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THE EVOLUTION OF HIGH TC SUPERCONDUCTOR MATERIALS USED IN ELECTRICAL ENGINEERING (A REVIEW)

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Fenomenul scăderii bruşte a rezistenţei electrice până la valori neglijabile s-a observat la multe metale şi aliaje în condiţii de temperatură scăzută şi s-a numit superconductivitate.

În afară de mercur, primul element care prezintă superconductivitate, s-au descoperit o serie de elemente, aliaje metalice şi semiconductoare, compuşi anorganici şi organici, izolatori şi materiale cu ordonare magnetică într-un domeniu restrâns de temperatură scăzută – care, la o valoare specifică fiecărui material numită temperatură de tranziţie sau temperatură critică, T_c, prezintă o scădere prin salt spre zero a rezistenţei electrice.

În prezent, este acceptat că rezistenţa unui material în stare supraconductoare este de 10^{-25} Ω, aceasta fiind limita actuală determinată experimental.

Lucrarea prezintă o retrospectivă privind evoluţia materialelor supraconductoare şi stadiul actual al acestor materiale utilizate în electrotehnică şi în alte diferite domenii, fiind prezentate metodele prin care s-au obţinut supraconductorii şi proprietăţile atinse de fiecare dintre ei.

The phenomenon of suddenly decrease of electrical resistance down to a negligible values was emphasized for a lot of metals and alloys in low temperature conditions and was named superconductivity.

Besides mercury, the first element which presents superconductivity, were discovered a series of elements, metallic and semiconductors alloys, inorganic and organic compounds, insulators and materials with magnetic order on a low temperature restricted domain – which, at a specific value for each material (named transition temperature or critical temperature, T_c) present a decreasing to zero through jump of electrical resistance.

In present, it is accepted that the electrical resistance of a material in superconductivity state is about 10^{-25}Ω, that being the actual limit experimentally determined.

The paper presents an overview regarding the evolution of the superconductor materials and the actual stage of these materials used in electrotechnics and in other different domains, being also presented the methods through which the superconductors were obtained and the properties achieved for each one.

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1. Hystorical background of high Tc semiconductors

After the first discovery of the superconducting ceramic system La-Ba-Cu-O with critical transition temperature between 30K and 40K, other families of copper-oxide based ceramics have been synthesized with higher critical temperatures. These oxides include the Y-Ba-Cu-O series (Tc ≈ 90K), the Bi-Sr-Ca-Cu-O series (Tc ≈ 80-115K), the Tl-Ba-Ca-Cu-O group (Tc ≈ 85-125K), and some others which do not form obvious classes (e.g., $Ba_{0,6}K_{0,4}BiO_3$), [1].

YBCO remains the best studied ceramic superconductor, although other ceramic oxide systems based on Bi/Sr/Ca/Cu/O or Tl/Ba/Ca/Cu/O have been prepared and found to have somewhat higher Tc than YBCO.

The basic structure of these compounds has been determined as a distorted, oxygen-deficient multi-layered perovskite structure. The properties of superconductors are strongly affected by subtle points of the structure; in particular the configurations of Cu-O seem to play an important role in the superconducting mechanism.

The discovery of superconductivity with Tc ≈ 39K in magnesium diboride (MgB_2) was announced in January 2001, [2]. It caused excitement in the solid state physics community because it introduced a new, simple (three atoms per unit cell) binary intermetallic superconductor with a record high (by nearly a factor of 2) superconducting transition temperature for a non-oxide and non-C60- based compound. The reported value of T_c seems to be either above or at the limit suggested theoretically several decades ago for BSC, phonon-mediated superconductivity. An immediate question raised by this discovery is whether this remarkably high T_c is due to some form of exotic coupling.

The superconducting properties of ceramic composites strongly depend on the used materials, the conditions and procedures. The most accessible method for obtaining superconductor oxides is the conventional ceramic method, [3]. The method requires repeated cycles of heating and grinding, therefore a relative big consumption of time and energy, but, comparatively with the another methods (co precipitation, sol-gel, chelation), [4-6], it allows the direct elaboration of important quantities of superconducting powder in simple installations. The powder-in-tube method using the specific metallurgical powders methods is used for obtaining superconducting composite wires.

2. Application of high Tc semiconductors

Superconducting materials are used in some applications known at the first sight, but incompatible parameters with classical materials, for example, wires and cables for electrical energy transportation (without losses in DC and with very low losses in AC), electromagnets with very high magnetic field, magnetic susceptibility of some types of vehicles for transportation. Generally, the applications in the field called “hard currents” belong to this category, [10].

A second category of applications of the field of “hard currents” contain the applications of Josephson effect in principal; for example, SQUID (Superconducting Quantum Interference Device), used as transducer, recognized the magnetic field of the human body and of all its organs separately (brain, heart, eye, muscle etc.), and as circuit element having the switching time of the order of some picoseconds.

The revealing of high temperature superconducting will allow the using on a large scale of the superconducting materials in industry in the purpose of reducing the energy losses and of miniaturization the electronic and electrical devices, in medicine for diagnosis and treatment, in research in physics and techniques.

The field of high critic temperature superconducting applications is very large, from the lines able to transport currents larger than 10^6A, magnets which have fields higher than 10^5Gs, storage larger energy than 10^7 Joule, up to devices with sizes of some microns, sensors capable to measure 10^{-11}Gs or 10^{-17}V, shields that could make a zero magnetic field.

Very low electrical resistance, zero practically in DC of superconducting materials and elimination of Joule losses could represent arguments in introduction super conductivity in electrical energy distribution. However, economical studies had demonstrated that the superconducting electrical lines are not competitive with classical high voltage cables, the problem of cooling of these cables presenting specially difficulties. The passing from liquid He for metallic superconductors to liquid N_2 for HTSC, is not leading to economical efficiency rising of cryogenics electrical lines.

Superconducting solenoids or superconducting magnets are the first type of applications made on large scale because superconducting alloys with low critical temperature present very high critical currents. Superconducting magnets are used already on large scale in industry and laboratories, wherever is necessary a high intensity and an especial stability in time of magnetic field, which is obtained by operation in short-circuit regime of a solenoid. Superconducting magnets are used in chemical industry for synthesis of special materials, obtained only in magnetic fields. Magnetic separators used in mining industry are another application of superconducting magnets. The manufacture of monofilament conductors and later multifilament has enlarged the application field of HTSC.

In the past this type of application was believed to remain long time the advantage of conventional superconducting materials because the HTSC materials present critical density of very low currents. However, at present, electrical motors, electric generator from HTSC multifilament conductors are made. HTSC materials can be used in the field of electronics and electrical engineering, too.

3. Composition, structure, fabrication

The first superconductor found with $T_c > 77$ K is yttrium barium copper oxide ($Y_1Ba_2Cu_3O_{7-x}$), commonly termed “123”. Its structure appears in Fig. 1. It is related to the perovskite structure as follows: by tripling the perovskite (ABO_3) unit cell and substituting one yttrium atom for every third barium atom, the formula $Y_1Ba_2Cu_3O_9$ results. However, a little more than two oxygen vacancies are required for superconductivity. The formula can be thought of as $Y_1Ba_{3-1}Cu_3O_{9-2-x}$. The unit cell is orthorhombic, almost but not quite three cubes stacked upon one another.

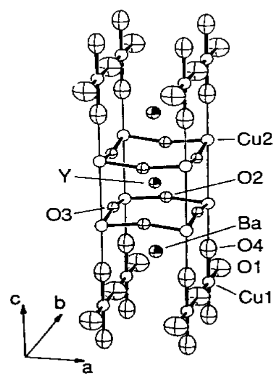

Fig. 1. Structure of the double layered $YBa_2Cu_3O_7$ compound.

This material has been produced as single crystals, polycrystalline thin film, or pellets. In polycrystalline materials the critical temperature and field, as well as the critical current density, have been shown to depend strongly on the microstructure, particularly grain boundaries and grain orientation, and therefore on the processing conditions.

The other superconductor, MgB_2 crystallizes in the hexagonal AlB_2 type structure, which consists of alternating hexagonal layers of Mg atoms and graphite like honeycomb layers of B atoms. This material, along with other 3d-5d transition metal diborides, has been studied for several decades, mainly as a promising technological material, [2]. Fig. 2 shows a typical structure of MgB_2 taken at room temperature, [7]. The peaks in the X ray diffraction pattern can be indexed assuming a hexagonal unit cell, with a = 3.086 Å and c = 3.524 Å.

As shown in Fig. 2, the boron atoms are arranged in layers, with the atoms Mg interleaved between them. The structure of each boron atom is the same as that of a layer in the graphite structure: each atom is here equidistant from three other boron atoms. The material MgB_2 is composed of two layers of boron and magnesium and the a and c axis in the hexagonal lattice.

In order to obtain the superconductor material by the solid-state reaction procedure mixtures of binary oxides, oxides and carbonates, oxides and azotates have been used. The technologies elaborated until present mostly depend on materials, especially on the purity and type of powders.

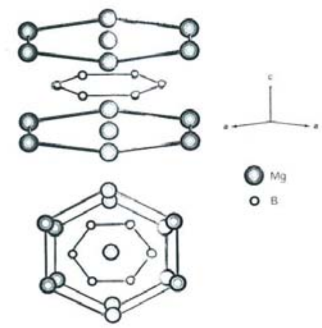

Fig. 2. Structure of MgB_2 at room temperature.

The chemical reaction for the synthesis of $YBa_2Cu_3O_{7-\delta}$ superconducting composite can be written as:

$$Y_2O_3 + BaCO_3 + CuO \Rightarrow Y_xBa_yCu_3O_{7-\delta}$$

with x = 0.3, ...,1.85 and y = 0.2, ..., 2.

The δ deficit of oxygen must not exceed the value 0.6 because $YBa_2Cu_3O_6$ up to $YBa_2Cu_3O_{6.4}$ have a tetragonal structure without presenting superconducting properties. The composites $YBa_2Cu_3O_{6.41}$ up to $YBa_2Cu_3O_7$ have an orthorhombic structure with better superconducting properties to $7-\delta = 7$, [8].

In a series of our own experiments [9] we used carbonates or nitrates as raw materials, and so supplementary calcinations operations for removing carbon and nitrogen oxides were needed. Generally, these calcinations take place in air at temperatures extending from 800^{o}C up to 1100^{o}C, for 8 ... 40 hours.

The pressing procedures used for powders compacting are in $10^5 \div 7.5 \times 10^8$ N/m^2 domains. The solid-state reaction between the raw materials from the obtained samples takes place in oxygen at temperatures 880 ^oC ÷ 1200 ^oC. For cooling, we generally used cooling rates between 1^oC/min and 5^oC/min, [8].

In the technological researches in the achievement of superconductor composite $YBa_2Cu_3O_{7-\delta}$ we used the following raw materials: Y_2O_3 (purity > 99.99 %; Johnson Matthey), $BaCO_3$ (purity 98.38 %, Fluka AG) and CuO (purity > 99.99 %, Fluka AG), [9].

The mechanical grinding was realized in an agate mill, for 1 hour. The calcinations were made at 840^oC for 4 hours, [9]. This thermal process is necessary to remove the volatile impurities of the mixture and the decomposition of carbonates. In order to assure a good homogeneity of the mixture, 3 calcinations-grinding cycles were made. The obtained mixture was cold pressed at a pressing of $10tf/cm^2$. The sintering process was made at 925^oC in 5 torr oxygen atmosphere. The cooling speed was established at approximately 7^oC/min. Some of the electrical properties in the superconducting state, electrical resistance for the sample treated at 925^oC, for 50 hours are presented in Fig. 3, [9].

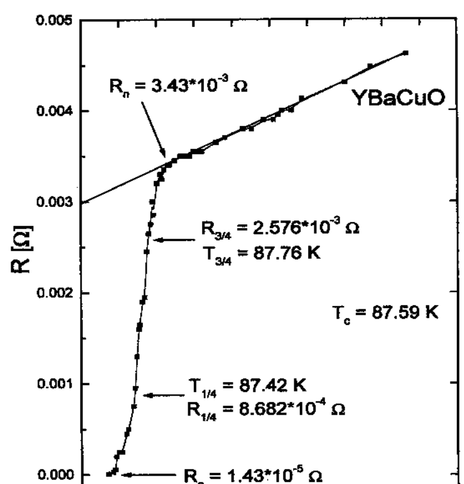

Fig. 3. The electrical resistance dependence vs. temperature for samples sintered 50 hours at 925^oC.

The definition of the critical temperature from an R = R(T) graphic can be achieved using the relation Rc = (Rn+Rsc)/2 where Rn is the resistance of the sample in the normal state, Rsc is the resistance of the sample in the superconducting state and Rc is the electrical resistance at critical temperature Tc, [10]. Using this definition, from the R vs. T dependence in Fig. 1 we obtained Tc = 87.59K, [9].

4. Conclusions

An improved and correct appreciation of the experimental results can be made using the evaluation of the transition interval. Using some notes of the Tc definition on the graph R=R(T), we think that the width of transition is: $\Delta T=T_{1/2}=T(R_{3/4})-T(R_{1/4})$, where $R_{3/4}=(3/4)(Rn+Rsc)$; $R_{1/4}=(1/4)(Rn+Rsc)$. For the analyzed sample it was obtained a transition interval of 0.34K, [9].

We appreciate that the technological parameters to obtain the best superconductor characteristics for the YBaCuO material are sintering at 925^{o}C in oxygen atmosphere for 50 hours, [9].

The field of electronics based on superconductors includes digital integrated circuits with large integrated scale (LSI), because no semi conducting devices have simultaneously delay times of 10ps order and consumption powers of 10^{-7}–10^{-6}W. The most used circuit element is three junctions interferon.

The using of superconducting materials in applications of electrical field is limited in present by low values of the critical currents and by high instabilities which are presenting the electrical conductors from these materials. Researches have been made in the field of superconducting limiting device of current.

R E F E R E N C E S

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