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ABSTRACT

The process of sintering refractory solids at room temperature by high pressures is described. The effect of purity, particle size, and calcining temperature is discussed. A possible mechanism for the sintering is discussed. Two applications are presented: First, the determination of spectra of solids which in general cannot be obtained because they are available only as powders; and second, squeezing out the pores of a catalyst support which permitted determination of the rate of growth of platinum particles on an alumina support as a function of temperature.

The primary objective of our high pressure program is the study of the electrical and magnetic properties of solids. With our present apparatus we can reach pressures as high as 500,000 atmospheres. In pursuing the main objective we have stumbled on a phenomenom that we wish to describe in this paper, namely, the compaction of finely divided solids into transparent discs which must have densities very close to the theoretical density of the solid. For want of a better term we have called this pressure sintering. In the ordinary sintering process the material is subjected to a pressure of several hundreds of atmospheres at an elevated temperature. In the present process, a similar result is obtained at room temperature but at very high pressures, the pressure required being a function of the material. This process is only partially understood at the present time; however, a reasonable explanation can be given for the results obtained.

The compression of a solid to transparency is really not new. A standard technique in infrared spectroscopy is the use of mulls made of the heavier alkali halides. These materials are squeezed transparent at relatively low pressures. However, when these low pressures are used, evacuation of the sample is essential. In our work, evacuation is not necessary. A reasonable review of the alkali halide work is given by Ford, Wilkinson, and Price.[1]

Our attention was first called to the possibility of sintering at room temperature some five or six years ago when we found that lithium aluminum hydride was as transparent as glass after having been subjected to a pressure of 100,000 atm. With the passage of time we also have been able to squeeze many oxides to the transparent state. The discs remained

transparent even after several years aging. Some of the discs developed cracks, but this was not unexpected due to the strain that was introduced by subjecting the materials to stresses beyond their elastic limits.

The criterion that we use for the approach to theoretical density is that of optical transparency. This criterion limits the work at the present time to materials that are transparent in the visible or have absorption bands that do not extend over the entire visible region. In general, and for mechanical reasons alone, the size of the sample is about 10 mg. We are not equipped to measure directly the densities of such small samples with high precision. However, if we start with particles that are as small as 100 A on edge, and the final sample is transparent, it is reasonable to suppose that the number of scattering centers is very small. The very small number of scattering interfaces indicates that the particles have come into intimate contact with each other, i.e., the large number of solid-air interfaces have been replaced by solid-solid interfaces. On this basis we assume that the samples have approached theoretical density. For example, after application of 60,000 atm pressure, a 0.02 cm thick sample of magnesium oxide showed 85% light transmission.

In order to understand the pressure sintering process, first, consider the behavior of a single crystal placed in a pressure chamber whose volume is greater than that of the crystal. In this case, the course of events as pressure is applied to and incurred on the sample can be easily predicted. At the lowest applied pressure, the crystal would deform elastically. At a pressure above the strength of the material, the crystal would flow until the pressure chamber is entirely filled by the crystal. Further application of pressure would merely compress the materials.

In our studies, we start with finely divided powder. This complicates the analysis to the point where it is not possible to present more than a simple qualitative explanation of the pressure sintering process. In general, the apparent density of a powder is about 50% of that of a single crystal. Furthermore, the particles are randomly oriented. When pressure is applied to this conglomeration, particles certainly can move with respect to each other to fill the space more completely. Also, it appears reasonable that a certain number of particles are oriented so that they can undergo plastic flow. What is certain is that at some pressure, the total force will be sufficiently great so that plastic flow will occur in all particles. When this pressure is reached, in the absence of any gases, the particles would flow until they came into contact and the flow would continue until no void space remained within the sample.

Bridgman [2] has found in his studies of the compression of nitrogen and argon that these gases diffused through steel containers so rapidly at pressures above 30,000 atmospheres that equation of state work could not be extended above this pressure at room temperature. It is reasonable to assume that ordinary air would behave in a similar manner. Thus, one would expect that at a pressure of about 30,000 atmospheres that the air surrounding the powder particles would start diffusing out of the sample, and that the flow of the material would not be restricted by the gas that originally was present. In short, at pressures above 30,000 atmospheres, one would not expect the atmosphere to impede the flow of the individual particles due to the formation of an air pocket. For this reason, if the compaction is done at the very high pressures we use, it is not necessary to evacuate the sample before sintering.

There is one further condition that is necessary that has not been discussed. In the foregoing discussion it was tacitly assumed that the deformation and flow of the container was small compared to that of the sample. If the material in the pressure cavity is harder or stronger than the apparatus, then the flow will occur in the apparatus and not in the sample. However, when we attempted to pressure sinter diamond dust, it was the apparatus that flowed and not the diamond particles. Besides the high pressure, it is essential that the sample is softer than the material of the apparatus. This last limitation precludes very few materials from study, since the parts of the apparatus in contact with the sample are compacted tungsten carbides, such as G. E. Carboloy 999, which is extremely hard.

The pressure vessel used in these experiments was a set of anvils similar to that described by Bridgman [3]. The necessary thrust was developed with a hydraulic press of 100, 200 or 500 ton capacity, depending on the total force needed. The total force required depends on the nature and diameter of the sample.

Before the actual sintering, the powder was pelleted in a small die. The pellets varied from 7/16 to 3/16 in. in diameter and were about 0.006 in. thick. After pelletization, the sample was placed between the faces of the anvils. A ferric oxide coated pyrophylite ring was used to contain the sample. Pressure was increased in 10,000 atm increments. About two minutes were allowed for the dissipation of the heat generated by each compression. The sample was maintained at the maximum pressure for about ten minutes, after which pressure was reduced continuously until the press rams opened, permitting withdrawal of anvils.

Three general observations have been made which seem to influence the

pressure at which transparency for a given solid was obtained. In general higher pressure was required when (a) the particle size increased, (b) the purity of the sample lowered, and (c) the calcining temperature of the solid before application of pressure was raised. The first two factors are in accord with temperature sintering. The latter seems to have no counterpart, and it seems difficult to account for this behavior. However, this behavior has been observed repeatedly. For example, eta-aluminum oxide calcined to 600°C became transparent at a pressure of 100,000 atmospheres. If the same sample was calcined to 800°C, a pressure of 400,000 atmospheres was necessary before sintering was accomplished. This observation gives rise to a great deal of speculation, but no one argument leads to a reasonable explanation at the present time.

Earlier it was stated that the transparency of the sample was maintained at room temperature for several years. If the sample of an oxide is annealed at a sufficiently low temperature, no change in transparency or structure of the sample was apparent to the human senses. However, as the annealing temperature was increased, opaqueness and mechanical weakness set in at a temperature characteristic of the solid. At about 100 to 200° after this degeneration sets in, the sample crumbled and appeared to revert to its initial condition.

A plausible explanation for this behavior is based on the existence of hydroxide on the surface of the individual particles. It is known that the surfaces of most oxides are hydroxide rather than oxide. In some oxides this is true of the surface alone, while for others, the complete sample can be converted to hydroxide on prolonged contact

with the atmosphere. When the temperature is raised sufficiently, the hydroxide decomposes to water and oxide. Gaseous water is certainly formed at the grain boundary. At a sufficiently high temperature the pressure of the water vapor probably becomes great enough to separate the particles from each other.

A partial X-ray study of magnesium oxide gave some insight to the details of the internal changes. These measurements were made by L. Grossman. The magnesium oxide was obtained from Professor Norman Phillips of this department. The specific area as measured by nitrogen adsorption was such that if the particles were in the shape of cubes, the cubes would be 100 A on edge. This sample showed transparency when pressed at 30,000 atmospheres or higher. Figure 1 exhibits the half-width of the 200 line as a function of the pressure to which the oxide had been subjected. Due to the very large line width, this was the only line that could be studied. The half width increases by nearly two between 30,000 and 200,000 atmospheres.

Figure 2 shows the effect of annealing on the half width of the 200 line for a sample that had been originally compacted at 60,000 atmospheres. The disc was heated to 350°C for 15 minutes, its half width measured. The same sample was then annealed for the same length of time, increasing the temperature at 50° intervals until the sample crumbled. For reference, the same treatment and measurement was made on the original powder. These results are shown in the same graph.

The initial anneal to 350° showed a very marked narrowing of the half width of the line. Further heat treatment to 550°C showed a small decrease in the half width of the line. Above this temperature, where crystal growth

sets in, the two become indistinguishable, indicating that crystal growth was the most important factor in the determination of the X-ray line width when heated above this temperature.

The X-ray experiment is not conclusive because only a single line could be studied. The increase in line width could have been due to a decrease in the particle size or to the introduction of strain. If the increase in line width was caused by the diminuation of the size of the particles, then the half width could have been proportional to $\tan^2 \theta$ if the increase in width was due to the introduction of strain in the sample. The rapid decrease in line width at temperatures below that at which crystal growth normally occurs indicates that a large part of the line width increase was due to strain. The remaining increase in line width indicated that there also has been a decrease in the size of the particles. Considering the manner in which the compaction occurs, this appears to be a foregone conclusion without the X-ray evidence.

Apart from the intrinsic interest in the process, there are a number of applications of pressure sintering. We would like to mention two. First, this compaction permits the determination of the spectra of solids which cannot be obtained when the sample is in its usual form. For example, Conway[4] of the Lawrence Radiation Laboratory, Berkeley, has determined the adsorption spectrum of gadolinium oxide down to 2000 A. A similar study is being made on europium oxide by Nathans [5] of the same laboratory at Livermore.

The second application has a direct bearing on catalysis. Powell, Somerjai, and Montgomery [6] have used this pressure sintering process to determine the rate of growth of platinum particles on a catalyst support.

A summary of their experiments and results follow.

The basic experimental problem was the determination of the rate of growth of platinum particles on an eta-alumina support. The method that these authors wished to use to detect the growth was low angle X-ray scattering. The difficulty in this experiment is the scattering from the alumina-air interface, which is large. When the metal is introduced, the scattering is changed, but the observed scattering is now due to alumina-air, and alumina-platinum. There is no way in which the scattering can be correlated directly to the platinum size, since no way can be found for the correction of the background scattering.

A possible solution is to fill the pores with a material that is volumetrically isoelectronic with alumina. These authors, however, found it more convenient to squeeze the pores out of the alumina. The scattering of the alumina could be reduced to the point where it was negligible. Figure 3 shows the low angle X-ray scattering through pressed alumina as a function of the pressure to which the sample had been subjected. At 100,000 atmospheres, the difference between air and alumina scattering is negligibly small and measurable only at the lowest angles. At a pressure of 300,000 atmospheres, the presence of the alumina in the beam is undetectable at any angle measured by these investigators. By using this technique, it thus becomes possible to look at the platinum scattering completely uncomplicated by any other scattering process.

Figure 4 shows the effect of platinum concentration on the scattering. From data such as this the authors were able to study the growth rate of platinum as a function of temperature and atmosphere. They were able to obtain sufficient data to formulate a theory for the growth

rate. Their forthcoming paper should be consulted for the details of their experiments. Obviously this technique is not restricted to platinum and alumina. This technique should be applicable to the study of the growth of any metal on any support as long as the scattering from the metal is different from that of the support.

In conclusion, our experiments, which are truly only preliminary, indicate that much is yet to be learned concerning the manner in which the compaction occurs. It appears that much information can be obtained from this approach that cannot be conveniently obtained by more standard methods.

REFERENCES

(1) M.A. Ford, G.R. Wilkinson and W.C. Price, Molecular Spectroscopy, Institute of Petroleum, 1955.

(2) P.W. Bridgman, Phys. Rev. 46, 930(1934).

(3) P.W. Bridgman, Proc. Amer. Acad. Arts and Sci. 81, 165(1952).

(4) J. Conway, Private Communication.

(5) M. Nathans, Private Communication.

(6) R.E. Powell, G. Somerjai, and P.W. Montgomery, Private Communication.

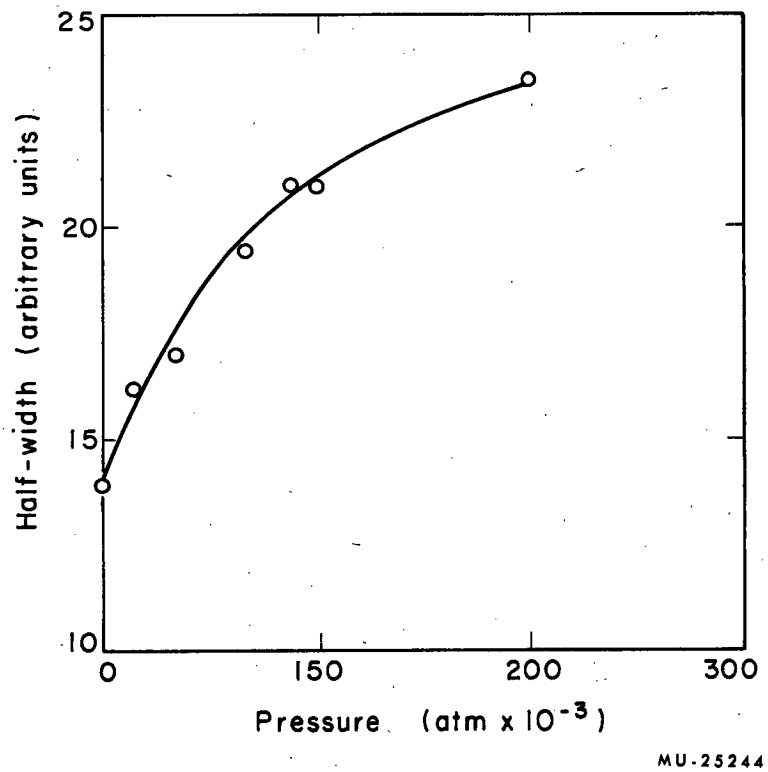


Fig. 1. Effect of pressure on the half-width of the 200 line of MgO.

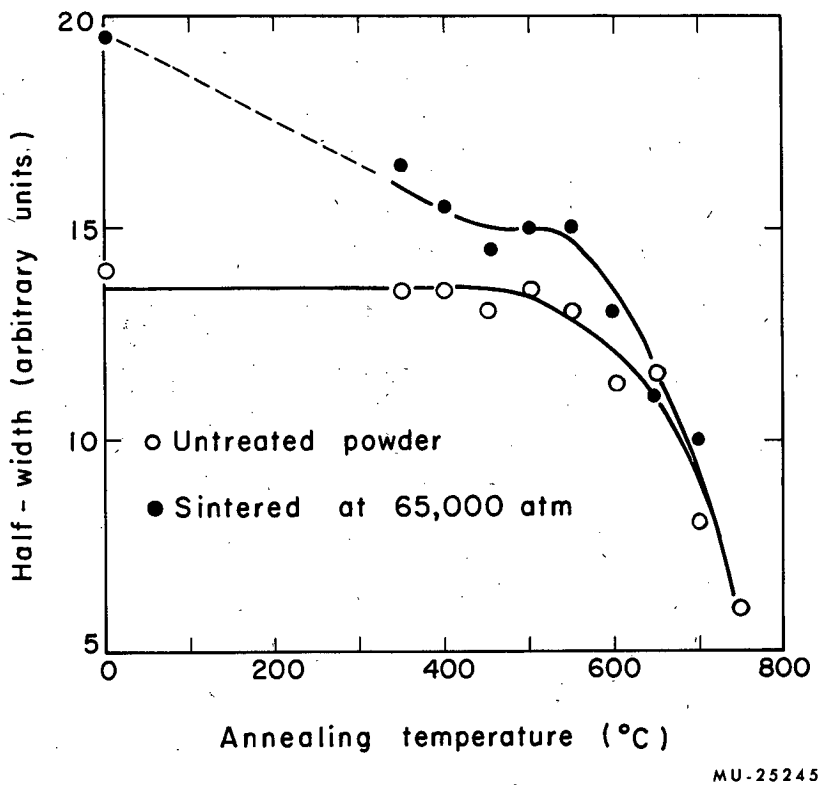


Fig. 2. Effect of annealing on the half-width of the 200 line of MgO. Shown are the original powder and a sample sintered at 65,000 atmospheres.

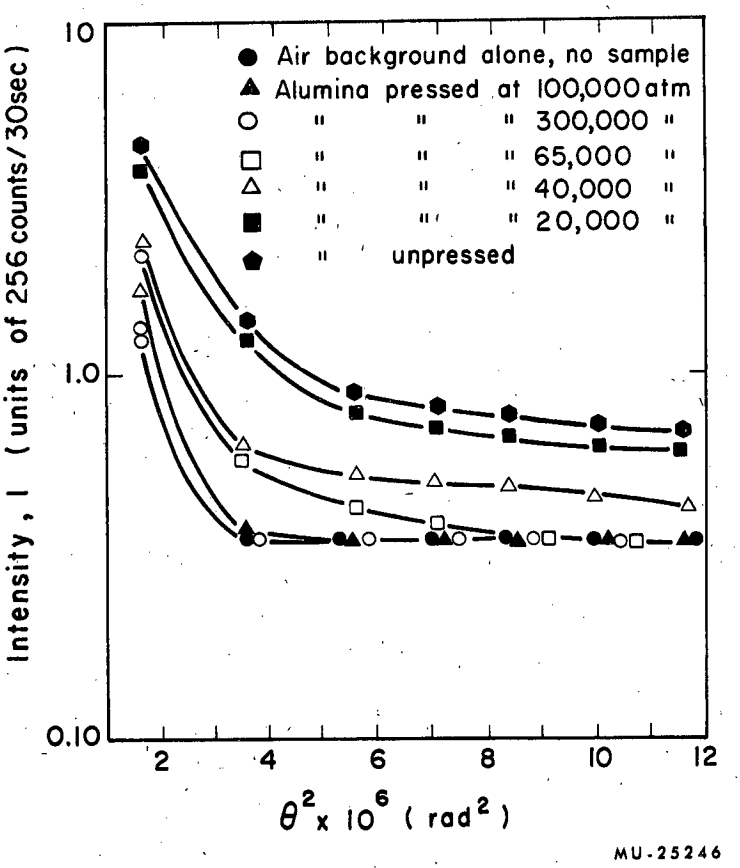
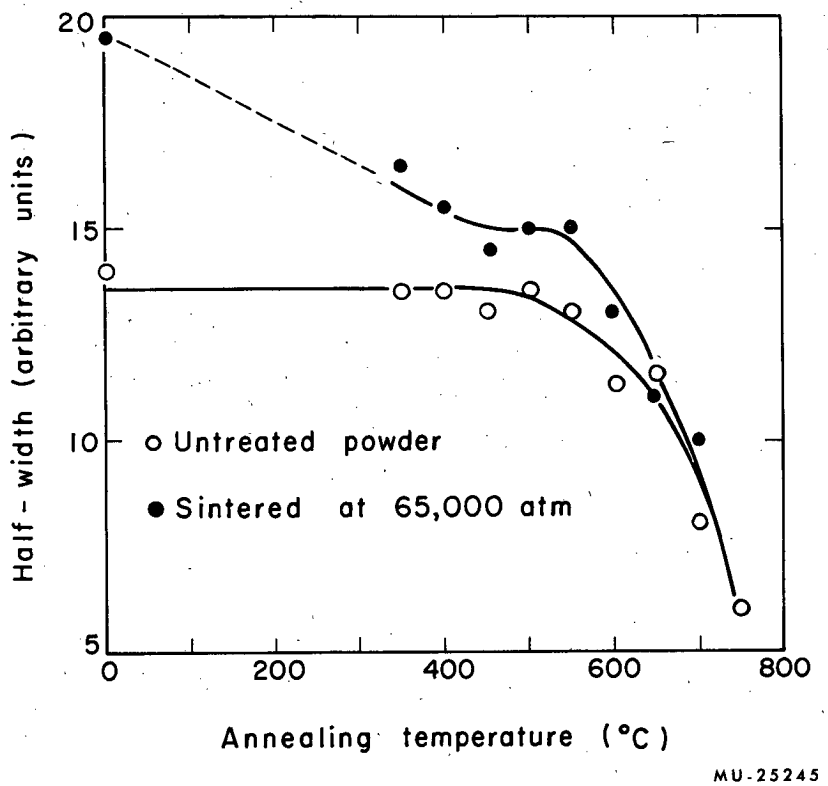


Fig. 3. Effect of pressure on the low angle X-ray scattering of eta-alumina.



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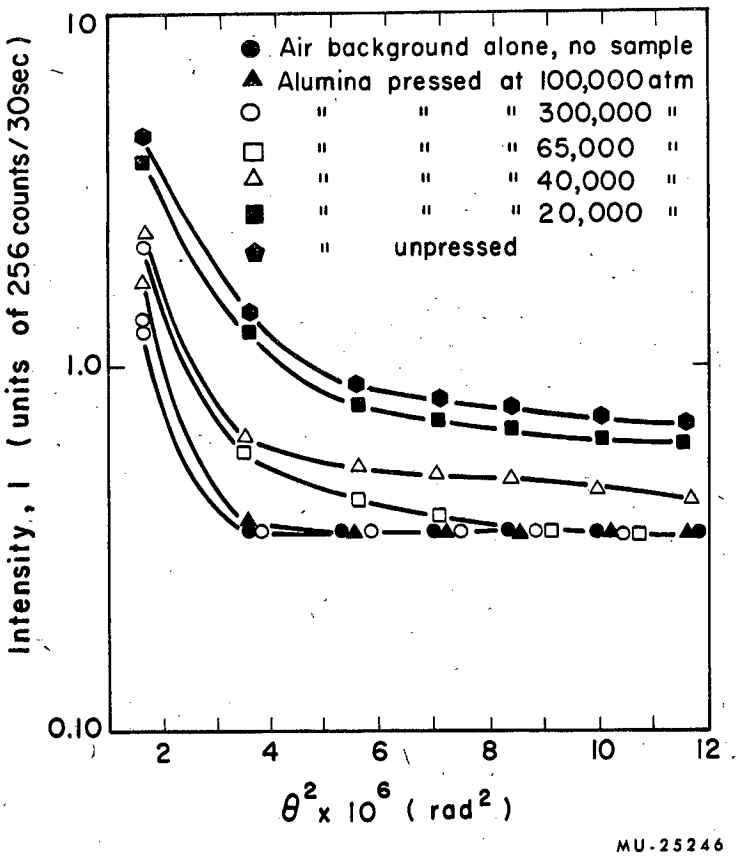

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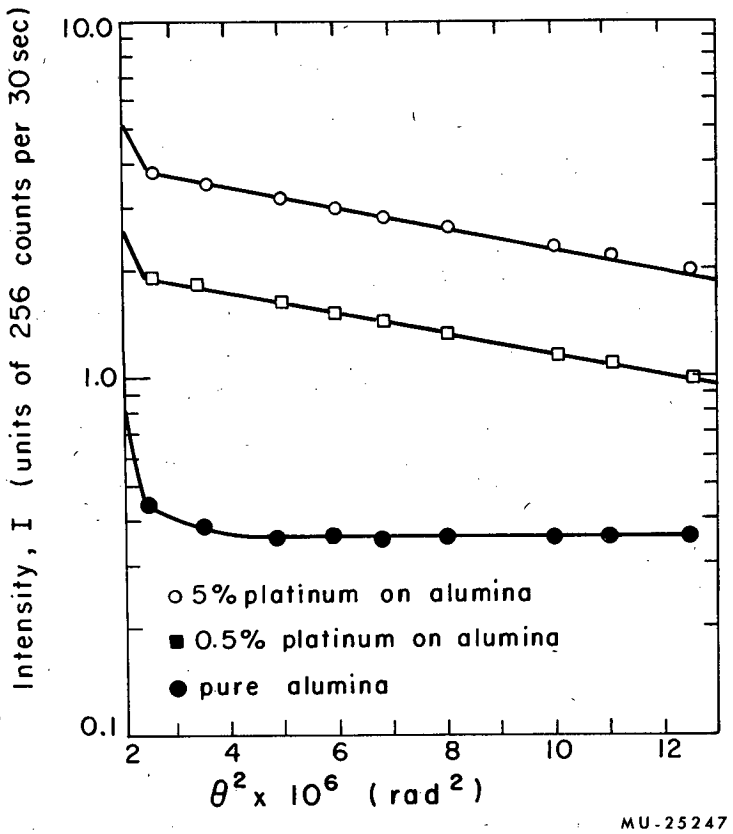

Fig. 4. Low angle X-ray scattering of platinum particles on an alumina support.

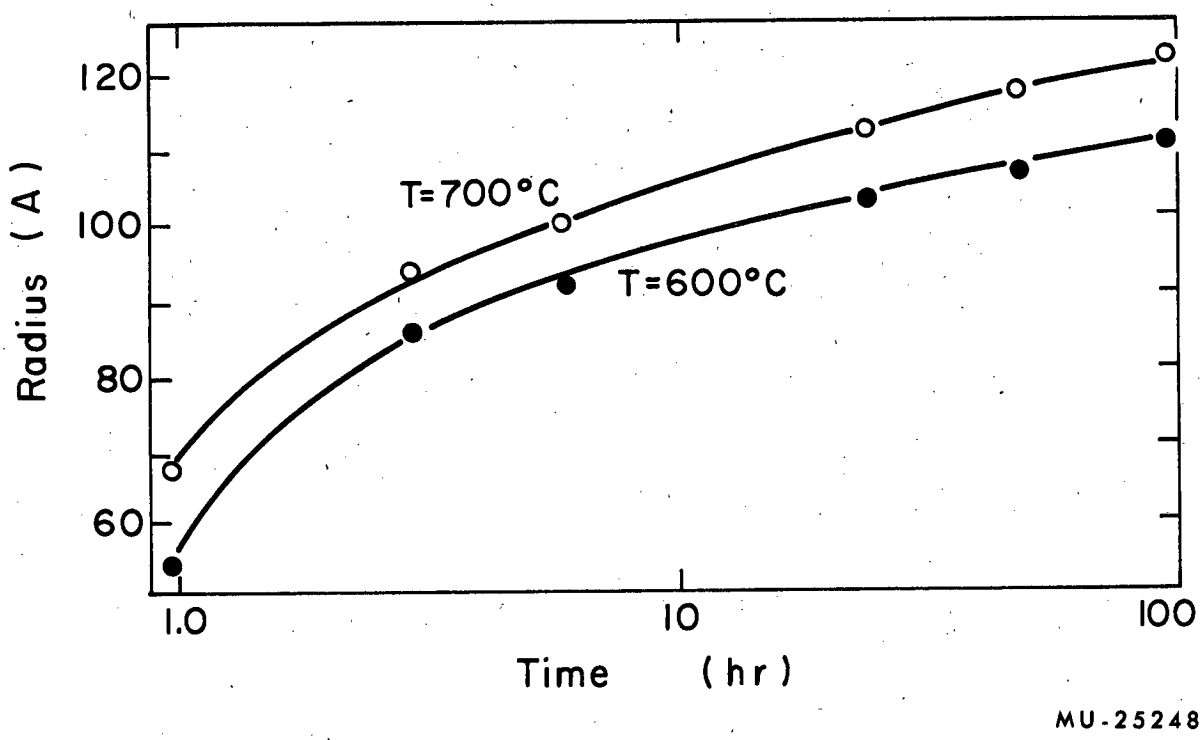

Fig. 5. Effect of time at temperature in a reducing atmosphere on the mean radius of platinum particles. These values were obtained from data as shown in Fig. 4.

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