



# RARE-EARTH INFORMATION CENTER INSIGHT

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## Follow-up - High $T_c$ Superconductors

In the October 1, 1988 issue of RIC Insight we wrote that Art Sleight reported at the 18th Rare Earth Research Conference that DuPont had developed a new method for preparing the best precursor powders of the  $YBa_2Cu_3O_x$  (1:2:3) superconductor he had ever seen. In the January 6, 1989 issue of Science (243, 66) they report the first details of their method for making these precursor materials.

Their process involves solution-derived, carbon-free precursors which are decomposed at 650° to 700°C in  $CO_2$ -free atmospheres to form the tetragonal phase of the 1:2:3 compound. This decomposition temperature is ~200°C lower than those normally used to form the 1:2:3 material. The tetragonal phase is then oxidized at 400°C to give the superconducting orthorhombic phase, which has an onset  $T_c$  of 87 K. The absence of carbon in any step in this process is important since any carbon in the grain boundaries of the 1:2:3 superconductor has an adverse effect on the critical current. One process involves hyponitrite precursors and the other uses hydrated metal oxides which are derived by hydrolysis of organometallic solutions.

## Follow-up - High Strength Glassy Alloys

In the November 1, 1988 issue of RIC Insight, we reported that a new class of high strength aluminum-base, rare earth containing glassy alloys had been discovered by S. J. Poon and co-workers from the University of Virginia. We have subsequently learned that Japanese scientists from the Institute for Materials Research, Tohoku University had obtained results similar to those reported by the University of Virginia scientists. Indeed the first paper published by A. Inoue and co-workers was published about five months earlier [Jap. J. Appl. Phys. 27, L479 (1988)], but since the title of their paper contained no mention of rare earths it was overlooked. Subsequent papers, which appeared in the September and October issues of the same journal (27, L1579, L1583 and L1796), included the chemical symbols of some of the rare earth elements in the titles. Thus it appears that these unusual alloys were independently discovered, but the Japanese have the earlier priority date. Basically the latest results published by both teams confirm their earlier claims, and this discovery potentially still looks like a great market for the rare earth metals.

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### Oxygen Containing Nd-Fe Permanent Magnets

Schneider *et al.* have found an oxygen stabilized magnetically hard phase in Nd-Fe alloys [Mater. Lett. 7, 215 (1988)]. This phase,  $\text{NdFe}_4\text{O}_x$ , has a coercivity of 0.5 T (5 kOe) and a Curie temperature of 235°C (~60°C below that of  $\text{Nd}_2\text{Fe}_{14}\text{B}$ ). This discovery adds a lot to our understanding of the magnetic behavior of the iron-rich alloys. The existence of a second magnetically hard phase in the Fe-Nd-B alloys has been known for some time, and the data presented by Schneider *et al.* strongly suggests it is  $\text{NdFe}_4\text{O}_x$ , since no commercial Nd-Fe-B magnets are ever oxygen free. Furthermore, their results explain the 1935 report by Drozzina and Janus [Nature 135, 36] of a Nd-Fe alloy with an extremely high coercivity (0.43 T), which at that time the alloy surely contained a large fraction of oxygen. Furthermore, they believe this explains the high coercivity in the boron-free melt spun ribbons of Nd-Fe reported by Croat in 1981, which was the start of the technological development of the Nd-Fe-B permanent magnets.

### Fuel Cells

Fuel cells are expected to be one of the important alternate sources of energy in the future, perhaps as early as the late 1990's. Recent work by H. Yahiro and co-workers [J. Electrochem. Soc. 135, 2077 (1988)] suggest that rare earths may be among the lead materials used in fuel cells, especially those operated at 600° to 1000°C. They found that a  $\text{CeO}_2\text{-Y}_2\text{O}_3$  solid electrolyte exhibited much higher conductivities than that of the usual electrolytes CaO or  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$ . They solved the problem commonly associated with  $\text{CeO}_2$  based electrolytes, namely the reduction of the  $\text{CeO}_2$  to  $\text{Ce}_2\text{O}_3$  by hydrogen, by RF sputtering a thin film of stabilized  $\text{ZrO}_2$  coating onto the  $\text{CeO}_2\text{-Y}_2\text{O}_3$  electrolyte. The open-circuit voltage of the fuel cell approached the theoretical value. The output of this  $\text{CeO}_2$ -based fuel cell greatly depends on the cathode material used because of the low operating temperatures. The mixed oxide  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  cathode was found to produce the highest power density.

### High Temperature Red Ceramic

The lack of suitable high temperature red pigments in the ceramic industry has led R. Olazcuaga and co-workers [J. Solid State Chem. 71, 570 (1987)] to develop a Ce-Pr oxide ceramic which will provide the stable red colors required. The classical red pigments either had a pale red to pink color ( $\text{Fe}_2\text{O}_3$  in zircon matrices or  $\text{Pb}_3\text{O}_4$  in tin oxide matrices), or were poisonous and unstable above 900°C [ $\text{Cd}(\text{S},\text{Se})$  or Na uranates]. The French investigators studied the  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  system over the range of  $0.03 \leq x \leq 0.10$ . The color varied from brick red at  $x = 0.05$  to a dark red at  $x = 0.10$ . The most attractive red color was obtained for  $x = 0.05$ . Thermal tests revealed that the pigments were stable up to 1000°C, but at higher temperatures the color changes toward orange.

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