Thallium 2223 High Tc Superconductor in a silver matrix and its magnetic shielding, thermal cycle and time aging properties

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ABSTRACT

Superconducting Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_{10}$ (Tl2223) was ground to powder. Mixture with silver powder (0--80% weight) and press to desired shape. After proper annealing, one can get good silver-content Tl2223 bulk superconductor. It is time-stable and has good superconducting property as same as pure Tl2223. It also has better mechanical property and far better thermal cycle property than pure Tl2223.

I. INTRODUCTION

From practical view, one hope bulk superconductor has good superconducting property, good mechanical property, time-stable, and good thermal cycle property (one cycle means rapidly temperature change 25°C --> liquid nitrogen --> 25°C).

Unfortunately, pure Tl2223 does not have all above mention properties. It has good superconducting property and it is time stable. But, its mechanical property is not good. It is not easy to form it. Its thermal cycle property is bad. After a few thermal cycle, it loses transport superconductivity.

For practical application, need to improve its mechanical property and thermal cycle property.

Tl2223 superconductor in silver matrix can give better mechanical property and far better thermal cycle property than pure Tl2223 and still give good superconducting property.

We have made some high Tc superconducting shielding devices using this kind of material two years ago. By thermal cycle test and time aging test, we can say Tl2223 with 10%--80% weight silver is good superconducting engineering material.

II. SAMPLE PREPARATION
Synthesizing Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ raw superconducting material

Tl$_2$O$_3$ (>99%), BaO$_2$ or BaO (>95%), CaO (>99%), and CuO (>99%) with the molar ratio of cations of 2:2:2:3 are mixed and ground in an agate mortar. Then the ground powder is pelletized in a die with a hydraulic press at an applied pressure of about 7000 kg/cm$^2$. The pellets are then placed in a tubular alumina crucible and covered with an alumina plug. The crucible with contents is placed in a tube furnace; The power turned on and the temperature of the furnace raised to about 895$^\circ$C at an ascending rate of 20 degrees per minute. The samples are heated at 895$^\circ$C for 50 hours and then cooled within the furnace at a descending rate of 1 degree per minute to 600$^\circ$C. Finally the furnace is turned off and the samples cooled to room temperature within the furnace. Oxygen is flowing in the furnace during sintering.

Fabrication of Ag-content Tl2223 superconducting cylinder

The pellet of raw superconducting Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ is then broken and pulverized to a particle size of 1-5 microns. The ground powder is then mixed uniformly with silver powder (99.9% purity, 0.7-1.3 microns particle size) with the weight percentages of Ag:0, 10, 20, 40, 60, 80, 100. The mixed powders are then pressed into cylinders which are then annealed in a tube furnace. Oxygen is flowing in the furnace tube during the annealing. The temperature of the furnace is raised from room temperature to 790-820$^\circ$C at a rate of 0.5 - 1 degree per minute and then maintained at this temperature for 30 hours. The furnace temperature is then reduced at a rate of 1-2 degrees per minute to 200$^\circ$C, at which point the cylinders are then removed from the furnace.

About two years ago (May--July, 92), we made several Tl2223 cylinder with 10%, 20%, 40%, 60% weight silver. A few months later, we made cylinder with 0%, 80%, 100% silver for comparison.

Sample dimensions and weights as following:

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>#7</th>
</tr>
</thead>
<tbody>
<tr>
<td>SILVER CONTENT (%)</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>INNER DIAMETER (mm)</td>
<td>14.7</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>OUTER DIAMETER (mm)</td>
<td>24.5</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>23.0</td>
<td>25.0</td>
</tr>
<tr>
<td>HEIGHT (mm)</td>
<td>68.0</td>
<td>30.0</td>
<td>25.0</td>
<td>22.0</td>
<td>20.0</td>
<td>25.0</td>
<td>26.0</td>
</tr>
<tr>
<td>WEIGHT (g)</td>
<td>112</td>
<td>60</td>
<td>60</td>
<td>59</td>
<td>60</td>
<td>79</td>
<td>79</td>
</tr>
</tbody>
</table>
III. TEST

We use Fig.1 measurement system to measure magnetic shielding attenuation of cylinder samples.

Then all samples underwent thermal cycle. After every 20 cycles, measure shielding attenuation again. As the first batch of test, total 61 thermal cycles were done.

Each thermal cycle is following: Rapidly immerse sample in liquid nitrogen for about 5 minutes, take out and put in open air. So, a lot of frost first and then water condense on surface of sample. When sample reaches room temperature again and dry, immerse it in liquid nitrogen again. As you see, the thermal cycle is very harsh test.

After all samples were in open air for more than one and a half year, all underwent another 50 thermal cycles, then measure shielding attenuation again.

Then, another 50 cycles thermal cycles. Now, this test is continuing.

IV. RESULT AND DISCUSSION

All test results are shown in fig. 2 - 9. At beginning, all samples are good. Magnetic shielding attenuations are 70-90 db at f=60 Hz.

After 20 thermal cycles, pure T12223 (no Ag) sample lost its magnetic shielding property. All silver-content samples are still good.

The first batch of thermal cycle test is 60 cycles. All silver-content samples are still good after 61 cycles.

In fact, when superconductor is rapidly colding and warming, it rapidly expands and contracts. For pure T12223, all grains are hard ceramic. So, contacts between grains are hard to hard. When expansion and contraction, hard to hard contact produces very high stress and it causes many microcracks inside. After several thermal cycles, there are so many microcracks inside that all transport paths are cut off. So, there is no screen current and lost magnetic shielding property.

When add silver into pure superconductor, silver locates between superconducting grains. So, many contacts between grains are soft. Less microcracks are produced during thermal cycles. So, Ag-content superconductor has good thermal cycle property.

According to above analysis, low Ag-content sample produces more microcracks than high Ag-content sample during one thermal cycle. So, if we continue to do thermal cycle test more and more, low Ag-content sample will loss its shielding property more early than high Ag-content sample. Test result proved it.

After all samples were in open air for 1 1/2 years, we did thermal cycle test again. The second batch of test is 50 thermal cycles. After 50 cycles, measure shielding attenuation again. Test results are:

a. 10% Ag sample was dead, lost its shielding property.

b. Other high Ag-content samples with Ag-content more than 10% are still good.

The results agree with above analysis. The results also mean that Ag-content T12223 superconductor is time stable.
V. INCREASE MAGNETIC SHIELDING EFFECT

The all Ag-content samples of the first batch are very short. They have low length diameter rate (L/d see Fig. 10).

\[ H = 2L \]

\( d \)-inner dia.

All L/d are = 1 - 1.5

For more high magnetic shielding attenuation, need to increase critical current density \( J_c \) of superconductor, L/d value and more thick of wall.

We have fabricated more longer cylinder:

- 10% Ag + 90% Ti2223, ID=9.7mm, OD=19.1mm, L=89mm;
- 20% Ag + 80% Ti2223, ID=9.8mm, OD=19.0mm, L=88mm.

The first one reached 132 db attenuation;

The second one reached 126 db attenuation.

The effect of increasing length is shown in Fig. 11.

Inside field dependence of applied field is shown in Fig. 12.

VI. CONCLUSION

Ag-content Ti2223 is a good superconducting engineering material. It is time-stable and good superconducting property as same as pure Ti2223. It has better mechnical property and far better thermal cycle property than pure Ti2223.

References

1. J. Wang and M. Sayer, "Low frequency magnetic shielding of YBa\(_2\)Cu\(_3\)O\(_7\) : Ag\(_x\) high temperature superconductors," Cryogenics 1993 Vol 33, No 12


Fig. 1. Measurement System Diagram
Thallium 2223 + 0% Silver
1.0 G applied field

![Graph](image)

Fig. 2. Magnetic field attenuation as a function of frequency for Thallium 2223 tube with 0% added silver. The magnetic field was applied parallel to the tube axis. The graphs show measurements made during the 1st, 21st, 41st and 61st cycles between room temperature and 77.3 K.

Thallium 2223 + 10% Silver
1.0 G applied field

![Graph](image)

Fig. 3. Magnetic field attenuation as a function of frequency for Thallium 2223 tube with 10% added silver by weight. The magnetic field was applied parallel to the tube axis. The graphs show measurements made during the 1st, 21st, 41st and 61st cycles between room temperature and 77.3 K.
Thallium 2223 + 20% Silver
1.0 G applied field

Fig. 4. Magnetic field attenuation as a function of frequency for Thallium 2223 tube with 20% added silver by weight. The magnetic field was applied parallel to the tube axis. The graphs show measurements made during the 1st, 21st, 41st and 61st cycles between room temperature and 77.3 K.

Thallium 2223 + 40% Silver
1.0 G applied field

Fig. 5. Magnetic field attenuation as a function of frequency for Thallium 2223 tube with 40% added silver by weight. The magnetic field was applied parallel to the tube axis. The graphs show measurements made during the 1st, 21st, 41st and 61st cycles between room temperature and 77.3 K.
Fig. 6. Magnetic field attenuation as a function of frequency for Thallium 2223 tube with 60% added silver by weight. The magnetic field was applied parallel to the tube axis. The graphs show measurements made during the 1st, 21st, 41st and 61st cycles between room temperature and 77.3 K.

Fig. 7. Magnetic field attenuation as a function of frequency for Thallium 2223 tube with 80% added silver by weight. The magnetic field was applied parallel to the tube axis. The graphs show measurements made during the 1st, 21st, 41st and 61st cycles between room temperature and 77.3 K.
Fig. 8. Magnetic field attenuation as a function of frequency for a pure silver tube. The magnetic field was applied parallel to the tube axis. The graphs show measurements made at room temperature and 77.3 K.

Fig. 9. Results of test after 1 1/2 year in open air, another 50 thermal cycles, and total 111 thermal cycles. 10% Ag sample is dead and others are OK.
At 20 G of DC Field

At DC Field

Figure 11

Figure 12

(A) Critical field measurement