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Contents

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ABSTRACT

Superconducting niobium-tin composites containing filamentary Nb_3Sn were fabricated by powder metallurgy technique which involved powder rolling, sintering, infiltration, mechanical reduction and diffusion heat treatment. The influence of various process parameters at each step was experimentally examined. Optimal values have been recommended to be incorporated in a pilot plant for continuous production of the composite. Potential problems in the design and operation have been discussed and possible solutions presented. Finally, areas requiring additional investigation are indicated.

I. INTRODUCTION

Since the discovery by Kunzler, et al.[1] in 1961 that Nb_3Sn, an intermetallic compound of niobium and tin, was superconductive at cryogenic temperatures many investigators have explored different ways to fabricate a conductor out of the material for practical usage. Some conventional methods, like vapor deposition of crystalline niobium-tin on a flexible stainless steel ribbon[2] and a diffusion process to obtain a thin continuous layer of Nb_3Sn on niobium strip[3] have been tried. However, because of the extreme brittleness of the compound, none of them has been really successful as far as the capability of mechanical handling is considered. The recent approach to this problem has been to support the Nb_3Sn layer between a number of ductile metal plates or coatings.

At the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, a different and unconventional method for the manufacture of the superconductive material in the form of a strip containing thin filaments of Nb_3Sn has been developed.[4] It is based on the three powder metallurgy techniques: roll compacting of Nb powder, sintering and infiltration with tin followed by mechanical reduction and chemical reaction. Extensive experimentation has been done to achieve the best material properties by optimizing the operating variables at each production stage. This report describes studies carried out to freeze the parameters and to collect necessary data to aid the design and fabrication of a pilot plant for manufacture of tapes up to a mile long. A number of problems developed during the pilot plant design. Among them were the method of powder feed to the rolls, the prevention of poor

edge compaction, the selection of sintering atmosphere and the process start-up for continuous production. Some feasible solutions to these and other problems are developed in this report. The first half of the report deals with the influence of operating parameters on the properties of strip with particular emphasis on powder rolling and sintering stage conditions. A plot of ductility versus time of sintering for varying temperatures is given. Design aspects of rolling mill and hot zone are discussed in the second half. Finally, areas requiring further study before pilot plant fabrication are outlined.

II. PROCESSING OF THE STRIP

A. Flow Diagram

The entire process involves seven steps as shown in the schematic flow chart (Fig. 1) which closely represent the final system. The steps in the order of their occurrence are:

1. roll compaction of pure niobium powder to form a porous strip,
2. sintering of the green strip to make it strong and ductile,
3. infiltration with tin to obtain an interconnected network of tin pockets in niobium matrix,
4. metal cladding or coating of the ribbon,
5. mechanical reduction by cold rolling which elongates the tin clusters into fine filaments,
6. chemical reaction to form Nb_3Sn filaments, and
7. metal cladding with copper or aluminium.

To greatly simplify the design, fabrication and operation the entire system is divided into two stages between steps 3 and 4. The coiled strip after the first stage serves as input to the second. In addition to simplicity parting just before cold reduction has the advantages of not harming the flow of tape in one stage in case of a breakdown in the other, of not necessitating synchronism in speeds of tape at various points, and of eliminating a vacuum seal between steps 3 and 4 when the first stage is to be enclosed in high vacuum.

B. Suitability of P/M Processes

Most of the conventionally produced superconducting tapes have been in the form of one or two thin layers of Nb_3Sn with comparatively thick and flexible supporting layers of one or more metals like copper, silver and stainless steel. The extreme brittle nature of the intermetallic compound makes the composite incapable of taking any appreciable strains without breaking. This limits the usage of the composite where it has to be bent, wound and unwound. But the tape produced by the powder metallurgy processes listed above solves this problem because the thin filaments allow more elastic deformation than the solid layer before breaking. Furthermore the soft matrix of Nb surrounding the filaments and some residual tin in the core of the filaments give the tape more flexibility. In addition to this mechanical ruggedness the loss of power when conducting alternating currents is reduced considerably for the same area of cross section of Nb_3Sn. This is due to the filaments' size, shape and configuration (being respectively, thin, long and running almost parallel) which minimizes the hysteresis and eddy current losses and improves the stability of the tape as a high field super conductor. It is expected that these fascinating outcomes of the P/M processes make the product most outstanding.

III. OPERATING PARAMETERS AND THEIR INFLUENCE

Porosity, strength and ductility of sintered strip are the most important properties that have to be given first consideration, because they determine all other properties of the final product. The green powder compact is required to have adequate porosity to ensure a good volume fraction of tin after infiltration. Also the strip should be strong enough to withstand its own weight during sintering and any tension imposed on it by guiding rolls. Finally, ductility of sintered ribbon is essential to obtain heavy mechanical reductions. Since porosity and strength are conflicting parameters a sort of balance is reached between the two. Tapes with green porosity around 30% were found to suit the purpose very satisfactorily.

A. Powder Characteristics

The variables inherent with the powder being rolled are: 1. particle shape and 2. size distribution. As the powder is bought from suppliers little control could be exerted on particle shape. Effect of size and its distribution on porosity has been studied by Prakash Babu.[5] The smaller the size and the narrower the distribution the finer and more uniform the pores will be. This would bring in fine filaments with desirable disposition. Thus it was discovered that an optimum porosity, with an extremely fine distribution of pores, appeared to be in the range -20 + 10μ.

Due to the scarcity of classified powder in sufficient quantities tests were done with -325 mesh Nb powder with the following data:

Purity: 99.92%
Apparent density: 3 gms/cc
Sieve Analysis:
- 270 + 325 Mesh: 1.5%
- 325 + 400: 26.0%
- 400 : 72.5%

Scanning electron micrograph of the powder is shown in Fig. 2. The angular and highly irregular shape of the particle seems to contribute to the good green strength of the rolled strip.

B. - Powder Rolling

During roll bonding the variables associated with rolls are roll diameter, surface quality, peripheral speed and roll gap. Rolling was done in both air and vacuum to observe the dependency of green porosity on these variables. The mill that was employed is shown in Fig. 3. It had 2 inch diameter steel rolls with 0.250 in., 0.285 in. and 0.475 in. wide rolling surfaces separated by grooves to accommodate powder-feed hoppers. The quarter inch surfaces were roughened using 320 grit emery paper to improve friction. As this was the only rolling mill available the effect of diameter could not be examined. However, literature on powder rolling[6] says that the usual ratio of roll diameter to strip thickness is in the range of 100 to 300 : 1.

Observations of rolling tests are listed in Table I. The porosity was calculated by accurate measurement of dimensions and weight of the green samples. The flow of powder was found to be retarded in vacuum, as would be expected. If it were in air, the air pockets escaping from

the coherent zone,* through the powder in the incoherent region, stir the particles so that they settle down uniformly. There is no such fluidisation taking place in vacuum rolling. As a result the vacuum rolled strip was slightly thinner and had nonuniform strength due to weak spots along the length, especially when the quarter inch wide strip was rolled. When wider strips were produced in vacuum the strength was found to be more even, suggesting that stationary end walls of the hopper were hindering the flow of powder adjacent to them. The latter fact led to poor edge compaction which along with the poor flow of powder in vacuum aided breakage in less wide ribbons. This is highly undesirable from the standpoint of quality control and necessity of trouble free passage of strip to the sintering furnace in a continuous system. This difficulty was overcome when a vibrator (60 cps electric buzzer with the dome removed) was attached to the hopper (Fig. 3). There was much better compaction along the width in general and at the edges in particular. This could be evidenced by the decreased porosity (Table I) and reduced loss of loose powder falling near the edges during rolling. Other methods to achieve good edge compaction will be discussed under the subheading--Edge Restraint.

The effect of roll speed on porosity, as could be seen from the observations in Table I, is not as profound as of roll gap or use of vibrator. The surface condition of the rolls also plays an important role. The rougher the surfaces the more is the compaction because of increased grip angle. Powder head does not seem to have any appreciable

*Defined by the arc of rolls corresponding to angle of grip.

effect on porosity. Now it is only a matter of common sense to expect a thicker green strip with adequate and uniform porosity from sandblasted rolls fitted with a vibrating hopper.

C. Sintering

During sintering the mechanical bond between individual particles of the porous strip becomes a metallurgical one, thereby imparting strength and ductility to the strip. Sintered strip should have enough ductility for two reasons. It should be able to be cold rolled to reductions of the magnitude of 80 to 90% without undue cracking. Also as pointed out earlier the final product has to be flexible in order to be put to uses like coils for magnets. Ductility together with adequate porosity can be obtained only by careful selection of dwell time and temperature of sintering. Another equally important variable that has to be judiciously chosen, is the sintering environment.

1. Sintering Atmosphere

Pure niobium is highly reactive at elevated temperatures. So even the slightest presence of impurities, chiefly O_2, H_2 and N_2 in the sintering atmosphere leads to the formation of their respective chemical compounds which embrittle the strip. Hence, the choice lies between very pure inert atmosphere and vacuum. Because of the apparent advantages of more reliable seals at feed throughs and eliminating the need for elaborate pumping equipment, sintering under helium and argon were first tried. Earlier investigators[5,7] used commercially available highest purity helium and argon with total claimed active impurity levels* of

*Argon: O_2 = 3, H_2 = 1, N_2 = 5 ppm; Helium: O_2 =.2, N_2 = 1 ppm.

1.2 and 9 ppm respectively. They reported embrittlement of the strip irrespective of sintering duration. This had led to the building of a small gas purification plant on a laboratory scale.

The idea was one of Zaklad.[8] The flow diagram of the plant is shown in Fig. 4. It consisted of a stainless steel tube filled with copper catalyst called BTS (manufactured by the BASF) and a coil of stainless steel tubing containing molecular sieve granules of grade 4Å (made by the Linde Corporation). Oxygen present in the argon was removed when the latter is passed through the BTS kept at 200°C. The molecular sieve maintained at liquid nitrogen temperature entrapped the water vapor, CO_2, hydrocarbons and nitrogen. The purifier was connected directly to the sintering furnace. The gas was purified continuously as it flowed in a closed loop. This purification procedure was believed to get the total impurity level from 9 to approximately 3 ppm. Sintering under such an environment, unfortunately proved fruitless. Also helium was tried in a similar way but with no success. The ductility was still unacceptable as the sintered strip could not take any appreciable bending. It broke when bent around a radius of one inch. So it was concluded that the purity of the inert gas was not sufficient to prevent the formation of oxides, hydrides and nitrides of Nb which are responsible for embrittlement.

The only alternative then left was vacuum. The existing Abar furnace whose sectional view is shown in Fig. 5 has pumping equipment that can pump down to pressures in the range of 10^{-5} mm of mercury. Sintering in vacuum of this order was found to be very encouraging. In

spite of the fact that a vacuum system requires elaborate pumping equipment and often trouble shooting seals, utilization of vacuum as a sintering medium has the following major advantages.

1. A relatively poor vacuum of 1 micron (= 10^{-3} mm of Hg) corresponds to a "high purity" gas having a residual impurity content of 3 ppm. A vacuum of 10^{-6} mm of Hg corresponds to an impurity content in the gas of 3 ppb which is possible to obtain only in a static (completely sealed) system of comparable vacuum integrity.[9]

2. Vacuum being the cleanest available processing atmosphere cleans niobium strip during sintering thereby making it ductile.

2. Effect of Time and Temperature

A series of experiments was conducted to investigate quantitatively the dependency of ductility of ribbon on time and temperature of sintering. The same kind of powder as mentioned before was used throughout. Green strips were made by rolling in air with a roll gap of 0.015 in. and roll speed of 30 ipm. The rolled strips were 0.019 in. thick and 0.4 in. wide after edge trimmings. They had a green porosity of 28 ± 1%. In each of the experiments about 4 in. specimen was tied to the bottom of a tantulum rod and hung in the extension tube of the Abar furnace (Fig. 5). The furnace was pumped down to the 10^{-5} mm of Hg range, heated up and maintained at 1000°C for ten minutes for outgassing of the furnace walls. The temperature was then raised to the sintering range. When it stayed constant at a predetermined value, the specimen was introduced into the hot zone. After sintering for a specified time the specimen was taken back into the extension tube for cooling. The pressure in the furnace used to increase from 1.1×10^{-4} to 2×10^{-4} mm of Hg in the first few

seconds of sintering and drop down to where it started after a period of 30 to 40 sec. The increase in pressure was due partly to degassing of the strip and partly to fresh surface of tantulum rod coming into the furnace. The sample was removed from the furnace after it had been cooled.

The strip was now ready for testing. Because of its physical dimensions a standard tension test was considered unsuitable for noting the percentage elongation which is a direct measure of ductility. Instead a rather crude but effective method was employed. The specimen was cut into two equal pieces and each one was bent around rods of varying diameter in order, beginning with the largest diameter. The diameter around which the bending results in a visible crack in the strip was recorded for both top and bottom pieces. The smaller this "critical diameter" for a specimen, the more is its ductility. Keeping the temperature constant similar experiments were done for varying durations of sintering. Next the temperature was fixed at another value and the same procedure was repeated. The observations were used for plotting critical diameter versus residence time for different temperatures. The plots are shown in Fig. 6. It is now possible from the plots to interpolate any set of sintering variables namely time and temperature for a particular ductility.

D. Infiltration with Tin

The third step in the manufacture of the super conductive tape is the infiltration of sintered strip with tin. This was done in the Abar furnace after it has been modified as shown in Fig. 5. A quartz tube housed the tin bath contained in a graphite crucible. The bath could be heated to any desired temperature from outside by means of a movable electrical heater. The procedure of infiltration included heating the tin to the required temperature while the sample was in the furnace, dipping for a predetermined duration and raising the sample back into the cold zone for cooling. This could be done in either vacuum or in an inert atmosphere.

For good infiltration the liquid tin should wet well the niobium strip without any reaction and flow readily into the pores by capillary action. An increase in temperature of tin causes a decrease in viscosity. Thus, liquid tin which is very viscous at 240°C (viscosity = 212 c.p.) becomes thin at 650°C and flows like water (viscosity = 1 c.p.). Surface tension which is responsible for capillarity, is actually reduced with temperature; but the reduction being very small (from 526 dynes/cm at 253°C to about 515 at 650°C) does not affect the process at all. But since at too high a temperature, diffusion reaction to form the brittle compounds of Nb and Sn is favored, one has to guard against this. Even though the formation of Nb_3Sn is time dependent little of the compound was detected in the microstructure analysis of the strip which was infiltrated in tin at 650°C for as long as 5 minutes. Samples with infiltration times varying between 1/2 to 1 minute at 650°C showed absolutely no difference in the content of tin and the infiltration was quite satisfactory.

Complete infiltration can be attained only when all the pores are interlinked. The question of disconnected pores, fortunately, does not arise because the sintered strip has a porosity of the order of 20%, whereas according to Caputo and Pels[10] a porosity of 10% or more in a powder compact would be a network of pores with interconnections.

Infiltration under inert atmosphere proved inferior to that in vacuum. The cross sections of infiltrated strips were studied under the microscope after anodizing the polished surface, using Picklesimer solution. One usual observation was the difference in size and amount of pores between the centre and the edges of the cross section. Porosity was higher with larger pores near the edges than in the centre. This difference disappeared to a large extent in wider and carefully rolled specimens using a vibrator. This is of course due to uniform distribution of roll pressure in wider strips and improved flow of powder when the vibrator is used. Micrographs shown in Fig. 7 indicate the difference of porosity between edge and centre of a typical infiltrated sample.

E. Cold Reduction

The aim of reduction by rolling the infiltrated strip is to elongate the interconnected network of tin to form filaments. The thinner the filaments are, the better the super conductor properties of the finished tape will be. The possible percentage of reduction without deleterious edge cracking depends on the constituents of the strip and their ductility. The softer tin with a lower flow stress flows more readily than the niobium matrix and there is a danger of its loss due to "squeeze-out" at higher reductions. This has been observed by Prakash Babu in

microscopic examination of longitudinal sections of 90 to 95% reduced specimens. They contained cavities resulting from tin squeeze-out and subsequent elastic springback of niobium boundaries. Also mechanical reductions beyond 90% showed wrinkling when the initial strip thickness was less than 16 mils. Therefore, the selection of % reduction should be based on optimal agreement between electrical and mechanical properties. Since roll pressure is responsible for tin squeeze-out it is advisable always to reach the final thickness in as many passes as possible.

Edge cracking is another problem associated with rolling. When the strip is relatively thin and the pass reduction heavy, the edges barrel and are forced to elongate by the dragging effect of the bulk of the material. If the ductility of the material is limited, the combined action of secondary tensile forces developed due to this dragging and compressive forces of rolls results in cracking. The ductility of a strip is impaired by the presence of a phase (tin) which has a low melting point.[11] Trimming of the edges between passes reduces the propagation of already developed cracks. Tapes worked to 85 to 90% reductions using a 4 high mill (1.625 in. dia rolls backed by 4.50 in. dia rolls) in about 6 passes with two intermediate edge trims seem to possess optimum characteristics including very good flexibility. They could take approximately 0.2 in. diameter bends. Photomicrographs of Fig. 8 show the longitudinal sections at 50, 65, 75 and 90% reductions of a sample sintered at 2250°C, 1×10^{-4} mm of Hg for 2 minutes and infiltrated at 650°C for one minute. The gradual change in the thickness of the filaments can be seen from these pictures.

F. Reaction by Diffusion Heat Treatment

Reaction between niobium and tin is a diffusion process. It could take place at varying conditions of time, temperature and environment. The same arrangement of the tin bath under the Abar furnace mentioned earlier was employed for studying the effect of these parameters. Useful ranges for temperature and time were reached after a number of trials. A 0.004 in. thin 75% reduced strip required 3 to 4 minutes treatment at 950 to 970°C for complete reaction of tin. In a 90% reduced tape which was only 0.0016 in. thin, a dip for 40 to 60 seconds at the same tin bath temperatures converted almost all the impregnated tin to Nb_3Sn. This was so because the area of contact between niobium and tin of the 90% reduced tap was much greater than that in the lower reductions. Also, it was believed that the amount of coldwork might increase the rate of diffusion. The rate of cooling after the dip was suspected to be playing an important role in the reaction phenomenon. Samples that were cooled very slowly just above the tin bath contained a noticeable amount of Nb_6Sn_5, another intermetallic compound. Nb_6Sn_5 shows up as a reddish brown phase after anodizing. Consequently the samples carried less critical current when tested. Hence, it is recommended to cool sufficiently fast in order to avoid this shortcoming.

Earlier investigators have conducted diffusion treatment under different environments. In vacuum heat treatment evaporation of tin from the surface was a serious problem. Use of inert gas atomosphere (He or A) minimized vaporization. But heat treatment in a tin bath proved to be better because when the strip was removed from the tin bath a layer of tin was left on its surface. This tin coat improved

flexibility and facilitated soldering of the strip which was hard to achieve otherwise. Diffusion in tin has an additional merit that the open pores resulting from tin squeeze-out at heavier reductions would once again be filled with tin. For the sake of stability of the composite as a super conductor and mechanical flexibility for handling, a heavy coating of tin is essential. Another dip for a short time in tin maintained at about 300°C is all that is necessary. Also partial reaction leaving some tin in the centre of the Nb_3Sn filaments (Fig. 9) was found to contribute to additional flexibility. Furthermore, incomplete reaction might be necessary if the preference is towards finer filaments.

IV. PILOT PLANT DESIGN CONSIDERATIONS

Primary design involves a complete understanding of all the processes and knowledge of all the problems associated with each of the processes. Since the preceeding section of the report had dealt essentially with the processes and the influence of their variables on the properties of the tape, attention is now focussed on to the problems that have been encountered during the course of experimentation and discussions to aid the design and assembly. The problems are analysed in the sequence of their occurrence, after the following summary of feasible ranges for operating variables.

A. Quantitative Recommendations for the Operating Variables

Assuming that 0.016 to 0.018 inch thick green strip has to be produced and processed to the final form, the following recommendations could be made based on the tests conducted so far.

Rolling:

1. Diameter : 2.0 in.
2. Peripheral speed : 30 ipm
3. Roll gap : 0.013 to 0.014 in.

Sintering:

4. Temperature : 2300 to 2340°C
5. Residence time : 60 to 40 sec
6. Vacuum : 10^{-5} to 10^{-6} mm of Hg

Infiltration:

7. Tin bath temperature : 650 ± 20°C
8. Dwell time : 30 to 40 sec

Cold reduction:

9.	% reduction	: 80 to 90 %
10.	No. of passes	: 6 to 10

Diffusion:

11.	Reaction tin bath temperature	: 950 to 1000°C
12.	Dwell time	: 1 to 4 mins

B. Powder Feed Mechanism

The objective is to supply Nb powder to the rolls at a constant rate to ensure not only continuous compaction but consistent green porosity along the length and across the width of the strip. Since the entire system would be enclosed in vacuum the powder lot should either be stored in one or more hoppers inside the system itself or be supplied in batches intermittently from outside, through a double door mechanism. Calculations showed that the powder required for quarter mile, 1 in. wide and 4 mil thick (75% reduction from 16 mils or 90% from 40 mils) weighs nearly 14 pounds and occupies a volume of 2 litres. So the entire mass of powder could simply be stored inside the system without any difficulty.

The inherent poor flow of the powder which is due to a wide size distribution and a large fraction of fines, causes a problem in its feeding. Furthermore, the flow would be worsened in vacuum than in air, for there is no air to act as a lubricant between particles. To avoid bridging of powder masses it is necessary to have two hoppers--one, a storage bin from which the powder is steadily fed to a second hopper installed on the rolls. Two possible methods of feeding from the bin

to the roll hopper are shown in Figs. 10a and 10b. In screw-feed, the drive could be taken from one of the rolls through an endless chain. The feed rate could well be adjusted at any desired value by varying the aperature through which the powder comes in contact with the screw. In case of the other method, the bottom gate of the bin is shaken by some means to prevent the powder from bridging. However, vibrations of any kind result in highly intolerable segregation of powder after a short time. Since the screw-feeder causes little segregation, it is preferred to vibrating cone feed. The only drawback is that it requires an additional motion inside the vacuum. The powder would flow well on the second hopper if it is let fall by gravity from a small height. Otherwise shaking as it enters the roll gap by means of a vibrator is inevitable.

C. Rolling Mill Design

The first and foremost requirement for the rolling mill is the precision without which quality control becomes impossible. Good wear resistance is the next important factor for the roller material in order to maintain a desired surface condition until after a long run. But, irrespective of hardness of the rolls initial roughness would change with time, the change being more in the initial periods if the surface is too rough to start with. So it might not be unreasonable to assume that a fairly steady roughness would prevail after a few hours of rolling. If a gradual smoothening is detected due to wear, the surface could be conditioned continuously by some type of scratching from below.

As the entire mill has to be mounted in vacuum, above the sintering furnace, special bearings which operate trouble free in vacuum are to be used. The power could be transmitted from outside to the mill through both the roller shafts universally coupled to two other shafts driven by an electric motor. There must be a means to vary the speed from about 2 to 8 rpm. It was estimated from the roll torque (600 in. lbs for 1 in. wide tape), a morot with a 0.5 hp rating would provide a safety factor of 2. Keeping all these requirements in mind, the following selections have tentatively been made.

Roll Material: (one of the three)

	Type	Hardening Temp. °F	Tempering Temp. °F	Hardness Rc	Impact Strength*
a)	AISI D2	1875	325	62-63	75
b)	AISI D7	1975	325	64	19
c)	AISI A7	1750	400	65	

Bearings:

Needle bearings: Torington Co. W. J.-243024

Capacity 12000 lbs.

1. Edge Restraint

In the practice of powder rolling the problem of poor edge compaction is inevitably encountered. A simple way of testing the distribution of porosity along the width of a rolled strip is to dip it vertically in a good wetting solution (kerosene in the case of Nb powder) and to observe the extent of infiltration while holding the specimen steady. Two reasons seem to be responsible for poor edges. It is known from the

*Unnotched Izod Impact Strength in ft. lbs.

theory of rolling that in the flat rolling of powders the roll interface pressure changes not only along the arc of contact corresponding to the angle of grip, but also along the width of the strip. The gradual drop of interface pressure toward the edges which is due to plane-strain conditions prevailing in the central portions, leads to variation in porosity. This was evidenced when a one inch wide strip was rolled without any end constraints on the ungrooved portion of the rolls. The second reason for poor edges is the static end walls sitting in the grooves to confine the flow of powder. As pointed out earlier, the stationary walls retard the particle flow adjacent to them like a flat plate in a laminar flow of a liquid. As a result the powder feed at the edges is quantitatively less than in the centre. Quite often, it so happens that the amount of powder there is too insufficient to form a mechanical roll bond between particles. This means that the loose powder would fall off at the end walls of the hopper. Thus the wall-effect is doubly determintal.

One way of reducing to a great extent the effect of pressure drop along the width is to make the roll surface slightly concave, the curvature being confined to the edge region where the change in porosity is most noticeable. When the quarter inch roll surfaces were ground concave with a maximum dimentrical difference of 0.0008 in., the edge compaction was observed to be improved markedly.

Various means of edge restraint to eliminate the harmful end-wall effect have recently been developed. Some of them which might prove applicable are discussed below. The principle in all the examples shown in Figs. 11, 12 and 13 lies in the fact that the static walls are replaced by moving members which keep the relative velocity between

themselves and the roll surface as small as practical. In Fig. 11, the restraining elements take the shape of endless belts to facilitate continuous rolling. Even though the thickness of such belts is necessarily limited by their flexibility, they are expected to give adequate strength because of the support they receive from the rolls. The belts should, of course, move at the same speed as that of roll surfaces. The second example of Fig. 12 is a more compact arrangement in which the restraining element is made in the shape of a ring. The only disadvantage with this is that the surface velocity of the ring is not constant over the thickness of the powder strip, i.e., the plane of the paper, and the rolled strip might tend to curl toward the roll on the left.

A further application of the principle is illustrated in Fig. 13. It consists of two flexible rings made out of stiff rubber-like material, mounted one on each roller shaft as shown in the plan view. The rings are held tight against the rolls by means of coiled springs which could be fixed on one end to flanges on the shafts. The outer diameter of the rings should be such that the dimension H (the height of point of intersection of roll diameter and ring diameter from the line of centres) is greater than the height of the coherent zone which depends on the gripping angle and the diameter of the rolls. The merits of this kind of setup are that a pressure could be exerted on the powder being rolled from the sides because of the springs and that the tape deflection present in the second example might be avoided. All the three means of edge restraint discussed above require specially constructed housings to hold powder on the rolls depending on the shape of constraining elements.

D. Design of Hot Zone

A good deal of time was spent to investigate the possibility of cutting the sintering time down to half a minute by increasing the temperature so that the furnace length could be reduced. Because of the limitation in getting and difficulty in maintaining a temperature higher than 2330°C, even after the power boosting, sintering behavior could not be studied at higher temperatures. But from the observations made already, there is no reason why it should not be possible to obtain adequate sintering at temperatures in the neighborhood of 2350°C for 30 seconds. But then the question is whether or not the Nb strip can support, at that temperature, its own weight in the hot zone and any tension caused by the ribbon-guiding rolls below the furnace. The green strength does not pose any problem because according to reference No. 7 the green tape with a porosity in the range of our interest is capable of support lengths of the magnitude of several hundred inches. So tests have been conducted to evaluate the hot strength. A carefully rolled 0.25 inch wide, 16 inch long specimen was hung in the furnace. The top end was fixed to the tantulum rod by means of a clip. Known weights were attached at the bottom of the strip, and could be seen hanging free in the quartz tube. The middle portion of the ribbon was then heated in vacuum to 2280°C and maintained for 3 minutes. The specimen did not break. Another similar test was performed with increased weights with the intention of breaking the strip, but as in the previous case, it supported all the load. The results are summarized on the next page.

	Total Weight	wt/inch of Tape	Supported Length
Test 1	15.6 gms	0.333 gm	52 in.
Test 2	27.0 gms	0.333 gm	81 in.

The supported tape lengths were calculated taking into account the weights as well as the weight of the specimen below the centre of the hot zone. Though it is now clear that a 30 inch hot zone does not pose a problem at 2280 °C, the hot strength at temperatures beyond 2300°C is yet to be observed.

Various methods of heating including graphite element and quartz filament have been explored. Tungston mesh element seems to suit our purpose best. As 30 inch long mesh in one piece would be very slender and weak when hot it is safer to employ more than one element. Use of standard sizes makes the replacement easy and economical, in case of damage to any one of them. The diameter of the elements should be at least 2 inches to leave a clearance of half an inch on either side of the one inch wide ribbon. Any modified shape, for instance an elliptical or even rectangular cross section for the element, would not only bring in uniform heating along the width but reduce the power input to the furnace. But unfortunately it was learnt from several suppliers that limitations of existing manufacturing equipment make the fabrication of shapes other than circular more tedious and uneconomical. Therefore, two 15 inch long, 2 inch diameter and single phase tungsten Brew Mesh elements each having a resistance of ~120 m ohms and a price of approximately 750 dollars could be specified.

It is hard to make an exact estimate of power requirement to maintain a suitable temperature in the range of 2300-2400°C under the

dynamic conditions of sintering because of complex heat transfer. The power input is largely dependent on the efficiency of heat shields enclosing the hot zone. By assuming that the power is proportional to the volume of the working space, it could be roughly estimated at 90 to 100 kVA. This range is reached on comparison with existing furnaces.

If no means of edge restraint is adopted in powder rolling for reasons of simplicity, care should be taken to stop the passage of loose powder into the hot zone. Otherwise the elements get covered with powder and will cease to function efficiently. One way of solving this is to run the strip as it comes out of the mill, through a narrow slit in an inclined sheet of metal. Two possible schematic configurations of such a gate are shown in Fig. 14. The retained powder could be collected in a tray. Another way of achieving the same goal is by shadowing the tungsten mesh with a high temperature metal sheet like tantulum at the very top and letting the powder fall through until the bottom where is could be collected.

E. Pumping Equipment

The higher the vacuum the better it is for sintering. To ensure good ductility and cleanliness for the rolled strip, a vacuum of the order of 10^{-6} mm of Hg should prevail in the furnace. For any vacuum system, the pumping capacity and the speed are directly related to the vacuum chamber's volume and the amount of outgassing of both inside surfaces and the strip itself during sintering. In a continuous system, the major factor is, of course, the last one, because the chemically combined gases as well as those adsorbed by the large surface

of the powder, evolve when the porous body is heated. A sintering test was conducted to determine the amount of gas evolution. A precisely weighed powder compact was heated at 2150°C for 5 minutes and from the observed weight loss the percentage gas evolution by weight was found to be 0.16. For a more accurate estimate, other tests are being done where the furnace pressure variation is recorded during heating with and without hanging the sample in the hot zone. Superimposition of the two pressure records should give us the information on gas evolution if all other furnace conditions are assumed to be identical in both cases. The actual selection of pumping equipment would be possible only after showing these test results. However, it has been decided to use an oil diffusion pump backed up by a mechanical pump.

F. Infiltration Tank

A 40 second impregnation would require a 20 in. long tin bath. Calculations show that a quarter mile of 1 in. wide and 0.018 in thick (or one mile of 0.25 in. wide and 0.018 in. thick) tape would consume approximately 115 cubic inches of tin. So a tin bath having a shape like a deep tub with dimensions 20 in. × 2 in. × 4 in. deep could be used satisfactorily. The tub material could either be ceramic or graphite since tin wets to or reacts with none of them. Multiple electric resistance coils placed along, around and beneath and tub could maintain uniform temperature throughout the bath.

G. Operation of Stage I

After most of the Stage I design aspects are dealt with a tentative arrangement of all the plant elements has been agreed upon. Figure 15 illustrates the main features of the stage. The powder is stored in 4 hoppers which can turn in a circle about the central support. The powder can be released into the smaller hopper on the rolls at a constant rate from any one of these bins by rocking the shaft connected to the bottom gate. The rolled strip finds its way through the 30 in. long hot zone situated right below the rolling mill. After the sintering process the tape is guided by 4 sets of rolls of which the top one is driven with a small constant torque exerting a predetermined force on the tape to keep it straight. Then the tape is twisted through 30° over a length of 32 in. and directed into the tin bath for impregnation. Finally, the coiling device takes up the infiltrated tape. The speed of the take-up coil is controlled by a set of photocells which senses the tape's position when it takes a turn at the bottom of the vacuum chamber.

The only problem remaining unsolved till now is that of start-up, that is, how to start the whole operation. Two ways have been looked into to find their applicability with minimum trouble. The first one is to roll-clad between Nb powder, a thin refractory metal tape which has been taken through all the path from take-up coil to the roll gap. The cladding to a solid tape appeared to be inadequate and the junction where the cladded tape ended was weak. Next a perforated tape and a thin wire mesh were used with some success with the latter. The second solution is to powder-roll a long tape, sinter it while the rolls are stopped, open the system to atmosphere and run

the rolls once again, until the sintered tape pass through the guiding rolls and enter the bottom chamber. There the end of the Nb strip is spot welded to any solid metal tape that has been taken through the rest of the path. It was observed that sintered strip spot welded very well to stainless steel tape. Breaking the vacuum could possibly be eliminated if provision is made inside the system to weld the two ends together.

V. AREAS FOR FURTHER STUDY

Since all the operating variables of Stage I are either frozen or brought down to narrow ranges, the pilot plant fabrication could now be initiated for the stage. However, if a thicker final product is favored for reasons of mechanical handling, rolling behaviour of the powder has to be restudied, using a set of bigger rolls. Areas requiring more detailed investigation before building the second stage of the plant are discussed below.

1. When a reduced sample is heat treated in tin, not only the niobium surrounding the inside network of tin but also that at the strip surface in contact with the tin bath participates in the diffusion reaction. Thus, there form two layers of Nb_3Sn enclosing the filamentary structure. These layers, whose thickness depend on the duration of reaction, help increase the current carrying capacity. Now, a study has to be made to relate the layer thickness, reaction time and grain in current.

2. Though the filaments are interconnected, at certain points along the length they are fewer in number and at certain other regions they are thinner than the average section. Thus, when the tape is conducting high currents there are bound to be hot spots where the total cross-sectional area of Nb_3Sn is less, and these may cause a local rise in temperature sufficient to change the superconductor to the resistance state. In order to overcome this instability, at least partially, bonding the superconductor to a normal metal is necessary which not only provides a temporary alternative current path but acts as a thermal shunt. This could be achieved in a number of ways: a) by rollcladding

the strip between two metal tapes (copper, aluminum or silver) after the diffusion process; b) by vapor deposition of a stabilizing metal; and c) by dipping once again in tin maintained at a fairly low temperature, after the diffusion treatment. Though the last one appears simpler and less expensive of all, a further investigation has to be made to compare the different approaches with regard to their electrical, thermal and strength behaviors.

3. The percentage mechanical reduction is one of the most important factors whose selection should be reasoned by actual critical current tests. From the few tests conducted so far by Dr. Gilbert, it has been observed that 90% reduced tapes had higher dc critical current density* than 75% reduced ones. At this stage it is believed that the ac properties of the tape would be improved with higher reductions. However, an accurate and detailed experimentation has to be carried out to find the influence of mechanical reduction and diffusion reaction time on both dc and ac properties. A plot similar to Fig. 6 relating diffusion time and temperature with the critical current is very essential to make optimal choice of the variables.

4. It is reported that doping the Nb with Zr or ZrO_2 increases the critical current independently of the production method.[2] So useful work could be done in the future to utilize the principle of doping in the present P/M technique.

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*Amperes per square inch cross section of the tape.

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Table I.

Sl #	Variable	Roll Gap (mils)	Surface Speed (ipm)	Environment	Vibrator	Strip Thickness (mils)	% Green Porosity
1	Roll gap	13	30	vac.	yes	16.7	21.4
2		14	30	vac.	yes	17.6	23.9
3		15	30	vac.	yes	18.5	26.5
4	Speed	13	20	vac.	no	16.9	21.8
5		13	30	vac.	no	16.8	23.9
6		13	45	vac.	no	16.7	25.0
7		13	20	vac.	yes	16.8	20.5
1		13	30	vac.	yes	16.7	21.4
8		13	45	vac.	yes	16.6	23.0
9	Environment	14	30	air	yes	17.0	20.3
2		14	30	vac.	yes	17.6	23.9
10		14	30	air	no	18.0	25.8
11		14	30	vac.	no	17.2	28.7
2	Vibrator	14	30	vac.	yes	17.6	23.9
11		14	30	vac.	no	17.2	28.7
3		15	30	vac.	yes	18.5	26.5
12		15	30	vac.	no	18.2	31.4

Width of the strip: 0.5 inches

Powder head above the centerline of the rolls: approximately 2 inches.

FIGURE CAPTIONS

1. Flow chart, 1. powder rolling, 2. sintering, 3. infiltration, 4. cladding, 5. cold reduction, 6. reaction and 7. copper cladding.
2. Scanning electron micrograph of -325 mesh niobium powder.
3. Rolling mill.
4. Flow diagram of inert gas purification plant.
5. Abar furnace, 1. extension tube, 2. tantulum rod, 3. back filling port, 4. electrical leads, 5. tungsten mesh heating element, 6. Nb specimen, 7. radiation shields, 8. water cooled wall, 9. W -5% Re vs W -26% Re thermocouple point, 10. vacuum connection, 11. quartz tube, 12. graphite crucible, 13. liquid tin bath and 14. electric heater.
6. Plot of sintering time vs ductility for varying temperatures.
7. Photomicrographs of as infiltrated strips showing porosity at a) edge and b) centre; areas 1. tin and 2. niobium (roll gap: 15 mils, roll speed: 30 ipm and no vibrator; sintered in vacuum at 2260°C for 3 minutes and infiltrated in tin at 650°C for 1 minute).
8. Photomicrographs showing longitudinal sections of the strip at a) 50%, b) 65%, c) 75% and d) 90% reductions; areas 1. tin and 2. niobium.
9. Photomicrographs of an 80% reduced specimen heat treated in tin at 960°C for 3 minutes; a) longitudinal section and b) cross section; areas 1. tin, 2. niobium and 3. Nb_3Sn.
10. Powder feed mechanisms; a) screw feed and b) vibrator feed.

11,12,13. Edge restraining methods.

14. Loose powder collecting methods.

15. Stage I of the pilot plant.

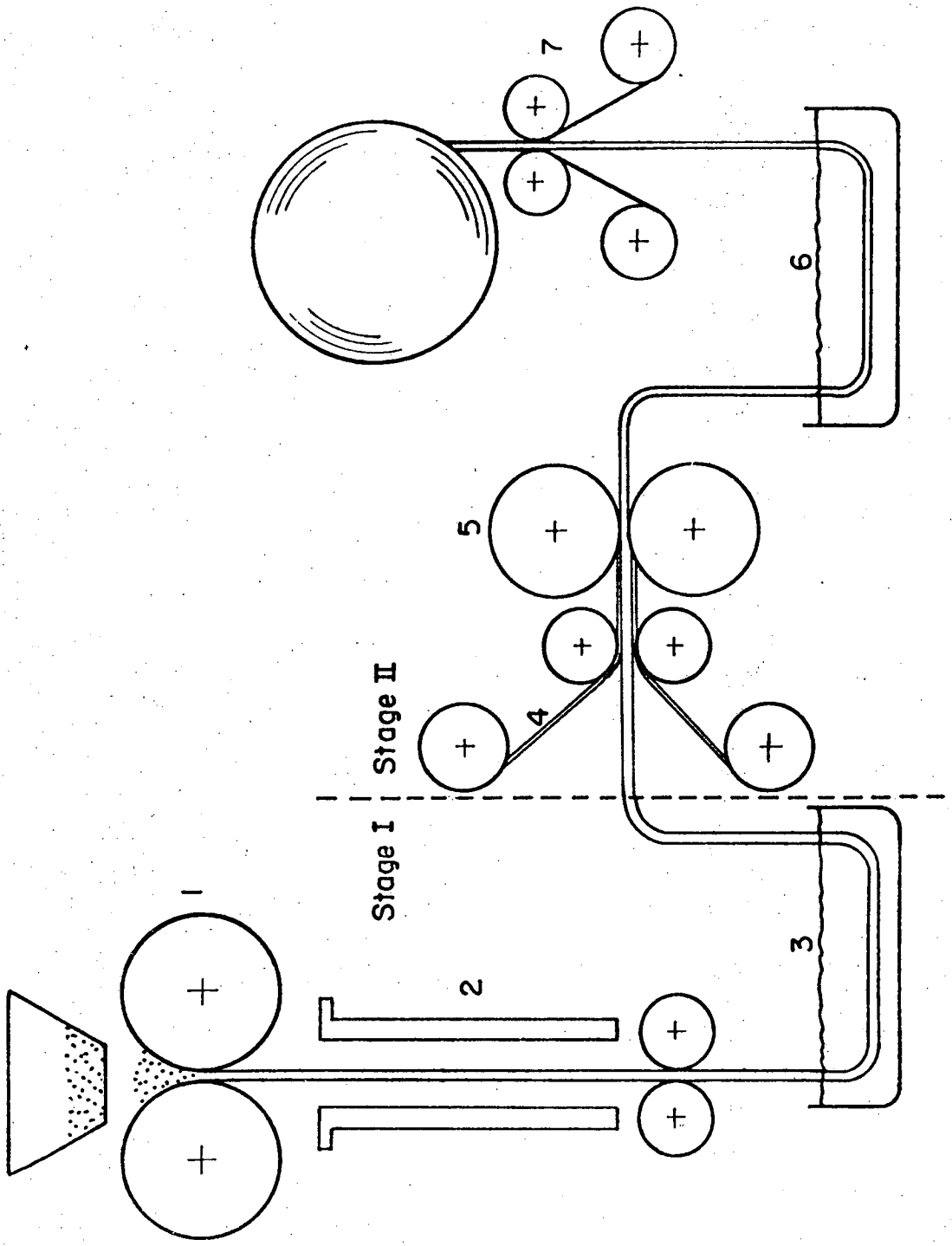

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Fig. 1

XBB 731-433

Fig. 2

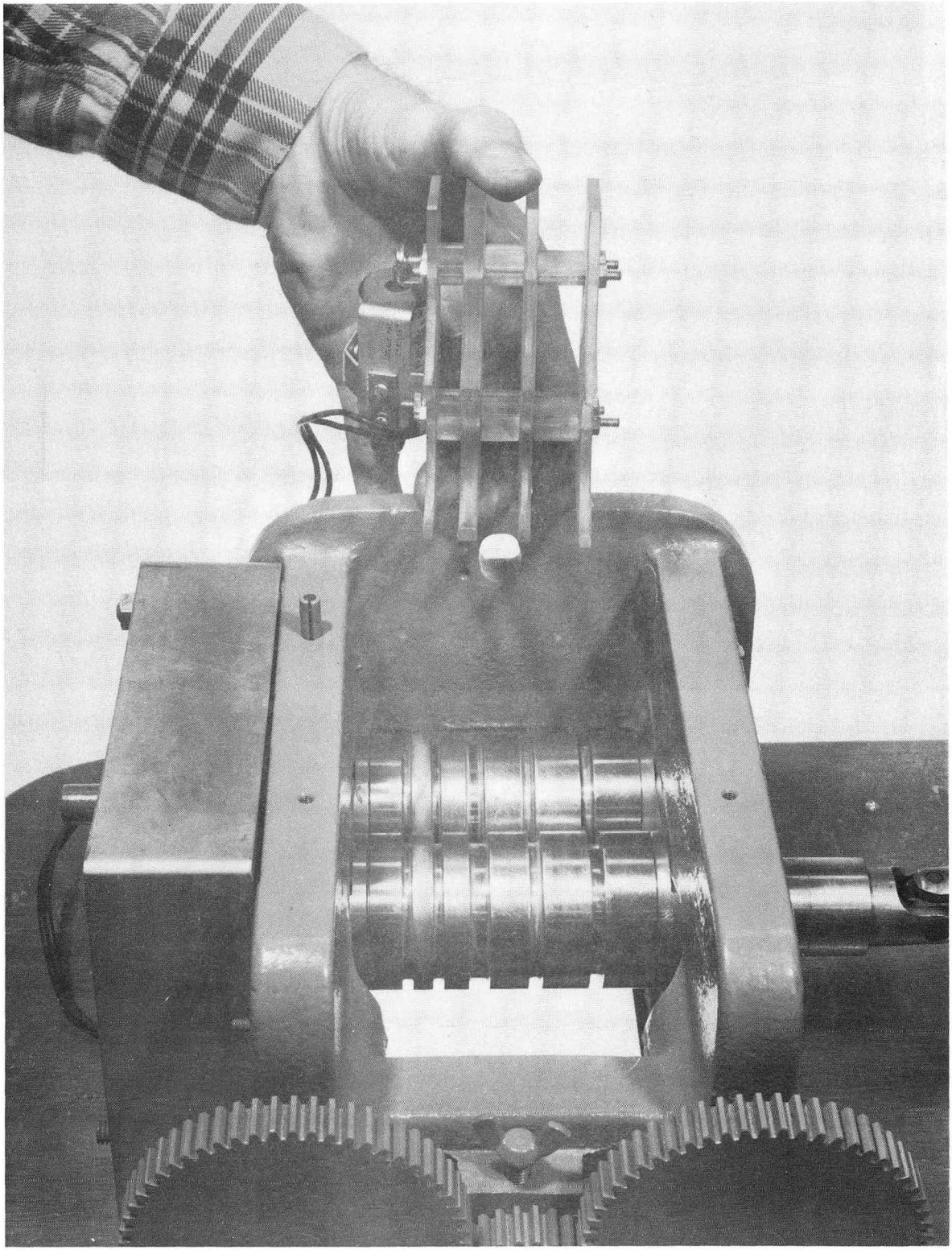

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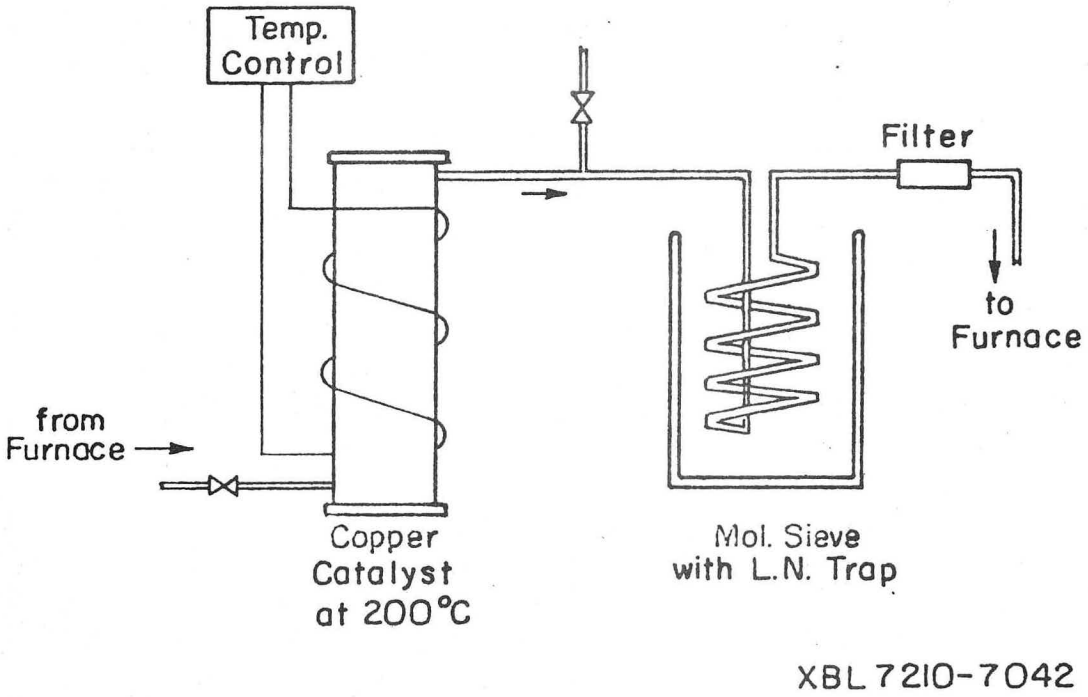
Fig. 3



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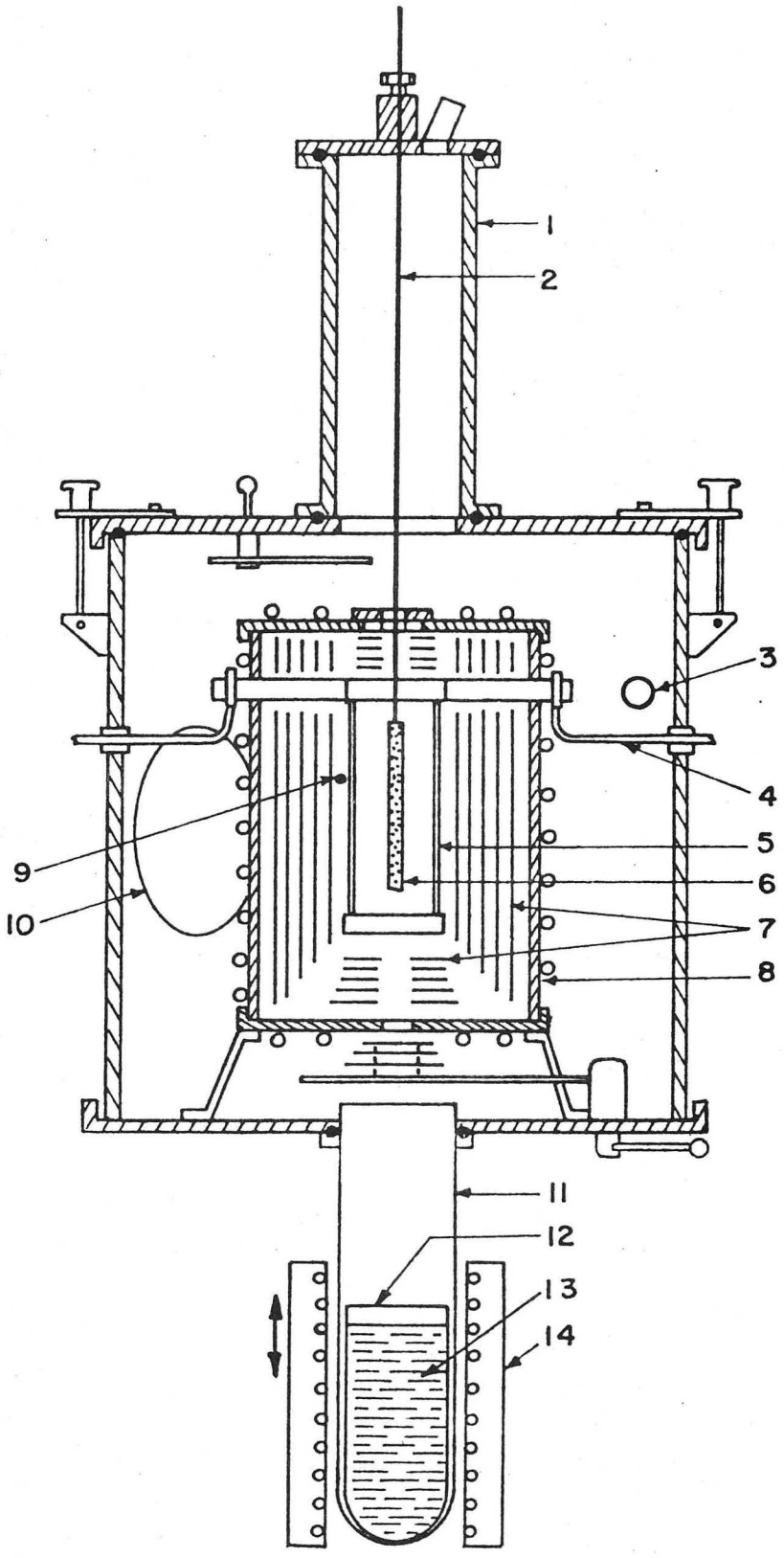

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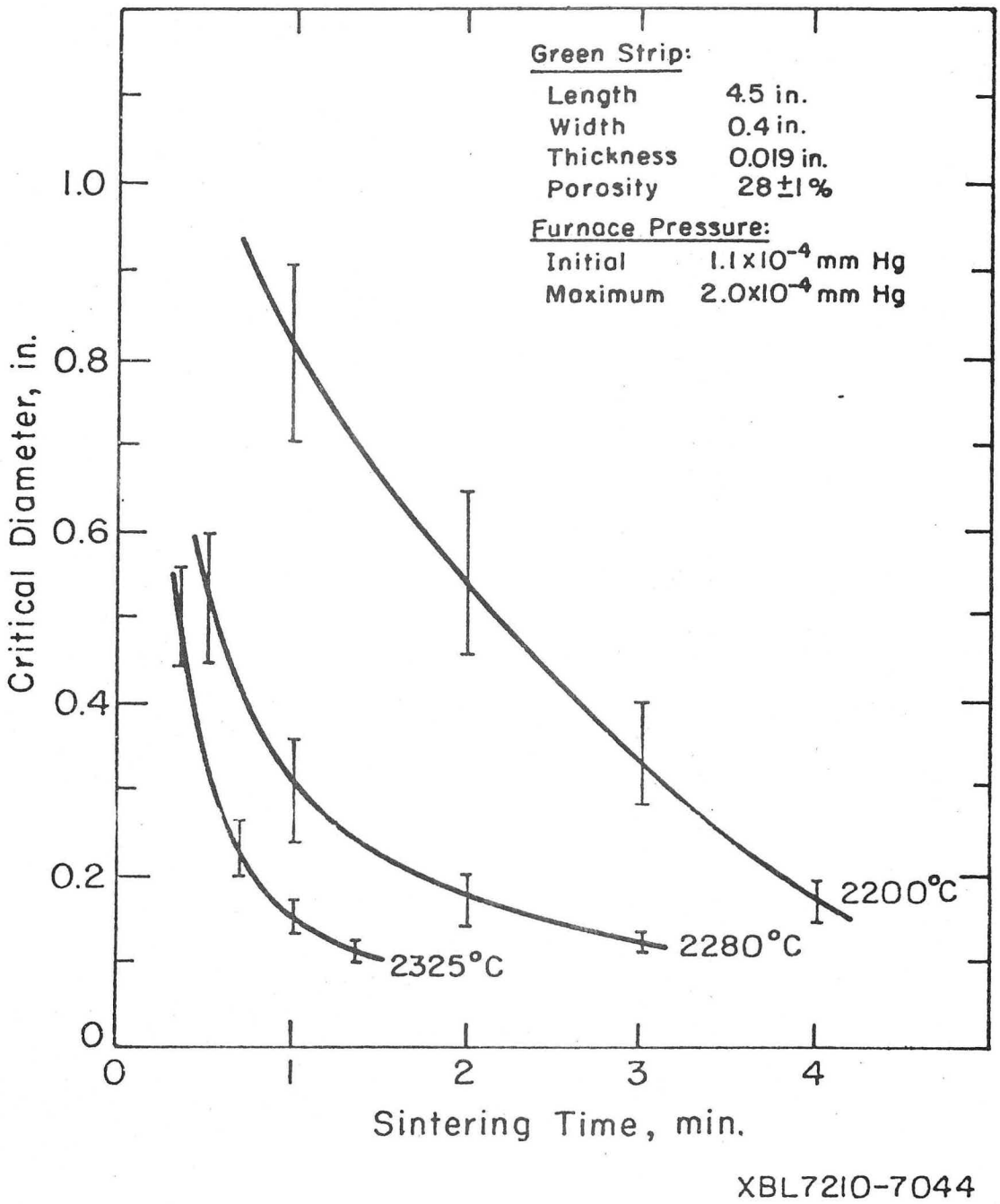
Fig. 5



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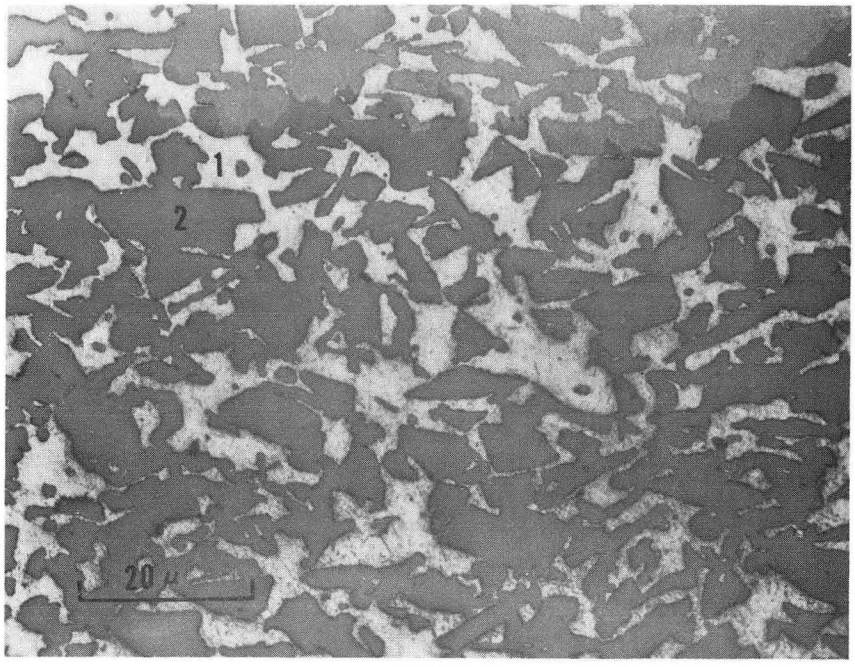


Fig. 7a

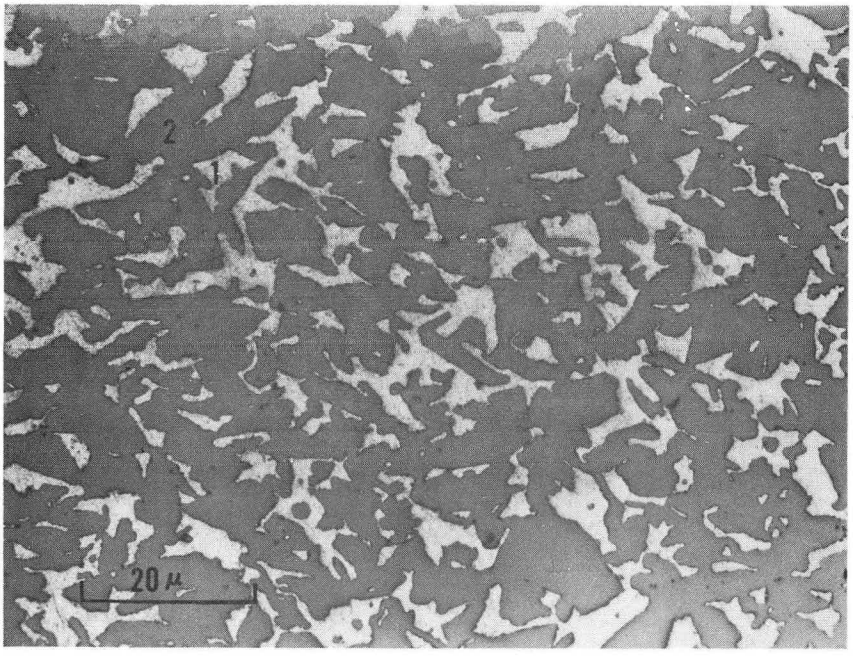


Fig. 7b XBB 731-437

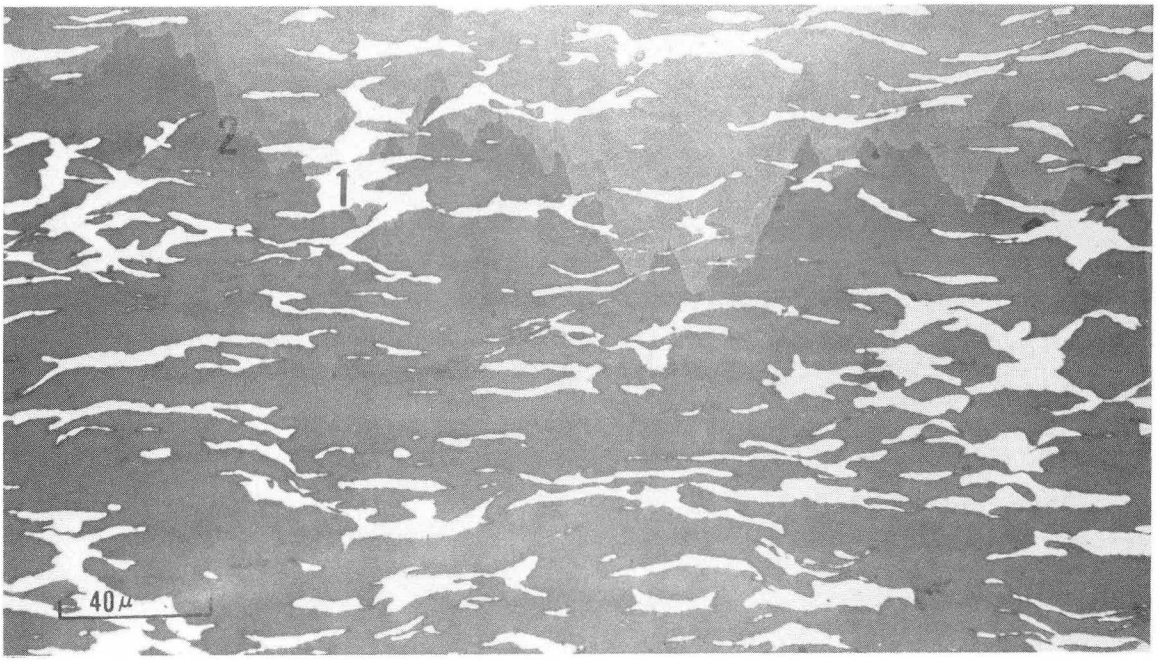
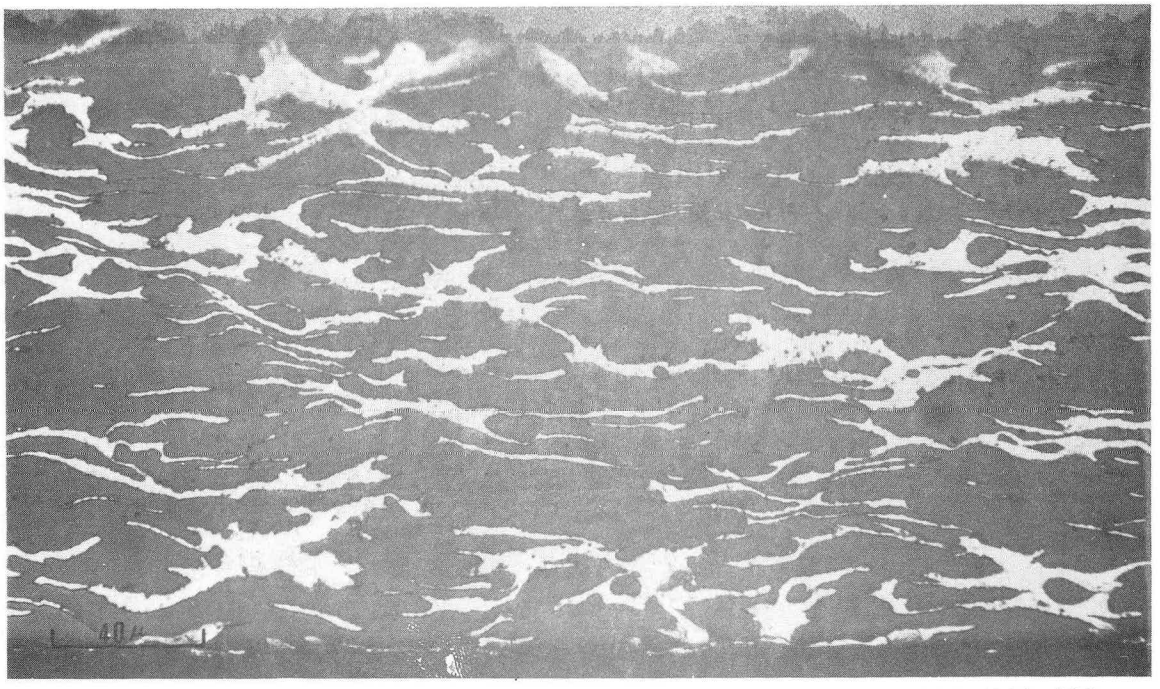


Fig. 8a



XBB 731-435

Fig. 8b

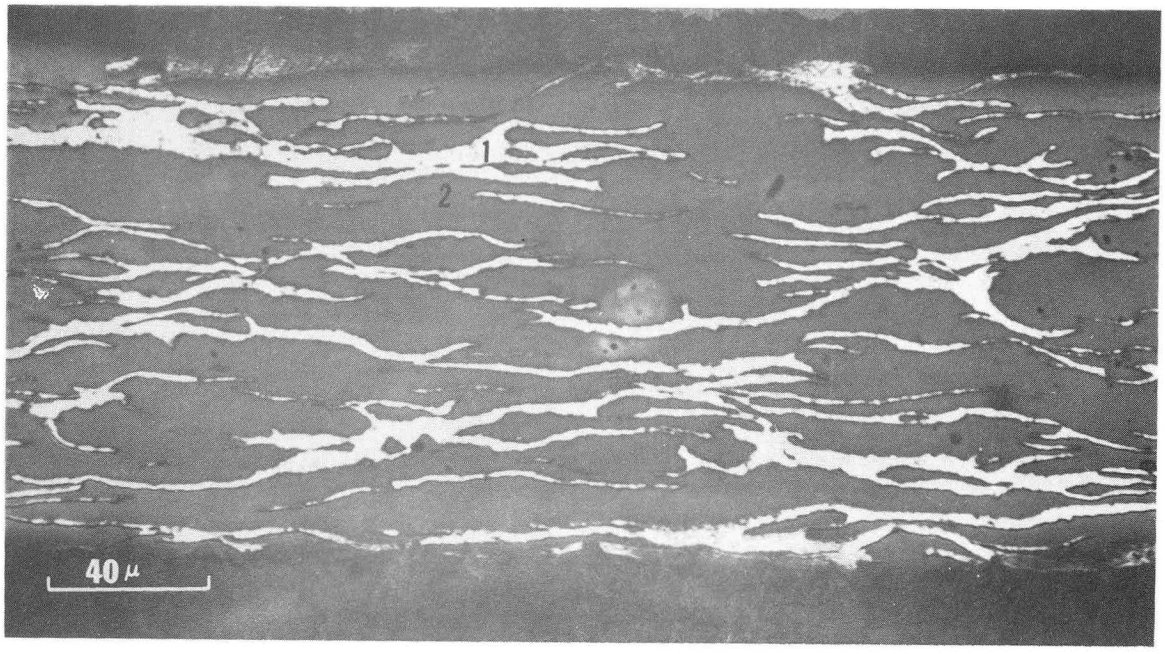


Fig. 8c

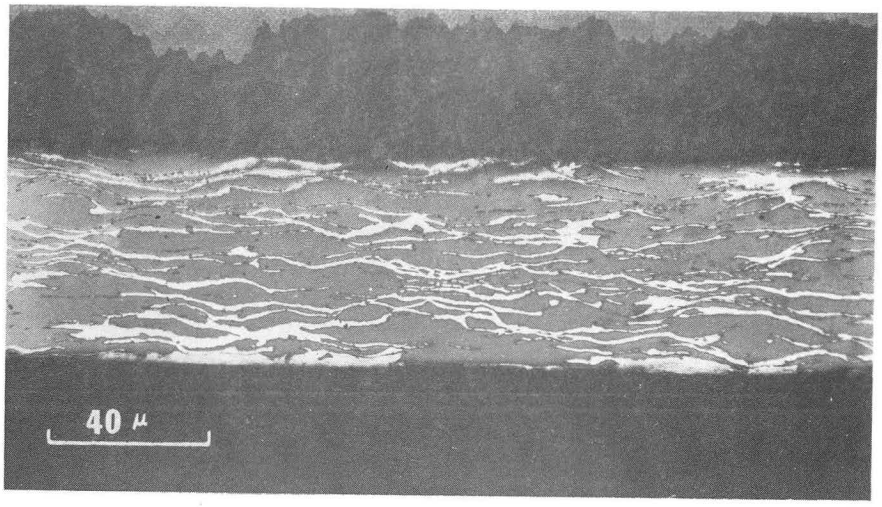


Fig. 8d

XBB 731-434

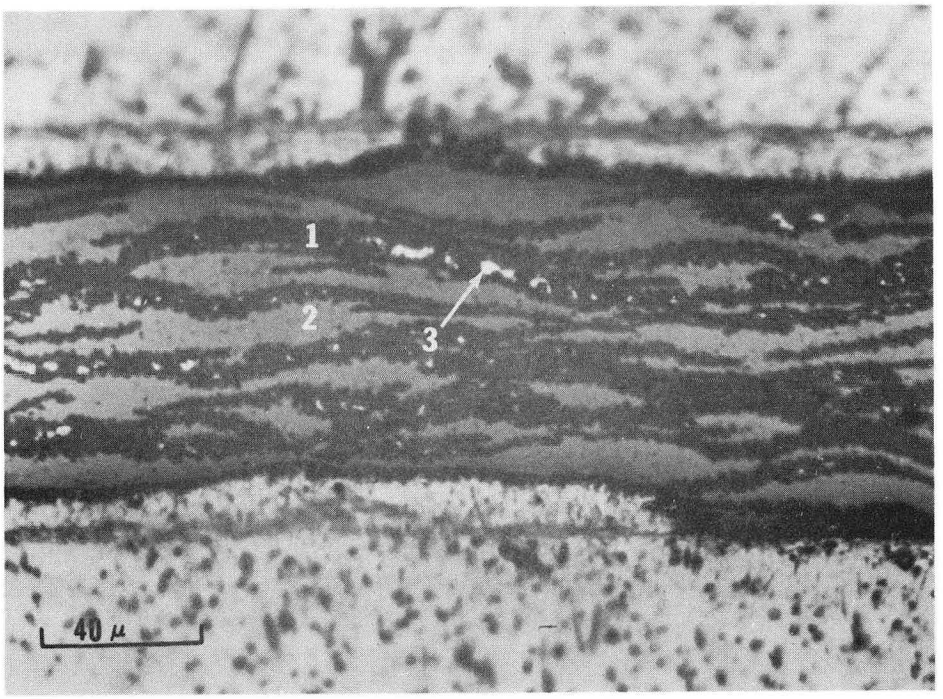


Fig. 9a

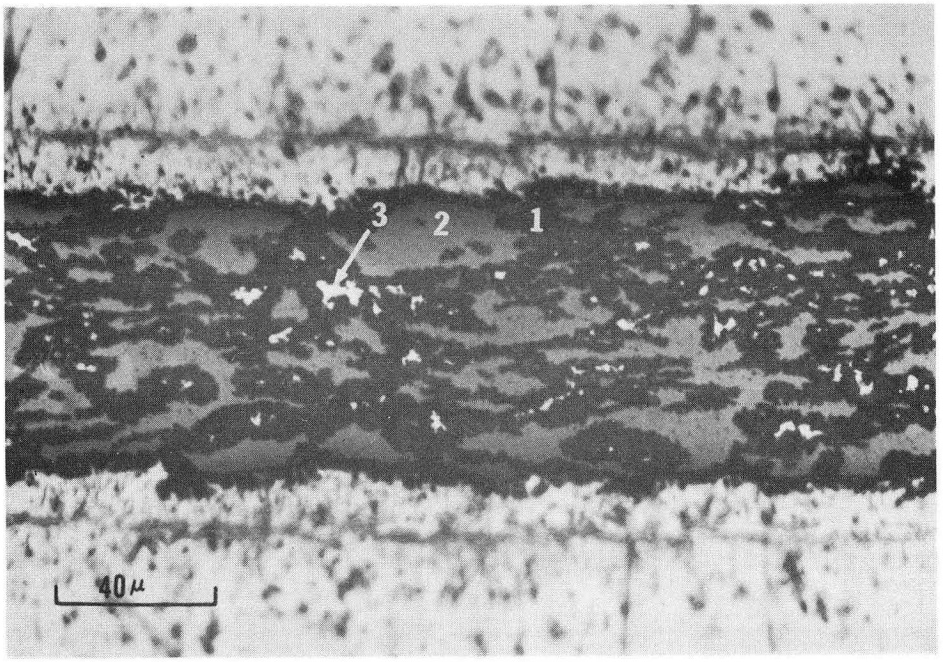


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Fig. 9b

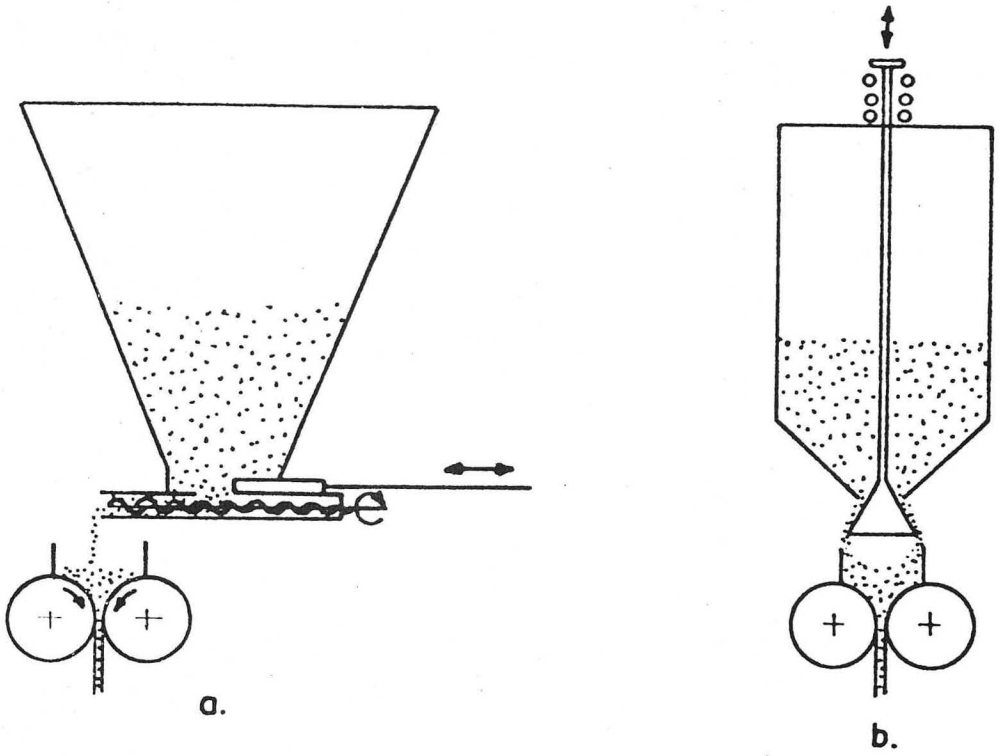

Fig. 10

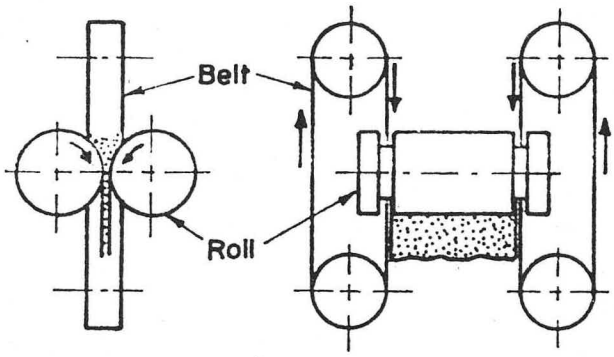

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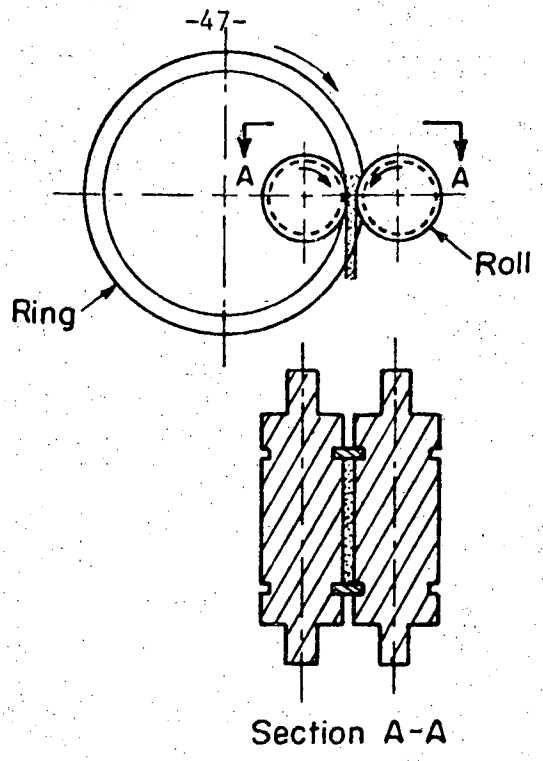
Fig. 11



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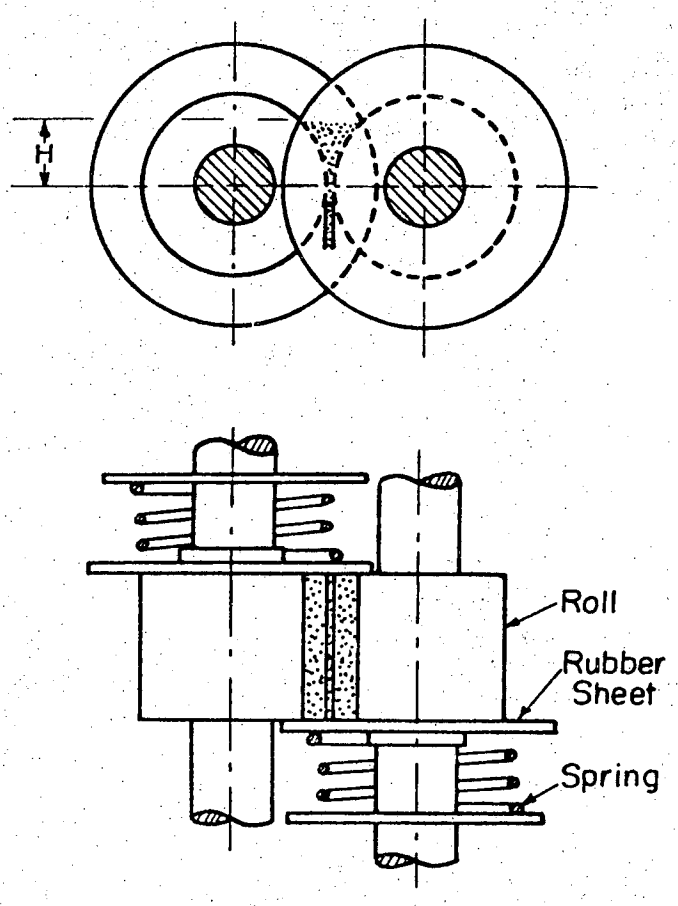

Fig. 13

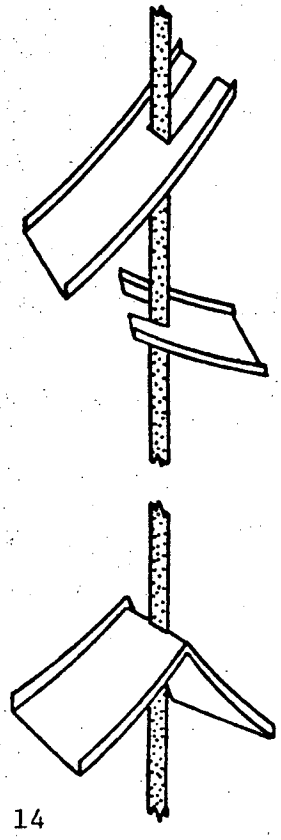

Fig. 14

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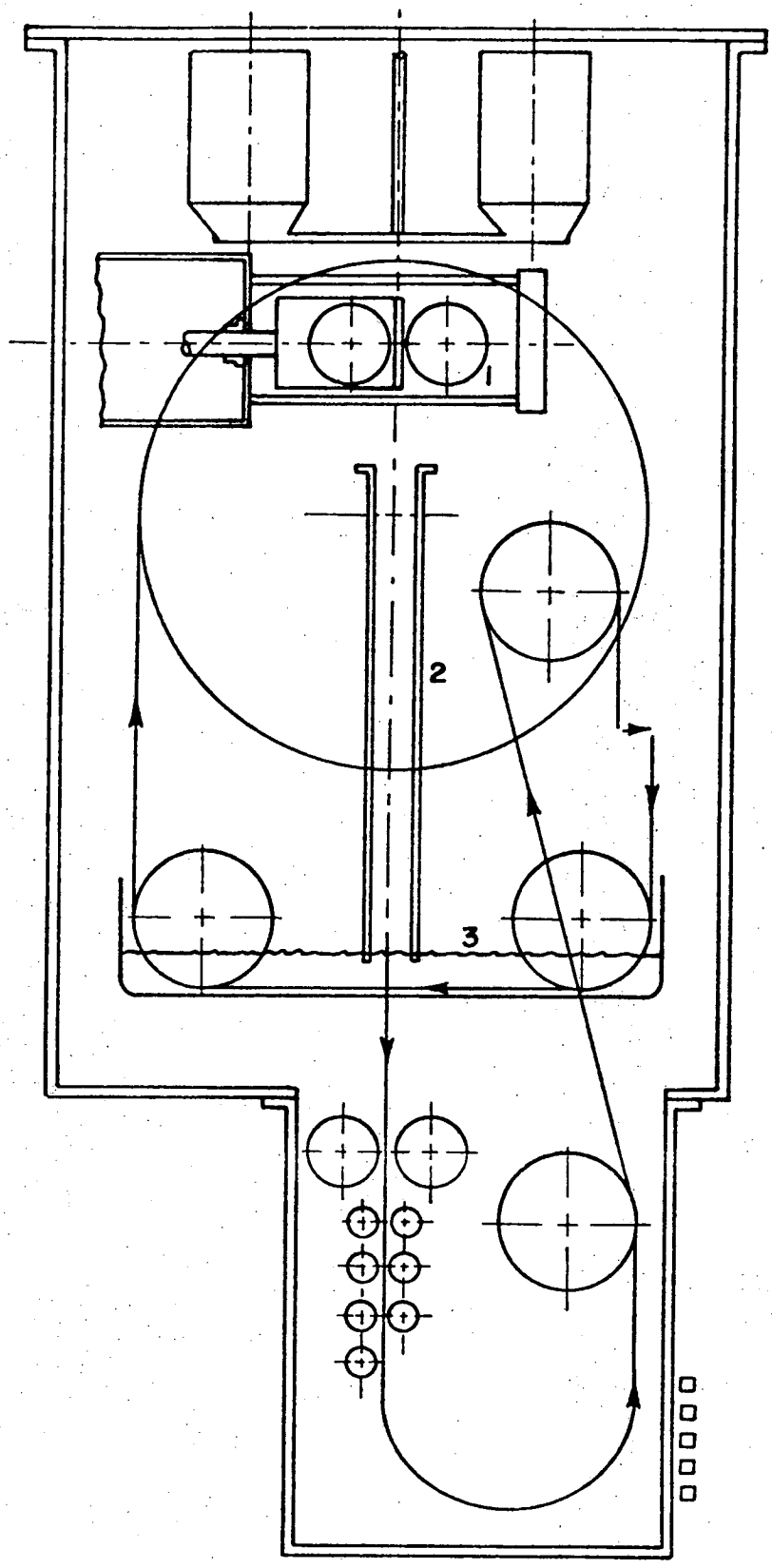

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Fig. 15

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