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Submitted to Powder Metallurgy

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A TECHNIQUE FOR EXTRUSION FORMING OF
BRITTLE AND REFRACTORY COMPOSITIONS

Milton R. Pickus and Molly Wells

May 1965

Introduction

Over the past decades the usage of the term refractory material has been extended to include - in addition to the oxides, silicates and graphite - an expanding variety of compounds among which may be noted the metal carbides, nitrides, borides and silicides. The importance attributed to these compounds is indicated by the number and scope of the studies being reported in the literature. Among the first of them to have a significant impact on industrial practice was the carbide of tungsten in the field of high speed cutting tools. Now they find many applications involving exposure to severe abrasion and high temperatures. Recently their electrical properties have commanded attention, for it has been found that a number of compositions, particularly the carbides and nitrides of some transition metals, exhibit high critical temperatures and magnetic field strengths at the transition between their superconducting and normal states.

These compounds are characterized by such properties as high melting point, great hardness, high strength at elevated temperatures, and varying degrees of resistance to attack under corroding and oxidizing conditions. Most are quite brittle. This property, together with the high melting points, gives rise to a need for special fabricating techniques, whether from the standpoint of production in industry or of the preparation of test samples for use in the research laboratory.

A process that has had a long period of successful application is that of powder metallurgy. Historically, this process may be considered to have evolved from the early experiments of Wollaston on the preparation of wrought forms of platinum from chemically prepared platinum sponge.

Modern techniques had their inception in the solution of problems peculiar to the growth of the incandescent lamp industry. Tungsten had been found to be the best choice as a material for filaments. Large scale production of tungsten wire became possible as a result of Coolidge's development of a powder metallurgy process at the General Electric Company. Essentially, the process consisted of compressing tungsten powder in steel dies, and then heating the compacted bars in hydrogen to high temperatures by direct passage of heavy electric currents. The bars developed considerable strength, fully adequate to withstand hot working operations. In a carefully controlled sequence, the area of cross section was gradually reduced to a degree where conventional wire drawing could be employed. Because of the hardness of tungsten, it was necessary to use diamond wire drawing dies. The high cost of maintaining these dies led to a search for less expensive materials possessing the necessary wear resistance. This effort was rewarded with the development of the "sintered carbides", a mixture of tungsten carbide and cobalt powders, pressed in steel dies and then heated in a reducing atmosphere, usually hydrogen, to 1350-1400°C. The sintered carbides, which now often contain the carbides of tantalum and titanium in addition to that of tungsten, found many other applications, particularly in the manufacture of tools for cutting and shaping, and of components required to withstand severe abrasion. As a result of the demand for these products, powder metallurgy became an important industrial process and consequently was the subject of intensive study. As techniques improved with continued research, the methods of powder metallurgy were applied to other high melting metals, alloys, and compounds. Prior to the introduction of

electron beam melting, practically all production of tantalum, niobium, molybdenum, and tungsten commenced with sintered bars of compacted metal powders.

Some obvious limitations of preparing the compacts by compressing powders in steel dies are the restrictions to simple, symmetrical shapes; to a narrow range of length to diameter ratio; and to materials having some degree of ductility. The admixing of lubricants and binders (in the case of the sintered carbides the relatively ductile cobalt may be considered a binder) such as stearates and paraffin, improved matters considerably. By reducing the friction between the die walls and the powder, lubricants permitted a much greater uniformity of density throughout the compact, and reduced substantially the required pressure. Binders, on the other hand, made it possible to obtain adequate strength after compacting even with quite brittle materials. The choice of lubricants and binders must be limited to those substances which not only fulfill the intended function but which also leave behind no complicating residue to interfere with sintering.

The problem of length to diameter ratio and the restriction to simple shapes were both appreciably resolved by the development of hydrostatic pressing. This technique consists of loading the powder into a thin elastic membrane having the desired form. The membranes may be of intricate design and contain reentrant angles. The loaded membrane is suspended in a suitable fluid contained in an hydraulic apparatus by means of which the necessary pressure can be transmitted. Since the pressure is applied equally in all directions, compacts with great uniformity of density are obtained. This method has been used successfully with a wide range of materials.

The method of hot pressing - though providing only limited latitude in length to diameter ratio or in variety of form - is especially advantageous in coping with the very brittle compounds. Generally, pressure is applied while the material is at a high enough temperature to undergo plastic flow. However, since the required temperatures vary from about 1000°C for aluminum oxide to 2500°C for some of the metal carbides, there are very few substances available for the construction of dies. Graphite is the one most commonly employed and generally is quite adequate, except for compositions adversely affected by the presence of carbon. Hot pressing is frequently carried out in vacuum, and one of the great virtues of the method is that, under favorable conditions, with no binders or lubricants, very nearly the theoretical density can often be attained.

One interesting solution to the problem of length to diameter ratio is the procedure of sheath rolling, wherein a ductile metal tube is filled with powder, sealed off, and then swaged or rolled to effect compaction. In this manner wire of small diameters has been made. This process is useful for powdered materials containing at least some ductile constituent to aid in compaction. The method is not satisfactory, however, for use with brittle materials of high melting point, and especially where reaction between the sheath and its contents must be avoided.

Extrusion: General Description

Since situations are encountered with brittle and refractory materials wherein none of the powder compacting techniques described is really convenient, a versatile extrusion method in use at this laboratory will be described. In its essential features, the method consists of coating the particles of a powdered material, either metallic

or not, with a selected thermoplastic substance in such a manner and proportion that the mixture as a whole takes on the characteristics of a typical thermoplastic. The preparation may then be subjected to the forming methods commonly employed with plastics such as molding, extrusion, and heat forming. Brittle materials may thus be shaped into rod, ribbon, or wire. The parts so formed are subjected to a programmed heating cycle in an appropriate atmosphere, during the course of which the thermoplastic substance is volatilized, and sintering of the powdered material takes place with retention of the original shape. Under favorable conditions sintering may proceed to a point where nearly theoretical densities are attained. Among the materials processed by this method are the carbides of tantalum and niobium; carbon nitrides of niobium; tungsten carbide-cobalt mixtures and aluminum oxide.

It is preferred, in general, to work with powders of fine rather than coarse particle size. If the material is sufficiently frangible to make particle size reduction by ball-milling effective, it is customary to commence with this operation. This is especially desirable where two or more constituents are involved because of the efficient mixing accomplished. With ductile material ball milling is not practical; it is therefore advisable to use powders of a size corresponding to at least -325 mesh.

Polystyrene was selected as the thermoplastic. After experimentation with a number of alternatives, a conclusion was made to avoid formulations containing oxygen, to minimize the residue left when samples were heated for the purpose of volatilizing the plastic. The choice was narrowed to polymerized hydrocarbons and among them polystyrene was considered to have the best overall combination of properties. It was found expedient, however, in order to have better control over extrudability to modify the

properties of polystyrene by the addition of diphenyl, or the eutectic mixture of diphenyl and diphenyl ether. Toluene is used as the solvent for both the polystyrene and the diphenyl. The former is made up as a 3% solution, and the latter, as a 10% solution (100 cc of solution containing 3 grams and 10 grams respectively). The solutions are made up separately rather than as a composite for a reason that will be indicated in the following section. The diphenyl or the diphenyl-diphenyl ether eutectic will be referred to as the plasticizer, a function either performs satisfactorily.

In the section that follows, extrusion of the monocarbide of tantalum as 1/8" diameter wire will be described in some detail to illustrate the procedure. The point of view will be primarily that of a research laboratory concerned with only the relatively small quantities of material required for specimen preparation. Appropriate variations may of course be made to accommodate larger quantities.

Procedure for Extrusion of Tantalum Carbide

A quantity of tantalum carbide is ball-milled for about 48 hours in a steel mill, using steel balls, and toluene to fill the free space. The milled powder is then treated in boiling hydrochloric acid to convert to soluble chlorides the iron and other contaminants picked up during the ball-milling. The acid is decanted and the powder is washed in a sufficient number of changes of distilled water to give a test indicating freedom of chloride. A weighed portion of dry powder is placed in a large evaporating dish, and to it is added a volume of the 3 percent polystyrene solution such that the weight of polystyrene will be 4-1/2 percent of the total weight of the batch being prepared. Heat is applied by means of an

electric hot plate to evaporate the toluene, with continuous stirring of the mixture being maintained, to assure a uniform distribution of the polystyrene that is precipitating from the solution. The evaporation is allowed to proceed until only enough toluene remains to keep the mixture from thickening. At this point the plasticizer is added in such quantity that its weight is related to the weight of polystyrene by the ratio of one to five. The plasticizer is added at this stage rather than simultaneously with the polystyrene to prevent excessive loss during the evaporation of the bulk of the toluene. Since the vapor of toluene is both flammable and toxic, suitable safety precautions must, of course, be observed.

The evaporation (and the stirring) is continued until the mixture becomes rubbery in consistency. Further stirring being impractical, the mixture is then oven dried for about 1/2 hour at 110°C to remove residual solvent. As a result of this treatment the powder particles are coated with polystyrene and the entire mixture will behave as a thermoplastic. The batch may then be extruded as 1/8" diameter wire (or other diameters or cross-sections as desired). Since only moderate temperatures and pressures are involved, the extrusion apparatus may be of simple design. In fact, a die set and heater assembly of the type used for mounting specimens for metallographic work can be used quite satisfactorily, it being necessary only to substitute an extrusion die for the base plug. Fig. 1 shows a typical set-up. A temperature in the range of 160° to 175°C is suitable for extrusion. Pressures are usually well below 20,000 psi and can be less than 4000 psi, depending on such factors as the amount of residual solvent present, a greater or lesser proportion of polystyrene, and the diameter of the wire being extruded. Whereas a proportion of polystyrene corresponding to 4-1/2 percent of the total weight makes possible the extrusion of tantalum carbide, other proportions will be

required for different substances. In practically all cases it has been found a sufficiently close adjustment (assuming the particle size of the powders to be approximately in the same range) to increase the percentage of polystyrene inversely with the specific gravity of the material to be extruded, maintaining a five to one ratio between the polystyrene and plasticizer.

The selection of a proper sintering temperature is influenced by a number of factors, and is treated adequately in the literature on powder metallurgy. Especially in working with unfamiliar compositions, it is largely a matter of empirical determination and consideration of the properties desired. For example, if mechanical properties are the primary concern, it is important to approach as closely as possible the theoretical density. On the other hand, certain studies involving gas-metal diffusion or reaction may be more expeditiously carried out on specimens having a controlled residual porosity. When temperatures higher than about 1400°C are required, it has been found convenient to do the sintering in two stages. With all of the materials thus far encountered, sufficient strength is developed after heating to 1400°C to permit the handling necessary to transfer the specimens to a high temperature furnace. Problems relating to support of the specimens and to reactions with support materials differ so markedly in the two temperature ranges they are best managed separately.

Sintering at 1400°C will be considered first. The extruded tantalum carbide is cut (with a scissors - or simply snapped between the fingers) into convenient lengths of about 4 inches, and placed on a graphite support of the form shown in Fig. 2. In the extruded condition, machining is easily accomplished, and if desired, small holes may be drilled in the ends of the specimens so that they may be later suspended by tungsten wire

hooks during the second stage sintering. The support is set in position in a horizontal globar tube furnace, having a gas-tight, closed-end mullite combustion tube. The arrangement, as shown in Fig. 3, provides facility for working in vacuum or with controlled atmosphere. With the combustion tube rigidly supported at the open end by means of a brass manifold, the furnace, mounted on roller bearings and riding on two sections of track, may be easily moved along its axis, making for convenience in loading and unloading, and changing tubes when necessary. The two smaller diameter mullite tubes, one serving as the gas inlet and the other containing a thermocouple, are also independently mounted in the same manifold and carry the specimen support. A positioning peg is so placed that when the furnace is brought up against it, the specimen support is centered in the hot zone. With this arrangement, all of the components are readily placed in the correct relative position for each run. The gas inlet and specimen support are positioned at the end of the combustion tube, and in the hottest part of the furnace, in order to avoid recirculating over the specimens any of the distillation products of the polystyrene and plasticizer. Another advantage is that the last contact with the distillation products will occur while the specimens are at the lowest possible temperature.

It is important that the rate of distillation be controlled. If it is too rapid, internal pressures can develop sufficient to split the specimens. An automatically programmed heating cycle that gives satisfactory results is as follows: from a cold start to 375°C in four hours; hold at 375°C for four hours; increase to 1400°C in four hours; hold at 1400°C for three hours; furnace cool to room temperature. The heating rate is approximately linear. Possibly a shorter cycle could be used, depending mainly upon the diameter of the specimens. However, this cycle is convenient

in that a run can be started in the morning and be completed, with the furnace cool and ready for another charge, the following morning. The choice of protective atmosphere (usually inert gas or vacuum) and composition of the specimen support will naturally be determined with respect to the particular material being treated.

It will be noted from Fig. 2 that the test samples are supported over their entire length. This is necessary because, as the temperature rises above approximately 350°C, and distillation of the thermoplastic progresses, there will be a period during which the samples lack sufficient mechanical strength to sustain their own weight. Support can, of course, be provided in a number of ways; for example, the samples may be imbedded in powdered graphite or alumina contained in a suitable boat. Where avoidance of contamination is critical, they may be supported on material of the same composition as the samples themselves.

Upon completion of this heating cycle certain compositions, such as tungsten carbide - cobalt mixtures, will have been adequately sintered, and are ready for use. Other materials, tantalum carbide, niobium, and aluminum oxide for example, require much higher temperatures and must be transferred to another furnace. For this purpose a vertical graphite tube furnace, resistance heated and designed to operate under vacuum or controlled atmosphere, has given satisfactory service, although any of several other types would do just as well. Proper support of the specimens during this high temperature treatment poses no particular problems other than the usual precautions taken to avoid undesired side reactions.

Discussion of Results

A few observations of a general nature may be in order. Since the material undergoing extrusion is in a thermoplastic condition, it cannot

support any appreciable pressure gradient; therefore, uniform density throughout the compact would be expected. This behavior is in contrast to the case of cold pressing in steel dies where bridging due to friction between the powder and die walls can occur. With respect to the minimum residual porosity attainable, extrusion, cold pressing, and hydro-pressing are all similar, but differ from hot pressing. This is a consequence of the fact that only in hot pressing (or some variation such as high temperature extrusion without benefit of additives) is pressure applied while the material per se is undergoing plastic flow.

Whenever additives are employed, either to facilitate compaction or, as in the present case, to render a material extrudable, the possibility of contamination by a residue must be considered. One of the principal reasons for selecting polystyrene was the fact that in the event of some dissociation, the small amount of residue would be carbon; and carbon in many instances can be tolerated, or even made useful. In working with any of the metal carbide systems, for example, the effect of a small carbon residue would generally be minimal. On the other hand, it should be noted that one of the most prevalent impurities in metallic powders is oxygen. Especially in the case of refractory metals, where temperatures encountered during sintering are high enough to make favorable the kinetics of the reaction between carbon and oxygen, the deliberate addition of carbon can yield a product lower in both carbon and oxygen than the starting material. Thus a residue of carbon will often have a purifying rather than contaminating effect.¹ This is illustrated by the following experiment. A sample of niobium powder was prepared for extrusion in accordance with the procedure described herein. The extruded wire was heated to 1350°C under conditions considered favorable for some dissociation of the polystyrene: recirculation of the distillation products over the heated samples.

The carbon content was determined for the niobium powder (supplied by Kawecki Chemical Company); for the extruded rod after heating to 1350°C; and after heating for one hour in vacuum at 2050°C. The oxygen content was determined for the original powder and for the extruded samples after 2050°C treatment. The results are shown in the following table.

Table I

Chemical Analyses (weight percent)

	Niobium Powder as received	Extruded Niobium Rod heated to 1350°C	Extruded Niobium Rod heated to 2050°C
Carbon	0.11	0.29	0.0014
Oxygen	0.43		0.20

A number of extrusions prepared by this technique are shown in Fig. 4. They illustrate the applicability of the method to a variety of materials, and indicate the facility with which complex forms may be prepared. Coils and twists were made from pieces of extrusion warmed over an electric hot plate. Samples are shown both in the as extruded condition and after varying degrees of sintering. The niobium specimens were sintered only partially, so that advantage could be taken of the residual porosity in the gas-metal reaction studies for which they were intended. The extrusions of a tungsten carbide-cobalt mixture and the flat strip of aluminum oxide were sintered fully. The flat strip of aluminum oxide included in Fig. 4 developed considerable transparency after only one hour of firing at 1960°C. This is shown in Fig. 5. As would be expected a substantial decrease in physical

dimensions occurs as sintering progresses towards completion. Table II shows the reductions in diameter observed at several sintering temperatures for an extrusion of aluminum oxide rod.

Table II

Reduction in Diameter as a Function of Sintering
Temperature for an Extrusion of Aluminum Oxide

Diameter	Condition	Percent Reduction
0.0805"	as extruded	---
0.0755"	1 hour at 1400°C	6.2
0.0662"	1 hour at 1800°C	17.8
0.0640"	1 hour at 1920°C	19.8

The progressive consolidation with increasing sintering temperature is indicated for aluminum oxide by the photomicrographs of Figs. 6, 7, and 8. These photomicrographs suggest that at temperatures up to about 1700°C the specimens are fairly porous. As the temperature is increased above 1900°C there is a rapid reduction in residual porosity.

In conclusion it may be said that since extrusion involves a somewhat more detailed preparation procedure, its use would be recommended especially for applications involving either intricate shapes, or high ratios of length to diameter. In these situations where conventional techniques are inadequate, the extrusion procedure described has proved its usefulness.

ACKNOWLEDGEMENT

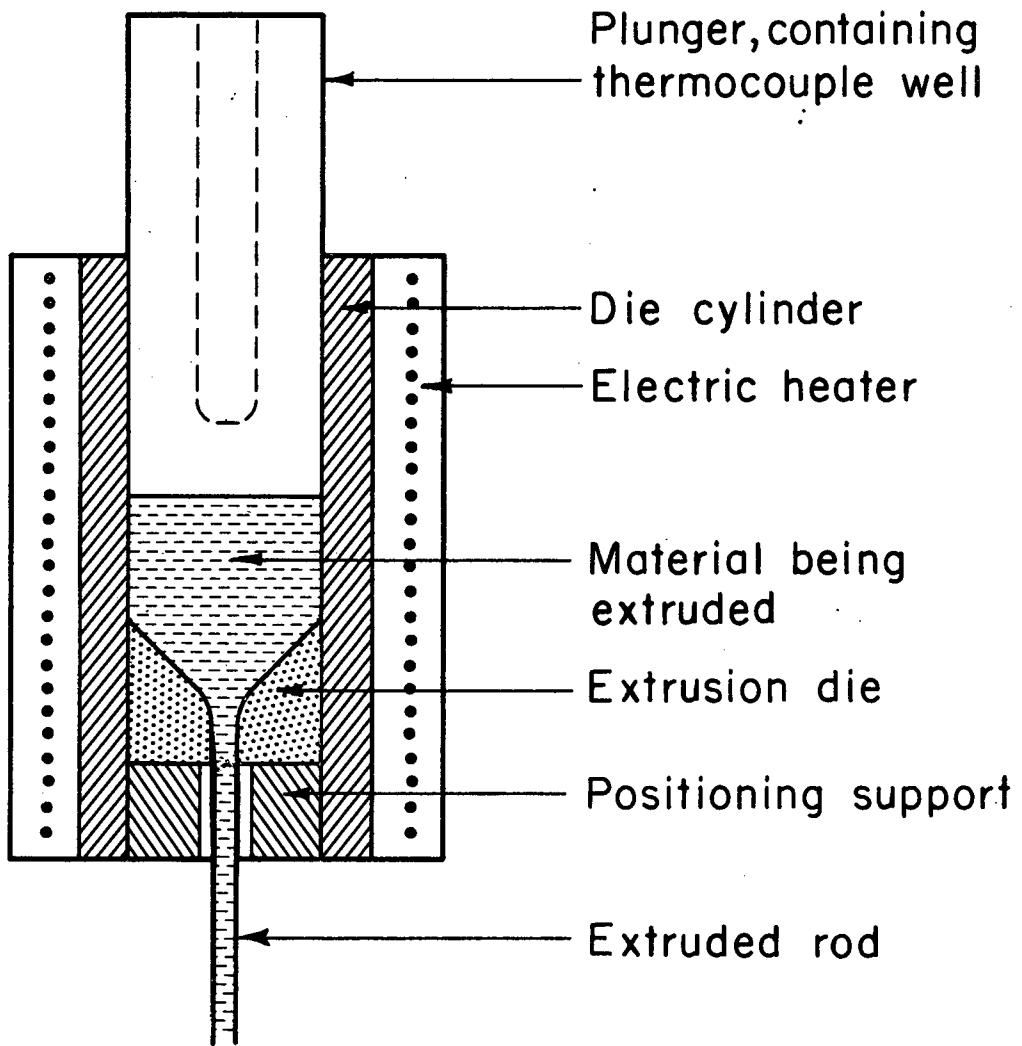
The authors express their appreciation to Mr. Donald J. Wixson for his assistance in specimen preparation and metallography. This work was supported under the United States Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

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1. E. M. Grala and R. J. Van Thyne, Columbium Metallurgy, Interscience Publishers, New York, 1960, p. 139.

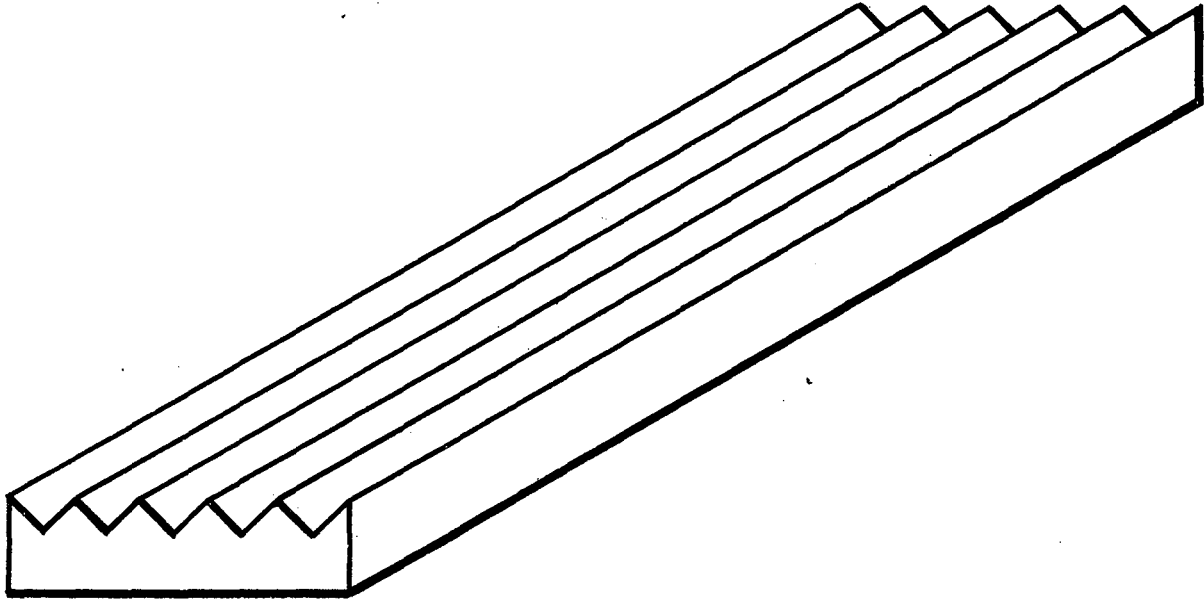
Figure Captions

- Fig. 1. Section through extrusion apparatus.
- Fig. 2. Shape of the graphite form for supporting extrusions during initial sintering.
- Fig. 3. Plan view of apparatus for initial sintering.
- Fig. 4. An assortment of unfired and fired extrusions. The pairs on the left from top to bottom are niobium, niobium carbide, and tantalum carbide - the lower ones are unfired. Middle group (white): aluminum oxide - the twisted piece on the right is unfired; the other pieces are fired. Group on the right: tungsten carbide cobalt mixture - the three pieces on the right are unfired.
- Fig. 5. Transparent piece of extruded alumina fired at 1960°C.
- Fig. 6. Extruded aluminum oxide fired 1 hour at 1750°C. Dark areas are residual porosity. X250.
- Fig. 7. Extruded aluminum oxide fired one hour at 1850°. X250.
- Fig. 8. Extruded aluminum oxide fired 1 hour at 1960°C. Etched with phosphoric acid. X250.



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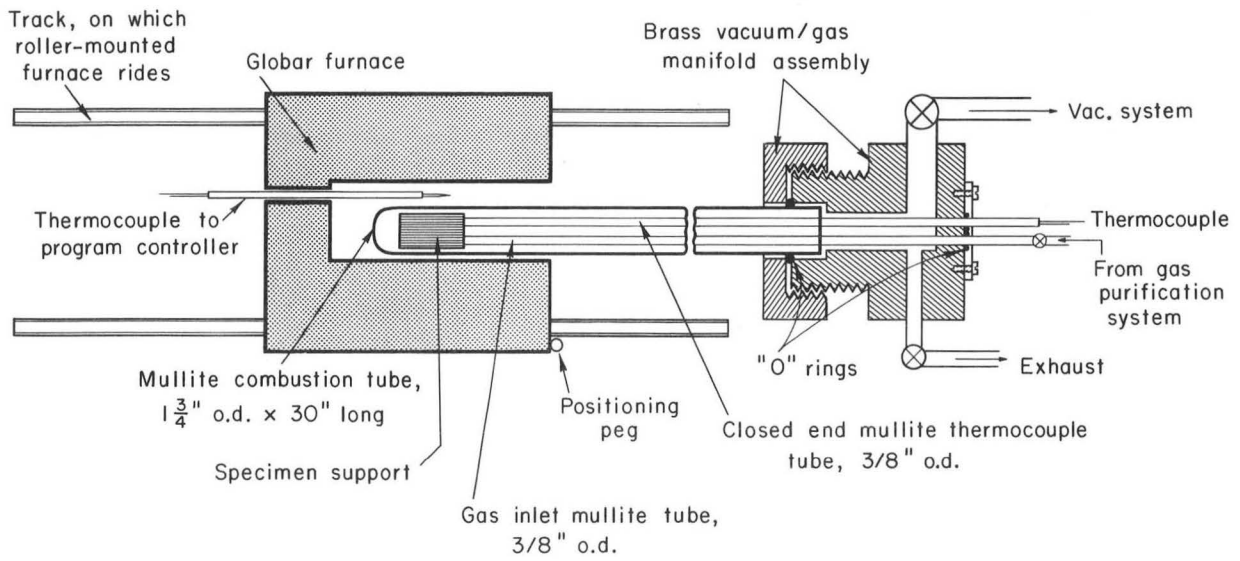
Fig. 1



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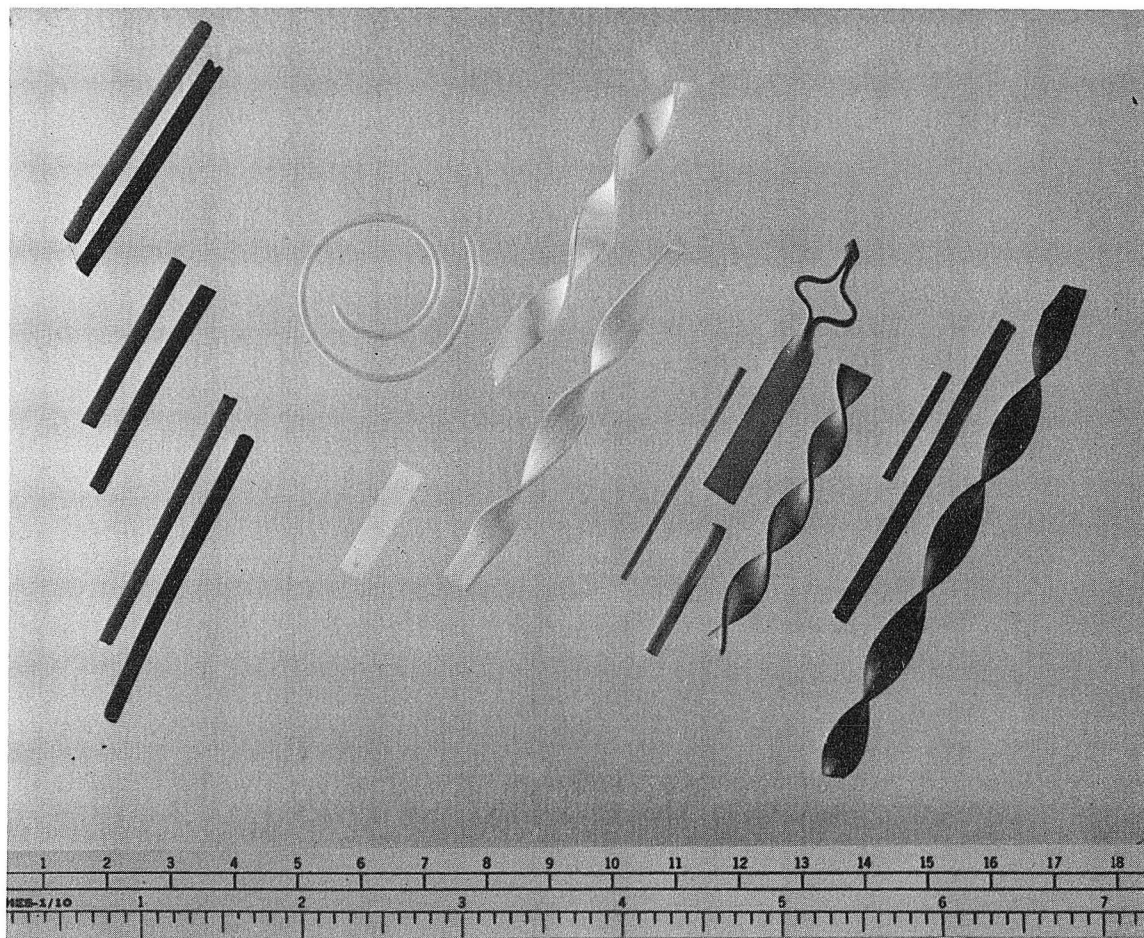
Fig. 2

Plan view



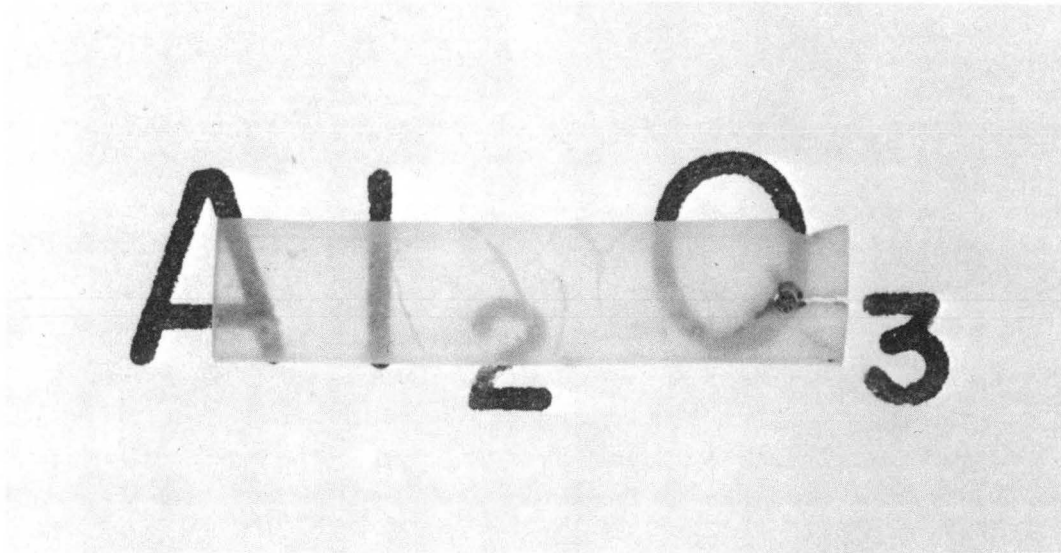
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Fig. 3



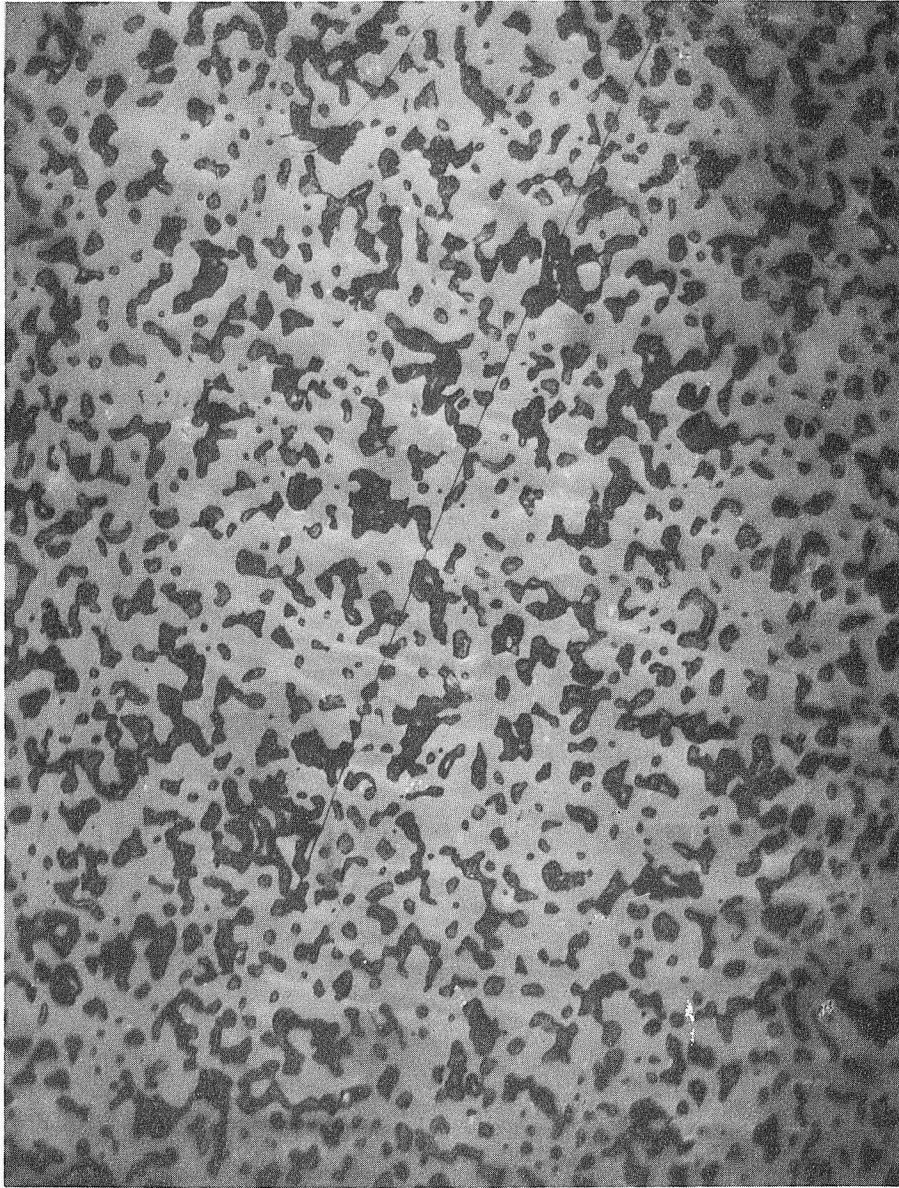
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Fig. 4



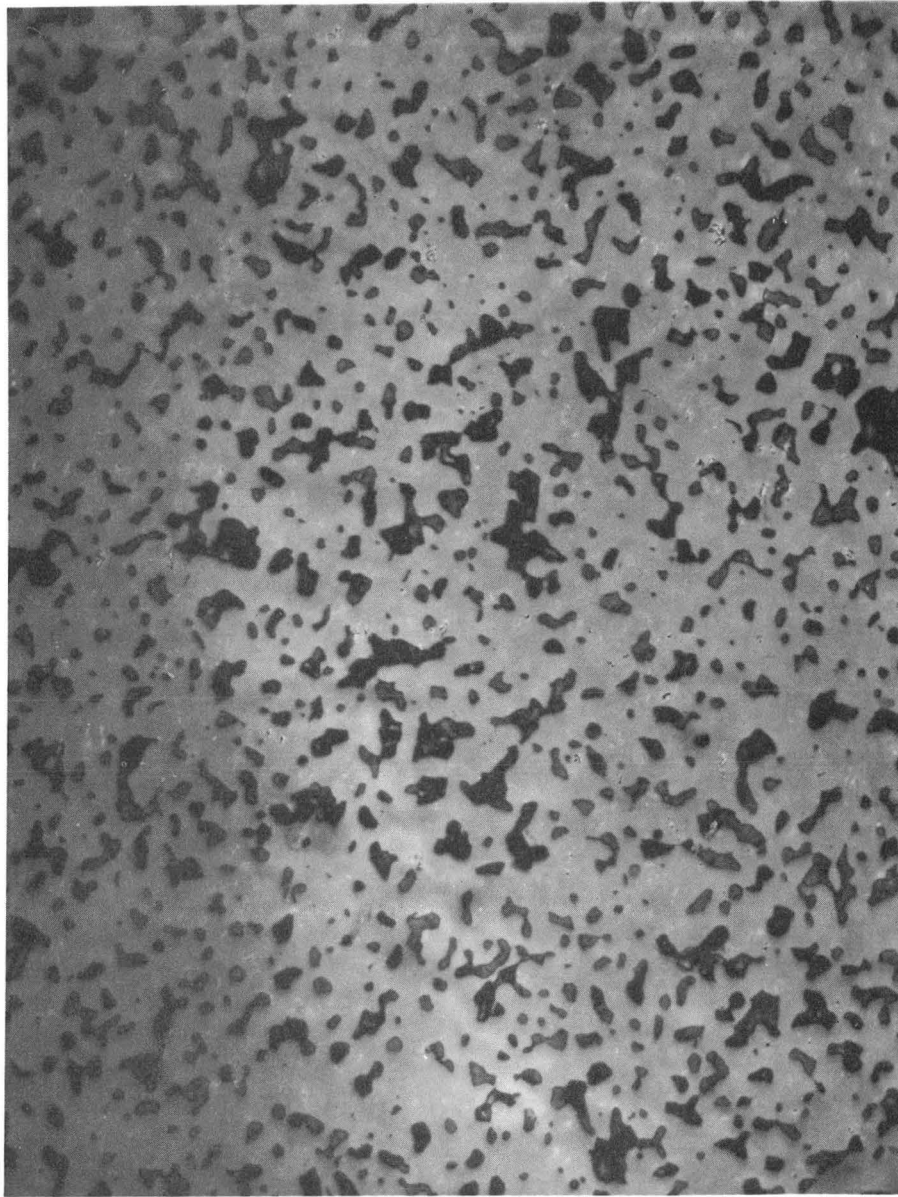
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Fig. 5



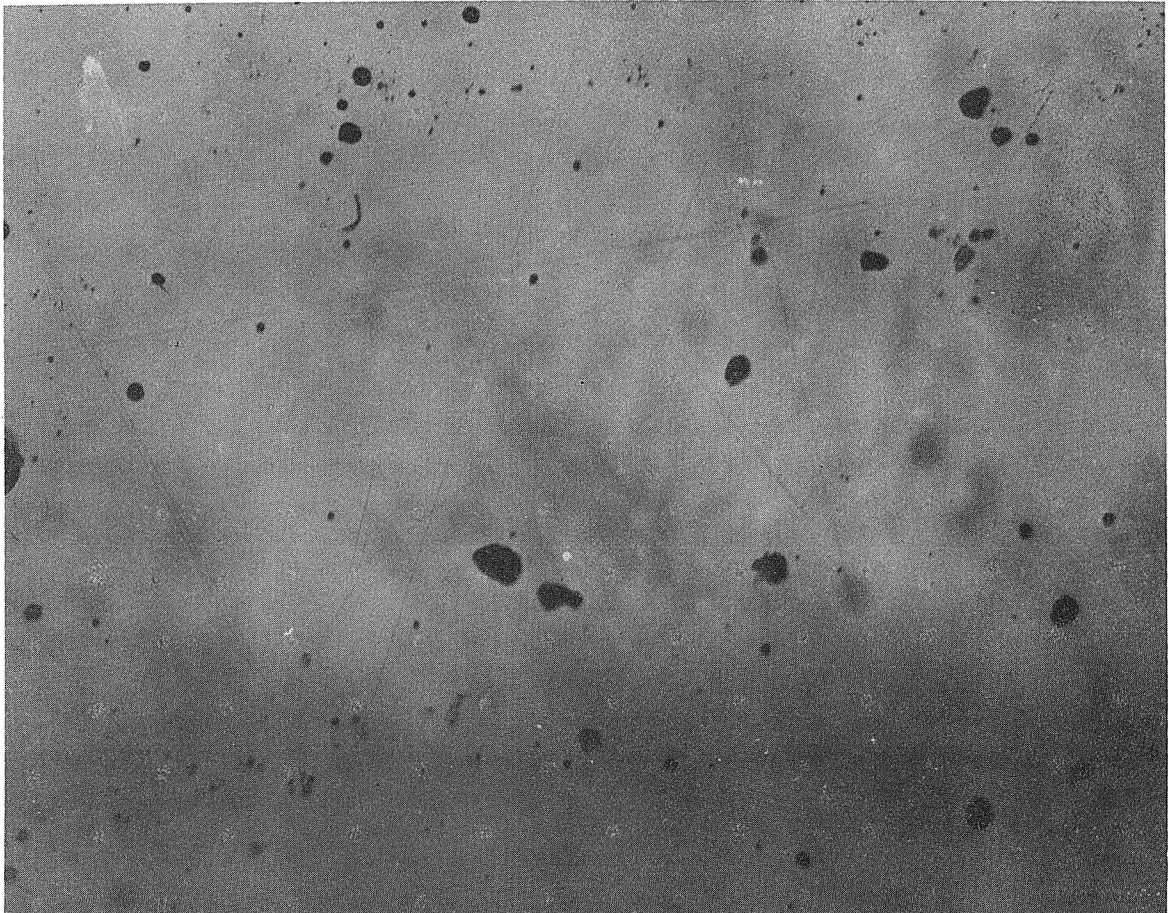
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Fig. 6



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Fig. 7



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Fig. 8

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