Thermochimica Acta, 148 (1989) 53-56
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Report on the workshop entitled:

CHEMICAL AND PHYSICAL PROPERTIES OF SUPERCONDUCTING MATERIALS CHARACTERIZED BY THERMAL ANALYSIS

Held at the IX. ICTA, 22. 8. 1988, Jerusalem, Israel
Organized by A. Reller, University of Zürich, Switzerland

This workshop was organized in order to pay due attention to the actual developments in the field of superconducting ceramic materials. The present situation proves that the preparation as well as the detailed characterization of these enormously interesting phases is a matter of intensive efforts by means of many different methods of investigation. Oxidic as well as the earlier known sulfidic superconductors represent a class of complicated materials with respect to their preparation, composition, structure as well as thermochemical reactivity. This is a field where thermal analysis proves to be an important, actually indispensable technique. Moreover, the quantitative measurements of physical properties, in particular superconductivity, represents a branch of thermal analysis and certainly requires due attention.

In summary, the present situation for the organizing committee of the *IX ICTA* was certainly well-suited to gather researchers at a round-table discussion or at a workshop dedicated to the presentation of recent findings or to the open discussion of related problems such as instrument performance, interpretation of thermoanalytical measurements, etc.

The workshop was organized in a manner that five participants of the conference presented their oral contributions. After each contribution the presentation was discussed by all participants of the workshop. A panel-discussion took place at the end of the gathering.

After a short introduction by the author of this report *Prof. M. Taniguchi (Tokyo Institute of Technology, Japan)* gave a short overview on the present state of research activities in the field of sulfidic superconducting materials. His contribution was entitled: *Stable range of Chevrel phases and their superconducting properties*. It is noteworthy that these phases were known to exhibit superconducting properties well before the discovery of the mixed copper oxide phases by Bednorz and Müller (Z. Phys. B. 64 (1986) 189). The sulfide phases, however, never attracted so much attention as the recent mixed copper oxide phases do, most probably because the measured T_c's never reached the values of the then known superconducting alloys. In addition their mechanical machinability is as problematic as the one for oxidic phases. Nevertheless,

---

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

0040-6031/89/$03.50

superconducting metal sulfides remain an interesting class of materials not only from the standpoint of rather fundamental studies on superconductivity, but also from the standpoint of possible compositional variability. In the field of superconducting metal sulfides thermoanalytical techniques prove to be a valid tool, be it for the definition of optimal parameters for synthetic procedures, be it for the characterization of the thermochemical reactivity of the products under various atmospheres. As indicated in the title of Prof. Taniguchi's contribution, thermal analysis allows the determination of partial or complete phase diagrams, which in turn represent the foundation for any detailed characterization as well as for any potential practical application of these compounds.

Whether or not new superconducting metal sulfide phases will be found by variation of the composition of the known systems or by the synthesis of basically new phases exhibiting Chevrel-type or other structures can only be answered by forthcoming experimental studies. One important impact of these phases, however, will certainly remain: they represent one part of the basis for the discussion and theoretical description of the phenomenon as such as well as of its underlying mechanistic aspects, i.e. of superconductivity in metal sulfides and in metal oxides.

The second oral contribution was entitled *Phases and partial phase diagrams of the Y-Ba-Cu-O system* and it was presented by *Prof. J. Sestak (Institute of Physics,Prague, CSSR).* Prof. Sestak outlined the possibilities of determining the stability range of a number of modifications of the high-T_c mixed copper oxide $YBa_2Cu_3O_{7-x}$, where the metal cations of the original phase were partially substituted by various different metal cations. He emphasized the importance of thermal analysis for the determination of reliable phase diagrams, in particular for such complicated systems like those phases containing at least three different metal cations in various stoichiometric ratios. Moreover, any thermoanalytical measurements require well-defined experimental conditions, not only by means of a best possible temperature control, but also by means of the defined pressure and atmosphere. The presentation clearly proved that complementary methods of investigations, above all structural investigations by means of X-ray diffraction techniques, have to be applied in order to achieve the necessary data for a detailed interpretation of the thermoanalytically obtained results on processes such as melting, phase segregations, etc. The discussion of this contribution was focussed on the various posssible phases and their stability range within the partial phase diagrams. One principal result of this dicussion was the clear demand for further experimental data on these challenging phases including the correlation between composition, structure, stability and physical properties.

The following contribution by *Prof. H.G. Langer (Dow Chemical Company, Midland, Mich., USA)* was dedicated to the reactivity of $YBa_2Cu_3O_x$. It was entitled: *The role of oxygen in $YBa_2Cu_3O_x$ systems.* Prof. Langer reported on unusual phenomena observed during thermogravimetric measurements of the thermal reactivity of the well-known high-T_c phase $YBa_2Cu_3O_{7-x}$. It is well-established, that this phase undergoes reversible thermal reduction and reoxidation processes within the compositional range of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. It is noteworthy, that the fundamental structural features are conserved. Prof. Langer suggested the probable formation of intermediate peroxide species during the thermal treatment of strongly oxygen deficient phases. The discussion of his results indicated that these observations might have been caused by traces of oxygen within the inert gas atmosphere. Obviously, these mixed copper oxide superconductors exhibit a high affinity towards oxygen and therefore, the importance of a best-possible control of the actual atmosphere has been clearly demonstrated by these investigations.

The influence of various atmospheres on the thermal behaviour of the high-T_c Y-Ba-Cu-O phases was impressively demonstrated by the results of the investigations carried out by *Dr. P.K. Gallagher and his coworkers G.S. Grader and H.M. O'Bryan (AT & T Bell Laboratories, Murray Hill, New Jersey, USA)*. Their contribution was entitled: *Some effects of CO_2, CO and H_2O upon the properties of $YBa_2Cu_3O_7$*. Dr. Gallagher presented thermogravimetric curves for heating $YBa_2Cu_3O_7$ up to 1000° in CO_2, CO, several mixtures of CO_2 in O_2, as well as in wet O_2 and wet CO_2. In pure CO_2 a small weight loss up to about 400° was measured, which is presumably due to O_2 evolution caused by its low partial presssure. This decrease in weight is followed by a large weight gain up to about 950° at which point the carbonate formed starts to decompose again. The thermal reactivity in CO turned out to be similar except that the initial loss of oxygen was much greater. In wet O_2 a very slight weight gain was observed beginning around 300° followed by the normal loss of weight associated with O_2 evolution and the decomposition of any hydroxides formed earlier. Sintered toroids and bars of $YBa_2Cu_3O_7$ were exposed to thermal treatments in pure CO_2, 1% CO_2 in O_2, and wet O_2 at selected temperatures. Treatments in CO_2 for 1000 minutes at 100° intervals led to a progressive decrease in conductivity and critical current J_c until at 500° the material proved to be completely semiconducting. The behaviour in 1% CO_2 in O_2 was similar. In wet O_2 the conductivity and J_c went through a minimum at about 300°. Finally, samples degraded by CO_2 or H_2O could be nearly regenerated by firing above 900° in O_2 and either annealing or slow cooling in O_2.
This sum of very informative results demonstrates that the thermal reactivity of such phases is extremely complicated. It also gives evidence that at present one is far from understanding the mechanistic and kinetic course of all these processes. As clearly shown, however, the detailed characterization of thermoanalytical data represents one important step towards a better understanding of the thermal behaviour and the concomitant changes of structure, stoichiometry and physical properties of these materials.

The last oral presentation by *Prof. I. Felner (Dept. of Physics, Hebrew University, Jerusalem, Israel)* was entitled: *Thermal decomposition of $YBaKCu_3O_x$*. This contribution was of particular interest with respect to the possibility of substituting the bivalent Ba cation by the monovalent K cation. Apart from the difficulty in preparing such a compound in a pure form, the impact of the presented results for the better understanding of the phenomenon "superconductivity in ceramics" is important. Such investigations evidence above all the importance of achieving basic knowledge on the significance of formal oxidation states, be it of the metal cations or of the oxygen anions. As a consequence of Prof. Felner's statements such type of investigations have to be pursued intensively.

After these oral contributions the general discussion was opened. In summary the role of thermoanalytical techniques was critically analyzed. From the various discussions one could clearly deduce, that for the present research activities in the field of superconducting ceramics thermal analysis proves to be an indispensable tool. The nowadays available instruments, however, cannot fulfill completely the requirements for reliable measurements. Above all, the facilities for a best-possible control of pressure and atmosphere - parameters of utmost importance for the detailed characterization of the thermal reactivity and stability of these materials - need to be improved. Moreover, the interpretation of thermoanalytical measurements only then yields valid results if a correlation with investigations by complementary methods is guaranteed. All in all, the frantic development of the field "superconductivity" will certainly lead to an improvement of the significance of as well as of the quality of results obtained by thermal analysis.