as 0·1 mho/m at 1600 °K. This value is of the same order as the value predicted theoretically.

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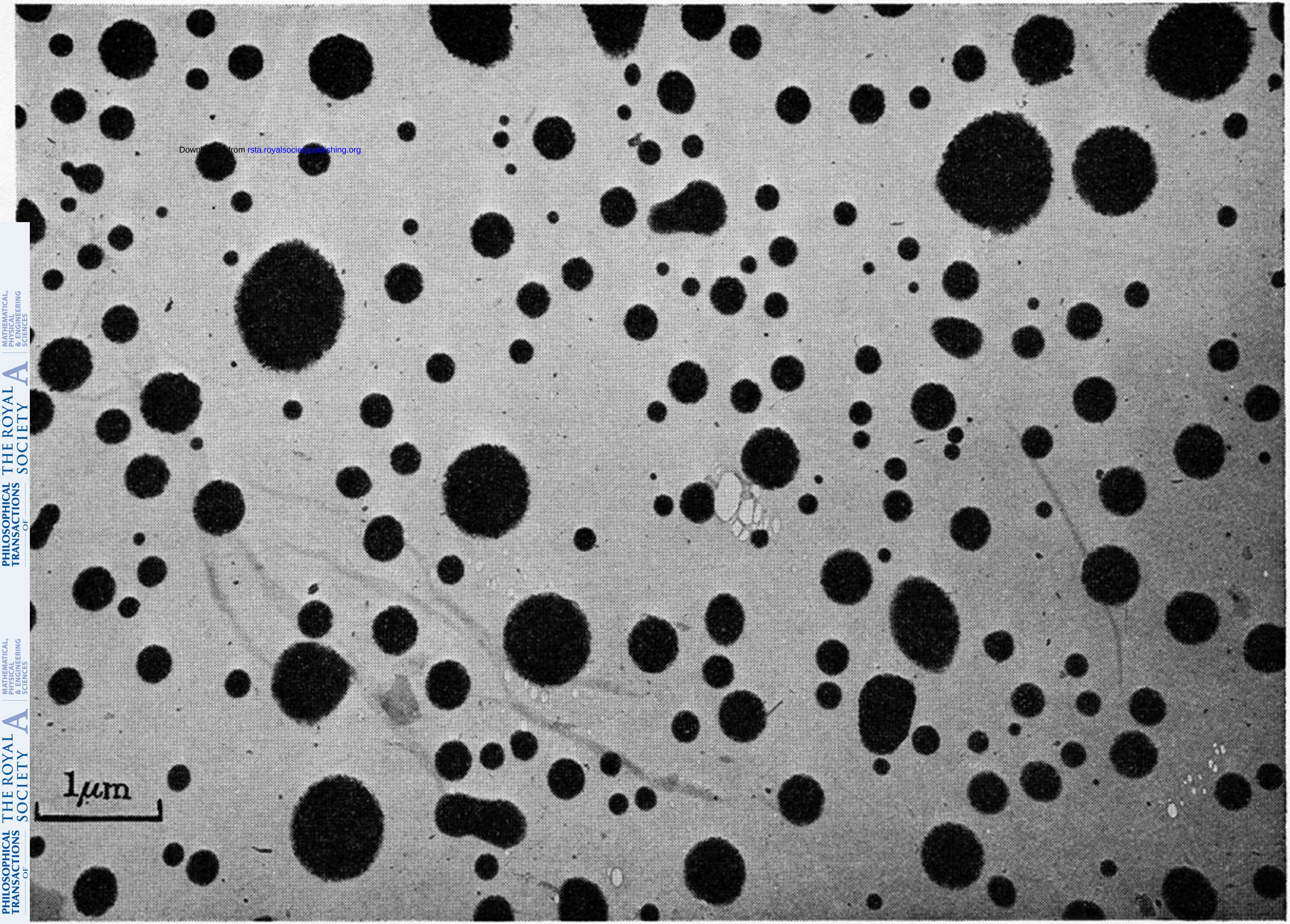

Figure 3. Electron micrograph of barium oxide.