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D E C I S I O N
of 16 May 2001

Case Number: T 0268/98 - 3.3.5

Application Number: 89906475.2

Publication Number: 0374263

IPC: C01G 3/00

Language of the proceedings: EN

Title of invention:

Oxide superconductive material and process for its production

Patentee:

Nippon Steel Corporation

Opponent:

Hoechst AG

Headword:

Oxide superconductor/NIPPON STEEL

Relevant legal provisions:

EPC Art. 54(1), 56, 83

Keyword:

"Sufficiency of disclosure - yes, practicable within functional limitation of the claim"

"Novelty - yes"

"Inventive step -yes, unexpected improvement of a product, non-obvious method for making a desired product"

Decisions cited:

T 0595/90, T 0233/93

Catchword:

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Case Number: T 0268/98 - 3.3.5

D E C I S I O N
of the Technical Board of Appeal 3.3.5
of 16 May 2001

Appellant:
(Opponent 01)

Hoechst Aktiengesellschaft
Zentrale Patentabteilung
Postfach 80 03 20
D-65903 Frankfurt am Main (DE)

Representative:

Ahrens, Gabriele, Dr.
Jasperallee 1A
D-38102 Braunschweig (DE)

Respondent:
(Proprietor of the patent)

Nippon Steel Corporation
6-3 Otemachi 2-chome
Chiyoda-ku
Tokyo 100-71 (JP)

Representative:

Kador & Partner
Corneliusstrasse 15
D-80469 München (DE)

Decision under appeal:

Decision of the Opposition Division of the
European Patent Office posted 30 January 2001
rejecting the opposition filed against European
patent No. 0 374 263 pursuant to Article 102(2)
EPC.

Composition of the Board:

Chairman: R. K. Spangenberg
Members: G. J. Wassenaar
M. B. Günzel

Summary of Facts and Submissions

I. The appeal is from the decision of the Opposition Division to reject the opposition against European patent No. 0 374 263. The patent was based on the European patent application No. 89 906 475.2 having the international filing date of 6 June 1989 and claiming the priority of two earlier patent applications filed in Japan on 6 June 1988 and 19 October 1988, respectively. The patent was granted with the following claims:

1. An oxide superconductive material composed of oxide of RE (a rare earth element including Y), Ba and Cu, which has a micro structure in which grains of a RE_2BaCuO_5 phase having a diameter smaller than $20 \mu m$ are dispersed in a single crystal of a $REBa_2Cu_3O_{7-y}$ phase.
2. A process for the preparation of an oxide superconductive material, which comprises melting oxides of RE (a rare earth element including Y), Ba and Cu having a superconductive substance-forming composition, rapidly cooling and solidifying the melt to form a plate or wire, once heating the plate or wire at a high temperature of 1000 to 1350°C to produce a partially melted state, and thereafter, gradually cooling the plate or wire at a rate lower than 200°C/hr.
3. A process for the preparation of an oxide superconductive material, which comprises molding an oxide having a superconductive substance-forming composition, which is obtained by mixing RE_2O_3 (RE represents a rare earth element including Y) and BaCu oxide, into a plate, or wire, heating

the molded body at a high temperature of 1000 to 1350°C to produce a partially melted state, and gradually cooling the molded body at a rate lower than 200°C/hr.

4. A process according to claim 2, wherein the thickness of the plate or wire is smaller than 5 mm.
5. A process according to claim 3, wherein the thickness of the molded body is smaller than 5 mm.

II. In the decision, inter alia, the following prior art documents were considered:

- D2: Appl. Phys. Lett. 52(24), 13 June 1988, pages 2074 to 2076,
- D3: Physical Review B, 37(13), 1 May 1988, pages 7850 to 7853,
- D5: Japanese Journal of Applied Physics, 26(7), July 1987, pages L1148 to L1149,
- D9: Japanese Journal of Applied Physics, 26(5), May 1987, pages L865 to L866.

The opposition grounds were insufficient disclosure, lack of novelty and lack of inventive step (Articles 100(a) and 100(b) EPC). The Opposition Division held that D2 was state of the art for the subject-matter of claims 1 to 3 because these claims were not entitled to the priority date of 6 June 1988. Taking into account D2 as closest prior art document they held that the subject-matter of the

claims as granted was new and involved an inventive step. They also held that the invention as claimed was sufficiently disclosed to be carried out by a person skilled in the art.

III. In the statement of the grounds of appeal, the appellant (opponent) maintained the objections raised before the first instance. Novelty of claim 1 was attacked on the basis of D2. An inventive step of the processes according to claims 2 to 5 was denied in view of D3 and D5. The invention was insufficiently disclosed because claims 2 and 3 did not comprise all the essential features of the invention and the patent in suit did not disclose how to perform the processes according to claims 2 and 3 in order to produce any article having the alleged superconductive and mechanical properties. During the appeal proceedings further reference was made to the following textbook as evidence for the skilled person's common general knowledge:

Fachlexikon ABC Chemie, Band 1 A-K, 1987, pages 610, 611, 619 and 620.

IV. The respondent (proprietor) refuted the arguments of the appellant. The claims as granted enjoyed the priority date of 6 June 1998 so that D2 was not state of the art. But even if the priority were not acknowledged, D2 would neither destroy the novelty nor would it jeopardize the inventiveness of the subject-matter of the claims as granted.

V. Oral proceedings took place on 16 May 2001 at the end of which the decision was announced.

VI. The appellant's arguments may be summarized as follows:

Insufficient disclosure

Claims 2 and 3 comprised the production of superconductive articles thicker than 5 mm but the patent in suit did not disclose how to make articles thicker than 5 mm. On the contrary it was explicitly indicated that suitable products thicker than 5 mm could not be obtained.

Novelty

D2 disclosed Y-Ba-Cu-O superconductors obtained by melt-textured growth of polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ superconductor (123 phase) using directional solidification, having a dense structure consisting of long, needle- or plate-shaped crystals aligned parallel to the a-b conduction plane. The microstructure as shown in Fig. 2(b) revealed the presence of grains of Y_2BaCuO_5 (211 phase) with a size below 20 μm within the superconducting crystals. Even if the crystals contained only a small amount of grains, the latter were clearly dispersed into the crystals of the superconductive phase. Any mixture of two phases should be regarded as a dispersion. The superconductive crystals of D2 should also be regarded as "single crystals" within the meaning of the patent in suit, whereby it had to be taken into account that the crystals according to patent in suit might be twin crystals, which were not proper single crystals. The superconductive properties such as the critical current density, with or without an external magnetic field, were also at least as good as those of the product of the patent in suit. Thus D2 anticipated the subject-matter of claim 1.

Inventive step

It was known from D9 that the critical current density J_c could be increased by fluxoid pinning and that small Y_2BaCuO_5 grains present in the YBCO system may be effective pinning centers. It was thus obvious to provide a superconductive material from $YBa_2Cu_3O_{7-y}$ crystals comprising small Y_2BaCuO_5 grains in order to increase the critical current density. Thus the subject-matter of claim 1 was obvious in view of D2 and D9.

In the melt-textured process according to D2, the polycrystalline body was heated to 1050-1200°C. The cooling between 900°C and 400°C took place at a very low rate of 10°C/h. The cooling rate between the partly melted state and 900°C was not disclosed but since it took place in an isolated furnace it was certainly lower than the 200°C/h required by present claims 2 and 3. The processes according to claims 2 and 3 differed thus from the process disclosed in D2 only in the use of another starting composition. It was known from D5 to prepare a superconducting $YBaCuO$ phase from a quenched liquid of the oxides forming the superconductive phase in order to mix the elements at an atomic level. Since thorough mixing of the starting components was also mentioned in D2, it was obvious to apply the mixing method according to D5 in the process according to D2 and thus arrive at a process according to present claim 2.

According to D2 a mixture of barium carbonate, yttrium oxide and copper oxide was moulded. Since barium carbonate decomposed at the melting temperature to barium oxide it was obvious to replace barium carbonate with barium oxide right from the beginning and thus arrive at a process according to present claim 3.

VII. The respondent's arguments may be summarized as follows:

Sufficiency of disclosure

The patent in suit contained an example of how to perform the invention and by applying the claimed process the skilled person could easily produce superconducting plates or wires with a thickness of more than 5 mm. Reduced homogeneity which might arise in thicker plates might affect the quality but did not destroy the basic superconductive properties. Moreover a skilled person would know how to avoid inhomogeneity in thicker objects. The invention was thus sufficiently disclosed.

Novelty

The product of D2 might comprise grains of the 211 phase smaller than 20 μm , but they were lying between the cracked needle-like crystals of the 123 phase and were not present as a dispersion within the crystals of the 123 phase. The occasional presence of one or two particles of one phase in another phase could not be regarded as a dispersion.

Inventive step

Starting from D2, the problem to be solved by the present invention was to provide a superconductive material with improved superconductivity especially when used in high magnetic fields. This problem was solved by the combination of features pursuant to claim 1 as granted. The single crystal feature and the presence of grains of 211 phase with a diameter smaller than 20 μm were not predetermined by D2 or any combination with any other of the cited documents. There was no hint to change the directional melt-

textured growth of D2 to one of the methods of claims 2 and 3, comprising a cooling step at a rate lower than 200°C/h. The process according to D2 required the directional solidification of the melt by a temperature gradient of at least 50°C/cm. The process according to claims 2 and 3 as granted differed therefrom essentially in that the melt was gradually cooled at a rate lower than 200°C/h without a substantial temperature gradient. In D2 treatment took place in a small furnace which cooled down very rapidly when heating was discontinued. Without a special arrangement, of which there is no sign in D2, the cooling from the partly melted state to 900°C took place at a rate which was at least 3 times faster than required by the patent in suit, likely around 1000°C/h. According to claims 2 and 3 the precursor which was partly melted was a mixture of a rare earth oxide and an oxide of barium and copper. The use of such a precursor was not disclosed or suggested in any of the cited documents.

VIII. The appellant requested that the decision under appeal be set aside and that the European patent No. 0 374 263 be revoked.

The respondent requested that the appeal be dismissed and that the patent be maintained.

Reasons for the Decision

1. *Sufficiency of disclosure*

1.1 The independent claims 2 and 3 relate to processes for the preparation of a superconductive plate or wire. The thickness of the plate or wire is not limited. According to the description the plate or wire has a

thickness of several mm, suitably below 5 mm (column 2, lines 53 to 56). Further according to the description, the thickness is limited to 5 mm because at higher thickness a homogeneous material cannot be obtained (column 4, lines 30 to 35). According to the respondent the latter statement does not imply that with the method of the invention superconductive plates or wires thicker than 5 mm cannot be obtained. Even if some inhomogeneity occurs in thicker plates, still good or even excellent products can be obtained. In the absence of evidence to the contrary, the Board accepts that with the information provided in the patent in suit the skilled person can perform the processes according to claims 2 and 3 under such conditions to obtain superconductive plates or wires with a thickness higher than 5 mm. The Board does not exclude that plates or wires thicker than 5 mm have possibly not the same high quality as thinner plates or wires, but it does not affect the sufficiency of the disclosure of the claimed processes, as long as the product which is obtained has superconductive properties. It has not been demonstrated or made plausible that plates or wires thicker than 5 mm and having superconductive properties could not be made.

- 1.2 It is not disputed that with the process according to claim 2 or 3 superconductive plates or wires with a thickness of several mm can be produced. It is evident to the Board that beyond a certain thickness suitable products cannot be obtained. The processes of claims 2 and 3 do however not extend to the production of plates or wires of any size. The scope of these claims has a functional limitation in the requirement that the product produced by the claimed processes must be an oxide superconductive material. The fact that the patent in suit does not disclose the production of superconductive plates or wires having a thickness higher than 5 mm does not therefore, in the Board's

view, render the disclosure of the invention as claimed insufficient. Since no other objections under Article 100(b) EPC have been raised, the Board holds that the contested patent meets that requirement of the EPC.

2. *Priority*

The dispute between the parties concerning the patent's entitlement to the claimed priorities would only have been relevant if D2, published between the earliest priority date and the filing date, destroyed the novelty or inventive step of the claimed subject-matter. Since the latter is not the case for the reasons set out below and since the question to which degree a patent application may deviate from the priority document without losing the priority right was still pending before the Enlarged Board of Appeal (G 2/98) at the point in time when the Board's decision on the present case was taken, the Board has left the priority issue undecided.

3. *Novelty*

3.1 D2 discloses a melt-textured oxide superconductive Y-Ba-Cu-O material comprising three phases, $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, Y_2BaCuO_5 and CuO. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase consists of near-parallel cracked needles typically 100-3000 μm long and 5-20 μm wide, sometimes separated by an essentially copper-oxide phase (page 2075, right hand column). The morphology of the Y_2BaCuO_5 phase is indicated as being "blocky" (table 1). D2 comprises Figures 2a and 2b showing the microstructure of the melt-textured material. The copies of D2 originally provided by the appellant are of such a bad quality that it is impossible to determine the position of the Y_2BaCuO_5 phase with respect to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase. Later provided copies of electronic pictures of the original

publication show more details. Assuming that these electronic pictures really correspond to the Figures in the original publication, which has in fact not been contested, the Figures reveal that the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase is present as broken needles sometimes interrupted by a Y_2BaCuO_5 phase in the form of blocky particles with a size below $20 \mu\text{m}$. The majority of the blocky particles are clearly situated between the needles. There is no unambiguous disclosure of particles consisting of the Y_2BaCuO_5 phase present within a needle of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase. D2 certainly does not disclose the presence of particles of the Y_2BaCuO_5 phase dispersed in a single crystal of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase. In the Board's opinion the expression "dispersed in" should be given its common meaning of "a substantially homogeneous distribution of a discontinuous phase within a continuous phase". The appellant's interpretation that already the presence of one or two particles within an other phase should be considered as a dispersion has not been substantiated and cannot be accepted.

Therefore, the feature that grains of a $\text{RE}_2\text{BaCuO}_5$ phase having a diameter smaller than $20 \mu\text{m}$ are dispersed in a single crystal of a $\text{REBa}_2\text{Cu}_3\text{O}_{7-y}$ phase, renders claim 1 novel over D2. For the issue of novelty it can thus be left aside whether the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ phase needles of D2 are single crystals within the meaning of the patent in suit or whether the single crystals according to the patent in suit, which show a twin-crystal pattern, are pure single crystals within the definition given in Fachlexikon ABC Chemie.

- 3.2 The feature that grains of a $\text{RE}_2\text{BaCuO}_5$ phase having a diameter smaller than $20 \mu\text{m}$ are dispersed in a single crystal of a $\text{REBa}_2\text{Cu}_3\text{O}_{7-y}$ phase is undisputedly not disclosed in any other cited document. The subject

matter of claim 1 is thus novel within the meaning of Article 54(1) EPC. The process claims 2 to 5 are also novel. Since this has not been disputed no further observations in this respect are necessary.

4. *Inventive step*

4.1 It is undisputed that D2 represents the closest prior art if the priority cannot be acknowledged. The transport critical current density J_c of a ceramic bar, prepared by the melt-textured growth process disclosed therein, has been determined by the so called pulse technique at 77 K under zero field conditions and with an applied magnetic field of 1 T (10000 Gauss). The zero field transport J_c was about 17000 A/cm² and at 1 T the transport J_c was still 4000 A/cm².

According to the patent in suit (column 1, line 55 to column 2, line 4) the main problems to be solved are:

- (1) Improvement of the critical current density J_c in zero magnetic field and in a magnetic field.
- (2) Improvement of the shapeability.
- (3) Improvement of the mechanical strength.

Since no data are available concerning the shapeability and mechanical strength of the product of the patent in suit, the Board can only consider an improvement of the critical current density. Starting from D2 the problem underlying the invention can thus be seen in the provision of an oxide superconductive material having improved critical current density with and without an

external applied magnetic field. The patent in suit proposes to solve this problem by a material, according to claim 1, composed of single crystals having dispersed therein grains of the RE_2BaCuO_5 phase having a diameter smaller than $20 \mu m$.

According to Figure 2 of the patent in suit the transport J_c at 77 K of a sample cut from the material obtained according to the example, determined by the four terminal method, was more than $10,000 A/cm^2$ at $H=0$ and about $4000 A/cm^2$ at $H=1T$. According to the patent in suit the values obtained by the four-terminal method include a risk of an underestimation of the J_c by a generation of heat at the current terminal. This effect is confirmed by D3 (see, page 7850 right hand column). The values obtained by the measurements of the magnetisation characteristics are indeed much higher. According to Figure 4, with magnetisation measurement at 77 K on another sample the following J_c values were obtained: about $40,000 A/cm^2$ at $H=0$ and about $10,000 A/cm^2$ at $H=1T$. The J_c value at $H=0$ is even higher than recorded for a single crystal of $YBa_2Cu_3O_{7-y}$. In D2 magnetisation measurements of J_c were not made, so that direct comparison was not possible. The extremely high J_c values obtained by magnetization measurements of the product of the patent in suit is, however, in the Board's view an indication that the critical current density of the product of the patent in suit in the range from 0 to 1T, if measured with the same method, would likely be higher than that of the product of D2. The Board can accept the appellant's submission that by the magnetisation method essentially intra-crystalline currents are measured so that for a polycrystalline body, as in the patent in suit, magnetic measurements of J_c give a too high value. The appellant has, however, not provided evidence or convincing arguments that the overestimation of J_c by the magnetisation measurement is so large that the J_c

value of the product of D2 would have been equally high if measured by the magnetisation method. The Board therefore accepts that the product according to present claim 1 actually solves the above-mentioned problem.

4.2 D2 does not provide any indication as to how the critical current density can be further improved. In D9, a research report concerning the influence of an external magnetic field on the critical current density in type Y-Ba-Cu oxide superconductive wires, it was found that, at 77 K, J_c was dramatically reduced to almost zero at 2 T. Several methods are proposed to improve J_c such as to arrange the c plane, considered to be an electron path, to the wire longitudinal direction, optimization of heat treatment conditions, higher compaction density and increase in n (carrier concentration); see page L866, right hand column. The first of these methods has been followed by the authors of D2 and D3 by subjecting the sintered body to a melt-textured growth process under a temperature gradient of more than 50°C/cm, in order to create long needles of the 123 phase. In D9 it is further observed that the other known factor for increasing J_c is fluxoid pinning. The following comment was, however, given: "At present, we cannot refer to pinning mechanism; especially we must consider the above two dimensionality, contrary to the conventional metallic superconductor. However, we believe that effective pinning centers (magnetic impurity, the normal phase such as Y_2BaCuO_5 , small void and grain boundary) exist in this YBCO system." Thus D9 teaches that effective pinning centers are available but do not yield the expected result. In the Board's view, therefore, D9 does not encourage the skilled person to add additional pinning centers. D9 certainly provides no incentive to create grains of Y_2BaCuO_5 within a single crystal of $YBa_2Cu_3O_{7-y}$. None of the other cited documents discloses or suggests this feature either.

4.3 In addition, the prior art does not comprise any technical information as to how to obtain the "pinning centers" according to claim 1. Therefore, even if the claimed product were to be considered highly desirable, it must be taken into consideration that there was no obvious method in the art to make it (see, T 595/90, OJ EPO 1994, 695, point 5 of the reasons, and T 233/93, dated 28 October 1996, point 4 of the reasons). Thus the average skilled person not even could, let alone would, have been able to arrive at the claimed product. The Board, therefore, holds that the product according to claim 1 involves an inventive step within the meaning of Article 56 EPC.

4.4 The processes according to claims 2 and 3 differ from the process disclosed in D2 in the use of a different composition of the ceramic body which is partly melted and the cooling rate from the partly melted state. The Board cannot accept the appellant's allegation that by turning out the heating of the isolated furnace after partly melting the moulded body therein, the cooling rate will be automatically below 200°C/h. D2 does not comprise detailed information concerning the apparatus used for melting and cooling the sintered body. With respect to the used melt-textured growth process reference is made to D3. According to D3 the samples were melt processed by heating either to the single-phase liquid region using local heating similar to that used in zone melting, or to the two-phase (liquid + solid) region (page 7850, right hand column). Local heating seems to imply that the sintered body as a whole is not heated in an isolated furnace and that, after removal of the heating zone from one part of the body to another part thereof, the partly melted, but now unheated part of the body, cools down very quickly.

In any case, there is no convincing evidence that in the process according to D2 the cooling rate from the partly melted state to a temperature of 900°C was below 200°C/h.

4.5 The appellant's argument that it was known from D3 (page 7852, last paragraph) that reduction of grain boundaries would improve the superconductive properties of the YBCO phase, that it was self-evident that increasing the crystal size would reduce the grain boundaries and that it was common general knowledge that crystal growth was enhanced by slow cooling, so that it was obvious to reduce the cooling rate, is not convincing either. Since the discovery of the superconductive YBCO phase various specialist research teams throughout the world have tried to improve its critical current density, but as far as known to the Board, despite the above-mentioned common general knowledge, one has not proposed to slow down the cooling rate of a partly melted phase as required by present claims 2 and 3.

4.6 Moreover, the invention does not only reside in the slow cooling rate, it is the combination of the claimed cooling rate with a specific precursor which is melted. According to claims 2 and 3 the precursor is a moulded body of a mixture of a rare earth oxide and a BaCu oxide. According to claim 2 this mixture is obtained by melting the oxides followed by rapidly cooling and solidifying the melt. In D2 and D3 a different precursor is used, namely a sintered body made from barium carbonate, yttrium oxide and copper oxide. During the long sintering process near the melting temperature of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ composition (900-950°C for 16h) a sintered superconductive body is obtained, whereas according to the patent in suit the precursor is a non-superconductive intimate oxide mixture. The use of the claimed precursor in a melt-textured process

for the preparation of a ceramic superconductor is not disclosed or suggested in any of the cited documents. It is true that D5 discloses the preparation of a YBCO superconductor starting from a quenched liquid of the composing oxides but the solidified oxide mixture is then annealed at 900°C for 48h, forming a sintered superconductive body (see page L1148, second paragraph); ie the same kind of body which is used as precursor in the melt-textured growth process according to D2 and D3.

- 4.7 In the Board's view, therefore, the combination of the specific precursor and the cooling rate as now claimed, was not obvious to a person skilled in the art trying to solve the above-mentioned problem. The subject matter of claims 2 and 3 thus involves an inventive step within the meaning of Article 56 EPC. Claims 4 and 5, being dependent upon claims 2 and 3 respectively, involve an inventive step for the same reasons.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:



G. Rauh

The Chairman:



R. Spangenberg

