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D E C I S I O N
of 10 July 2003

Case Number: T 1030/01 - 3.4.3

Application Number: 95105193.7

Publication Number: 0676817

IPC: H01L 39/24

Language of the proceedings: EN

Title of invention:

Method of preparing high-temperature superconduction wire

Patentee:

SUMITOMO ELECTRIC INDUSTRIES, LTD., et al

Opponent:

Siemens AG

Headword:

-

Relevant legal provisions:

EPC Art. 56, 114(2)

Keyword:

"Inventive step (yes)"
"Late filed documents"

Decisions cited:

T 0468/99, T 0736/99

Catchword:

-



Case Number: T 1030/01 - 3.4.3

D E C I S I O N
of the Technical Board of Appeal 3.4.3
of 10 July 2003

Appellant: Siemens AG
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Representative: -

Respondent: SUMITOMO ELECTRIC INDUSTRIES, LTD.
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Decision under appeal: Interlocutory decision of the Opposition
Division of the European Patent Office posted
17 July 2001 concerning maintenance of European
patent No. 0676817 in amended form.

Composition of the Board:

Chairman: R. K. Shukla
Members: V. L. P. Frank
J. H. Van Moer

Summary of Facts and Submissions

I. European patent No. 0 676 817 was opposed on the ground of lack of inventive step (Articles 100(a) and 56 EPC). The patent was maintained in amended form pursuant to Article 102(3) EPC by the Opposition Division's interlocutory decision dispatched on 17 July 2001.

The following prior art documents were *inter alia* considered in the opposition proceedings:

D2: EP-A-0 356 969

D3: Advances in Superconductivity II, Proceedings of the 2nd International Symposium on Superconductivity (ISS '89), November 14-17, 1989, Tsukuba (JP), Springer-Verlag, 1990, pp. 419-422

D7: IEEE Transactions on Applied Superconductivity, Vol. 3, No. 1, March 1993, pp. 942-945;

D9: JOM, March 1991, pp. 21-25

D10: Applied Superconductivity 1993, Vol. 1, H. C. Freyhardt (ed.), DGM Informationsgesellschaft Verlag, pp. 217-220.

In their decision, the Opposition Division concluded that as the method of preparing a high-temperature superconducting wire according to the main request did not exclude further processing steps such as plastic working and heating between the two heat treatments at the first and second temperatures respectively, it was obvious having regard to the prior art method disclosed

in document D7. With respect to the auxiliary request, the Opposition Division observed that the problem addressed by the claimed method was the improvement of the critical current density of superconducting wires of Bi-2223 phase. This was achieved by the specific two-stage heat treatment according to claim 1 of the auxiliary request resulting in critical current densities as high as 38900 A/cm² (Sample 10, Table 3 of the patent in suit). None of the documents cited by the opponent, however, provided an incentive to perform on a starting material formed by Bi-2212 phase and non-superconducting phases a two step heat treatment without any plastic working between them. The purpose of the first heat treatment was to remove any negative influence on the starting powder mixture exerted by the plastic working procedure. The second heat treatment formed the sintered body of the superconducting Bi-2223 phase.

II. The opponent lodged an appeal on 5 September 2001 against the interlocutory decision of the Opposition Division, paying the appeal fee on the same day. The statement of grounds of appeal received on 12 November 2001 referred to the following further documents:

D11: EP-A-0 451 532

D12: DE-A-41 24 980

D13: EP-A-0 462 409

D14: Materials Research Society Symposium -
Proceedings, Vol. 275, 1992, Materials Research
Society, pp. 233-238

D15: Applied Physics Letters, Vol. 59, No. 6, 5 August 1991, pp. 736-738

- III. The respondent (patent proprietor) submitted with his letter of 18 March 2002 three sets of claims 1 to 5 according to a main, first and second auxiliary requests, respectively.
- IV. In a communication accompanying the summons to oral proceedings according to Rule 11(1) RPBA, the Board *inter alia* observed that the main and first auxiliary requests submitted by the patent proprietor as a party to the proceedings as of right under Article 107, second sentence, EPC, were not admissible, since they were neither appropriate nor necessary, because the claims according to these requests extended the scope of protection with respect to the patent maintained by the Opposition Division in its interlocutory decision and the amendments made to the claims did not rise from the appeal (cf. G 9/92 and G 4/93, prohibition of *reformatio in peius*).

Furthermore, the Board announced that the relevance of documents D11 to D15 for the issue of inventive step would be discussed during the oral proceedings.

- V. In the course of the oral proceedings held on 10 July 2003, the respondent withdrew his main and first auxiliary requests, and requested the grant of a patent on the basis of his second auxiliary request. The claims of this request correspond to the version on which the Opposition Division based its interlocutory

decision to maintain the patent. The respondent thus requested that the appeal be dismissed.

The appellant requested that the decision under appeal be set aside and the patent revoked.

VI. The wording of the independent claim according to the respondent's request reads as follows:

"1. A method of preparing a high-temperature superconducting wire, comprising the steps of: charging raw material powder having an element composition capable of forming a 2223 phase of a bismuth-based oxide superconductor and mainly consisting essentially of a 2212 phase and a non-superconducting phase in a metal sheath;

carrying out plastic working on said metal sheath being charged with said powder for obtaining a wire;

carrying out a heat treatment at a first temperature on said obtained wire; optionally cooling said wire obtained by said heat treatment at the first temperature to room temperature and

carrying out a heat treatment at a second temperature, being higher than said first temperature, on said wire obtained by said heat treatment at the first temperature, or in case the cooling is performed after the first heat treatment, on the wire obtained by said cooling step, wherein

said heat treatment at said first temperature is carried out at a temperature in the range of 700 to 800 °C during 10 to 50 hours and substantially forms no sintered body of said oxide superconductor, said heat treatment at said second temperature being carried out

at a temperature higher than 800 °C and forming a sintered body of said oxide superconductor, and the critical current density of the finally obtained high-temperature superconducting wire is increased by said heat treatment at said first temperature as compared with a case of not carrying out said heat treatment."

VII. The appellant argued essentially as follows:

- Documents D11 to D15, although not filed within the opposition period, should be considered by the Board under Article 114(2) EPC, since they are relevant to the superconducting wire production method claimed and disclose, in particular, a multistep heat treatment for obtaining Bi-2223 phase superconducting powders and wires.

- The method of producing a Bi-2223 superconducting wire according to the invention in suit comprises as an essential feature a two-step heat treatment at different temperatures with no plastic work being performed on the wire between these two steps. The patent discloses that drawing and rolling the wire damages the crystal structure of the material, producing an amorphous state. The first heat treatment heals these defects and recreates the Bi-2212 phase, while the second heat treatment at a higher temperature produces the Bi-2223 phase from the Bi-2212 phase. It is, however, well known in the state of the art that the Bi-2223 phase is very difficult to obtain and that it has a very limited stability range (cf. D3, Figure 1). Moreover, it was usual to form the 2223

phase from the previously formed 2212 phase, whereby the starting materials used for obtaining the 2212 phase were completely irrelevant (cf. D2, D7, D10 and D14). Document D15, furthermore, discloses that cold worked 2223 tapes showed severe structural damage due to mechanical deformations of the core and that these results were consistent with previous reports on Ag-clad 2212 tapes. For these reasons, it would have been obvious to follow the standard way of obtaining the 2223 phase from the 2212 phase and to realize that any mechanical damage done to the 2212 phase needs to be healed before transforming it to the 2223 phase.

VIII. The respondent argued essentially as follows:

- Documents D11 to D15 were not submitted in due time and should, therefore, be disregarded under Article 114(2) EPC, since they are not relevant to the present invention. In particular, documents D11 to D13 do not relate to the oxide powder in tube (OPIT) method of the invention in suit. Furthermore, documents D14 and D15 are no more relevant than document D10 or the other documents already on file.

- According to the patent in suit, it is an essential aspect of the invention that the second heat treatment is done on the wire obtained by the first heat treatment, ie that plastic working is carried out on the wire between both heat treatments. The examples disclosed in the patent show a large increase in the critical current

density (Jc) when the steps of the claimed method are followed. Document D10, ie the closest state of the art, discloses a two step heat treatment which is, however, used only when the starting material is formed of non superconducting powders (identified as 'phase composition of type I' in this document). For starting material formed by the 2212 phase and non superconducting powders (phase composition of type II) no pre-heat treatment at lower temperature is required. The starting materials used in the method according to claim 1 of the patent in suit correspond to the type II phase composition. There was, however, no reason to modify the teaching of document D10 in order to subject the type II starting materials to a pre-heat treatment at lower temperature, as it is specified in the method of the present invention, since in this document the highest Jc's were obtained for the type II starting powder composition.

Reasons for the Decision

1. The appeal is admissible.
2. *Late filed documents*
 - 2.1 The appellant submitted that documents D11 to D15 were cited in response to the reasoning of the Opposition Division to maintain the patent in amended form, according to which the exclusion of any plastic deformation between the heating steps involved an inventive step. The feature that no mechanical

deformation is carried out between the first and second heat treatment was not present in the claims according to the main request before the Opposition Division. The documents, it was submitted by the appellant, were therefore filed in due time.

- 2.2 The Board agrees with the appellant that since these documents are filed in direct response to the reasoning of the Opposition Division leading to the maintenance of the patent in amended form within the four-month time period allowed under Article 108 EPC for filing the statement of grounds of appeal, they are to be regarded as filed in due time. The Board has therefore no discretion to disregard them under the provision of Article 114(2) EPC (cf. eg T 468/99, point 1.1 of the "Reasons for the Decision"; T 736/99, point 2.2.1 of the "Reasons for the Decision"). In the following discussion of inventive step, these documents are therefore taken into consideration.

3. *Inventive step*

No formal objections were raised by the appellant against the claims in suit and the novelty of the method according to claim 1 has also not been contested. The only issue in this appeal is therefore that of inventive step of claim 1.

- 3.1 The patent in suit relates to the fabrication of superconducting wires using (Bi,Pb)-Sr-Ca-Cu oxide ceramic material by the 'oxide powder in tube' (OPIT) method. Three compound families of this ceramic material having a varying number of copper oxide layers are of interest: the one-, two- and three- layer

compounds which are usually referred to as the 2201, 2212 and (Pb)2223 phases, respectively. The 2212 phase has a critical temperature (T_c) of about 80 K while the 2223 phase has a T_c of about 110 K. The most interesting phase for practical applications is the 2223 high- T_c phase. This phase, however, is difficult to obtain and is stable only in the temperature range of 830 to 860°C (cf. D3, page 419 'Introduction'; page 420, 'Results and Discussion'; Figure 1 and D9, page 21, 'Introduction').

- 3.2 According to the OPIT method, oxide powders of the desired stoichiometry and phase content are placed inside a metal tube. The packed tube is deformed into the desired geometry, which is either round wire or flat tape, and annealed to produce the desired superconducting properties. The type and distribution of phases in the powder for a given overall powder composition will affect the microstructural evolution during the thermomechanical processing of the wire. A key feature of OPIT conductors with the highest critical currents is a high degree of crystallographic alignment of the superconducting oxide after the thermomechanical processing. In the case of the 2223 conductors, repetitive pressing and annealing increases the degree of oxide texture (c axis perpendicular to the plane of the tape) and the critical current density, at least for up to two or three repetitions. Post-deformation heat treatment is used to form and homogenize the high- T_c phase and to sinter the superconducting oxide grains for good electrical connectivity (cf. D9, page 21, 'The OPIT process'; page 22, left hand column, second paragraph and middle

column, 'Thermomechanical processing'; page 23, right hand column, second and third paragraph).

3.3 It is common ground that document D10 is the most relevant state of the art. This document discloses the effect of the ceramic core's initial phase composition on the Ag-sheathed Bi-2223 tape's critical current density (J_c). Two different initial powder mixtures were used as starting materials for obtaining the Bi-2223 phase. In the type I phase composition a mixture of non-superconducting oxide powders (OP) was employed. The type II phase composition was formed by 50% OP and 50% Bi-2212 phase. Both powder compositions had the overall 2223 phase composition and were used for fabricating Ag-sheathed superconducting tapes by the conventional OPIT method described above (cf. page 217, 'Experimental details').

According to this document, the highest J_c 's ($1.6 - 1.9 \times 10^4$ A/cm²) were obtained with the initial phase composition of type II after two heat treatments at 840°C in air with an intermediate cold pressing step at 1.0 GPa.

Similar J_c values, however, could be achieved in document D10 also with the initial phase composition of type I, but only after a pre-heat treatment of the wire in the temperature range of 800 - 820°C. It is thought that this pre-heat treatment transforms part of the non-superconducting oxide powders of the type I composition into the Bi-2212 phase within the tube, resulting thus in a phase composition similar to the one of the type II (cf. page 218, 'Results and Discussion'; page 320, 'Conclusion'; Figure 1).

3.4 The method of preparing a high-temperature superconducting wire according to claim 1 differs, therefore, from the method disclosed in document D10 essentially in that on a wire with the initial phase composition of type II (ie a mixture of non-superconducting and Bi-2212 powders) a first heat treatment in the temperature range of 700 - 800°C is performed prior to the second heat treatment at 840°C while no mechanical deformation is done on the wire between the two heat treatments.

3.5 The problem addressed by the invention as claimed is disclosed in the patent in suit, which is to increase further the critical current density of a Bi-2223 superconducting wire (cf. page 1, lines 31 to 32).

This formulation of the technical problem is also valid having regard to the closest prior art document D10, since the critical current densities achieved by the claimed method are higher than the maximum J_c disclosed in this document (ie above 2×10^4 A/cm² according to the Examples 1 and 3 of the patent in suit compared to a maximum J_c of $1.6 - 1.9 \times 10^4$ A/cm² disclosed in document D10).

3.6 The Board agrees with the appellant that it was known in the prior art, disclosed *inter alia* in documents D2, D3 and D10, that Bi-2223 superconducting wires obtained by converting the 2212 phase exhibited relatively high current density (cf. D2, page 5, lines 1 to 6; D3, page 420, 'Results and Discussion' and Figure 1; according to document D10 the best results are achieved

when the 2223 phase is obtained from the 2212 phase, ie the type II phase composition).

Moreover, as has been argued by the appellant, the specific starting materials for obtaining the 2212 phase are not important. What is crucial is that this phase is obtained before converting it into the 2223 phase. Document D10 discloses that the 2212 -> 2223 phase conversion can be done while the material is already in the tube, while document D2 teaches to start mainly with the 2212 phase (cf. D10, page 218, fifth paragraph; D2, page 4, lines 47 to 49).

Document D7, on the other hand, discloses a method in which the starting material used for the superconducting core is formed by the Bi-2223 phase. In the process disclosed in this document each mechanical deformation step is followed by heat treatment. The multifilament wires obtained by this method had J_c 's in the range of $2 - 3 \times 10^4$ A/cm². It is suggested that this may be due to the fact that the multifilamentary array was highly distorted and/or the heat treatment procedure no yet fully optimized (cf. page 942, right hand column, 'Experimental'; page 944, 'Conclusion' and Figure 1).

These documents thus show that the most promising method for obtaining superconducting wires with high J_c 's was not yet established at the priority date of the patent in suit and that different approaches were still followed by the persons skilled in the art.

3.7 Documents D11 to D13 relate to the formation of the Bi-2223 phase. However, they are not concerned with the 'oxide powder in tube' (OPIT) method for producing a superconducting wire as in the patent in suit. A skilled person would not have consulted these documents in order to improve the critical current density (J_c) of a Bi-2223 based superconducting wire, since these documents do not address this issue.

Document D14 relates to the parameters that influence the growth and stability of the 2223 phase in the OPIT method. It discloses that this phase is stable in a limited temperature interval and that the growth of this phase follow a S-shaped profile. This information, however, is disclosed in document D3 (cf. Figure 1).

Document D15 concerns the critical currents and the processing of Ag-sheathed Bi-2223 superconducting tapes obtained by the OPIT method. The fabrication method used comprises the successive application of deformation and sintering (DS) schedules. According to this document, severe structural damage to the superconducting core due to mechanical deformation was observed and these results were consistent with earlier reports on DS alignment of 2212 tapes (cf. page 736, right hand column and Figure 1; page 737, right hand column, last eleven lines). However, there is no indication in this document that this damage to the core could have a detrimental effect on J_c and had to be 'healed' before any sintering step. For these reasons, the disclosure of this document does not go beyond that of document D7, which was published about two years after the publication of document D15, both documents having two authors in common.

3.8 Moreover, the Board concurs with the respondent in that none of the documents of the state of the art discloses a two-step heat treatment with no mechanical deformation done on the wire between the two steps when using 2212 phase powder as precursor material. According to the patent in suit, the first heat treatment step at the first temperature heals the defects produced in the superconducting core of 2212 phase reestablishing its crystalline state, but without creating the 2223 phase. Only during the second heat treatment step at a temperature above 800°C is the 2223 phase grown from this healed 2212 core (cf. the patent in suit, page 4, lines 26 to 37; Figures 1 and 2).

In the method disclosed in document D10 the pre-heat treatment is carried out before the heat treatment at 840°C. However, this pre-heat treatment is done **only** for the type I phase composition, ie the composition comprising **only** non-superconducting oxide powders, and is used to produce the 2212 phase within the tube before converting this phase into the 2223 phase during the heat treatment at 840°C. The skilled person would not apply this pre-heat treatment when the starting powders already comprise the 2212 phase, as in the method of the patent in suit, since according to document D10 there is no need for a pre-heat treatment under these circumstances (cf. page 220, 'Conclusion').

3.9 The Board is convinced from these facts that the core's crystalline state is disturbed by the mechanical deformation process. However, no prior art document discloses that such a disturbed crystalline state of the 2212 phase may have detrimental consequences on the

critical current density, probably because it was believed that the defects introduced by the mechanical deformation process were healed during the heat treatment for converting the 2212 phase into the 2223 phase. As it is stated in the description of the OPIT process, this heat treatment forms and homogenizes the high-T_c phase and sinters the oxide grains together (see point 3.2 above and document D9). It would thus appear that a pre-heat treatment would not have been regarded as useful to improve the final J_c.

Summarizing, the state of the art does not direct the skilled person to take into account the crystalline state of the core before the final 2223 phase is formed.

- 3.10 For these reasons, in the Board's judgement, the method according to claim 1 involves an inventive step in the sense of Article 56 EPC and accordingly meets the requirements of Article 52(1) EPC.

The dependent claims concern further particular embodiments of the invention and are patentable for the same reasons.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar:

The Chairman:

P. Martorana

R. K. Shukla