NIOBIUM TIN AND RELATED SUPERCONDUCTORS*

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I. INTRODUCTION

If we attempt to categorize the useful or promising superconductors, we find that they fit into three distinct groups. These are the brittle intermetallic compounds, the ductile metal alloys, and the pure metals. The pure metals are low critical field superconductors, several of which are important for rf cavities. The best compounds have critical magnetic fields and critical temperatures almost twice as high as the best known alloys. For this reason the superconductivity group at Brookhaven has worked mainly with Nb_3Sn, the only compound available in useful form, in preference to the alloys. This paper will review our knowledge of the superconducting (hereafter SC) compounds and their properties, and who is developing each type. A review will also be made of our experiences with several conductors and of a technique for testing a complete conductor prior to using it in a device.

To show where the compounds fit into superconductivity, Table I gives comparative data about a few of the compounds, alloys, and elements. The difference in ductility of alloys vs compounds is stressed because it determines the geometry in which a material is useful. The compounds may be imagined to be like a ceramic. If they are strained appreciably, they fracture and the SC path is damaged. Therefore the commercially successful compound, Nb_3Sn, has been made in ribbon form wherein the thickness of substrate plus SC is no more than 0.004 in. This theoretically allows the conductor to be wound about a diameter of 1 in. without damage. In actual practice, conductors with a 0.003 in. over-all thickness for the substrate and Nb_3Sn have operated well when wound about a 0.25 in. diam post.

The alloys, by comparison, are ductile, and therefore they are practical and lowest in cost when manufactured as round wires. The cross-sectional shape of the alloy and compound conductors has had considerable effect on the winding design of magnets, particularly the paraxial conductor radial field beam magnets which have been recently constructed.

II. THE SUPERCONDUCTIVE COMPOUNDS

Looking now at the compounds, the most unusual type of compound conductor is fabricated by the multiwire process, Fig. 1, developed by Professor Saur of the University of Giessen, West Germany. The wire starts as a tube about 0.5 in. in diameter into which fine tin-coated wires of niobium are inserted. Up to 900 wires are used in one conductor. The composite is then drawn to an over-all diameter of around 0.020 in. after which it is heat-treated at 900-1200°K to form Nb_3Sn by a diffusion process at all interfaces between the Nb wires and the Sn matrix. The small size of the SC strands raises the critical field, H_c, to about 250 kG and results in an over-all current density of 20 000 A/cm^2 at 210 kG. The current density of this conductor is relatively flat over a wide field range so that at fields below 150 kG it is surpassed by that of the Nb_3Sn ribbons. With the 0.020 in. diam, this conductor must be used on

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TABLE I

Brittle Intermetallic Compounds	Critical Temperatures at B = 0	Critical Fields at 4^oK	Comments
$Nb_3 (Al_{0.8}Ge_{0.2})$	20.7^oK		
Nb_3Sn	18.2	245 kG	Only available compound
Nb_3Al	17.5		
NbN	15.6	153	
Nb_3Ga	14.5		
NbC	14.0		
V_3Si	17.1	235	
V_3Ga	16.8	210	
MoN	12.0		
$MoGa_4$	9.8		
<u>Ductile Alloys</u>			
Nb-42Ti-6Ta	10 - 11	140 kG	Japanese development
Nb-48Ti	9.5	122	Best available alloy
Nb-33Zr	10.7	80	Becoming obsolete
Nb-25Zr	11.0	70	Becoming obsolute
Pb-56Bi	8.8	15	
Mo-50Re	~ 10.0	~ 15	Used as fine wire for low fields
Bi50, Pb25, Cd12.5, Sn12.5 = Wood's metal	~ 8.0	12	
<u>Pure Metals</u>			
Nb	9.25	1985 G	Rf cavities
Tc	8.22	-	
La (B)	6.3	1600	
V	5.3	1020	
Ta	4.48	830	
Pb	7.19	803	Rf cavities and suggested for ac cables
Sn	3.72	309	
Re	1.698	198	
Ga	1.09	51	
Zr	0.546	47	
Ti	0.39	100	

a form of at least 2.5 to 3 in. diam or the SC filaments will be fractured. It would appear that flattening this conductor into a ribbon prior to heat treatment would make it more flexible and useful for bending around small diameters. If this material can be developed to withstand a small bending radius, it should find immediate use for the cores of high field solenoids. Since the Nb_3Sn is formed by diffusion, one could undoubtedly form other SC compounds such as V_3Ga by the same process.

The most popular type of Nb_3Sn ribbon is the diffusion-formed material illustrated in Fig. 2. The manufacture begins with a niobium ribbon which is coated with tin, heat-treated at 900-1200°K for several hours, and then either clad or plated with a normal conductor such as copper or silver.

The ribbon in bare and copper-plated form was first available in 1964 as Niostan from the National Research Corporation and later from Supercon,[1] a division of the same company. The copper-plated material 0.25 in. wide by 0.0025 in. thick performed well in the first Panofsky-type quadrupoles at Brookhaven. Current densities of about 30 000 A/cm^2 were obtained at a peak field in the corners of about 20 kG. The copper-plated form of this ribbon 0.5 in. wide x 0.0013 in. thick next became available from CSF[2] in 1965. CSF now offers single and double ribbon substrates with Cu plating or cladding in various total thicknesses from 0.0012 to 0.011 in. Standard widths are 6.4, 10, 12.7, and 20 mm. In the United States, CSF superconductors are now distributed by Kawecki.[3]

A diffusion-type Nb_3Sn ribbon with copper cladding (Cryotape) was offered next by GE[4] in November of 1965. Their commercial ribbons have typically been 0.5 in. wide by 0.0032 and 0.0037 in. thick with ratings of 150 and 300 A respectively at 100 kG. Ribbons with thicker copper — up to 0.010 in. total thickness — as well as more Nb_3Sn — up to 600 A rating — are available on special order. Figures 3, 4, and 5 are microphotographs of cross sections of GE 150, 300, and 600 ribbons. GE can also produce several of their ribbons with either a single or double substrate, as is observable by comparing Figs. 3 and 4 with Fig. 5. They also offer stainless steel cladding for use in solenoids where the product of radius times current times field yields a force which exceeds the yield strength of soft or hard copper cladding.

In March of 1968, Plessey[5] introduced a diffusion type Nb_3Sn ribbon (Super Magloy 1) which is available copper clad on one or both sides with a thickness of 0.002 or 0.003 in. Standard width at present is 0.25 in.

A V_3Ga ribbon of the diffusion type has been developed by Tachikawa[6] during the past year and was tested to current densities of about 20 000 A/cm^2 at 200 kG. The critical field is above 200 kG. The process includes tinning a V ribbon with Ga,

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1. Supercon Division of National Research Corporation, 9 Erie Drive, Natick, Massachusetts 01762.

2. Compagnie Générale de Télégraphie Sans Fil (CSF), 12 Rue de la République, 92 Puteaux, France.

3. Kawecki Chemical Company, 220 East 42nd Street, New York, N.Y. 10017.

4. General Electric Vacuum Products, 1 River Road, Schenectady, New York 12305.

5. The Plessey Company, Ltd., Preformations Division, Cheney Manor, Swindon, Wiltshire, England.

6. Kyōji Tachikawa, Satoshi Fukuda, and Yoshiaki Tanada, National Research Institute for Metals, Mogūro-Ku, Tokyo, Japan.

plating the Ga with Cu, and then heat-treating at around 980°K for 10 hours. This ribbon is not available commercially.

The vapor deposition process has been equally successful for forming Nb_3Sn ribbon as illustrated in Fig. 6. The leader in development and sole commercial producer of this material since the summer of 1963 has been RCA.[7] The process uses a quartz furnace heated to 970°K, which is fed with $SnCl_2$, $NbCl_4$, HCl, H_2, and He gases, through which the heated ribbon (1270°K) passes. The high thermal energy of the ribbon is sufficient to cause decomposition of the molecular gases on contact such that Sn and Nb appear at the surface in the proper proportions to form superconductive NbSn compounds. The large number of variables in this process as compared with the diffusion process allows a greater degree of optimization to be attained. There apparently are differences in the final products since the vapor-deposited ribbon has a critical temperature around 15°K compared with 18°K for the diffusion process material.

Following the deposition of SC, the ribbon is electroplated with a thin layer of Ni and then it is either plated with 0.0005 to 0.0015 in. of pure Ag or clad with 0.001 to 0.004 in. of pure copper. Variations in thickness which originally occurred in the Ag-plated ribbon have now been reduced by a machining process that should hold the thickness tolerance to ± 0.0001 in.

RCA's commercial production has mainly been of 0.090 in. wide ribbon in at least three current ratings — 60, 110 and 220 A at 100 kG — with Ag plating or Cu cladding to order. With standard Ag plating the thicknesses are 0.0044 and 0.0052 in. A recent addition to their production has been 0.500 in. wide ribbon, developed under contract from Brookhaven. The wide ribbon is available in 300, 600, 900, and 1200 A ratings at 100 kG with either Ag plating or Cu cladding for electrical stabilization. Figures 7, 8, and 9 illustrate developmental ribbons with current ratings of 800, 1200, and 1100 A. The 800 and 1200 photos show defects that seem to be related to loss in stability of these ribbons — namely, delamination within the SC layer and porosity of the SC layer. Both of these ribbons were limited to around 35 000 A/cm^2 when tested in pie windings of around 200 m length. The 1100 sample, which contains a dense SC layer, is from a ribbon length which carries 72 000 A/cm^2, the highest current density ever achieved in a solenoid at Brookhaven. The "1100" was obtained by extrapolation from 68 kG at which field this 0.005 in. thick ribbon carried 1600 A.

In making coils for use with pulsed currents or 60 Hz current, it is essential to avoid electrical shorts between turns. To do this without greatly reducing the turn density is easiest when redundancy is used in the insulation. This has been accomplished by using insulated ribbon in combination with 0.0005 to 0.002 in. Mylar interleaving for a total insulation of no more than 0.001 to 0.003 in. per turn. When bare ribbon is used, Mylar of 0.005 to 0.010 in. is usually required to avoid shorting by burrs on the edges.

All of the commercial diffusion-type ribbons are offered either bare or insulated with varnish about 0.0003 in. thick per side. The vapor-deposited ribbon has not yet been offered with insulation.

A comparison between most of these superconductors may be seen in Fig. 10 where useful current density, J_c, taken from manufacturers' curves has been plotted against B, the magnetic field perpendicular to the length of the conductor and parallel with its surface. "Useful" is used here to indicate that the current densities have been based on the area per turn in a typical winding rather than the area of a bare conductor.

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7. Marketing Department, RCA Superconductive Products, Building 18-3, Harrison, New Jersey 07029.

It must also be understood that the currents are based on short sample measurements, and in actual use in an inductive coil, instabilities will occur which tend to prevent current densities at low fields from exceeding those usually obtainable at 80 to 100 kG. When coils are used as inserts and operated in high background fields, the instabilities tend to disappear and straight sample performances are more likely to be obtained.

At fields above 140 kG, it may be seen that V_3Ga ribbon and Nb_3Sn multiwire promise large current density gains over the present commercial products.

At fields below 140 kG, it is painfully clear that the 20 000 A/cm^2 recommended by RCA as proper design for solenoids is far below the current densities obtainable in noninductive samples.

III. STABILITY

The question now arises as to why a solenoid or inductive sample of SC has a lower quench current than a noninductive SC. There is no concise answer at the present time, but a few facts are considered to be relevant. First, no SC is at present used alone as a high field magnet conductor, mainly because the spontaneous occurrence of a normal (and therefore highly resistive) region in the conductor can cause a sudden burst of joule heating which exceeds the heat transfer capability to the He bath. The result is a rapid local temperature rise and associated increase in the length of the normal region, with an ensuing radial spread of the normal region throughout the solenoid, more commonly referred to as a "quench." The universally accepted method for reducing this "quench" problem is to combine a normal conductor (NC) in parallel with the SC. Now the NC (high purity Ag or Cu) can have a very low resistance in comparison with the normal SC, in fact perhaps only 1/2000 to 1/10 000 as much for an equal thickness. This low resistance material in parallel with the SC apparently serves to reduce greatly the I^2R joule heating and also to conduct this heat edgewise so that it may transfer to the He bath. The result is a composite conductor which is capable of much higher current densities before the onset of instability, or inability to recover from a normal spot. The optimum amount of NC for 0.5 in. wide ribbon appears to be about 0.001 in. of copper per 0.00025 in. of Nb_3Sn SC. In actual fact, the stability of the composite is affected by many parameters, including $dB_\perp/dI$ and B at the position of the conductor and the exposure of the edges and faces of the conductor to liquid helium. $dB_\perp/dI$, in this case, is the change in field perpendicular to the ribbon face per unit change in ribbon transport current. B is the background field surrounding the conductor in which the coil is situated.

IV. EXPERIMENTAL RESULTS

A few results which have been obtained in Sampson's laboratory with devices made from Nb_3Sn are shown by the points on Fig. 10. Δ_2 is a 1.25 in. bore solenoid made in 1964 which operates at 43 000 A/cm^2 and 83 kG. Δ_1 is a 1.0 in. solenoid made in 1966 which operates at 39 000 A/cm^2 and 103 kG. Δ_3 is a 0.62 in. i.d. × 1.25 in. o.d. insert which operates at 51 000 A/cm^2 and 119 kG. This same coil, operated by itself in superfluid He, produced 48 kG at a J of 71 000 A/cm^2. The preceding coils were made of 0.090 in. wide vapor-deposited, silver-plated ribbon wound in layers.

Various coils of 0.500 in. wide ribbon are shown by Δ_4, a 1.5 in. bore pie which produced 69 kG at 71 000 A/cm^2, Δ_5, which is a 5.0 in. bore pie winding that produces 50 kG at 41 000 A/cm^2, and Δ_6, a quadrupole of 4.0 in. bore × 24 in. length which carries 26 000 A/cm^2 at 20 kG.

Δ_7 shows, for comparison purposes, a Nb25Zr solenoid which operates stably at

26 000 A/cm^2 and 53 kG. Since the coil forms are identical, Δ_2 and Δ_7 would lie on the same load line.

One characteristic of Nb_3Sn ribbon which is closely related to stability is flux jumping in inductive solenoids. Flux jumping is observed as voltage spikes that override the emf seen across a coil when the current level is being swept up or down. The size and frequency of flux jumps are always small in coils which are capable of reaching I_c (where the load line crosses the B-I curve for the conductor), while jumps are large and numerous in unstable coils that quench prior to reaching I_c.

When all other conditions are held equal, flux jumping is probably dependent on the ratio of superconductor to normal conductor. In other words, a conductor with a very thick Nb_3Sn layer (say 0.0005 in. or greater) and an Ag or Cu layer less than 0.001 in. thick would make a jumpy or unstable coil.

Stability in coils has been shown by Morgan and Dahl[8] to be related to inductance and, therefore, presumably to dB/dI, by a test of an inductively wound vs a noninductively wound pie of identical geometry and ribbon length. A current of 1350 A was not sufficient to drive the noninductive coil normal while the inductive coil had an instability limit around 800 A.

V. TESTING TECHNIQUES

Since work was begun at Brookhaven on Nb_3Sn ribbon, there has been a search for better methods to test materials prior to actually building a device with them. The first method was to cut a short (~ 1.0 in. long) sample from each end of each ribbon length, clamp it between copper blocks, and measure its critical current as a function of magnetic field perpendicular to the current flow. Then if a solenoid were made from this batch of ribbon, the lengths would be wound such that the highest current densities were on the inside. The problem with short sample tests is that they indicate almost nothing about the stability of a long length of ribbon, as may be seen from the high current densities obtainable at low fields in short samples compared with the low current densities which are actually possible in coils.

Once a solenoid is assembled, an obvious test is to measure the current limit of each length of ribbon in it. This is most informative when tests are performed at various current sweep rates and at several levels of fixed background field produced by the outer sections. Any length which operates poorly in the coil is then replaced.

A third method for testing is to energize a complete solenoid in series and put it into the persistent mode with a shorting switch. After it has stabilized, emf's are read across each section to locate bad joints and poor lengths of ribbon.

A continuous testing method for Nb_3Sn ribbon has also been developed. The ribbon is passed through a Dewar at a rate up to 0.5 m/sec and, en route, it passes through a magnetic field of 50 kG. At the entrance to and exit from the field, coils encircle or lie close to the face of the ribbon and produce an output which is related to the diamagnetic properties of the SC ribbon and to the nature of the NC bonded to it. With an integrator driven by the coils connected in opposition, the diamagnetic strength of the SC layer has been measured and defects have been detected in the SC and in the SC to NC bond.

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8. G.H. Morgan and P.F. Dahl, Brookhaven National Laboratory, private communication.

Another test which has been used by Sampson recently is measurement of the conductivity of the normal conductor at close to SC temperatures. It has been found that Cu cladding used by manufacturers has around twice the conductivity of Ag plating. It has also been found that the Ag plating will increase in conductivity by a factor of about two (becoming equal to the Cu) when it is properly annealed. Even after annealing, the Ag plating is poor (resistance ratio ~ 60) compared with commercial fine silver foil (resistance ratio ~ 200). In tests of solenoids made of 0.090 in. ribbon as well as pies made of 0.500 in. ribbon, there appears to be a positive correlation between conductivity of the plating and stability of the coil. This has been shown with two coils each containing approximately 1000 m of 0.090 in. ribbon which operated unstably and would only carry 60-70 A. After annealing, the current limits were raised to around 95 A, which was still not at the B-I limit.

Another test which we have made on superconductors to understand their performance is to measure their critical temperatures. A coil containing approximately 1 ft of conductor with thermocouples and current leads attached to each end is enclosed in a copper sheet to provide a uniform temperature environment. With 10 A flowing through the coil, it is slowly raised out of the helium bath while thermocouple emf is read from each end of the coil. When the emf across the sample reaches 1 mV, it is assumed to be above T_c at the high temperature end. The two ends were never more than 0.5^oK apart. The only difference found to date is that vapor-deposited ribbon has a $T_c < 15^oK$ while diffusion ribbon has a $T_c \approx 17.5^oK$.

A newly established method[9] by which we can test complete lengths of 0.500 in. ribbon for stability is the 5.0 in. bore pie test. The usual run of lengths is from 180 to 500 m and over this range, the value of $dB_\perp/dI$ at the inner turn is a very weak function of the amount of ribbon being tested. These coils are very easy to construct and test compared with useful magnets, so it is advantageous to test lengths of ribbon in this fashion prior to winding them into a more complex design. At present, some 20 pieces of ribbon (approximately 300 m each) have been tested this way and current densities have varied from 22 000 to 54 000 A/cm^2 at fields to 70 kG. The time saving with the pie test is large when you consider that four ribbon lengths for a quadrupole may be wound as pies and tested in two man days compared with eight man days required to perform the same experiments with the quadrupole.

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9. Specification for Superconductive Ribbon, Brookhaven National Laboratory SPEC. AGS-481, June 18, 1968.

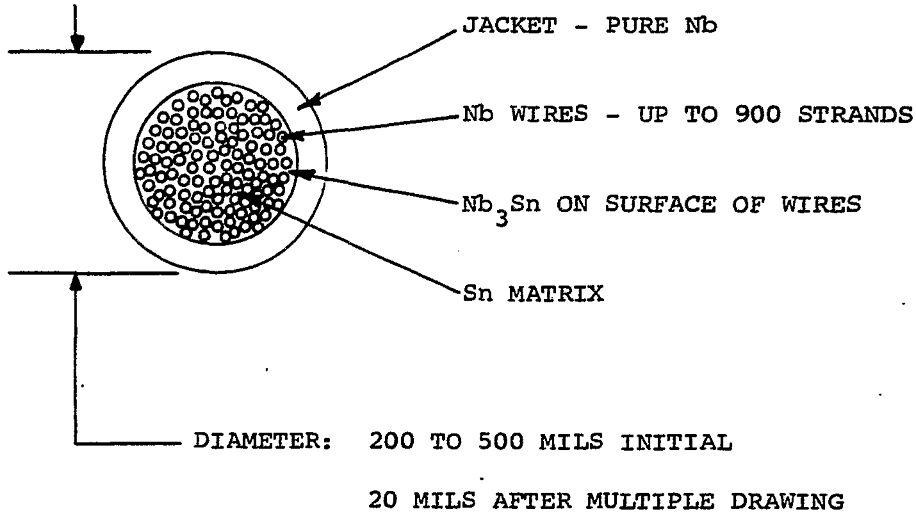

Fig. 1. Multiwire diffusion process.

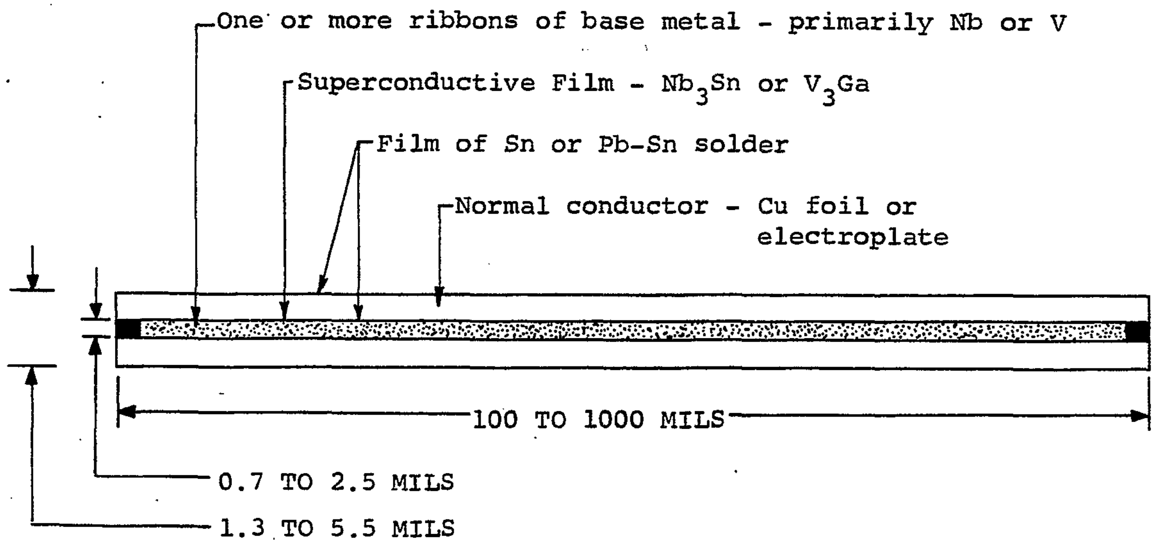

Fig. 2. Diffusion process — Nb_3Sn or V_3Ga ribbon.

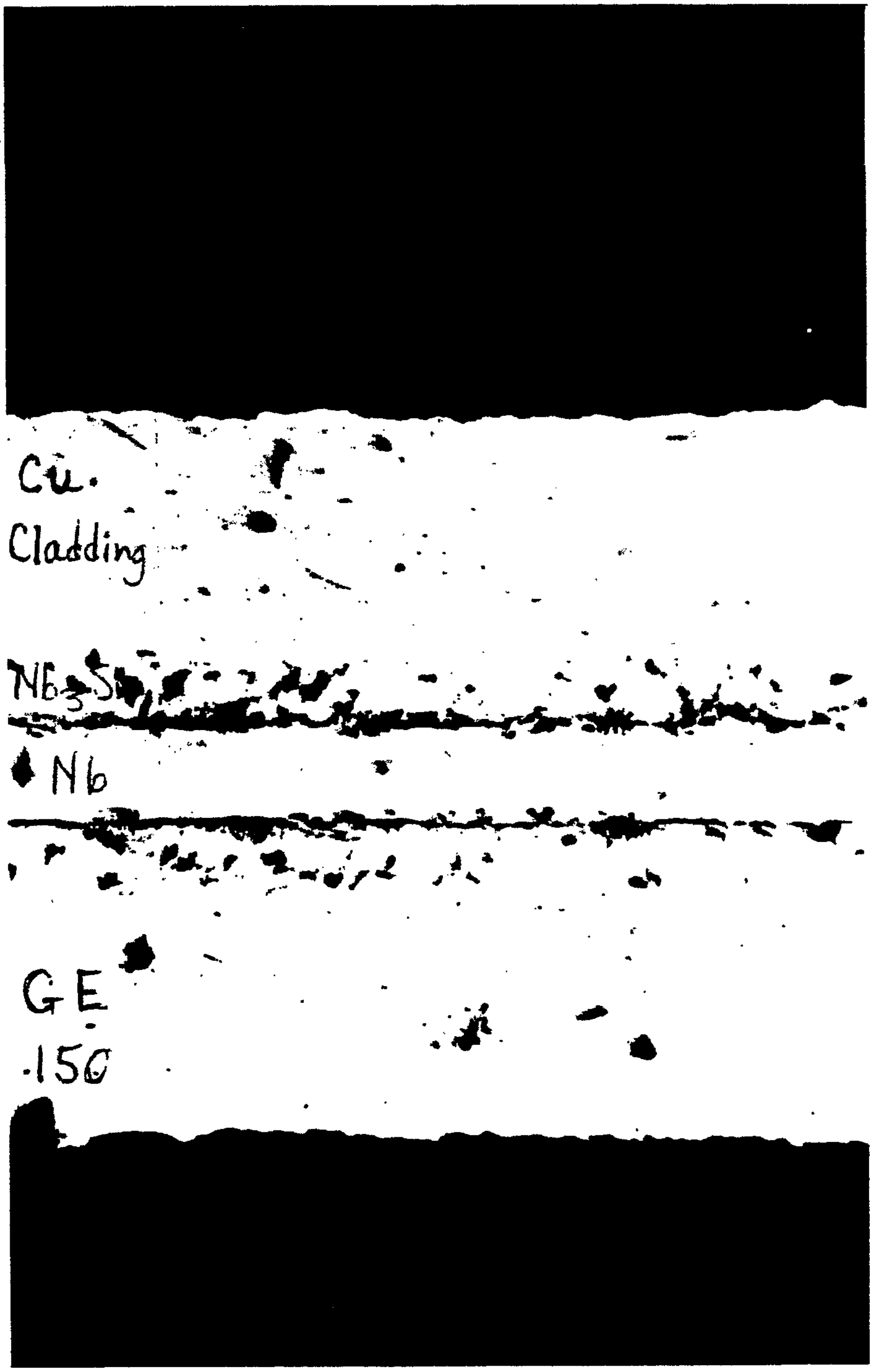

Fig. 3. Microphotograph of cross section — GE 150 ribbon.

GE 300

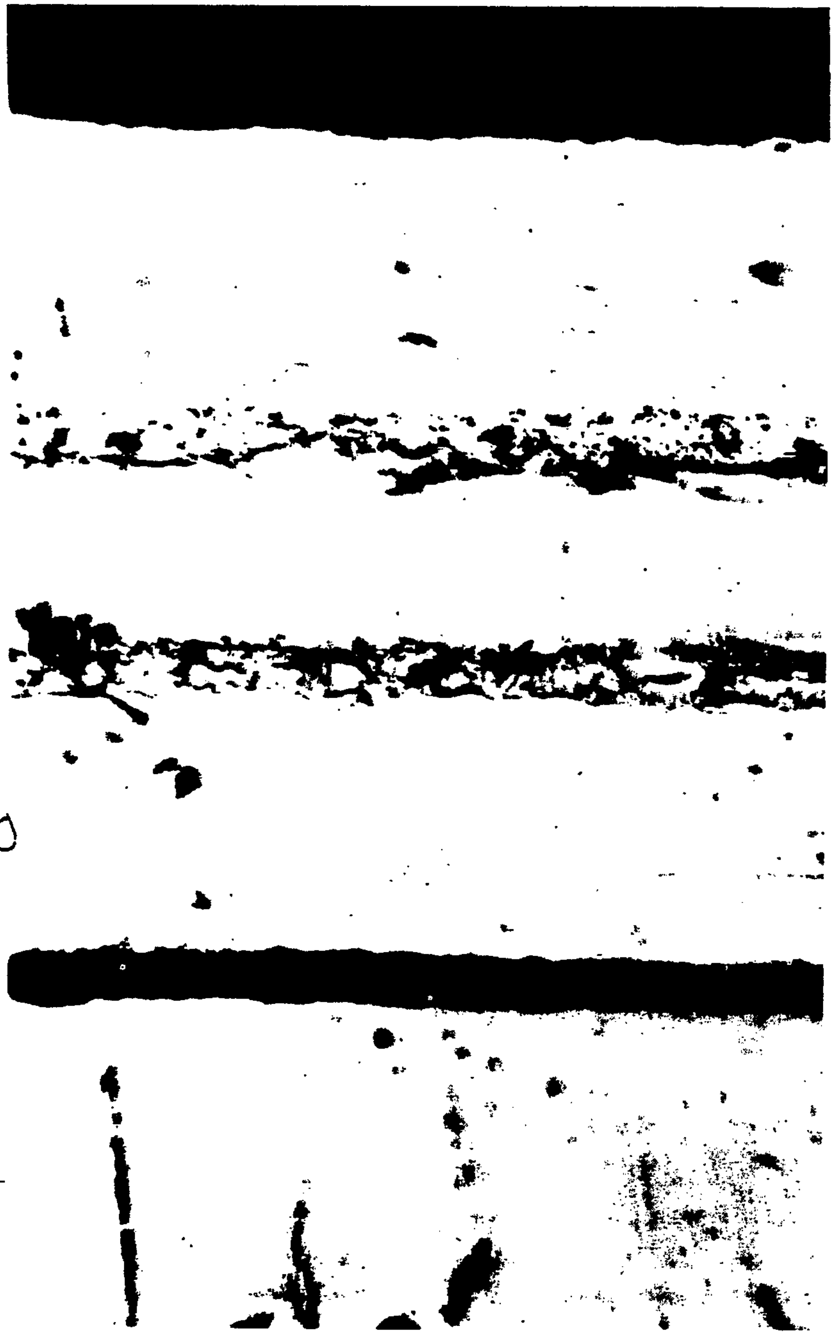

Fig. 4. Microphotograph of cross section — GE 300 ribbon.

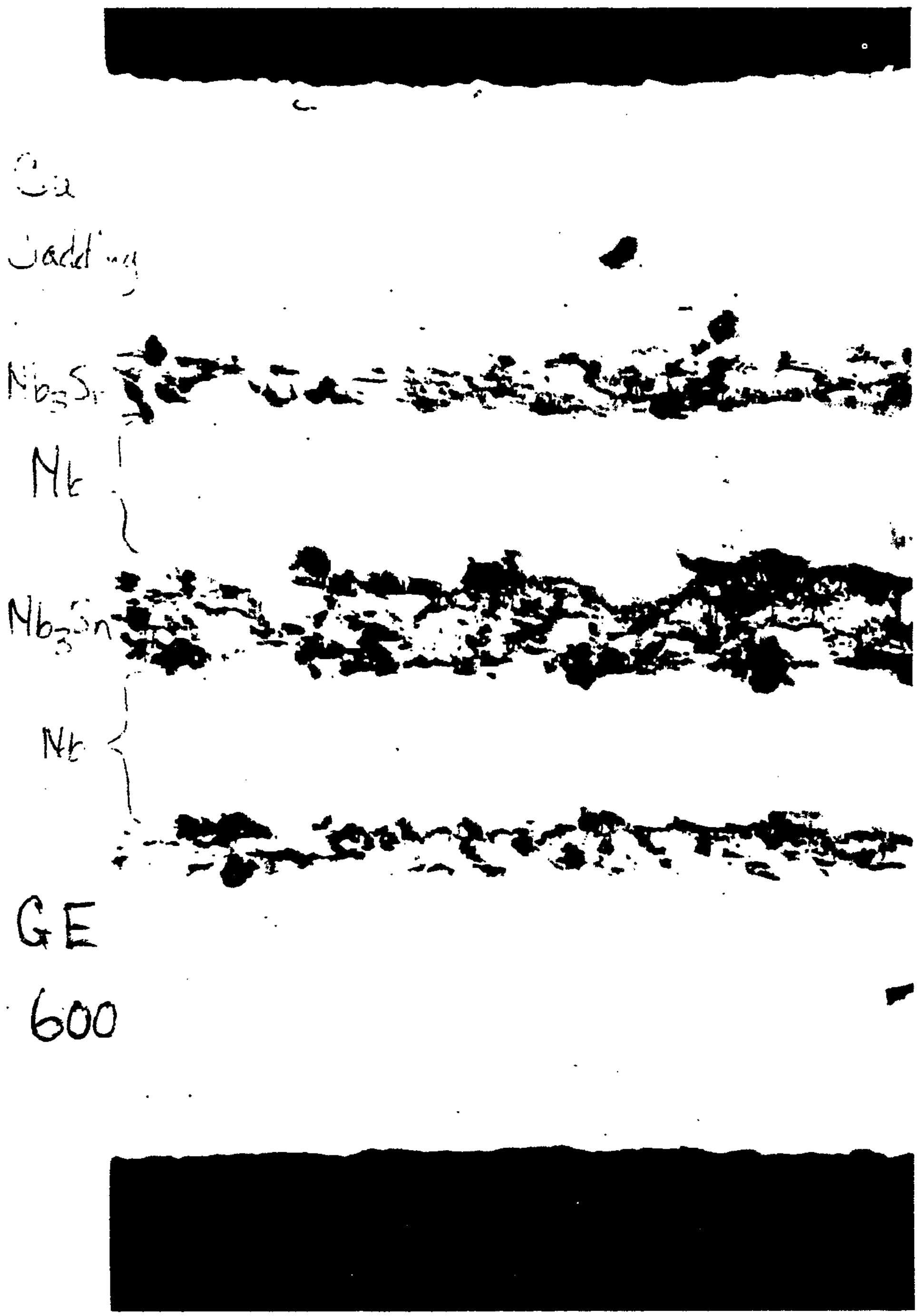

Fig. 5. Microphotograph of cross section — GE 600 ribbon.

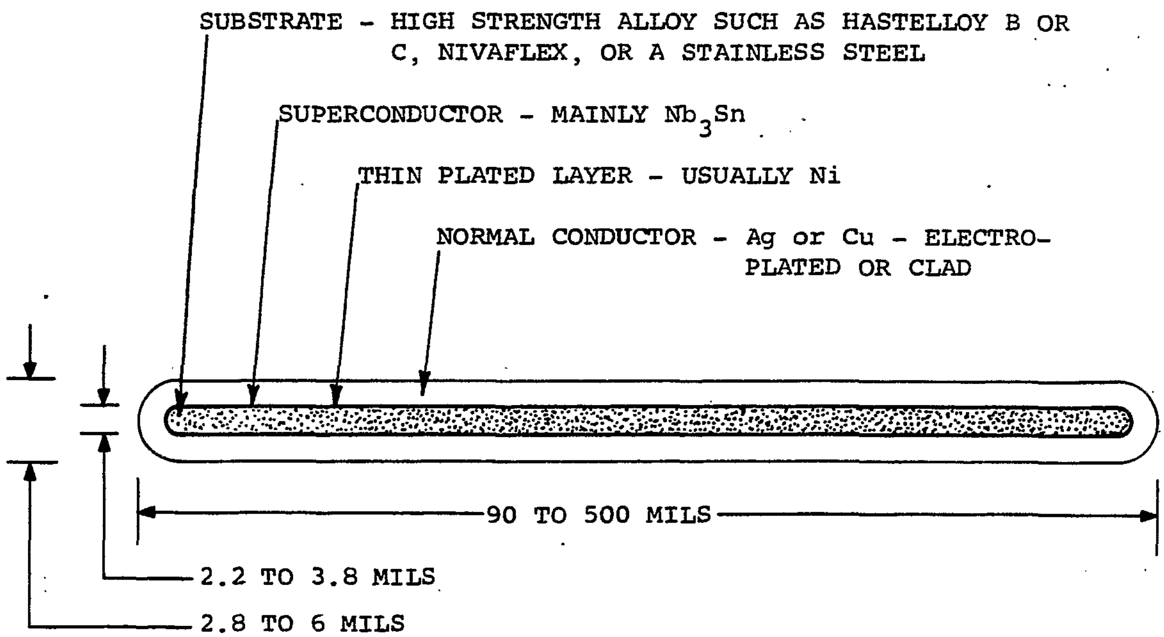

Fig. 6. Vapor-deposition process — Nb_3Sn ribbon.

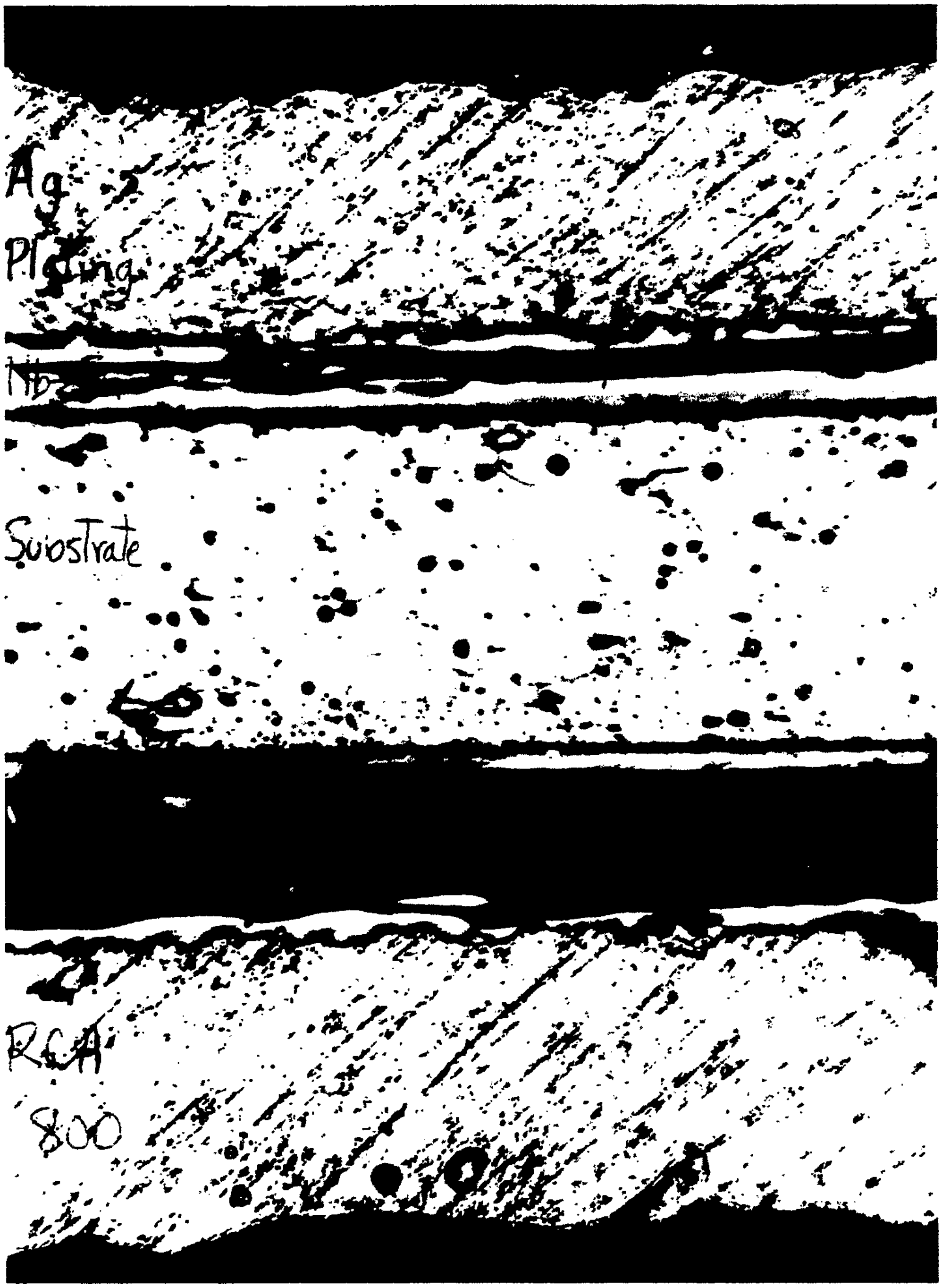

Fig. 7. Microphotograph of cross section — RCA 800 developmental ribbon.

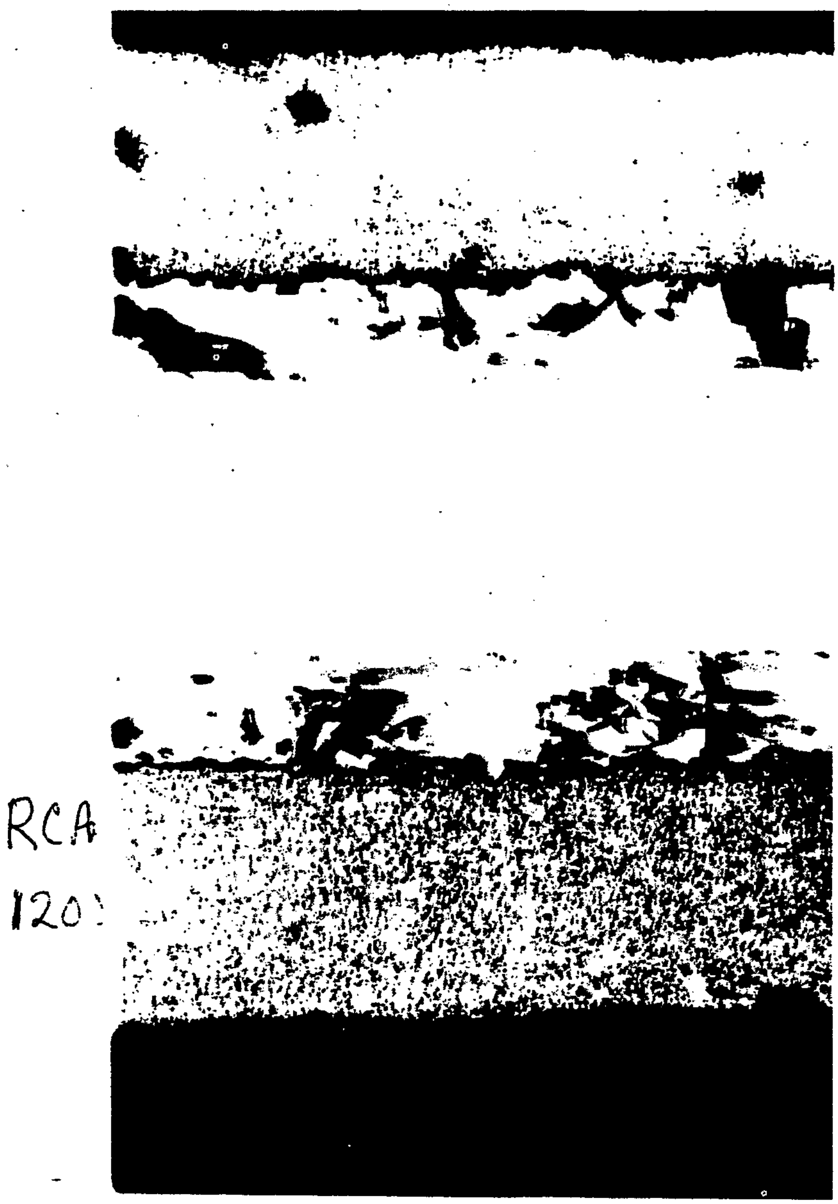

Fig. 8. Microphotograph of cross section — RCA 1200 developmental ribbon.

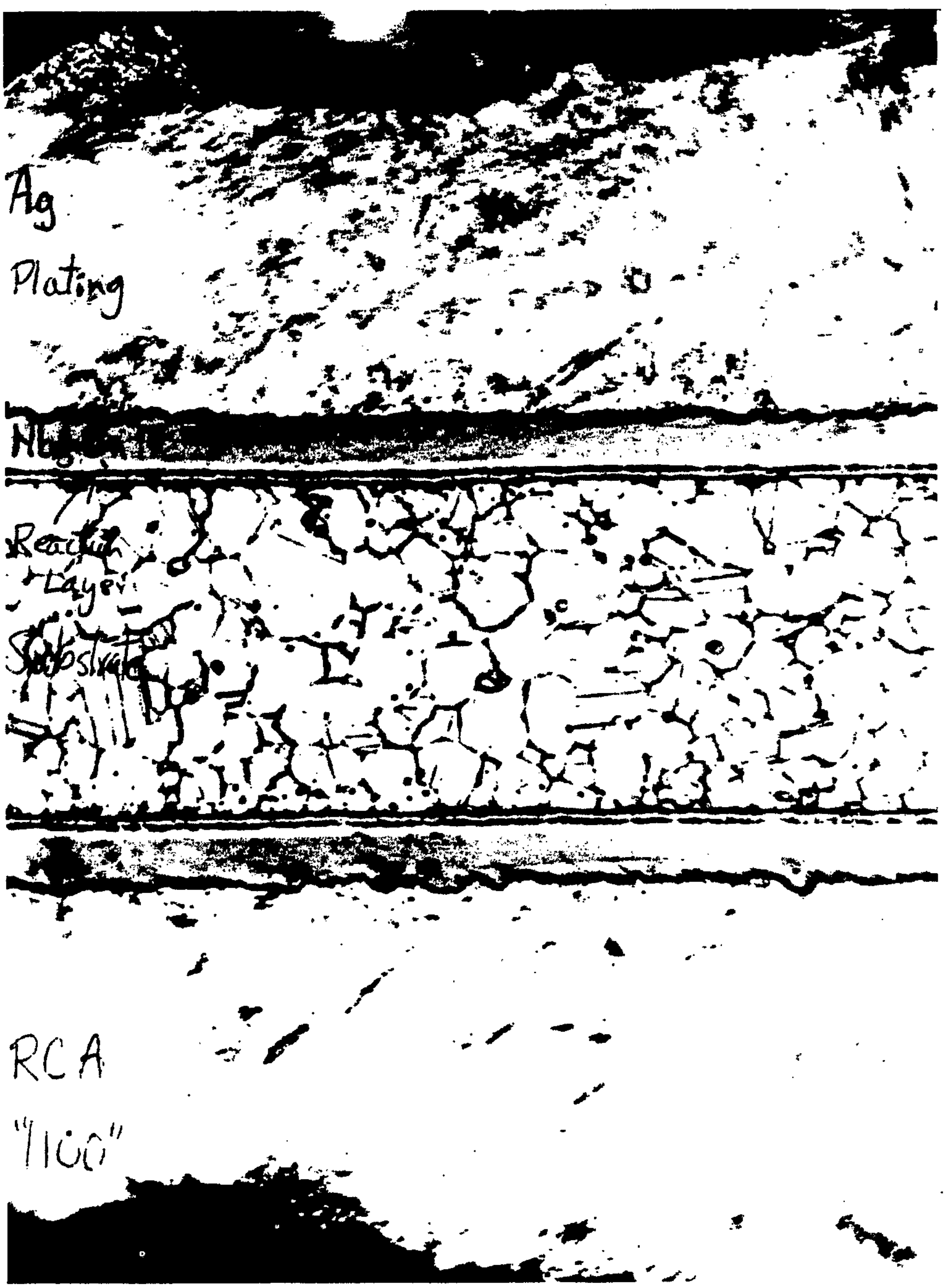

Fig. 9. Microphotograph of cross section — RCA "1100" developmental ribbon.

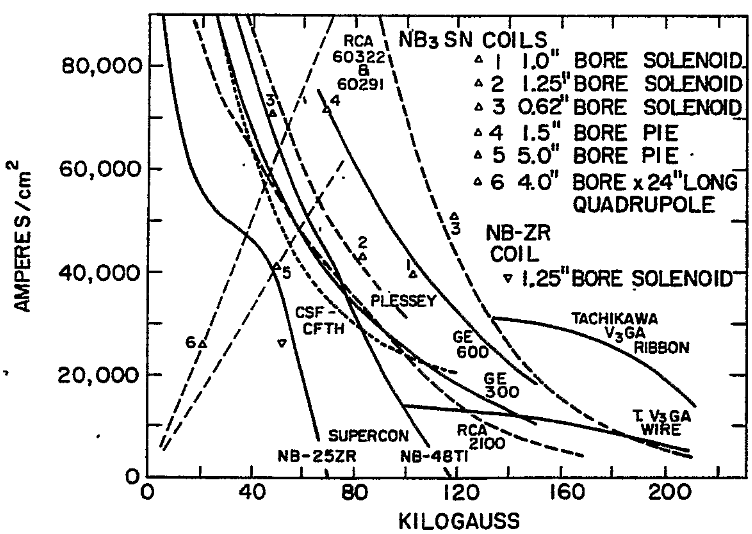

Fig. 10. Useful current density vs field at $4.2^{o}K$