(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
06 October 2022 (06.10.2022)

WIPO | PCT

(10) International Publication Number
WO 2022/207464 A1

(51) International Patent Classification:
C09K 5/14 (2006.01) *F25B 9/14* (2006.01)

(21) International Application Number:
PCT/EP2022/057823

(22) International Filing Date:
24 March 2022 (24.03.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2104559.6 31 March 2021 (31.03.2021) GB

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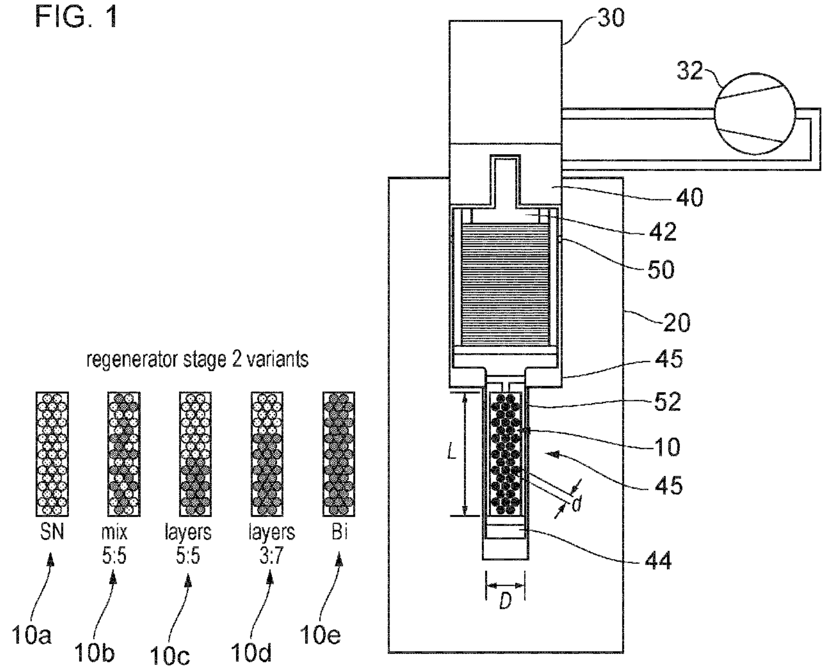
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: REGENERATOR MATERIALS, REGENERATORS AND REFRIGERATION SYSTEMS HAVING REGENERATORS

FIG. 1



(57) Abstract: A regenerator material, a regenerator comprising the material and a low temperature refrigeration system having such a regenerator are disclosed. The regenerator material comprises a plurality of balls; between 25% and 75% of the balls being formed of bismuth; and between 75% and 25% of the balls being formed of a tin antimony alloy.

WO 2022/207464 A1

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Published:

— *with international search report (Art. 21(3))*

REGENERATOR MATERIALS, REGENERATORS AND REFRIGERATION SYSTEMS HAVING REGENERATORS

FIELD OF THE INVENTION

The field of the invention relates to regenerator materials for use in refrigeration systems such as cryocoolers and to regenerators comprising the material.

BACKGROUND

Regenerator materials are used in closed-cycle refrigeration systems that use refrigerants such as helium as the working fluid. The regenerator material forms a matrix through which the working fluid flows. The regenerator material absorbs heat from the working fluid as the working fluid leaves the compression volume and flows towards the expansion volume, thereby cooling the working fluid. Following expansion and cooling of the working fluid, the flow is reversed, and the regenerator material releases its stored heat to the working fluid flowing past it, thereby cooling the regenerator material.

It is advantageous if the heat capacity of the regenerator material is high compared to that of the working fluid. With very low temperature refrigeration systems such as cryocoolers, many materials have very reduced heat capacities. At temperatures below 100 K - which is the typical temperature range of a cryocooler - the heat capacity of non-magnetic or non-superconducting materials typically decreases considerably as described by the Debye model, ultimately leading to a vanishing value approaching 0 K. Lead has one of the highest heat capacities at these low temperatures and has conventionally been used. However, lead is toxic and it would be desirable to find an alternative material to lead.

SUMMARY

A first aspect provides a regenerator material for a low temperature refrigeration system, said regenerator material being formed of a plurality of balls; between

25% and 75% of said balls being formed of bismuth; and between 75% and 25% of said balls being formed of a tin antimony alloy.

With the use of lead as a regenerator material becoming unacceptable, both tin and bismuth have been considered as replacement materials in low temperature refrigeration systems. The properties required for a regenerator material are a large specific heat capacity across the thermodynamic process temperature range of operation, and where the material is a granular material then the material should not be too hard or brittle as hard and brittle materials are difficult to fabricate into a spherical shape and may disintegrate into powder over time. Low toxicity is also important and the reason that lead is no longer considered suitable.

Bismuth has many of the desired properties but is relatively expensive. Tin is also quite suitable and is less expensive but in its elemental form has the drawback of reverting over time to an allotrope that is not ductile. An alloy of tin and antimony has been found to address the allotrope problem.

The inventor of the present invention recognised the above problems and found that a regenerator material formed of a mixture of balls some formed of bismuth and some of a Sn-Sb alloy provided a particularly effective regenerator material particular at very low temperature operations such as between 10 and 50K and in some embodiments down to as low as 8K.

Using a mixture of the two different substances allows the properties of bismuth which might be more effective at the very low temperatures to be present, while reducing the costs by interspersing the bismuth balls with the lower cost Sn-Sb balls which have acceptable properties across much of the range of operational temperatures and indeed perform better than bismuth at the higher temperatures, that is above about 35K.

Furthermore, using a mixture of balls of different materials allows for greater flexibility when selecting the composition of regenerator material suitable for a particular regenerator and also provides reduced costs when compared to forming an alloy of this mixture of materials.

In some embodiments, a mean diameter of said bismuth balls is within 20% of a mean diameter of said tin antimony balls, preferably within 5%.

Although there are advantages as set out above with using a mixture of balls of different materials, one significant potential drawback is that where the balls vary in mean diameter by a significant amount then this can lead to a significant increase in the resistance to flow and a corresponding reduction in performance. This can be a particular problem with refrigeration systems using pneumatically driven displacers. The inventor recognised this potential drawback and designed a system where the balls were carefully selected such that there was little difference in the mean diameter of the balls of the different materials.

Where they are used in a layered format in the regenerator then a difference of up to 20% in size may be acceptable, however, in embodiments, where they are used as a mixture then a smaller difference of up to 5% is preferred.

In this regard it should be noted that a ball of a substantially spherical shape is preferred as such a shape provides many points of contact improving heat conduction between the balls. An aspect ratio of up to 2:1 of the smallest to the largest diameter of the balls is acceptable.

In some embodiments, said regenerator material comprises between 45 and 55% of balls formed of bismuth and between 55 and 45% of balls formed of a tin antimony alloy.

In some cases a regenerator material that has approximately half Sn-Sb and half bismuth may be effective. In other embodiments a regenerator material with more bismuth may be preferred depending on the temperatures of operation of the regenerator.

In some embodiments, said tin antimony alloy comprises between 80% and 98% tin by weight, preferably between 90% and 96% by weight.

In some embodiments the purity of the bismuth is 99.5% or higher.

In some embodiments, said balls comprise a mean diameter of between 150 and 300µm, preferably between 220 and 270 µm.

The size of ball selected affects both heat transfer and flow resistance. Larger balls have a smaller surface area to volume ratio and thus, reduced heat transfer properties, while smaller balls provide reduced size gaps between them and flow resistances rises. The optimum size will depend both on the properties of the material forming the balls and on the displacer of the refrigeration system that the regenerator is being used in. It has been found that for a regenerator material formed of a mixture of bismuth and tin antimony balls then balls of a diameter of between 150 and 300 µm are preferred, where the balls are being used in a refrigeration system having a pneumatically driven displacer for example then the resistance to flow is particularly important and larger balls may be preferred, perhaps in the range 220 to 270 µm.

A second aspect provides a regenerator filled with the regenerator material of the first aspect.

In some embodiments, said regenerator has a cylindrical shape, with a length of between 70 and 100mm and a diameter of between 15 and 30 mm.

A regenerator of the above size is particularly appropriate for use in a refrigeration system with a pneumatically operated displacer, where the displacer is mechanical then a regenerator that is larger, perhaps twice as large may be used. A larger diameter regenerator may provide for reduced resistance to flow, an increased heat capacity and a higher mass flow rate. This increase in mass flow rate needs however, to be carefully controlled as it needs to be supported by the first stage regenerator and the compressor.

In some embodiments, said bismuth and tin antimony balls are intermingled within said regenerator to form a mixed regenerator material.

Although there is a technical prejudice against intermingling regenerator materials mainly due to their differences in physical properties which may lead to the harder material grinding the softer material for example, it has been found that with bismuth and antimony, which have a fairly similar hardness and which are both sufficiently hard to resist pulverisation, this problem is not significant.

In other embodiments, said regenerator comprises two layers a first layer towards a warmer end comprising said tin antimony balls and a second layer towards a colder end comprising said bismuth balls.

Although the mixture of balls provided a surprisingly effective regenerator, in some cases it has been found to be advantageous to layer the regenerator material, such that bismuth that is more effective at the lower temperatures is held at the colder end of the regenerator, while the tin-antimony balls are at the higher temperature end.

In some embodiments, said regenerator comprises between 60% and 70% bismuth and between 30 and 40% tin-antimony.

It has been found that with a layered regenerator, in some cases and in particular in embodiments with low temperature operation, a regenerator that comprises more bismuth than tin-antimony may be preferred.

A third aspect provides a refrigeration system comprising a first stage regenerator and a second stage regenerator according to a second aspect.

The regenerator of the second aspect may be used in the second stage of a cryocooler for example where operation may occur in a temperature range of between 10 and 50K and in some cases between 8 and 50K.

In some embodiments, said refrigeration system comprises a pneumatically driven displacer.

A pneumatically driven displacer has the advantages of having fewer parts and therefore being less expensive to manufacture, more robust and easier to service. Furthermore, its performance degrades prior to failure making failures easier to predict and therefore avoid that with a mechanical displacer. A pneumatically driven displacer does require a regenerator material with not too high a resistance to flow and thus, the size of balls that is preferred for a mechanical displacer may be different to those used in a pneumatic displacer.

A fourth aspect provides a cryopump comprising a refrigeration system according to a third aspect.

Further particular and preferred aspects are set out in the accompanying independent and dependent claims. Features of the dependent claims may be combined with features of the independent claims as appropriate, and in combinations other than those explicitly set out in the claims.

Where an apparatus feature is described as being operable to provide a function, it will be appreciated that this includes an apparatus feature which provides that function or which is adapted or configured to provide that function.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will now be described further, with reference to the accompanying drawings, in which:

Figure 1 shows a refrigeration system according to an embodiment; and

Figure 2 shows the cooling power of different compositions of regenerator material across a temperature range of operation of the second stage regenerator.

DESCRIPTION OF THE EMBODIMENTS

Before discussing the embodiments in any more detail, first an overview will be provided.

Regenerator materials are used in in refrigeration systems such as cryocoolers as heat exchange materials for cooling the working fluid on its way from the compressor, the expanded working fluid then cooling the regenerator material on its return to the compressor.

These refrigeration systems often operate in two stages, the first stage providing initial cooling down to perhaps 50K and the second stage cooling to a much lower temperature perhaps down to 8 K.

The regenerator material of the second stage needs to have a high heat capacity at the very cold temperatures of operation of the second stage regenerator. It also should have a form that allows the working fluid to exchange heat with the material. A granular form may be used, the size of the balls being selected as a compromise between increased heat transfer and decreased resistance to flow. A smaller size provides an increased surface area to volume ratio and thereby improves heat transfer but also provides a more compact form increasing flow resistance.

Where a mixture of metal materials has been used this has generally been in the form of an alloy. However, alloys are expensive to make and their composition is set. Having a mixture of balls of different material reduces the costs and allows changes to be made in the composition in a straightforward manner.

Furthermore, as tin-antimony and bismuth are both of a similar and relatively elevated hardness, then potential problems that may arise with a mixture of balls of different materials, where one material preferentially wears when in contact with the other do not arise to any significant extent.

Figure 1 shows a closed loop refrigeration system in this case a Gifford-McMahon cold head according to an embodiment. Compressor 32 provides high pressure helium to the refrigeration system. Drive unit 30 controls both the in- and out-flow of the helium as well as the motion of the displacers 42, 44. Where the drive is a pneumatic drive then the control of the motion of the displacers is performed by the drive unit with the help of a guide socket 40. The displacers 42, 44 are situated in cylinder 45 and they are sealed by seals 50, 52 towards the cylinder wall to force the helium to pass through the regenerator material. The movement of the displacers 40, 42 forces the warm high pressure helium to flow through the first stage regenerator, and subsequently through the second stage regenerator 10, being cooled as it flows. The cooled helium is then expanded and absorbs heat from the cold finger which provides the cooling performance. The displacers 42, 44 are then driven back by the drive unit 30 towards the cold end and push the helium out of the cylinder through the regenerator material thereby cooling the regenerator material. The helium returns to the compressor 32 and the cycle starts again.

In general the cylinder 45 of the cold head is mounted within a vacuum chamber 20.

The displacers may be driven mechanically by a motor, or pneumatically by a separate flow of the compressed helium. A pneumatically driven system has the advantage of increased reliability and fewer servicing requirements but is more sensitive to increased flow resistance, such that an increased ball size in the regenerator matrix may be preferable with this system.

In this embodiment the second stage part of cylinder 45 has a 20mm diameter D and a length L of 75mm, and the displacers 42, 45 are pneumatically driven by a flow of helium (not shown) that is separate from the flow through the regenerators.

Figure 1 shows the different alternative compositions of the regenerator materials 10a, b, c, d, e within the second stage regenerator according to both the prior art and different embodiments.

The left-hand and right-hand examples 10a and 10e respectively show second stage regenerators according to the prior art filled with grains of bismuth 10e or a tin-antimony alloy 10a. The other three regenerators 10b, 10c, 10d are regenerators according to an embodiment and comprise grains of both bismuth and a tin antimony alloy.

The second stage regenerator 10b comprise a mixture of balls of tin-antimony and bismuth with the balls of the different materials being intermingled. In this embodiment the mean diameter d of the balls is 250µm, and the tin-antimony and bismuth balls are substantially the same size, the mean diameter of the balls differing by less than 5%. Different sized balls in a mixture can lead to increased compactness and increased resistance to flow, this can be problematic particularly where the displacers are driven pneumatically.

The second embodiment 10C has the same composition of regenerator materials, however, they are layered rather than intermingled, the layers comprising a bismuth layer at the colder end and a tin-antimony layer at the warmer end. Bismuth has a higher heat capacity than tin-antimony at the lower temperatures and thus, performs better than tin-antimony at the lower temperatures and it is therefore advantageous for this to be at the colder end. The layers may be separated by a separating element such as a copper mesh.

The third embodiment 10d has a slightly different composition of materials where there is more bismuth than tin-antimony, but the materials are still layered.

Figure 2 shows the difference in cooling power for different temperatures of the second stage cold finger, for the different second stage regenerators shown in Figure 1

As can be seen a conventional bismuth regenerator performs well down to about 9K, while a conventional tin antimony second stage regenerator does not perform so well at the low temperatures and in particular, at temperatures around 10K or lower its performance is very poor.

The regenerators 10b, 10c and 10d having the mixture of regenerator materials each perform significantly better than the tin antimony regenerator at the lower temperatures of operation and indeed provide acceptable performance down to temperatures at or even below 10K, for some of the layered examples acceptable performance down to about 8K is achievable.

The layered regenerators provide a performance that is very similar to that of bismuth and significantly better than might be expected, providing a high performance regenerator for a lower cost than a pure bismuth regenerator and one that has improved performance at higher temperatures.

The intermingled embodiment of 10b also provides significantly improved performance at the lower temperatures than the tin-antimony example and approaches the performance of bismuth at 20K and indeed will exceed the performance of bismuth at higher temperatures. This regenerator also has the advantages of ease of construction and ease of adaptation, so that the composition and ratios of the two materials may be tweaked according to particular requirements without requiring any redesign of the regenerator or refrigeration system.

Although illustrative embodiments of the invention have been disclosed in detail herein, with reference to the accompanying drawings, it is understood that the invention is not limited to the precise embodiment and that various changes and modifications can be effected therein by one skilled in the art without departing from the scope of the invention as defined by the appended claims and their equivalents.

REFERENCE SIGNS

10, 10a, b, c, d, e	second stage regenerator material
20	vacuum enclosure
30	drive unit
32	compressor
40	guide socket
42	first stage displacer
44	second stage displacer
45	cylinder
50, 52	seals

CLAIMS

1. A regenerator material for a low temperature refrigeration system, said regenerator material comprising a plurality of balls;

between 25% and 75% of said balls being formed of bismuth; and

between 75% and 25% of said balls being formed of a tin antimony alloy.

2. A regenerator material according to claim 1, wherein a mean diameter of said bismuth balls is within 20% of a mean diameter of said tin antimony balls, preferably within 5%.

3. A regenerator material according to claim 1 or 2, wherein said regenerator material comprises between 45 and 55% of balls formed of bismuth and between 55 and 45% of balls formed of a tin antimony alloy.

4. A regenerator material according to any preceding claim, wherein said tin antimony alloy comprises between 80% and 98% tin by weight, preferably between 90% and 96% by weight.

5. A regenerator material according to any preceding claim, wherein said balls comprise a mean diameter of between 150 and 300μm, preferably between 220 and 270 μm.

6. A regenerator filled with the regenerator material of any preceding claim.

7. A regenerator according to claim 5 or 6, wherein said bismuth and tin antimony balls are intermingled within said regenerator to form a mixed regenerator material.

8 A regenerator according to any one of claims 1 to 6, wherein said regenerator comprises two layers a first layer towards a warmer end comprising

said tin antimony balls and a second layer towards a colder end comprising said bismuth balls.

9. A regenerator according to claim 7 or 8, wherein said regenerator material comprises a regenerator material according to claim 3.

10. A regenerator according to claim 8, wherein said regenerator comprises between 60% and 70% bismuth and between 30 and 40% tin-antimony.

11. A refrigeration system comprising a first stage regenerator and a second stage regenerator according to any one of claims 6 to 10.

12. A refrigeration system according to claim 11, wherein said refrigeration system comprises a pneumatically driven displacer.

13. A cryopump comprising a refrigeration system according to claim 12.

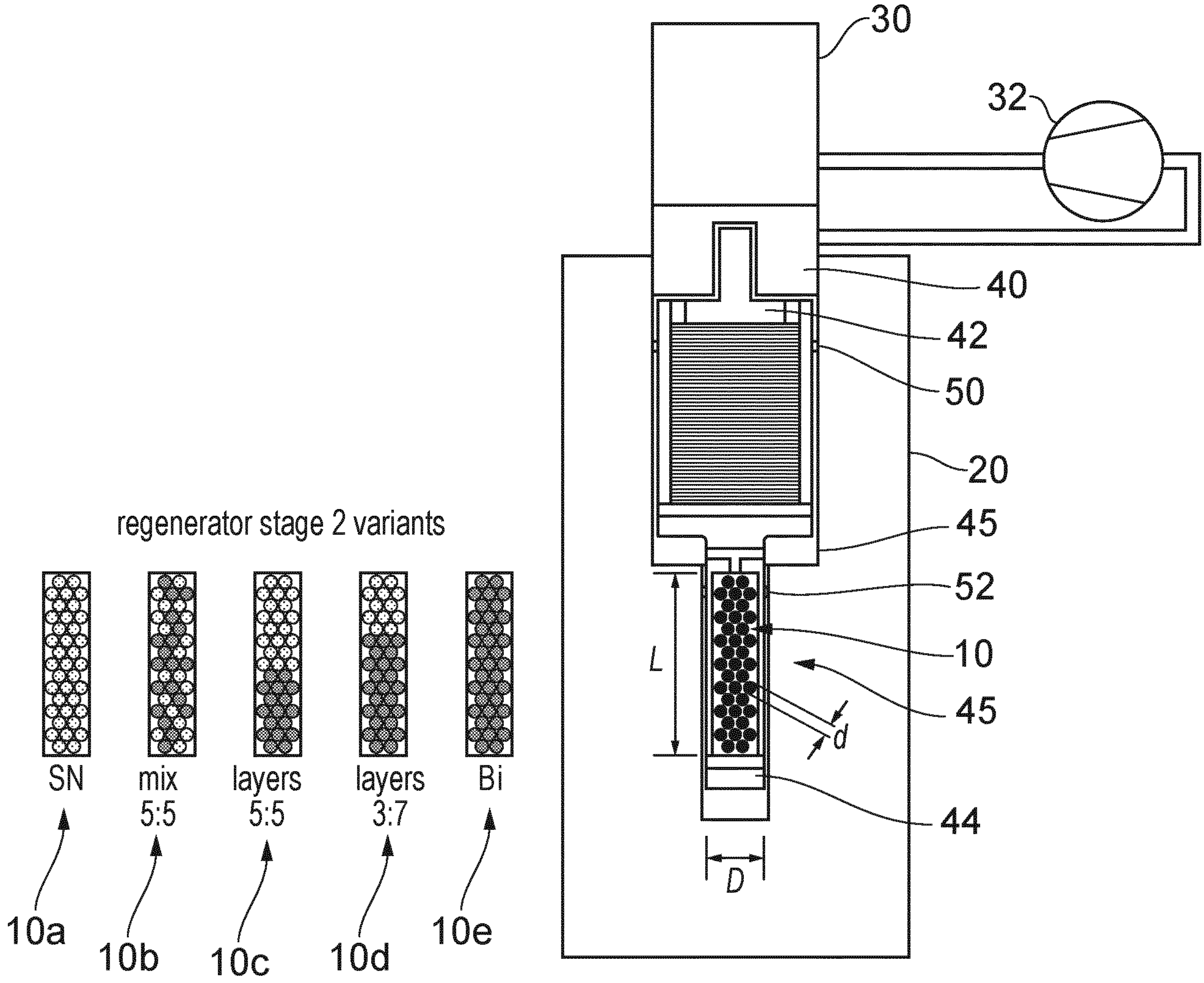
regenerator stage 2 variants
SN
mix 5:5
layers 5:5
layers 3:7
Bi
10a
10b
10c
10d
10e
30
32
40
42
50
20
45
52
10
45
L
d
44
D

FIG. 1

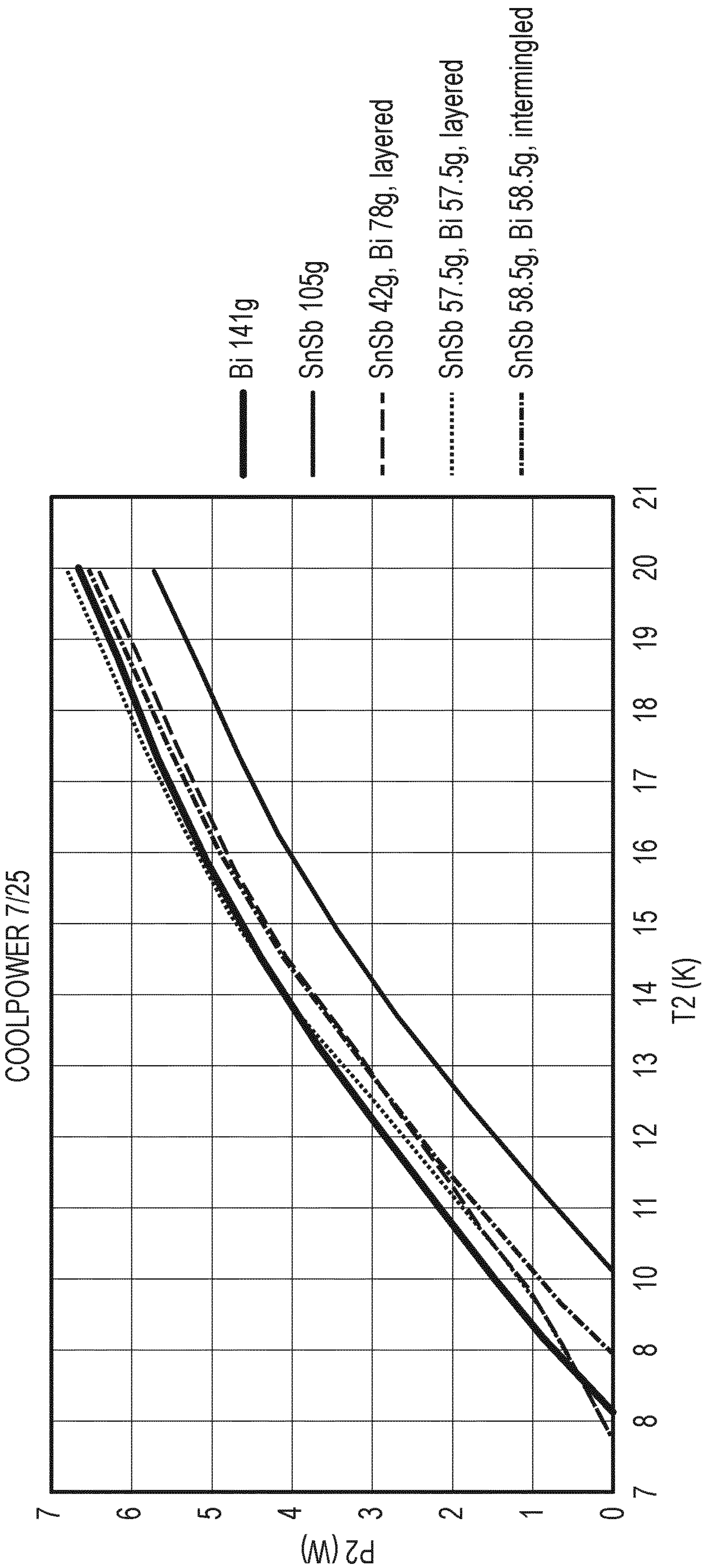
COOLPOWER 7/25
P2 (W)
T2 (K)
Bi 141g
SnSb 105g
SnSb 42g, Bi 78g, layered
SnSb 57.5g, Bi 57.5g, layered
SnSb 58.5g, Bi 58.5g, intermingled

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/057823

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/14 F25B9/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K F25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2011/126553 A1 (BALL-DIFAZIO DOREEN J [US]) 2 June 2011 (2011-06-02) paragraphs [0012], [0042] - [0044]; figures 1,2,10 -----	1-13
Y	WO 2019/232919 A1 (CSIC PRIDE NANJING CRYOGENIC TECH CO LTD [CN]) 12 December 2019 (2019-12-12) paragraphs [0001] - [0018], [0040], [0047]; figures 1-5; table 1 -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 June 2022	04/07/2022

Name and mailing address of the ISA/	Authorized officer
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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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