Questionnaire 3 COCIR Exemption 11 of RoHS Annex IV

Lead in alloys as a superconductor and thermal conductor in MRI

Acronyms and Definitions

TCB thermal conductor bonds

1. Background

Bio Innovation Service, UNITAR and Fraunhofer IZM have been appointed[1] by the European Commission through for the evaluation of applications for the review of requests for new exemptions and the renewal of exemptions currently listed in Annexes III and IV of the RoHS Directive 2011/65/EU.

You submitted information to substantiate your request for the renewal of the above-mentioned exemption. This information was reviewed and as a result, we ask you to kindly answer the below questions for further clarification of your request until 10 June 2021 if possible.

2. Questions

1) You mention in your exemption application that Siemens and Mitsubishi have developed demonstration electromagnets for MRI, although these are relatively small with coils being suitable for small animals such as a mouse only.

   What are these demonstration magnets intended to demonstrate?

   This research is to investigate the use of high temperature superconductors which can potentially be used at liquid nitrogen temperatures and so avoid the need for scarce liquid helium. If these higher temperatures could be used, the superconducting bonds will also be at a higher temperature and so potentially allowing the use of a wider choice of bonding materials. Mitsubishi stated in 2016[2] that they hoped to have a full size version by 2020 or 2021, however commercial full size MRI using high temperature superconductors are not yet available. COCIR also notes that Japan Superconductor Technology in their RoHS exemption request, state that in practice to achive optimum image quality, superconduction coils need to be used at liquid helium temperatures so this may not avoid the need for BiPb superconducting bonds.

2) The slides illustrating the Oxford study by Speller at al. which you reference with participation of Siemens were published[3] in 2015. This is more than five years ago. Speller et al. in particular rate as promising the results for cold pressing with the tinning solution to prevent oxidation of the NbTi filaments.

[1] It is implemented through the specific contract 070201/2020/832829/ENV.B.3 under the Framework contract ENV.B.3/FRA/2019/0017

[2] https://www.mitsubishielectric.com/news/2016/pdf/0524.pdf

[3] C.f. , c.f. https://stfc.ukri.org/search-results/?keywords=speller&page=1&perPage=10&sortBy=_score&sortDirection=desc&selectedYear=2015&

What happened since then as to spot welding and cold pressing technologies and possibly to other approaches to bring them from laboratory research scale closer to practice?

The latest progress reported by Speller's group in Oxford[4] concludes that $B_{c,2}$ may be too low for a 'drop-in' replacement for commercial MRI magnets, it has potential for use in small magnet systems.

Current research seems to be exploring the impacts of microstructure, such as 'The study in the atmospheric oxidation of NbTi superconductor'[5], and 'The effect of the size of NbTi filaments on interfacial reactions and the properties of InSn-based superconducting solder joints'[6]. The latter of which concludes that the property of bulk solder is regarded the limiting factor and not any interfacial reactions. Such developments of understanding are crucial to understanding of potential ways forward, however it shows that the commercialisation of such technologies is still some time off.

Further research work has been commissioned to investigate, at a scientific level, the physical boundary between superconducting materials and whether the superconducting behaviour extends across this boundary, a parameter known as coherence length. It is hoped that this research will allow the development of practical methods of forming superconducting connections, once this fundamental understanding has been developed.

3) You explain that two different cooling systems are used in MRI scanners:

- the immersion of the superconductor in liquid helium
- the thermal connection of the superconductor with a cooling system.

We would like to reference these as immersion cooling and indirect cooling for readability reasons.

a) We conclude from the above, that the thermally conductive bonds are used in indirect cooling only. Is this correct? You might have explained this in the previous questionnaire, but we were not sure that we can correctly interpret your answer.

In immersion cooling, everything is immersed in liquid helium and any heat will be removed by the liquid helium. However, in indirect cooling, the component creating heat is separated from the heat removal component by vacuum. In order to bridge them, thermally conductive bonds are sometimes required.

As such the requirement for thermally conductive bonds is predominantly an issue for indirect cooling systems, however as the operating level of liquid Helium in immersion systems is reduced, the thermal conductivity of components and their connections become more important, since the effect of the liquid cooling must be conducted from the reduced area which receives direct liquid cooling.

b) You said in the previous questionnaire that you will try to provide an outline of the indirect cooling situation. We would still be interested in this to better understand the design of these devices.

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4 https://indico.cern.ch/event/445667/contributions/2563682/attachments/1513660/2361336/TimothyDavies_MT25_Poster.pdf

5 Journal of Alloys and Compounds, V.848, 25 December 2020, T. Davies, C.R.M. Grovenor, S.C. Speller https://www.sciencedirect.com/science/article/abs/pii/S0925838820327092

6 Materials & Design, Volume 176, 2019, S. Santra, T. Davies, G. Matthews, J. Liu, C.R.M. Grovenor, S.C. Speller https://www.sciencedirect.com/science/article/pii/S0264127519302746

On further investigation, COCIR believes that thermal bonds are also covered by exemption 26. To avoid duplications and to speed up the evaluation process, we believe thermal bonds can be removed from exemption 11 wording.

4) From your answers to the previous questionnaire we understand that all thermally conductive bonds at the same time function as electrical conductors, i.e. that none of the lead alloy bonds functions as a thermal conductor only.

   a) Is it correct to turn this around saying that each lead-containing superconducting electrical connection acts as TCB as well in indirect cooling and possibly in immersion cooling?

   b) Could you please explain why electrical currents need to pass through the thermally conductive bonds in indirect cooling? In case immersion cooling requires thermally conductive bonds as well, please include immersion cooling in your explanation as well, keeping the two types of cooling separate.

   c) We asked in the last questionnaire which materials are bonded with the TCBs and you answered that the TCBs mechanically and thermally conntect the superconducting wire entering and exiting the superconducting coils to the electrical circuit of the magnet, and that each MRI manufacturer may use different materials that are most suitable and used. Given this your statement and the that you also said that each TCB has electrical function, and that the TCBs are exposed to high magnetic fields in the range of 0.3 to 7 T and higher:

      Why is it necessary to mention the thermal conductivity in the exemption wording if all of these bonds are superconducting electrical connects?

Please refer to the answer for Question 4.

5) You indicate the H_C of PbBi-solder with 1.77 T at 4.2 K. The above indicated operational range of 0.3 to more than 7 T to which TCBs are exposed exceeds the critical magnetic field strength considerably and would result in the loss of superconductivity.
Could you please explain how the TCBs are still superconductive above 1.77 T in this situation, or is superconductivity not required?

MRI manufacturers are aware that H_c of PbBi solder is lower than the quoted field strength values of some MRI. However, this is possible because the advertised field strength values, such as 3T or 7T are the field strength inside the bore of the magnet and in which the patient is located. The magnet is designed so that the solder bonds are at locations where the field strength is less than H_c to ensure that the bonds are superconducting. There is only limited flexibility with choosing the location of these bonds so that they are below H_c and it is not technically possible to locate these bonds at locations with much lower field strength values. TCBs may be used at field strengths of more than H_c if these are used for heat transfer and electrical signals but do not need to be superconducting.

6) You answered question 3 of the previous questionnaire.

   a) The critical field you indicate for PbBi (3.5 T) considerably deviates from the 1.7 T at 4.2 K which you indicate in table 1 of your exemption request. Could you please explain the difference?

      The two values are from two different publications. The difference in measured values is likely to be due to the measurement method used (e.g. design of equipment), measurement conditions and alloy composition, especially the presence of impurities. COCIR is not able to determine from the publications why these values are not the same, but both are much higher than published values obtained with lead-free solders.

b) You provided material parameters for SnInBi. We ask you to kindly provide these parameters for the second ternary alloy (BiSnIn) mentioned in your exemption request as well. Please make sure that the values are comparable, e.g. that critical field, current etc. are related to the same temperature (4.2 K).

We indicated in our exemption request that two alloys had been considered, which were SnInBi and SnInSb. There are not two different alloys containing Sn, In and bismuth. Equivalent parameters for SnInSb are not published, so we are not able to provide this data. However, a recent review, published in 2020, on superconducting solders indicates that addition of antimony (Sb) to Sn-In alloys is detrimental to its superconducting properties[7].

7) You state that MRI usually uses NbTi but NbSn may also be used. NbSn may be used at higher magnetic fields than NbTi, but NbTi is easier to process so is more common in commercial MRI.
Do the issues you report with bonding to superconducting materials apply to NbSn-superconductors as well, or are there differences in terms of manufacturability, consistency and reliability of lead-free solutions?

There has been research carried out mainly with NbTi as this is the most commonly used MRI superconductor. However, the technical difficulties with bonding to NbTi and NbSn are mainly due to the very inert nature of niobium oxide that readily forms on the surface of niobium alloys. Therefore, the issues found with NbTi are likely to be the same with NbSn.

8) In the answer to question 4 of the previous questionnaire you point out that there are no "lower limits", and that higher H_c is always better since image quality increases with the field strength. Since MRI scanners are built for a specific field strength (1 T MRI, 5 T MRI, etc.) not each MRI scanner may require the highest H_c. As long as the critical field is not exceeded, the image quality should be identical at a given field strength even if bonding materials with lower Hc are used in low-T MRI scanners. Since lower field strengths require lower currents, this should apply to the critical current density as well.

a) In the light of the above, why can MRI scanners with lower field strengths not use lead-free bonding materials?

Commercial MRI are designed to give the best image quality that is achievable and currently, most MRI are 1.5, 3 or 7T. A few special designs have slightly lower field strength and one MRI with 0.55T is available. An MRI with a smaller field strength cannot give the same image quality as a higher power magnet, so lower power MRI are limited in the diagnostic procedures that they can be used for.

There is also a corelation between the size of the equipment and field strength (see below images as a basis of comparison), with the practicability of positioning the bonds far enough away from the bore in low Tesla MRIs posing significant limitations.

[7] https://iopscience.iop.org/article/10.1088/1757-899X/957/1/012059/pdf

 

Even with a 0.55T magnet, the solder bonds will be inside a powerful magnetic field and so to ensure sufficient reliability, PbBi must be used. If superconductivity of the bonds were to be lost (e.g. if H_c were to be exceeded), the high current used for MRI (many hundreds of amps) will generate a lot of heat, causing the loss of liquid helium, and resulting in the MRI not being able to be used for long periods, as well as fires being a possibility.

b) Was pure lead used – or possibly is still used - in MRI scanners with lower field strengths?

COCIR is not aware that pure lead is currently used in MRI scanners.

Please note that answers to these questions may be published as part of the review of this request. If your answers contain confidential information, please provide a version that can be made public along with a confidential version, in which proprietary information is clearly marked.

It would be help the review process if you could kindly provide the information in formats that allow copying text, figures and tables to be included into the review report.