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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : B05D 5/12, C23C 8/10, C04B 35/50

A1

(11) International Publication Number: **WO 88/ 08338**

(43) International Publication Date: 3 November 1988 (03.11.88)

(21) International Application Number: PCT/US88/00892

(22) International Filing Date: 21 March 1988 (21.03.88)

(31) Priority Application Number: 042,318

(32) Priority Date: 23 April 1987 (23.04.87)

(33) Priority Country: US

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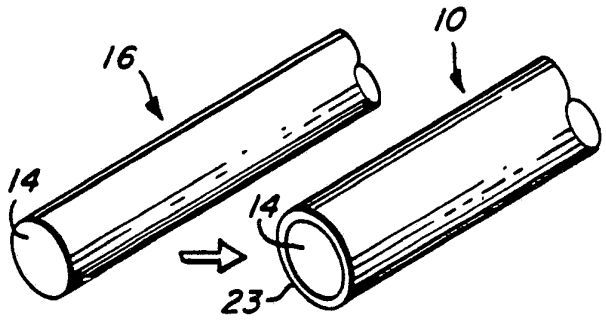
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(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PREPARATION OF SUPERCONDUCTING CERAMIC MATERIALS



(57) Abstract

A method of preparing a selected device geometry (10) of a superconducting compound. A high critical temperature superconducting compound is prepared from a starting metal composition (14) which is formed in a predetermined base geometry (16) and then subjected to an oxidation reaction to generate the superconducting compound (23) in the final selected device geometry.

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PREPARATION OF SUPERCONDUCTING CERAMIC MATERIALS

The present invention relates generally to superconducting compounds and methods of preparing the superconducting compounds. More particularly, the invention relates to preparation of superconducting ceramic materials having extremely high critical temperatures with the materials being prepared from metallic alloys having initial predetermined base geometries which are subjected to oxidation reactions to produce selected superconducting device geometries.

There has recently been substantial progress toward developing superconducting materials which exhibit extremely high critical temperatures (T_c). Some perovskite materials composed of Y-Ba-Cu oxides have a T_c above the boiling point of liquid N_2. The commercial implications of such materials are enormous; but the subject ceramic materials exhibit mechanical properties typical of ceramics, thus making the fabrication and preparation of devices of the superconducting compounds quite difficult. Presently these materials are prepared by sintering mechanical mixtures of oxides and carbonates or by coprecipitating oxalates and carbonates followed by calcining and sintering steps. These types of preparation and fabrication techniques are extremely difficult to carry out and expensive to implement in constructing suitable selected superconducting device geometries.

Brief Summary Of The Invention

It is therefore an object of the invention to provide an improved method of producing superconducting ceramic materials in a selected superconducting device geometry.

It is another object of the invention to provide a novel method of fabricating a starting composition as part of a predetermined base geometry to produce a selected superconducting device geometry.

It is a further object of the invention to provide an improved method of forming a predetermined base geometry of a starting metal composition as part of a normal conductor and oxidizing the starting metal composition to produce the desired superconducting device geometry from the predetermined base geometry.

It is also an object of the invention to fabricate a selected superconducting device geometry with various transitional, or intervening, compositional layers which bond a base metal or normal electrical conductor to a superconducting ceramic material.

In accordance with the invention a method is provided for preparing a selected device geometry of a superconducting compound by beginning with a starting metal composition, constructing or forming a predetermined base geometry of the starting metal composition and subjecting the starting metal composition to a chemically generic oxidation reaction, such as reacting the starting metal composition with selected

chalcogenides or halogens in order to produce the superconducting compound in the selected device geometry as derived from the predetermined base geometry. In another embodiment the method involves constructing a base metal structure, such as a copper block with channels, for receiving the starting metal composition and then subjecting the starting metal composition to a generic oxidation reaction to generate the superconducting compound in the selected device geometry, such as the copper block with a set of channels filled with superconducting compound.

Further objects and advantages of the present invention, together with the organization and manner of operation thereof, will become apparent from the following detailed description of the invention when taken in conjunction with the accompanying drawings wherein like reference numerals designate like elements throughout the several views.

Brief Description Of The Drawings

FIGURE 1 is a wire having a starting metal composition in the core region and an outer layer of a superconducting compound;

FIGURE 2 is a wire having a base metal core with an outer layer of superconducting compound;

FIGURE 3 illustrates two methods of assembling a starting metal composition with a base metal structure which receives the starting metal composition, (a) placing a bar of starting metal composition into open channels of the base metal structure and (b) pouring molten starting metal composition into partially closed channels of the base metal structure;

FIGURE 4 is a base metal container for receiving a molten starting metal composition to be oxidized while in the molten state;

FIGURE 5 is a base metal block and a thin overlayer of starting metal composition;

FIGURE 6 is a molten bath of starting metal composition for coating a wire of base metal which is passed through the molten metal bath; and

FIGURE 7 illustrates a furnace and coupled gas source for use in a batch processing mode of subjecting a starting metal composition to an oxidation reaction to generate a superconducting compound.

Detailed Description Of Preferred Embodiments

Referring now to the drawings, various aspects of preparing a selected device geometry 10 of a superconducting compound 12 are illustrated. The superconducting compound 12 generally has the chemical formula MX where M is at least one metal and X is an appropriate component for forming the superconducting compound 12. In a preferred embodiment the superconducting compound 12 has the chemical formula MNX where M is a metal selected from the group consisting essentially of the lanthanide rare earths or the group III B metals (such as Y and Sc), N is a metal selected from the group consisting essentially of the alkaline earth or alkali elements and X is a complex selected from the group consisting of a 3d, 4d, or 5d metal combined with chalogenide elements, such as O, S, Se and/or halogen elements, such as F, Cl, and I.

In the embodiments of FIGS. 1, 2, and 6 the method of preparing the selected device geometry 10 of the superconducting compound 12 involves: (a) preparing a starting metal composition 14, (b) constructing a predetermined base geometry 16 for the starting metal composition 14 and (c) subjecting the starting metal composition 14, as prepared in the predetermined base geometry 16, to a chemically generic oxidation reaction. This oxidation reaction then generates the superconducting compound 12 in the selected device geometry 10 and derived from the predetermined base geometry 16. This method of preparation greatly simplifies the construction of the selected device geometry 10 for the superconducting compound 12.

One example of preparing the superconducting compound 12 is shown in FIG. 2A where the starting metal composition 14 is fabricated as an outer wire layer 17 surrounding a base metal core 18, such as copper or aluminum. It is this outer wire layer 17 having the starting metal composition 14 which forms one example of the predetermined base geometry 16. To complete preparation of the superconducting compound 12 the wire layer 17 is then subjected to a chemically generic oxidation reaction (metal atoms reacting to reach a more positive valence, hereinafter referred to as, "oxidation reaction"). For the example of FIG. 2A, this oxidation reaction is carried out by heating a coil of processed wire (not shown) in a furnace 20 having a coupled gas tank 22 (see FIG. 7). This system shown in FIG. 7 provides a controlled temperature and a gas atmosphere

preferably of oxygen, or another chalcogenide, which enables formation of the superconducting compound 12. In other forms of the invention appropriate oxidation components, such as CO_2, SO_2, H_2S, Cl_2 and F_2, can also be used to form the desired superconducting compound 12.

The starting metal composition 14 is preferably a combination of a lanthanide, an alkaline earth and copper or a group III B metal, such as Y or Sc, an alkaline earth metal and copper. For example, the composition 14 can be, (a) $La_{2-x}M_xCu$ with M being Sr and/or Ba substituted for some of the La, or (b) $Y_xM_yCu_z$ with M, for example, being Ba. These starting metal compositions 14 are then oxidized to produce the preferred crystal structures composed of $La_{-x}M_xCuO_4$ (see the Examples) or $YBa_2Cu_3O_{7-\delta}$ where δ is about 0.1 to 0.3.

In preparation for carrying out the oxidation reaction to obtain the superconducting compound 12 in the selected device geometry 10, the starting metal composition 14 is first prepared in the predetermined base geometry 16. Any typical metallurgical fabrication technology can be used, such as, casting, rolling and powder sintering. As discussed hereinbefore, FIG. 2A illustrates one embodiment wherein the starting metal composition 14 has the predetermined base geometry 16 of the outer wire layer 17 over the base metal core 18. The selected device geometry 10 is then achieved by subjecting the predetermined base geometry 16 to the oxidation reaction. As depicted in FIG. 2B, the selected device geometry 10 includes the outer wire layer 17 of the

superconducting compound 12, an intervening layer of the starting metal composition 14 and the base metal core 18.

In FIG. 1A is another embodiment wherein the entire wire has the starting metal composition 14 and is the predetermined base geometry 16. The selected device geometry 10 is therefore readily achieved by carrying out the oxidation reaction to obtain the desired overlayer 23 of the superconducting compound (see FIG. 1B).

In FIG. 3 are shown two additional embodiments: (I) In the first embodiment a bar or wire 24 having the starting metal composition 14 is in position for placement in a base metal block 26, such as copper. Prior to carrying out the oxidation reaction, the bar 24 is electrically connected (such as by brazing or cold welding) to the block 26 to form the predetermined base geometry 16. The selected device geometry 10 is then achieved by performing the oxidation reaction under conditions resulting in preferential oxidation of the bar 24. (II) In the second embodiment in FIG. 3 the starting metal composition 14 is molten and is poured into a reservoir 28. While the starting metal composition 14 is still in the molten state, the oxidation reaction is carried out. Due to the increased reactivity in the molten state, the starting metal composition 14 is rapidly transformed and forms a solid form of the superconducting compound 12. Once the melt completely oxidizes the desired superconducting compound 12 solidifies in the block 26 in the selected device geometry 10.

In the second embodiment of FIG. 3 the electrical connection between the superconducting compound 12 and the block 26 is achieved by diffusion of atomic components into the solid block 26. This diffusion occurs most rapidly while the block 26 contains the molten starting metal composition 14 and superconducting compound 12 is at a high temperature in the solid form. This diffusion of atoms results in formation in the selected device geometry 10 of an intervening layer between the composition of the block 26 and the composition of the superconducting compound 12. Such an intervening transitional layer not only provides an electrical connection, but also provides a thermal expansion coefficient intermediate between that of the superconducting compound 12 and the block 26. This intermediate thermal expansion coefficient can prevent separation or spallation of the superconducting compound 12 from the block 26 which could arise from too large a difference of thermal expansion coefficient between the two materials. This intervening layer generated by diffusion of atoms can also be created for the first embodiment of FIG. 3 by means of a suitable heat treatment which is either separate from, or part of, the oxidation reaction.

In some forms of the embodiments of FIG. 3 the block 26 is joined with a cover block (not shown) of the same base metal composition. This cover block can be joined to the block 26 by a swaging operation in which exposed flat ends 29 of the block 26

are joined to the cover block. This final assembly partially isolates the superconducting compound 12.

A variation on the second embodiment of FIG. 3 is illustrated in FIG. 4. The starting metal composition 14 is in molten form and is poured into a base metal structure 30. The volumetric expansion associated with the oxidation reaction of the starting metal composition 14 ensures good thermal and electrical contact between the resultant superconducting compound 12 and the base metal structure 30. Furthermore, while the starting metal composition 14 is molten and the solid superconducting compound 12 is still at elevated temperatures, substantial diffusion takes place creating an intervening compositional layer having the attendant advantages described for the second embodiment of FIG. 3.

In FIG. 5 is illustrated another embodiment wherein the starting metal composition 14 is deposited in a film layer 32 on a base metal substrate 34. The film layer 32 can be deposited in a conventional manner, such as by vapor deposition, sputtering, electroplating, cladding, plasma spraying or by simply dipping the substrate 34 in a molten bath of the starting metal composition 14. The resulting composite of the substrate 34 and the film layer 32 is then subjected to the oxidation reaction to convert at least part of the film layer 32 to the superconducting compound 12 and form the desired selected device geometry 10.

In another form of the invention the film layer 32 of FIG. 5 can be formed in a stepwise manner with a series of layers of

different chemical composition being formed. The first of these layers adjacent to the base metal substrate 34 is formed to insure strong adhesion, such as by epitaxial growth. Succeeding layers are varied in composition in order to provide a compositionally graded metal layer culminating in a metal region which yields the superconducting compound 12 after the oxidation reaction. One can also utilize metal-ceramic compositions to assist in providing an adherent layer, or graded layers, while still generating the desired superconducting compound 12 in the selected device geometry 10.

In FIG. 6 is shown another method of preparing the predetermined base geometry 16 of the starting metal composition 14. A feed wire 36 composed of a base metal, such as copper, is passed through a molten bath of the starting metal composition 14 which coats the feed wire 36 to form the predetermined base geometry 16. This wire form of the geometry 16 can then be transferred to another location and be subjected to the oxidation reaction as part of a continuous process to produce the selected device geometry 10.

The following examples are merely illustrative and are not intended to limit the scope of the invention.

Example I

Appropriate molar quantities of Cu, La and Sr were melted together in a molybdenum crucible under a helium atmosphere to form an alloy of compositions 62 at. % La, 5 at. % Sr and 33 at.

% Cu, which is the metallic starting composition corresponding to a preferred pervoskite oxide: $La_{1.85}Sr_{0.15}CuO_4$. Droplets of the melt were quenched on a chill plate to inhibit phase separation. The alloy formed by this process was heated in air with the temperature raised slowly over a 24 hour period to 800°C and then air cooled. A $La_{2-x}Sr_xCuO_4$ type pervoskite layer was produced as verified by x-ray diffraction analysis.

Example II

In this example appropriate molar quantities of 5 at. % La and 0.5 at. % Sr were added to copper shot in a molybdenum crucible and brought to a melting temperature of about 970°C. This liquid was poured into a boron nitride crucible and subsequently remelted. The resulting ingot was removed from the boron nitride crucible and sectioned into 2 micrometer thick wafers. Some of the wafers were exposed to air at 800°C for various time periods ranging from 10 minutes to 18 hours. Samples exposed to air for 10 minutes were examined with back scattering electron imaging and x-ray diffraction analysis, and these technique detected an 80 micrometer thick perovskite oxide layer attached to the Cu alloy. For samples oxidized for longer periods of time, a layer thickness greater than 200 micrometers tends to separate from the metal base layer.

What Is Claimed Is:

1. A method of preparing a selected device geometry of a superconducting compound having the chemical formula MX where M is at least one metal and X an appropriate component reactive with said M metal to form said superconducting compound, comprising the steps of:

preparing a starting metal composition;

constructing a predetermined base geometry with said starting metal composition; and

subjecting said starting metal composition to a chemically generic oxidation reaction to generate said superconducting compound in said selected device geometry as derived from said predetermined base geometry.

2. The method as defined in Claim 1 wherein said step of subjecting said metal composition to a chemically generic oxidation reaction comprises a partial reaction.

3. The method as defined in Claim 1 wherein said predetermined base geometry comprises an electrically conductive metal wire having an outer layer of said starting metal composition.

4. The method as defined in Claim 3 wherein said electrically conductive metal wire comprises Copper.

5. The method as defined in Claim 1 where in said predetermined base geometry comprises a wire of said starting metal composition.

6. The method as defined in Claim 1 wherein said predetermined base geometry comprises a copper block and an attached layer of said starting metal composition.

7. A method of preparing a selected device geometry of a superconducting compound having the chemical formula MX where M is at least one metal and X is a complex selected from the group consisting essentially of a 3d, 4d, or 5d metal combined with a chalcogenide or halogen element, comprising the steps of:

preparing a starting metal composition;

constructing a predetermined base geometry with said starting metal composition; and

subjecting said starting metal composition to a chemically generic oxidation reaction to generate said superconducting compound in said selected device geometry as derived from said predetermined base geometry.

8. A method of preparing a selected device geometry of a superconducting compound having the chemical formula MNX where M is a metal selected from the group consisting essentially of the lanthanide rare earth elements or group III B metals, N is a metal selected from the group consisting essentially of the alkaline earth or alkali elements and X is a complex selected from the group consisting essentially of a 3d, 4d, or 5d metal combined with a chalcogenide or halogen element, comprising the steps of:

preparing a starting metal composition;

constructing a predetermined base geometry of said starting metal composition; and

subjecting said starting metal composition to a chemically generic oxidation reaction to generate said superconductor compound in said selected device geometry as derived from said predetermined base geometry.

9. A method of preparing a selected device geometry of a superconducting compound having the chemical formula MX where M is at least one metal and X is selected from the group consisting essentially of a transition metal combined with a chalcogenide or halogen element, comprising the steps of:

preparing a starting metal composition;

constructing a base metal structure for receiving said starting metal composition; and

subjecting said starting metal composition to a chemically generic oxidation reaction to generate said superconducting compound in said selected device geometry.

10. The method as defined in Claim 9 wherein said base metal structure comprises a molten bath of an electrically conductive metal.

11. The method as defined in Claim 10 wherein said electrically conductive metal comprises copper.

12. The method as defined in Claim 9 wherein said base metal structure comprises a solid electrically conductive metal and said starting metal composition is molten.

13. The method as defined in Claim 12 wherein said metal comprises a copper block having channels for receiving said starting metal composition.

14. The method as defined in Claim 9 wherein said base metal structure comprises a solid wire of electrically conductive metal and said starting metal composition is molten when received by said solid wire.

15. The method as defined in Claim 12 further including the step of diffusing said starting metal composition into said solid electrically conductive metal forming an intervening compositional layer between said conductive metal and said starting metal composition.

16. The method as defined in Claim 9 wherein M consists essentially of a lanthanide rare earth metal, a group III B metal and an alkaline earth metal.

17. The method as defined in Claim 9 wherein said step of preparing a starting metal composition comprises forming a melt of X and said step of constructing a base metal structure comprises forming a melt of M, said melt of M receiving said melt of X to form a surface layer of said melt of X on said melt of M.

18. The method as defined in Claim 9 wherein said oxidation reaction is part of a continuous processing operation beginning with generating said starting metal composition and ending with forming said selected device geometry.

19. A superconducting ceramic material having the chemical formula MNX where M is a metal selected from the group consisting

essentially of the group III B metals, N is a metal selected from the group consisting essentially of the alkaline earth or alkali metals and X is a complex selected from the group consisting essentially of a 3d, 4d, or 5d metal combined with a chalcogenide or halogen.

20. The superconducting ceramic material as defined in Claim 19 wherein said chemical formula comprises $YBa_2Cu_3O_{7-\delta}$ with said δ about 0.1 to 0.3.

21. A superconducting ceramic material prepared in accordance with the method of Claim 1.

22. A superconducting ceramic material prepared in accordance with the method of Claim 1 wherein said starting metal composition has the appropriate chemical composition to produce the desired composition for said superconducting ceramic material.

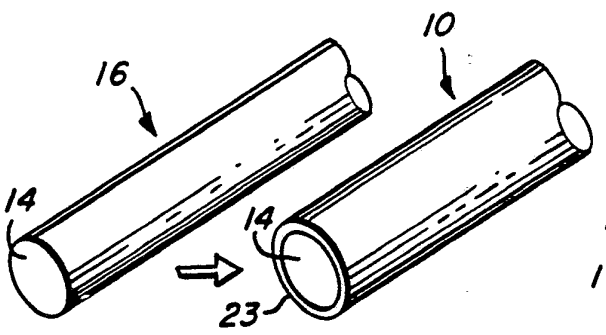


FIG. 1A FIG. 1B

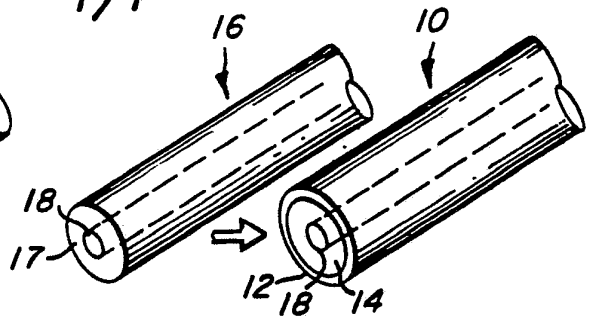


FIG. 2A FIG. 2B

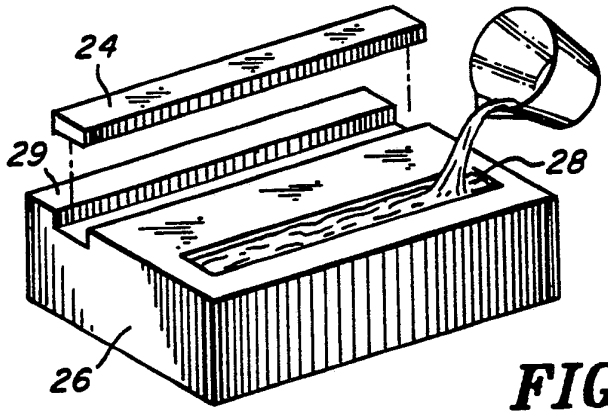


FIG. 3

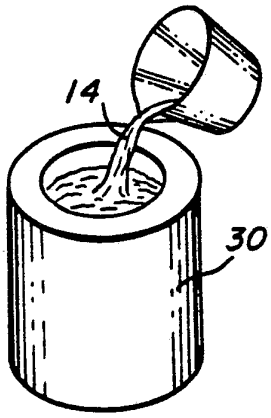


FIG. 4

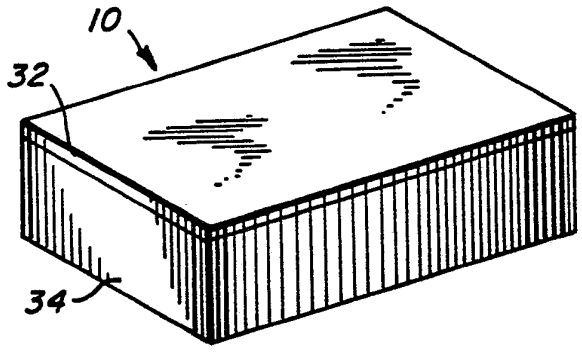


FIG. 5

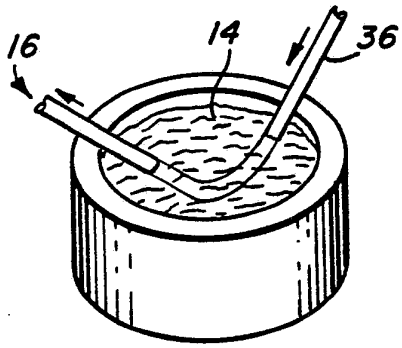


FIG. 6

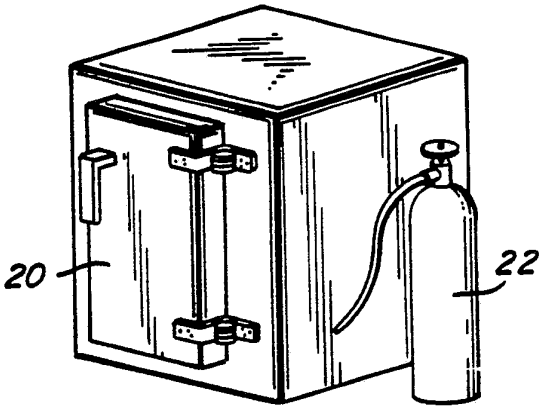


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/00892

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT.(4): B05D 5/12, C23C 8/10, C04B 35/50
U.S.CL.: 427/62, 252/521, 518; 501/152

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	427/62; 252/521, 518; 501/152

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JAPANESE JOURNAL OF APPLIED PHYSICS, VOL. 26, NO. 4, ISSUES 1987 APRIL (JAPAN). K. MATSUZAKI, PREPARATION OF A HIGH Tc SUPERCONDUCTOR BY OXIDIZATION OF AN AMORPHOUS La 1.8 Sr0.2 Cu ALLOY RIBBON IN AIR, SEE PAGES 334-336.	1-22
Y	ASAHI SHINBUN NEWSPAPER, ISSUE, 1987 MARCH 10, (JAPAN), SEE ENTIRE DOCUMENT.	1-22
Y	MATERIAL RESEARCH SOCIETY, PROCEEDINGS OF SYMPOSIUM S, 1987 SPRING MEETING OF M.R.S. 23 APRIL 1987, SEE ENTIRE DOCUMENT.	1-22

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
July 25, 1988	02 SEP 1988
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Sam Silverberg