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# Porous Metallic Substrates for Superconducting Coatings

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**Abstract**—By an example of porous metal tubes and thin plates prepared from the stainless steel powder a simple method is described of preparation of porous metallic substrates for superconducting coatings. The tubes outer diameter is 12 mm, length up to 300 mm, wall thickness about ~1.5 mm. The plate size is 85×85 mm, thickness 1 mm. We used the classic method of powder metallurgy, without any fillers. After sintering, the tube had a density 2.5–3.4 g $cm^{-3}$ and open porosity 55–65%. The microstructure of the tubes and plates surfaces and breaks was studied using scanning electron microscopy. The porous tubes were prepared also from powdered copper, nickel, titanium, and chromium, as well as from mixtures of stainless steel and copper, nickel and pseudoalloy Cu(30%)–Cr. The first coatings with superconducting compound $MgB_2$ were prepared.

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This research begun with the work on the creation of solid oxide fuel cell of the axial and planar geometry. As one of these structures an option was considered when as the supporting core of a membrane-electrode unit of fuel cell was taken gas-permeable metal tube or thin plate. In [1, 2] for this purpose porous tubes were used made of stainless steel powder 14X17H2. The technology developed for producing tubes from the steel powder has been successfully applied also to obtaining the tubes of different porosity from other metals and alloys. The porous tubes are used in various fields of science and technology, in particular, as substrates. With their strongly developed surface, they can serve as substrates for coatings with superconducting $Nb_3Sn$, $MgB_2$, and high-temperature superconducting ceramics.

It is known [3] that nickel and related alloys are used as substrates for high-temperature superconducting coatings because of their ability to form on the surface a texture favorable to the superconductor current-bearing capability. But recently again the interest increased in copper and its alloys as a material for the substrates for high-temperature superconducting coatings of the second generation [4], because they are not ferromagnetic and have an ability to form more sharp texture than nickel [5, 6].

In this paper, by the example of stainless steel porous tubes a simple and productive route is offered to produce such items. The possibility of obtaining porous tubes of copper, nickel, titanium, chromium is also demonstrated. The first results of the experiments of the coating the tube porous surface with a superconducting compound $MgB_2$ are presented.

**Methods of investigation**. The microstructural studies were carried out using scanning electron microscopy on a CamScan MV2300 microscope equipped with detectors of secondary and reflected electrons and with energy dispersive X-ray microanalyzer.

The important characteristics of porous products are apparent or open porosity $P_o$ and apparent density ρ. These properties were determined by the method of hydrostatic weighing. The experiment consisted in determining the mass $m$ of dry sample by weighing it in air, and the masses $m_1$ and $m_2$ of the same sample saturated with a liquid and weighed in air and in distilled water, respectively. Saturation with liquid was carried out by boiling the sample in distilled water. The density and porosity were calculated according to formulas:

$$\rho = m\gamma_{liquid}/(m_1 - m_2),$$

$$P_o = [(m_1 - m)/(m_1 - m_2)]\times 100$$

where $\gamma_{liquid}$ is the density of the fluid used, in this case water.

The tensile strength was calculated from the experiments of 3-point bending of the samples cut from the plate or the tube wall.

Electrical resistance was measured at room temperature by 4-pin method at passing a weak current.

**Characteristics of stainless steel powder.** As a material for tubes and plates was used powder of ferritic stainless steel of 14X17H2 brand. Its nominal chemical composition is 17.3 wt % of Cr and 2.5 wt % of Ni. However, according to X-ray analysis, the content in the powder was higher than the nominal: chromium by about 15%, nickel almost twice.

Sieve analysis of the 100 g control portion of the powder showed that main fraction (~64%) of the powder had the particle size less than 40 μm.

The bulk density of the powder calculated from two procedures of weighting two portions differed twice by weight equals 2.35–2.40 g $cm^{-3}$.

The supplied powder along with a large number of particles ranging in size from 5 to 10 μm contained the particles of the size 50 μm or larger. The particles were of irregular shape, with round edges. Fine particles had a tendency to agglomeration with the formation of conglomerates of several tens of micron in size.

**Producing the tubes.** The tubes size: length from ~80 to 300–320 mm, inner diameter 10 mm, outer diameter ~12 mm, wall thickness 1.0–1.5 mm. Open porosity was planned to be 45–55%.

Obtaining the porous tubes was based on the classical method of powder metallurgy, which excludes the use of any fillers in the formation of the powder billet [7]. The major technological steps were the formation of powder billet, sticking it in a hydrogen atmosphere or in a vacuum, and additional thermal treatment of sintered piece in a vacuum.

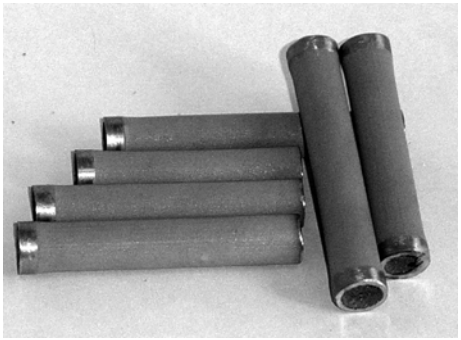

**Fig. 1.** A general view of steel tubes ~80 mm length from the powder fraction 60–100 μm with tips.

Producing a powder billet requires the following minimum set of components: quartz tube, metalic tube, two caps, and a funnel of the original design. The metallic tube is located inside the quartz tube. Their coaxial arrangement was fixed at bottom by the cap and at top with the funnel. The metallic powder was placed between the tubes. The inner diameter of the quartz tube defines the outer diameter of powder billet, and the outer diameter metal tube defines the inside diameter of the powder billet. Compaction of the powder was provided by vibration. Then the funnel was replaced by another cap, the same as at the bottom, and the metallic tube was filled inside with macrocrystalline aluminum oxide powder. The final operation of forming a powder billet was the removal of the metallic tube.

In the final version, the item to be placed into the furnace consisted of a quartz tube, rod of aluminum oxide powder, and powder billet. The caps were replaced by stoppers of kaolin wool.

Sintering of the powder billets was carried out at a temperature of 1050–1100°C for 1 h in hydrogen flow or in a vacuum. After taking from the furnace, the aluminum oxide was removed, and the sintered billet was liberated from the quartz tube. Additional heat treatment was carried out in a vacuum at 1150°C and higher in the bulk of $Al_2O_3$ powder. General view of the individual samples of the 80 mm tubes is shown in Fig. 1.

If the tube should be used as a substrate for superconducting coating, it should have at the ends the electrical contact tips made of solid metal for passing an electric current through it (Fig. 1). In this case, as the material served steel of the similar brand as the powder. The contacts can also be made of copper or aluminum.

Design of the contacts at the junction with the tube and the method of welding may be different. We have tested three methods of obtaining strong connection of the contacts with the tube: diffusion welding directly in the process of sintering of powder billets (in this case the powder blank has been formed together with the tips), laser welding and diffusion welding, as a separate operation, using a paste of finely crystalline powder of stainless steel in poly(ethylene glycol) .

In some cases the described method may be suitable for obtaining porous ceramic tubes.

**Producing the plates.** The substrate plates of the size 85× 85 mm and 1 mm thick were obtained by powder metallurgy. We used several sets of molds with two punches. The molds were of a high-strength graphite and the punches were of the same graphite or quartz with polished surfaces. The powder to 90% consisted of the fraction of the size no more than 40 μm.

The powder billet was formed in two steps: filling with powder the space between punches and leveling. Sintering of the billet was carried out directly in the mold under ~0.003 MPa pressure at 1050°C for 1–2 h in a vacuum or under hydrogen atmosphere.

**Microstructure of the tubes and substrates from the stainless steel powder.** At the initial stage of development of the technology, the presence of aluminum oxide rod in the powder billet caused fusing of its particles with the very hot inner surface of the sintered tubes. This did not have a negative effect on the gas permeability of the tubes, but the inner surface of the tube was not smooth.

The outer surface of the tubes (Fig. 2) was sufficiently smooth and uniformly packed with the powder particles. Since the powder of stainless steel was not sieved for removing the large particles, on the surface of the tubes were often detected the particles of the size up to 20–40 μm and larger. The bulk of the powder particles had a size less than 5 μm. It is seen that the powder particles are well fused. Two types of pores are seen: the small pores of the size less than 5 μm inside conglomerates composed of the fused small powder particles, and elongated pores of different shapes between conglomerates of the size reaching 50 μm or larger.

Producing the porous tubes with an improved version of the technology allowed to exclude fusing $Al_2O_3$ with the inner surface of the tubes. The microstructure of the inner surface (Fig. 2b) did not differ from the microstructure of the outer surface of the tube and remained smooth. The improved version differs from that above described in that the aluminum oxide powder is poured directly into the billet after the removal of a metal tube.

The microstructure of the surface of flat substrates differs from that of the outer surface of the tubes by reduced contact area between the powder particles. Due to the lack of vibration operation in the process of preparation, the powder billets density before sintering was less than in the case of the tubes.

**Properties of the tubes.** The behavior of tubes during sintering and subsequent annealing depended not only on temperature but also on the powder size. Therefore, we will consider the properties of the tubes produced from a powder containing 64% of the fraction smaller than 40 μm, and a powder with particle size from 100 to 160 μm.

After sintering, the density of the tubes produced from the fine powder was 2.5–3.4 g $cm^{-3}$ and the

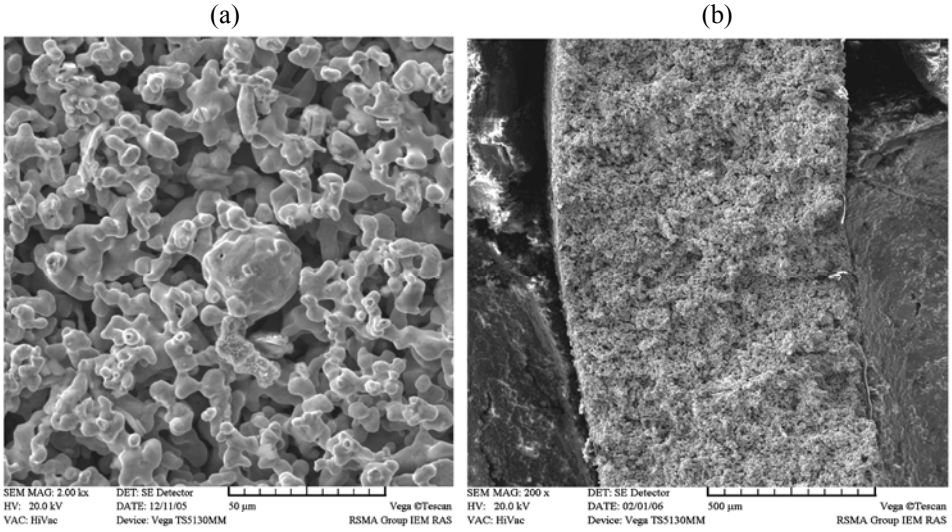


**Fig. 2.** (a) Microstructure of the outer surface of a stainless steel tube sintered at 1100°C and (b) the macrostructure of the surface of the fracture of the tube prepared by improved method, after sintering at 1050°C.

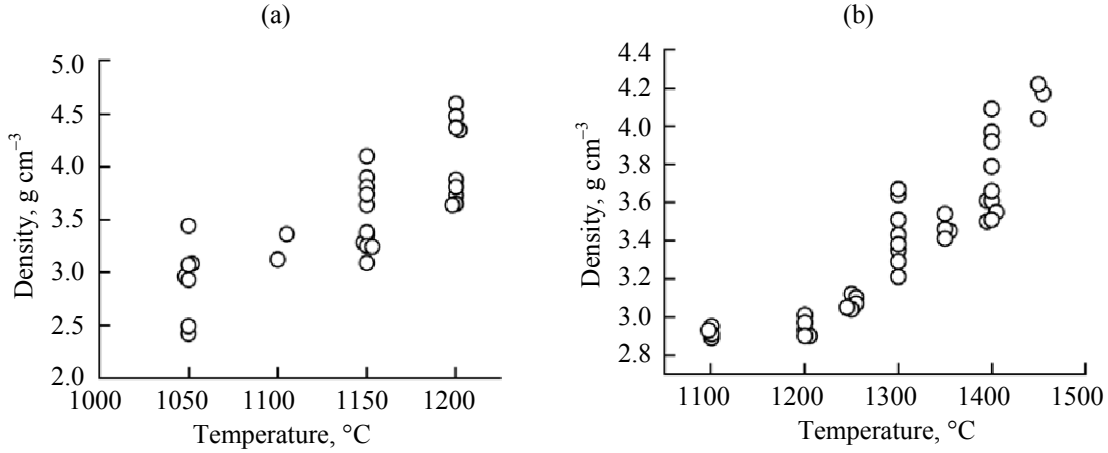


**Fig. 3.** Dependence of density on sintering and annealing temperature for the tubes made of the powder with the size: (a) 64% of the particles 40 μm and (b) 100–160 μm.

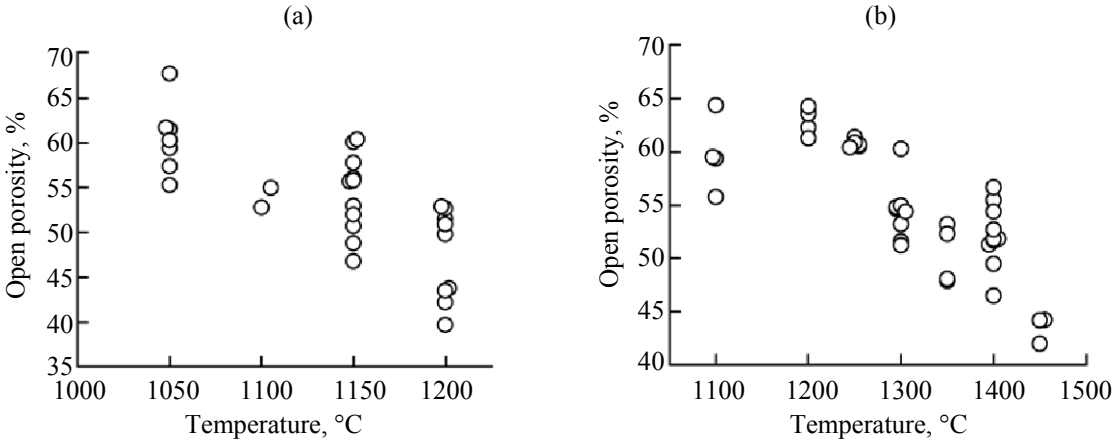


**Fig. 4.** Dependence of open porosity on the sintering and annealing temperature of the tubes made of the powder of the size: (a) 64% of the particles 40 μm and (b) 100–160 μm.

porosity 55–65% (Figs. 3a and 4a). After annealing even at 1200°C the density increased to 3.6–4.6 g cm$^{-3}$, open porosity decreased to 40–55%. In contrast, similarly annealing the tubes of the coarse powder did not alter density or porosity (Figs. 4a and 4b). To reach the properties approximately equal to the properties of the previous tubes annealed at 1200°C they should be processed with thermal treatment at 1400–1450°C.

Bending strength of the tubes made of fine powder after sintering at 1100°C was ~50 MPa, after additional annealing–sintering at 1200°C it increased markedly, from 55–60 to 130–140 MPa.

Bending strength tests of samples of the tubes made from the powder of 100–160 μm size were carried out at room temperature and at 500°C. The bending strength after sintering at 1200°C, regardless of the testing temperature, was not higher than 5–10 MPa. After sintering at 1400°C the bending strength increased to 30–40 and 55–65 MPa in the tests at 1400°C and at room temperature respectively.

The electrical resistance $R$ of the tubes made of the powder 100–160 μm monotonically decreased with increasing sintering temperature from 4 at 1200°C up to 1.2–2.2 mΩ cm$^{-1}$ at 1400°C, indicating better sintering of the powder particles.

The electrical resistance $R$ of the tubes obtained from the powder of ≤60 μm size varied from 1.0 to 1.8 mΩ cm$^{-3}$. To reduce the electrical resistance, to the powder of stainless steel can be added powder of a material with lower resistance and with low solubility in iron, the main component of steel. As such additives we selected copper, nickel and copper pseudo-alloy

with 30 wt % of chromium. The powders of these materials were mixed with the powder of stainless steel and the mixture was used for forming a billet. Powder mixtures were prepared by intensive stirring in the acetone medium in a planetary mill, followed by sieving. The data obtained in these experiments are summarized in the table.

We found that inclusion of copper in the amount of 5 wt % decreases electrical resistance of the tubes more than twice. Resistance decreases substantially also at adding the powder of Cu(30 wt %)–Cr pseudoalloy, but after additional annealing in hydrogen. Nickel additive resulted in the least effect on the resistance of the tubes. However, its content in the powder mixture does not exceed 10 wt %, while the maximum content of copper and pseudoalloy was twice as much.

Resistance of the sintered tubes from powder mixtures

| Powder composition, wt % | Thermal treatment | $R$, mΩ |
|---|---|---|
| 2Cu | Sintering: 1000°C, 1 h under | 0.9 |
| 5Cu | $H_2$ | 0.6 |
| 20Cu | | 0.3 |
| 5Cu30Cr | Sintering: 1000°C, 1 h under | 1.3 |
| 10Cu30Cr | $H_2$ | 1.0 |
| 20Cu30Cr | | 0.8 |
| 5Cu30Cr | Sintering: 1000°C, 1 h under | 1.2 |
| 10Cu30Cr | $H_2$ + annealing: 1100°C, 1 h | 0.5 |
| 20Cu30Cr | under $H_2$ | 0.4 |
| 2Ni | Sintering: 1100°C, 1 h under | 1.1 |
| 5Ni | $H_2$ | 0.7 |
| 10Ni | | 0.8 |

**Porous tubes made of copper, nickel, titanium, and chromium.** The method developed to produce porous tubes of stainless steel powder was used also for making the tubes of copper, titanium, nickel, and chromium.

This method is characterized by the feature that the powder billets during compaction were not processed by pressing. Therefore, the powder particles after sintering retain their original shape and size. Fusing of the billets occurred only in the points of contact of the powder particles. Judging from the microstructure of the tube surface we conclude that the original powder particles of nickel and chromium were in the form of granules of approximately equal size: 10–20 and 60–80 mm for Ni and Cr, respectively. The nickel powder particles had less regular form. The microstructure of the nickel tube surface is very similar to the microstructure of the surface of the tube of stainless steel. The initial size of the particles of titanium powder was considerably less, from a few tenths to 1–2 μm. As an example, Fig. 5 represents the microstructure of the tube surface of copper powder, which had a dendritic shape.

**$MgB_2$ coating.** Coating with a superconducting compound $MgB_2$ applied on the porous tubes from stainless steel and copper were made by the methods

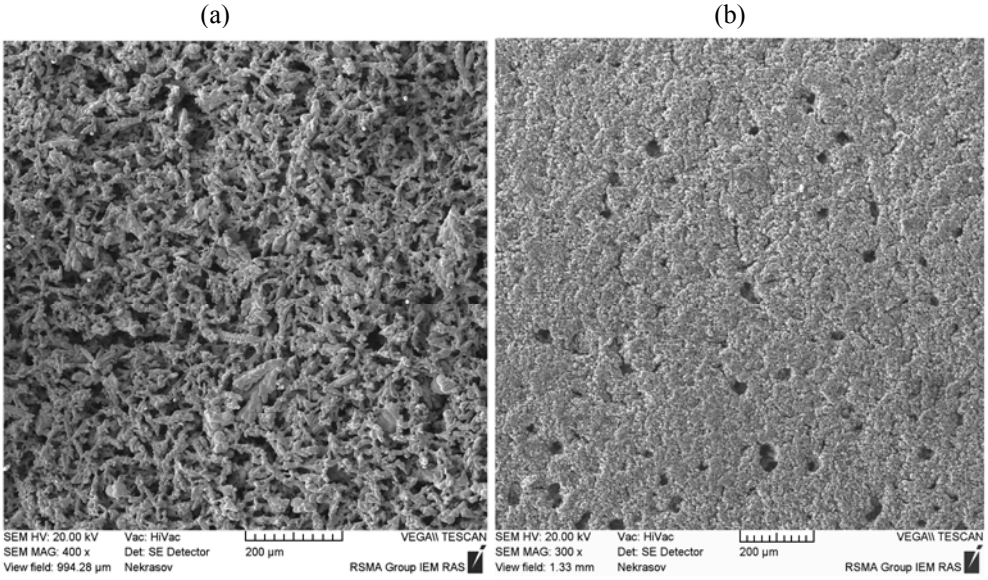


**Fig. 5.** (a) Microstructure of the outer surface of the porous copper tube and (b) of the coating of $MgB_2$ on this tube after sintering in argon at 850ºC for 2 h (b).

of impregnation and painting. Before applying, the surface of the stainless steel superconducting tube obtained from the powder of 100–160 μm size, was coated with a thin layer of powder of the same stainless steel, but with a particle size ≤40 μm by impregnating the tube with a suspension of the powder in polyethyleneglycol. After drying, the tube was immersed in the coarse aluminum oxide and subjected to vacuum annealing at 1050–1100°C for sintering the steel layer.

For application to the tubes of a superconducting coating they were impregnated with a suspension of the powdered $MgB_2$ in polyethyleneglycol. For painting was used a paste of superconducting powder in polyethyleneglycol. After the coating, the tubes were subjected to thermal treatment at 850°C for 2 h under argon.

The coating on the stainless steel tube obtained by the method of impregnation looks more uniform. On the surface of the coating obtained by painting of the steel and copper tubes a significant number of large cavities was observed formed at the outputs of the large pores (Fig. 5b). A positive result is the absence of macrocracks in coatings.

Thus, a simple method of obtaining porous metal tubes is developed. The porosity of the tubes of stainless steel powder is 40–60%, bending strength at room temperature 130–140 MPa. It is shown that by the described method it is possible to obtain porous tubes of other metals such as titanium, nickel, chromium, and copper, as well as from powder mixtures of stainless steel with copper, nickel, and Cu(30 wt %)–Cr pseudo-alloy.

It is suggested to use the tubes as porous substrates for functional coatings and a possibility is demonstrated of obtaining coatings with a superconducting compound $MgB_2$ on porous tubes made of stainless steel and copper by the method of impregnation followed by sintering.

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