

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 November 2003 (13.11.2003)

PCT

(10) International Publication Number
WO 03/094251 A2

- (51) International Patent Classification⁷: H01L 39/24
- (21) International Application Number: PCT/GB03/01920
- (22) International Filing Date: 2 May 2003 (02.05.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0210041.0 2 May 2002 (02.05.2002) GB
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 03/094251 A2

(54) Title: HIGH-FIELD SUPERCONDUCTORS

(57) Abstract: A method of increasing the upper critical field of a crystalline superconducting material is provided, which comprises the steps of converting the crystalline superconducting material to a substantially amorphous state, and then re compacting and crystallising the material. The method also has the effect of increasing the critical current density of the material, and is effective with both brittle and ductile superconductors.

1 High-Field Superconductors

2

3 The present invention concerns methods for the
4 manufacture of superconductor materials. More
5 particularly, the invention concerns methods of
6 increasing the upper critical field value (" B_{C2} ") of
7 crystalline superconductor materials to produce
8 high-field superconductor materials, e.g. for use in
9 superconducting electromagnets, or in power
10 transmission applications.

11

12 In relation to superconductor materials, the upper
13 critical field (B_{C2}) is the magnetic field strength
14 (Tesla, T) that delineates the superconducting phase
15 from the non-superconducting (or normal) phase.
16 Clearly a material cannot be used in magnetic fields
17 above B_{C2} in superconducting applications. The
18 critical current density (J_c) is the maximum useful
19 current density a superconductor can carry. J_c
20 depends on the magnetic field the superconductor is
21 exposed to. As a ball-park figure, when J_c drops

1 below about $4 \times 10^4 \text{ A.cm}^{-2}$, the size of the magnet
2 starts to increase and costs start to increase
3 rapidly.

4

5 High magnetic fields play an important role in
6 modern technological society. There are essentially
7 three areas of activity:

8

9 A) Magnetic Fields of up to ~ 12 Tesla: Medical
10 body scanners, particle accelerators, ore
11 separators, low field research magnets, maglev
12 trains.

13

14 The most important superconducting material
15 used in this field range is a ductile NbTi
16 alloy. A number of other ductile
17 superconducting materials have been
18 investigated in the past but ease of
19 fabrication and an upper critical field of
20 about 10- 12 T makes it the material of choice.

21

22 Note that even in magnets with a peak field
23 above 12 T, the low field parts use NbTi
24 windings because of the material's ductility.

25

26 The ductility of NbTi is critical, since it
27 directly translates into reliability and ease
28 of use. However its upper critical field is
29 about ~ 12 T so clearly is useless for
30 producing high magnetic fields above 12 T.

31

1 There are no known ductile superconductors that
2 can operate in magnetic fields significantly
3 above say 12 T.

4

5 B) Magnetic Fields of 12 - 22 Tesla.

6

7 Because there are no ductile superconductors
8 that can operate in this field range, brittle
9 superconductors have to be used, such as Nb₃Sn.

10

11 Multi-million pound demonstrators have been
12 built but handling brittle materials remains
13 problematic and the commercial market is
14 commensurately smaller.

15

16 Nevertheless there is still a significant
17 market in the range 12 T to 22 T including all
18 high field Research laboratory magnets and all
19 n.m.r systems (operating above 426 Mhz ~ 10
20 Tesla). There is also an application in Fusion
21 Tokamaks (currently designed to operate at 13.7
22 Tesla). It should be noted that there is an
23 enormous premium in increasing the field at
24 which Tokamaks operate - which is currently
25 set by the current carrying capacity and the
26 reliable use of brittle superconductors.

27

28 There are other brittle materials that compete
29 with Nb₃Sn, namely Nb₃Al and MgB₂ and ternary
30 and quaternary compounds of these binaries as
31 well as the developmental compounds.

32

1 C) Magnetic Fields above 23 Tesla

2

3 There are no superconducting magnets operating
4 in fields significantly above 22 T.

5 Above 22 Tesla, the commercial materials of
6 choice approach their upper critical field and
7 are no longer useful.

8

9 There is an enormous effort directed at trying
10 to improve the properties of developmental
11 superconductors for making magnets that can
12 operate above 22 T, and for power transmission
13 applications. This includes:

14 Chevrel phase superconductors which have
15 very high B_{c2} values of 60 T but do not have
16 sufficiently high J_c . J_c would need to be
17 increased up to about 4×10^4 A.cm⁻² at
18 operating fields above 22 T for these materials
19 to be useful.

20 Quaternary Nb₃Al which has higher B_{c2} than
21 binary Nb₃Al and very encouraging high J_c
22 values. The problem appears to be that the
23 manufacturing of these materials is complex and
24 currently unreliable in producing long lengths
25 of wire.

26 Improving Nb₃Sn. There are many
27 techniques that have been developed to
28 fabricate Nb₃Sn.

29 Development of High temperature
30 superconductors (e.g. Y₁Ba₂Cu₃O₇,
31 Bi₂Sr₂Ca_nCu_{n+1}O_{6+2n}, Tl₂Ba₂Ca_nCu_{n+1}O_{6+2n}, and
32 HgBa₂Ca_nCu_{n+1}O_{2n+4} compounds where n is an

1 integer). These materials are particularly
2 useful for both high-field and power
3 transmission applications.

4

5 Prior efforts to increase B_{C2} have concentrated on
6 doping high field superconductors. Many of the
7 improvements are explained using:

8

$$9 \quad B_{C2}(0) = 3.1 \times 10^3 \gamma \rho_N T_C$$

10

11 where γ is the Sommerfeld constant, ρ_N is the
12 normal state resistivity and T_C is the critical
13 temperature. So by doping the material and
14 increasing the resistivity, B_{C2} is increased.

15

16 The present invention provides a method of
17 increasing the upper critical field of a crystalline
18 superconducting material, comprising the steps of:

19 converting the crystalline superconducting
20 material to a substantially amorphous state; and
21 re-compacting the material.

22

23 It will be appreciated that a "crystalline
24 superconducting material" as referred to here
25 includes material that is only crystalline in part.

26

27 Preferably, the method further comprises the step of
28 crystallising the material.

29

30 Generally, the step of crystallising the
31 substantially amorphous material comprises
32 nanocrystallisation of the material.

1

2 The method may also have the effect of increasing
3 the critical current density (J_c) of the material.

4

5 The superconductor may be converted to a
6 substantially amorphous state by any means that
7 pumps energy into the material to increase its
8 energy state from a low level (crystalline) to a
9 high level (amorphous). This is most preferably
10 done by mechanical attrition (such as ball-milling),
11 but other equivalent methods may be used.

12

13 The substantially amorphous material may be re-
14 compacted and crystallised by means of heat and/or
15 pressure, most preferably by thermomechanical
16 processing (such as hot isostatic pressing (HIP)
17 and/or annealing).

18

19 The resultant material has a small grain size with a
20 high defect density, thereby increasing the
21 resistivity and thus B_{c2} as compared with the
22 original crystalline material. The grains
23 themselves may also have a high defect density.

24 These properties may also have the effect of
25 increasing J_c as compared with the original
26 material.

27

28 Existing high-field superconductors operating in
29 magnetic fields above 12 T tend to be brittle
30 materials. The application of the present invention
31 to such materials provides materials with increased
32 B_{c2} and/or J_c , enabling new and/or improved

1 applications of such materials. Existing ductile
2 superconductors tend to have relatively low B_{c2} ,
3 unsuitable for high-field applications above 12T.
4 The application of the present invention to such
5 materials may provide ductile materials suitable for
6 higher-field applications.

7

8 For example, the invention may be applied to improve
9 B_{c2} in existing commercial 12-22T field
10 superconductor materials, such as Nb_3Sn . The
11 invention may also be applied to improve B_{c2} in
12 existing commercial <12T field superconductor
13 materials such as NbTi (including doped NbTi),
14 extending the use of such materials to higher
15 fields. It may also be applied to elemental
16 superconductors such as Nb and Pb, or alloys of
17 these metals, where T_c is sufficiently high for
18 applications but B_{c2} is far too low. For example body
19 scanners could operate at higher fields with higher
20 resolution; all low field sections of high field (12
21 T - 22 T) large scale systems could use such
22 improved materials.

23

24 The invention may also be applied to superconductor
25 materials that are currently only of interest as
26 research materials, such as Chevrel phase materials,
27 potentially improving the properties of such
28 materials to the extent that they become
29 commercially useful.

30

1 The invention has been used to increase B_{C2} in a
2 Chevrel phase compound from 60 T up to 120 T by
3 using ball-milling followed by HIP/annealing.

4

5 It will be understood that B_{C2} is temperature
6 dependent and that, as is conventional in the art,
7 values of B_{C2} quoted herein are extrapolated values
8 for B_{C2} at zero Kelvin (" $B_{C2}(0)$ ").

9

10 The invention has also been applied to increase J_C
11 in a Chevrel phase compound (PbMo_6S_8 , "PMS") at zero
12 field by about a factor of 2 and to increase J_C in
13 high fields by at least a factor of 3. The
14 invention may also increase J_C in other materials by
15 a similar factor.

16

17 The resistivity of the superconductor material
18 increases markedly after ball-milling and compaction
19 and then decreases following HIP'ing/annealing. The
20 resistivity is strongly correlated with an increase
21 in B_{C2} (and kappa - the Ginzburg-Landau constant, κ).
22 See Table 1, below which shows how the resistivity
23 increases from $80 \mu\Omega\cdot\text{cm}$ ($B_{C2} \sim 47$ T) without any
24 milling up to $676 \mu\Omega\cdot\text{cm}$ ($B_{C2} \sim 139$ T) by ball-
25 milling and back down again $485 \mu\Omega\cdot\text{cm}$ ($B_{C2} \sim 107$ T)
26 to $363 \mu\Omega\cdot\text{cm}$ ($B_{C2} \sim 66$ T) with differing heat
27 treatments.

28

29 Table 1 Superconducting parameters obtained from
30 reversible magnetisation of PbMo_6S_8 samples

31

Sample	T_c (K)	$B_{c2}(0)$ (T)	κ	ρ_N (16 K) ($\mu\Omega\text{cm}$)
No. 1	14.42	46.65	124	80
No. 2	11.87	139.48	586	676
No. 3	12.36	106.77	402	485
No. 4	12.86	66.11	243	363

1

2 Processing condition:

3 No. 1: PMS, milling time: 0 h, HIP 800°C×8h.

4 No. 2: PMS, milling time: 200h, HIP 800°C×8.

5 No. 3: PMS, milling time: 200h, HIP 800°C×8h,

6 annealing: 800°C×40h.

7 No. 4: PMS, milling time: 200h, HIP 600°C×8h,

8 anneal: 600°C×40h, 1000°C×40h

9

10

11 As noted above, the invention uses ball-milling (or
 12 an equivalent process) to produce substantially
 13 amorphous superconducting material. The material is
 14 then recompact and crystallised to produce very
 15 small grain size material which probably has many
 16 scattering centres and pinning defects inside the
 17 grains. The small grain size and high defect
 18 concentration results in high resistivity with high
 19 upper critical field, B_{c2} .

20

21 It has been long known that in low magnetic fields
 22 the critical current density, J_c , increases when the
 23 grain size is decreased. The use of ball-milling to
 24 produce amorphous material which can then be

1 crystallised into material with very small grain-
2 size also increases J_c markedly.

3

4 Chevrel phase superconductors and Nb_3Sn have both
5 been used as powders to produce wires. High
6 temperature superconductors are also produced
7 routinely using powder metallurgy. Techniques such
8 as ball-milling may be used to thoroughly mix the
9 powders, however, this type of mixing is very
10 different from the present use of ball-milling for
11 producing amorphous material and crystallising.

12

13 It will be understood that suitable or optimal
14 parameters for ball-milling, HIP and/or annealing
15 (or equivalents) for the purposes of the present
16 invention may be determined empirically for
17 particular materials. The basic principle for the
18 crystallisation method is to control the
19 crystallisation kinetics of amorphous solids by
20 optimising the heat treatment conditions (for
21 example, annealing temperature, time and heating
22 rate) so that the amorphous phase crystallises into
23 a polycrystalline material with ultrafine
24 crystallites; i.e. to ensure that the nucleation
25 rate is high while the growth rate is small.

26

27 As used herein, "substantially amorphous" means
28 amorphous or nanocrystalline or a mixture thereof.
29 Also as used herein, references to crystallising the
30 substantially amorphous material means returning
31 amorphous material to a crystalline state and "re-
32 crystallising" any nanocrystalline components of the

1 "substantially amorphous material". It will be
2 understood that "re-crystallisation", when used in
3 its strict technical sense, generally means changing
4 a material with small crystals or strained crystals
5 into a material with larger crystals.
6 "Crystallised" is often used to describe changing an
7 amorphous material into a crystalline material. The
8 method of the present invention predominantly
9 involves "crystallising" amorphous material, but
10 since the material may not be completely amorphous
11 some limited "re-crystallisation" may also take
12 place.

13

14 Nanocrystalline (NC) materials are characterized
15 structurally by the ultrafine grains and the
16 numerous grain boundaries. The grain boundaries of
17 NC materials may be different from those of
18 conventional coarse grain, such as equiaxed grain
19 morphology, low-energy grain boundary structure and
20 flat grain boundary configuration. This produces
21 unusual physical, chemical and mechanical properties
22 with respect to the conventional coarse grained
23 materials. Ball-milling is one of the most
24 effective routes to fabricate NC materials of metals
25 and alloys. High-energy impact during ball milling
26 introduces severe plastic deformation of the milled
27 powder and forms nanocrystalline or amorphous
28 powder. Nanocrystallisation of the amorphous powder
29 results in formation of NC materials which usually
30 have dense and clean grain boundaries, low
31 microstrain and nearly perfect crystallite
32 structure.

1

2 By way of an example of the present invention,
3 nanocrystalline and amorphous PbMo_6S_8 (PMS) powder
4 was fabricated using ball-milling. The ball-milled
5 PMS powder was then subsequently hot isostatic
6 pressed (HIP'ed) and (in some cases) annealed to
7 obtain bulk samples.

8

9 Sintered PMS powder (5 g) with 6 Syalon balls with a
10 diameter of 20 mm was put into the Syalon pot and
11 ball-milled for 200 h at a rotational velocity of
12 300 revolutions per minute (rpm). The weight ratio
13 of ball to powder was ~16:1. Ball milling was
14 carried out in a steel box under Ar gas flow. The
15 milled powder was wrapped with Mo foil and stainless
16 steel and then HIP'ed at a pressure of 2000 bar and
17 temperatures of 600, 800 °C for 8 h. Some of the
18 HIP'ed samples were subsequently annealed at
19 temperatures of 600, 800 and 1000 °C for 40 h. The
20 details of the processing conditions are listed in
21 Table 1 above.

22

23 The milled powder has a relatively regular and
24 equiaxed morphology. The particle sizes are in the
25 range of 50 - 300 nm for the powder milled for 200
26 h. A preliminary TEM study reveals that the milled
27 particles consist of amorphous and nanocrystalline
28 phase with grain sizes of 10 - 20 nm.

29

30 As a second example, the invention has also been
31 used to increase B_{C2} at 2 K in Nb from 1.3 T up to

1 3.9 T by using ball-milling followed by pressing at
 2 room temperature.

3

4 B_{C2} is temperature dependent and measurements quoted
 5 for Nb are extrapolated values for B_{C2} at 2 K.

6

7 Table 2 Superconducting parameters obtained from
 8 irreversible magnetisation of Nb samples

Sample	T_c (K)	B_{C2} (2 K) (T)
1	8.6	1.3
2	7.9	3.9

9

10 Processing condition:

11 **No. 1: Nb, milling time: 0 h, Uniaxially pressed**
 12 **20°C×10 mins.**

13 **No. 2: Nb, milling time: 10h, Uniaxially pressed**
 14 **20°C×10 mins.**

15

16 The step of re-compacting the
 17 amorphous/nanocrystalline material is achieved by
 18 pressing the Nb at room temperature. The produced
 19 pressed powder exhibits the physical properties of a
 20 significantly increased upper critical field and
 21 critical current density. As the process is carried
 22 out at room temperature, that is, no special heat
 23 treatments are applied, there is no crystallisation
 24 involved. However, any form of heat treatment could
 25 be additionally applied, which may result in a bulk
 26 material being produced that exhibits an even larger
 27 increase in B_{C2} and J_c .

28

- 1 Improvements and modifications may be incorporated
- 2 without departing from the scope of the invention.

1 CLAIMS

2

3 1. A method of increasing the upper critical field
4 of a crystalline superconducting material,
5 comprising the steps of:

6 converting the crystalline superconducting
7 material to a substantially amorphous state; and
8 re-compacting the material.

9

10 2. The method of claim 1, further comprising the
11 step of crystallising the material.

12

13 3. The method of claim 1 or claim 2, wherein the
14 critical current density (J_C) of the material is
15 also increased.

16

17 4. The method of any preceding claim, wherein the
18 step of crystallising the substantially amorphous
19 material comprises nanocrystallisation of the
20 material.

21

22 5. The method of any preceding claim, wherein the
23 step of converting the crystalline superconducting
24 material to a substantially amorphous state
25 comprises pumping energy into the material to
26 increase its energy state from a low level
27 (crystalline) to a high level (amorphous).

28

29 6. The method of claim 5, wherein a mechanical
30 attrition method is used to achieve the increase in
31 energy state.

32

1 7. The method of claim 6, wherein the mechanical
2 attrition method comprises ball-milling.

3

4 8. The method of any of claims 1-7, wherein the
5 step of re-compacting the substantially amorphous
6 material is achieved by application of heat and/or
7 pressure.

8

9 9. The method of any of claims 1-8, wherein the
10 step of crystallising the substantially amorphous
11 material is achieved by application of heat and/or
12 pressure.

13

14 10. The method of claim 8 or claim 9, wherein the
15 application of heat and/or pressure comprises
16 thermomechanical processing.

17

18 11. The method of claim 10, wherein the
19 thermomechanical processing comprises hot isostatic
20 pressing (HIP) and/or annealing.

21

22 12. The method of any preceding claim, wherein the
23 crystalline superconducting material is a brittle
24 superconductor.

25

26 13. The method of claim 12, wherein the brittle
27 superconductor is Nb₃Sn.

28

29 14. The method of any of claims 1-11, wherein the
30 crystalline superconducting material is a ductile
31 superconductor.

32

- 1 15. The method of claim 14, wherein the ductile
2 superconductor is doped NbTi.
3
- 4 16. The method of any of claims 1-11, wherein the
5 crystalline superconducting material is an elemental
6 superconductor or an alloy thereof.
7
- 8 17. The method of any of claims 2-15, wherein, in
9 the step of crystallising the material in the
10 substantially amorphous state, the crystallisation
11 kinetics of the amorphous solid are controlled by
12 optimising heat treatment conditions so that the
13 amorphous phase crystallises into a polycrystalline
14 material with ultrafine crystallites.
15
- 16 18. The method of claim 17, wherein the crystallite
17 nucleation rate is high and the crystallite growth
18 rate is small.
19
- 20 19. The method of any of claims 8-18 when dependent
21 on claim 5, wherein suitable parameters for pumping
22 energy into the material and for the application of
23 heat and/or pressure to the amorphous material are
24 determined for the particular crystalline
25 superconducting material to which the method is to
26 be applied.
27
- 28 20. A crystalline superconducting material treated
29 according to the method of any preceding claim.
30
- 31 21. A crystalline superconducting material as
32 claimed in claim 19, having very small grain size,

- 1 with many scattering centres and pinning defects
- 2 inside the grains.