Induction Skull Melting of $\text{Y}_2\text{O}_3$-BaO-CuO in a Cold Crucible

T. Behrens, M. Kudryash, B. Nacke, D. Lopukh, A. Martynov, I. Loginov

Abstract

A new multi-functional melting installation will be put into operation soon at the Institute for Electrothermal Processes (ETP), University of Hannover, Germany. It will be used for high temperature induction melting of low conductive materials like oxides, ceramics and glasses utilizing induction skull melting technique. In cooperation with St. Petersburg Electrotechnical University (ETU), Russia, an appropriate material for first tests at ETP has been chosen to melt in a cold crucible, namely superconductor $\text{Y}_2\text{O}_3$ - BaO - CuO (YBCO). In view of the electrical data of the new furnace experimental tests with YBCO have been carried out at ETU. The choice of YBCO and the characteristics of the melting process are shown in the paper as well as the design of the cold crucible and of the inductor will be used at ETP. Numerical calculations concerning the starting process are presented, too.

Introduction

The induction skull melting technique (ISMT) is an excellent method to melt low conductive materials like ceramics, glasses and oxides. The high purity melt products are used as high-tech materials like optical glasses, synthetic gems and semi- as well as superconductors. A superconductor is an element, inter-metallic alloy or compound that conducts electricity without resistance below a certain temperature. Resistance is undesirable because it produces heat losses in the material. Superconductors are differently applied, for example, as current limiters, hysteresis and synchronous engines, bulk magnets and superconducting current leads.

YBCO is a high temperature superconducting ceramic usually produced by sintering technologies. It can be prepared in the solid state reaction of $\text{Y}_2\text{O}_3$, BaCO$_3$ and CuO in an oxygen rich environment. This reaction takes place at high temperatures (above 900 °C). Other methods like ISMT improve purity and productivity.

1. Multi-Functional Installation at ETP

A new melting furnace, unique by its design and size, is shortly before start-up at ETP. The installation works with ISMT which is especially suitable for high temperature induction melting of low conductive materials like oxides, ceramics and glasses. Such high melting temperatures up to over 3000 °C and chemically aggressive melts constitute enormous conditions unsuited for other conventional melting processes [1].

The induction melting process takes place in a vacuum chamber, as shown in Fig. 1, in different atmospheres such as air and inert gases or in vacuum. With the help of a charger further initial material or other materials can be added to the melt during the melting process. After liquefying the initial material the melt can be poured by turning the melting unit consisting of either a cold crucible or an inductor crucible (one-turn inductor) [2]. A lowering
The system makes possible directional solidification of the melt which is especially important for growing of big oxide crystals.

The power supply is a high frequency generator using transistors with an output power of about 300 kW and output voltage of about 460 V. With the aid of the compensation unit the frequency is variable in a range from 80 to 350 kHz. The series connection of capacitors and the use of an additional high frequency transformer allow a doubled or even quadrupeled converter voltage at the inductor.

2. Choice of Material for Melting in a Cold Crucible

2.1. Possibilities of Variation of Oxidic Materials

Because of the big range of electrical parameters a multitude of oxidic materials can be melted in the new melting installation. Different oxides and oxide systems have been investigated in order to find an appropriate material for the start-up tests in the new installation. A comparatively small cold crucible with an inner diameter of up to 200 mm is to be used for first experiments. Following materials are well suitable in order to be melted in a small crucible:

- glasses with melting temperatures between 1000 °C and 1700 °C and resistivities less than 2,5 - 3,5 Ω⋅cm, for example, phosphate glass (1000 °C), borosilicate glass (1300 °C) and silicate glass (1700 °C)
- monocrystal growth of ZrO₂ - Y₂O₃
- two-, three- and multicomponent oxide systems of crystalline and glass materials with a melting point of 1200 - 1600 °C and an electrical resistivity less than 1,0 - 1,5 Ω⋅cm, for instance, oxide mixtures of CaO, MgO, BaO, Al₂O₃, ZrO₂, SiO₂, Nb₂O₅, Na₂O, Li₂O, K₂O, FeOₓ, SrO, Y₂O₃ and others
- oxide system of ZrO₂₋ₓ - FeOₓ, for example,
  - the system ZrO₂ - Fe₂O₃ melted in air
  - the system ZrO₂ - FeO melted in inert gases
  - the system ZrO₂₋ₓ - FeO melted in vacuum
- high temperature ceramic superconductors (HTCS), for example, Y₂O₃ - BaO - CuO (YBCO).

2.2. Choice of a Material for First Tests at ETP

YBCO mentioned above has been chosen for first experiments in the new installation. Thereby, following characteristics have been taken into account: The melting point or liquidus temperature of the material should be low. A low temperature of the melt causes low heat losses from the melt pool to the environment, which makes possible to supervise the working of the installation with small values of power and simplifies the maintenance of the induction skull melting process of oxidic materials. Additionally, a low
electrical resistivity makes possible to carry out successful melting tests over the full frequency range provided by the power supply. While the melting process an intensive oxygen exchange between the melt and the air should be avoided in order to stabilize the chemical composition of the melt and its resistivity. Some characteristics of oxidic materials and of the melting process in that small crucible are shown in Tab.1. It results on the base of the geometric data of the crucible described in the following chapter.

Tab. 1. Characteristics of oxidic materials and of the melting process in a small crucible

<table>
<thead>
<tr>
<th>Material</th>
<th>Spec. heat flow (wall), W/cm²</th>
<th>Power (melt), kW</th>
<th>Temp., K</th>
<th>ε</th>
<th>Radiation losses, kW</th>
<th>Resistivity, Ω⋅cm</th>
<th>η</th>
<th>cosϕ</th>
<th>Power (ind.), kW</th>
<th>Voltage (ind.), kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>110</td>
<td>110</td>
<td>2573*</td>
<td>0,55</td>
<td>28</td>
<td>2,0</td>
<td>0,47</td>
<td>0,03</td>
<td>294</td>
<td>2,07</td>
</tr>
<tr>
<td>ZrO₂ - Y₂O₃</td>
<td>90</td>
<td>41</td>
<td>2000**</td>
<td>0,8</td>
<td>16</td>
<td>0,01</td>
<td>0,69</td>
<td>0,082</td>
<td>82,6</td>
<td>0,86</td>
</tr>
<tr>
<td>ZrSiO₄</td>
<td>90</td>
<td>41</td>
<td>2000**</td>
<td>0,61</td>
<td>12</td>
<td>4,3</td>
<td>0,3</td>
<td>0,025</td>
<td>176,7</td>
<td>2,95</td>
</tr>
<tr>
<td>Glass</td>
<td>35</td>
<td>17</td>
<td>1773*</td>
<td>0,5</td>
<td>6</td>
<td>1,0</td>
<td>0,67</td>
<td>0,042</td>
<td>34,3</td>
<td>0,87</td>
</tr>
<tr>
<td>Y₂O₃ - BaO - CuO</td>
<td>7</td>
<td>11,2</td>
<td>1533**</td>
<td>0,65</td>
<td>--</td>
<td>0,11</td>
<td>0,68</td>
<td>0,095</td>
<td>0,98</td>
<td>0,107</td>
</tr>
</tbody>
</table>

*- melt surface temperature  
**- crust temperature

First tests will be carried out with a composition of 5,62 Y₂O₃ - 45,13 BaO - 49,25 CuO wt. %. In this case the resistivity is low and the liquidus temperature is about 1200 °C. The induction skull melting technique guarantees obtaining recommended oxidic material of required purity and needed composition with many times higher productivity than with using solid-phase sintering technology.

Ceramic materials like Y₂O₃ - BaO - CuO are especially interesting during their transition to superconducting state at temperatures above the boiling point of liquid nitrogen. For example, the ceramic material 5,62 Y₂O₃ - 45,13 BaO - 49,25, obtained by liquid-phase synthesis in an induction furnace with a cold crucible and heat-treated in a resistance furnace afterwards, has got the temperature of transition to superconducting state equal to 94,2 K.

3. Design of the small Cold Crucible and of the Inductor

3.1. Small Cold Crucible

Fig. 2 shows the small cold crucible will be used for first experiments in the ETPs new installation. The crucible is made of 20 sections each of two water-cooled copper tubes. The inner diameter of the crucible is 160 mm. The air gaps between the tubes are smaller than 1 mm. The sections and the water collector are screwed with a non-conductive heat-resistant disc located between them. The upper part of the cold crucible is held together by a ring made of the same material as the disc. The bottom of the crucible is slitted several times to avoid eddy currents and must be cooled, too.
3.2. Inductor

The single-turn inductor forms a hollow cylinder with a height of 110 mm and an inner diameter of 220 mm. It is soldered to flat buses becoming gradually bigger up to 220 mm at the feeder connection. The whole construction is made of copper sheets of 3 mm thickness. The length of the buses is about 500 mm because the axis of the inductor and the axis of the lowering system have to agree.

To avoid electrical breakdowns between the inductor buses they are separated by a Teflon sheet of 1 mm thickness. The Teflon sheet should be fixed between the inductor buses.

In the stage of starting heating when the inductor voltage is maximum electrical losses in the inductor can reach 35 kW. The construction is provided with two parallel rectangular tubes made of copper for the purpose of cooling. The water pressure will be about 6 bar. The tubes are soldered to the inductor turn and to the buses on the full length. For soldering copper solder was used because of the high heat conduction.

Water supply for cooling of the inductor is given through the generator feeder. The seal between the feeder and the inductor flanges is provided by means of ring gaskets placed in special grooves.

4. Preliminary Investigations of YBCO

4.1. Melting Tests of YBCO at ETU in St. Petersburg

For reaching the similar melting conditions provided with the ETP installation following specially developed equipment was used for the ETU installation: The power supply is given by a vacuum tube generator working with a range of current frequency of 80 - 90 kHz, of output power of 0 - 60 kW and of inductor voltage of 0 - 4 kV. The ten-turn inductor used for the test shows an inner diameter of 210 mm and an outer diameter of 230 mm. The height is 118 mm. The cold crucible with an inner diameter of 160 mm is constructed by copper tubes with a diameter of 10 mm and a height of 250 mm. Therefore, the inner diameter of the crucible equals to the inner diameter of the small crucible is to be used in the ETP installation. The current frequency is equal to the minimum frequency value of the ETP installation.

For melting of 13,741 kg YBCO a mixture of Y₂O₃-, BaCO₃- and CuO-powders was prepared in such proportion so that after giving off carbon dioxide from the melt the calculated composition of the melt would be equal to 5,62 Y₂O₃ - 45,13 BaO - 49,25 CuO. A part of the powder mixture was put into the crucible. Then a graphite disk with a diameter equal to 60 mm and a height equal to 30 mm used as starting material was placed onto the powder surface. After forming the melt pool when it was able to heat itself by eddy currents the graphite disk was taken out of the melt. The left part of the powder mixture was gradually added into the crucible and thus the final melt pool was formed as shown in Fig. 3. Two temperature states of the melt pool were considered to find electrical parameters for a stable melting process and to estimate the value of the melt resistivity. Characteristics of some stages of the melting process in the small crucible are presented in Tab. 2.
Tab. 2. Characteristics of some stages of the melting process

<table>
<thead>
<tr>
<th>Temp. (melt), °C</th>
<th>Frequency (inductor*), Hz</th>
<th>Voltage (inductor), V</th>
<th>Electrical losses (inductor), W</th>
<th>Sum of heat losses (melt) and electr. losses (ind.), W</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>81600</td>
<td>1939</td>
<td>---</td>
<td>---</td>
<td>Starting heating</td>
</tr>
<tr>
<td>1200</td>
<td>81900</td>
<td>1016</td>
<td>903</td>
<td>9974</td>
<td>1st melting stage</td>
</tr>
<tr>
<td>1260</td>
<td>81900</td>
<td>1070</td>
<td>989</td>
<td>11235</td>
<td>2nd melting stage</td>
</tr>
</tbody>
</table>

* 10 turns

4.2. Numerical Simulation of the Starting Process

The method with graphite ring has been chosen to start the melting process. The graphite ring is heated up by electromagnetic field of the induction coil. In that starting time, the necessary voltage of power supply is used to heat the graphite ring up to the temperature of 1400 °C. It is assumed that 25% of the power, induced in the graphite ring, are spent in order to melt the powder and the other 75% are the power losses by radiation. It is also assumed that the power density $p_0 = 7$ W/cm² and temperature of the melt $T_{melt} = 1300$ °C are constant. This value of power density in the melt was obtained for $Y_2O_3 - BaO - CuO$ by the experiment made at ETU. Fig. 4 shows how the shape of the melt bath is developed in time. It is assumed that the position of the melt surface inside the inductor remains constant. The starting period is finished when the system does not react anymore on the existing of the graphite ring in the crucible. It is usually checked by removing the ring from the area of the inductor.

Parameters of the oxide system $Y_2O_3 - BaO - CuO$ at different steps of the starting process with a frequency of 95 kHz is listed in Tab. 3.

Tab. 3. Characteristics of two states during the starting process (frequency is 95 kHz)

<table>
<thead>
<tr>
<th>State</th>
<th>Temp. (melt), °C</th>
<th>Height (melt), cm</th>
<th>Voltage (ind.), V</th>
<th>Power (ind.), kW</th>
<th>Current (gen.), A</th>
<th>Current (ind.), kA</th>
<th>Power (melt), kW</th>
<th>Electr. losses (ind.), kW</th>
<th>Electr. losses (crucible), kW</th>
<th>Power (ring), kW</th>
<th>Power (bottom), W</th>
<th>cos $\phi$ (ind.)</th>
<th>$\eta$ (ind.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1400*</td>
<td>192</td>
<td>10,3</td>
<td>50,7</td>
<td>1,83</td>
<td>0,0</td>
<td>1,72</td>
<td>4,2</td>
<td>4,32</td>
<td>66,5</td>
<td>0,028</td>
<td>0,42</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>1300</td>
<td>117</td>
<td>14,9</td>
<td>115,9</td>
<td>1,10</td>
<td>12,8</td>
<td>0,63</td>
<td>1,5</td>
<td>---</td>
<td>24,3</td>
<td>0,105</td>
<td>0,86</td>
<td></td>
</tr>
</tbody>
</table>

* -- temperature of the graphite ring
The results of the numerical calculation show that the maximum voltage at the inductor does not exceed 192 V. Therefore, it is possible to melt YBCO at a frequency of 95 kHz. In this case the maximum power at the inductor will be 12.8 kW. The comparison of numerical and experimental results shows that values of the voltage and power in the melt are very close to each other at the first and the last stages of the starting heating, demonstrated in Tab. 4, in spite of some differences in frequency and temperature of the melt. It allows to use the constant value of the power density in the melt for investigation of starting heating in the furnaces with cold crucible.

Tab. 4. Comparison of numerical and experimental results

<table>
<thead>
<tr>
<th>Stage of starting heating</th>
<th>Inductor voltage (one turn), V</th>
<th>Power in melt, kW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Numerical *</td>
<td>Experimental **</td>
</tr>
<tr>
<td></td>
<td>Numerical *</td>
<td>Experimental **</td>
</tr>
<tr>
<td>first</td>
<td>192</td>
<td>193.9</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>last</td>
<td>117</td>
<td>107.0</td>
</tr>
<tr>
<td></td>
<td>12.8</td>
<td>11.2</td>
</tr>
</tbody>
</table>

* - Frequency 95 kHz, temperature of the melt 1300 °C.
** - Frequency 81.9 kHz, temperature of the melt 1260 °C

Investigations of the electromagnetic system described above were carried out on the basis of numerical calculations using the mathematical models developed in St. Petersburg Electrotechnological University [3, 4].

Conclusions

Experiments and numerical calculations have shown that first melting tests in the new melting furnace at ETP should be carried out with the high temperature superconducting ceramic Y_{2}O_{3} - BaO - CuO in a cold crucible. The low resistivity and low melting temperature of that material result in small voltages and heat losses and, therefore, allow an easy supervision of the melting process. The method with a graphite ring has been chosen to start the melting process.

References


Authors

Dipl.-Ing. Behrens, Torge
Dipl.-Ing. Kudryash, Maxim
Prof. Dr.-Ing. Nacke, Bernard
Institute for Electrothermal Processes
University of Hannover
Wilhelm-Busch-Str. 4
D-30167 Hannover, Germany
E-mail: ewh@ewh.uni-hannover.de

Dr.-Ing. Lopukh, Dmitry
Dipl.-Ing. Martynov, Alexander
Dipl.-Ing. Loginov, Ilya
Department of Electrotechnology
St. Petersburg Electrotechnical University
Prof. Popova str. 5
197376 St. Petersburg, Russia
E-mail: dblopuh@mail.eltech.ru