FACILITY FOR SYNTHESIZING AND ANNEALING SUPERCONDUCTING OXIDES IN A HIGH-PRESSURE OXYGEN ATMOSPHERE

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A facility for synthesizing and annealing of high-temperature superconductors in pure oxygen at pressures up to 3 kbar is described. The temperature in the cell and oxygen pressure are tuned independently. The cell can be manufactured either from metal (steel, stainless steel, nickel) or ceramic (Al₂O₃ or BeO). Its working volume is 7 mm in diameter and 10 mm long. Investigations of the oxygen doping of La₃CuO₄₋ₓ single crystals are discussed.

INTRODUCTION

Oxide superconductors are processed in an oxygen atmosphere at a high pressure in facilities producing a pressure of up to 200 atm and a temperature of up to 1000 °C [1].

The sample in such facilities is placed in a pressurized tubular cell with thick walls fabricated from very strong alloys used in aviation (for example, turbine vane alloys). Oxygen is directly fed into the cell from a high-pressure bottle at 150 atm, so an oxygen compressor is not needed. In addition to the obvious upper limit on pressure, these cells have many other flaws, namely, the inside temperature cannot much exceed 1000 °C, the materials technology is sophisticated and hence they are very expensive, and samples are contaminated with the metals from which the cell is made.

In order to generate an oxygen pressure over 200 atm at a high temperature in the laboratory, a more sophisticated facility is required. It must include an oxygen compressor, and the ambient pressure around the cell should be equal to the inside pressure, the outside chamber should be cooled, and the heater should be placed in the outside chamber, i.e., in the ambient gas. Since the best environment for a heater is a noble gas, the facility should also include a compressor for the noble gas. In such a facility the temperature can be raised up to 2000 °C without any risk of contaminating the sample because the cell can be fabricated from a high-melt ceramic (such as Al₂O₃ or BeO). A similar facility [2] has produced a pressure of up to 3 kbar at a temperature of up to 1700 °C. The first YBa₂Cu₄O₈ superconducting single crystals were produced under these conditions [3].

An intermediate version is also feasible. For example [4], a ceramic YBa₂Cu₄O₈ sample can be fabricated in a one-chamber device with an inside heater, the open cell with the sample and heater can be kept in an atmosphere of 80% of Ar + 20% of O₂ at a pressure of 1 kbar and a temperature of 1000 °C. It is evident that the processing cycle's total duration in such facilities is approximately equal to that in a two-chamber one, but the gas purity is sacrificed, and the heater in such an atmosphere has a shorter service life.

The aim of this project was to build a general purpose facility to process HTSC samples in the long-term in an atmosphere of pure oxygen for the widest possible range of pressure and temperature.

STRUCTURE OF THE FACILITY

The facility consists of two chambers (Fig. 1). Argon is compressed in a two-stage compressor 1. The first stage is a thermal compressor 2, which is a steel chamber with a volume of ~ 5 liters placed in a Dewar vessel with liquid nitrogen and has an external heater. The upper pressure in the first stage is 600 bar. Argon from this stage is fed under a multiplier 4 piston where it is compressed by a 60-ton PG-60 hydraulic press. The argon from the multiplier is fed via a
Fig. 1. Diagram of the facility: I) argon compressor; II) oxygen compressor; 1) argon pressurized bottle ($P < 150$ bar); 2) argon thermal compressor ($P < 500$ bar); 3) pressure gauge ($P < 1000$ bar); 4) multiplier; 5) pressure gauge ($P < 5000$ bar); 6) pressure gauge ($P < 600$ bar); 7) manganin pressure transducer; 8) pressure difference controller; 9) oxygen pressurized bottle ($P < 150$ bar); 10) pressure gauge ($P < 400$ bar); 11) oxygen thermal compressor ($P < 3500$ bar); 12) pressure gauge ($P < 5000$ bar); 13) cell; 14) graphite heater; 15) high-pressure chamber.

Fig. 2. Oxygen thermal compressor: 1) high-pressure chamber; 2) obturator; 3) oxygen channel; 4) heater; 5) oxygen volume.

high-pressure relief valve into a high-pressure chamber 15. The valve opens when the pressure inside the multiplier is higher than in the chamber. The upper pressure at the second-stage output is 5 kbar.

The pressure is measured by the calibrated spring gauges 5 and 6. A pressure transducer 7, (a coil of manganin wire mounted strain-free inside a high-pressure chamber with a volume of $<1$ cm$^3$) is used to record the argon pressure and to control the oxygen-argon pressure difference. The coil resistance is measured using the four-terminal scheme.

The main oxygen pressurizer II is built around a one-stage thermal compressor 11. Oxygen, which is fed from a bottle 9 under a pressure of $\leq 150$ bar, is condensed in a thermal compressor chamber with a volume of $\sim 350$ cm$^3$ immersed in a Dewar vessel of liquid nitrogen. The pressure is built up by heating the chamber using a 5-kW inside heater energized through a VRT-3 thyristor switch. Calculations of the structure strength indicate that the temperature inside the compressor should not be higher than room temperature, and a coil of nickel wire can operate as a heater under these conditions.

The maximum available pressure of $\sim 5$ kbar was calculated from the data in references [5] assuming that the isochores are linear. This pressure was included in strength calculations for the oxygen thermal compressor chamber shown in Fig. 2. The upper oxygen pressure in the thermal compressor of $\sim 3.5$ kbar was estimated using reference data on oxygen compressibility [6]. The oxygen pressure was measured using both a spring gauge 12 and a manganin transducer 7.

The pressures in the argon and oxygen chambers should be approximately equal, but to isolate the oxygen cell the argon pressure should be 20–50 bar higher. This pressure difference is generated by a pressure controller 8 (Fig. 1). This is a water-cooled high-pressure chamber with an inside volume of $\sim 1$ liter containing a 10-kW graphite heater located to heat the largest possible volume of argon inside the chamber. The heater power is controlled by a VRT-3 thyristor switch.

Pressurized oxygen is fed into a sealed cell 13 inside the high-pressure argon chamber 15. The oxygen pipe-lines are manufactured from stainless-steel tubes with an outside diameter of 3 mm and a wall 1 mm thick, their volume is about 2% of the total thermal compressor volume.
Fig. 3. High-pressure chamber with the high-temperature section: 1) high-pressure chamber; 2) obturator; 3) oxygen channel; 4) current lead; 5) argon volume 6) heat sink; 7) oxygen cell; 8) heater; 9) sample; 10) thermocouples; 11) argon inlet.

HIGH-TEMPERATURE SECTION OF THE HIGH-PRESSURE CHAMBER

The high-pressure chamber 1 (Fig. 3) is a cylinder with an outside diameter of 200 mm and a dead-end channel 50 mm in diameter. The chamber is produced from 38CrNi3Mo steel and tested to 5.5 kbar. The obturator 2 accommodates one oxygen channel 3, two high-current leads 4, and ten low-voltage (for thermocouples) leads. All the leads are self-sealing.

The cell 7 housing the sample 9 inside the crucible, which is made from a chemically inert material is connected to the oxygen channel 3 via a replaceable seal. Since the pressure exerted on the cell is fairly low, it can be fabricated from any material which is chemically stable in oxygen at high temperature, such as stainless steel, nickel, Al₂O₃, or BeO. The interval operating volume of the cell is 7 mm in diameter and 10 mm long. Note that these cells are not expensive. This is important in experiments with toxic or radioactive materials, for which a cell can only be used once.

The heater 8 around the cell is a thin-wall graphite pipe [7]. The copper heat-sink 6 is needed to lower the temperature of the seal. Three thermocouples 10 are inserted into grooves in the cell to monitor the temperature and control the heater operation. Presently we use chromel-alumel thermocouples operating at up to 1300 °C. At higher temperatures (up to 2000 °C) alundum cells and tungsten-rhenium thermocouples can be utilized [7].

The assembled high-temperature device is inserted into the high-pressure chamber. The obturator is sealed with a Teflon gasket, compressing rings, and a flange. Argon is fed from the argon compressor through hole 11.

TESTING THE FACILITY

The pressure inside the cell can be increased to 3 kbar. Figure 4 shows curves of parameters during one test at an oxygen pressure over 2 kbar and a temperature of 800 °C for two hours. The oxygen pressure dropped during the experiment from 2.35 to 2.1 kbar because of an inevitable oxygen leak and the absence of a backup oxygen volume. At a pressure of 1 kbar the experiment could last for 15 h.
Fig. 5. Magnetic susceptibility of La$_2$CuO$_{4-z}$ crystals after annealing under different conditions: 1) 600 bar, 650 °C, 120 min; 2) 1700 bar, 700 °C, 120 min; 3) 1700 bar, 750 °C, 15 min.

Figure 5 shows a typical curve illustrating the effect of oxygen doping on the superconducting properties of a La$_2$CuO$_{4-z}$ single crystal. This compound is interesting because samples containing excess oxygen are superconducting with a critical temperature of about 30 °K [7]. The curves indicate that the critical temperature increases with anneal temperature, and the volume of the superconducting phase is larger after the anneal at a higher pressure.

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LITERATURE CITED