



RARE-EARTH INFORMATION CENTER NEWS

SUPPORTED BY INSTITUTE FOR ATOMIC RESEARCH

IOWA STATE UNIVERSITY / AMES, IOWA

Volume VI

June 1, 1971

No. 2

University of Genova -

Italian Rare Earth Research Group

Hydrogen Containers



UNIVERSITY OF GENOVA - In the back row from left are G. Bruzzone, G. L. Olcese, A. Iandelli and A. Palenzona. In the front row from left are E. Franceschi, M. L. Fornasini and F. Merlo.

The Italian Rare Earth Research Group at the Institute of Physical Chemistry, University of Genova, is headed by Prof. A. Iandelli, who has been working on rare earths and their intermetallic and semimetallic compounds since 1933.

The research program is divided into four main branches:

1. Determination of binary phase diagrams of rare earths with other metals by means of differential thermal, metallographic, x-ray and magnetic analyses. Of special interest are Yb and Eu for their ability to become trivalent as well as being divalent. Recent work has been on the Yb-Cu, Yb-Ag, Yb-Au systems while Yb-Cd, Yb-Pd and Gd-Cd systems are currently under examination.

2. Determination of binary phase diagrams of alkaline earths with other metals for a comparison with the analogous Yb and Eu systems because of the similarity among these elements. Work now in progress is concerned with Cu and Pb systems.

3. Systematic investigations on the occurrence of intermetallic compounds of rare earths with a particular alloying partner. Such research involves the determination of the stoichiometry of the phases present, their crystal structures and the relations among these structures. Such a study has been completed for Zn, and Cd is now under examination. Another study on the Au compounds carried out jointly with Dr. K. A. Gschneidner at Iowa State University has also been completed.

(Continued on page 2)

Dutch scientists in the past year have reported on their discovery that some rare earth group VIII metal compounds are capable of retaining large amounts of hydrogen gas. Furthermore, they note that absorption and desorption is almost reversible at room temperature. At higher temperatures, 80°C, the hysteresis increases to 2.0-3.0 atm, compared to about 0.3 atm at 25°C.

Most of their work has been concentrated on LaNi_5 and SmCo_5 . The former compound absorbs 6.7 atoms of hydrogen per LaNi_5 molecule, and the latter 2.5 atoms. The absorption of hydrogen is accompanied by a volume expansion (25% for LaNi_5 and 10% for SmCo_5). By substitution of 30% of the La atoms by Ce, i.e., $\text{La}_{0.7}\text{Ce}_{0.3}\text{Ni}_5$, the hydrogen absorbed is increased to 7 atoms per RNi_5 formula unit.

The 6.7 atoms of hydrogen absorbed per LaNi_5 formula unit correspond to a density of hydrogen of 7.6×10^{22} atom/cc, which is twice as high as the hydrogen density in liquid hydrogen. There are several other materials which will exceed this density, TiH_2 -9.1, ErH_3 -8.1 and YH_3 -7.8, but none can be as readily desorbed to zero hydrogen concentration at room temperatures as the LaNi_5 compound.

These results were reported by J. H. N. van Vucht, F. A. Kuijpers and H. C. A. M. Bruning in *Philips Res. Rept.* 25, 133-140 (1970) and by Kuijpers and H. H. van Mal in *J. Less-Common Metals* 23, 395-398 (1971).

RE's Could Be Exhaust Catalyst

Nobel Prize winner W. F. Libby reported that his tests show that LaCoO_3 , as a heterogeneous catalyst from 25 to 450°C, appears to rival platinum as a catalyst for converting *cis*-2-butene to *n*-butane and other hydrocarbons. On the basis of this information and the fact that platinum is a good catalyst for reducing harmful exhaust emissions, Libby suggests that LaCoO_3 should be tested as a potential auto exhaust catalyst. Libby's note appeared in *Science* 171 499-501 (1971).

It has been estimated that 25,000 tons of catalysts will be needed per year to satisfy the new car demand when the new standards go into effect, *Metals Week* 42 [7] 20 (1971). At a cost of about \$1.00 per pound, LaCoO_3 is probably economically competitive with many of the other materials being considered.

In a later note, *Science* 172, 86 (1971), R. C. Vickery mentioned some of his previously unpublished 1958 data on the catalytic activity of Pr_6O_{11} and Tb_4O_7 he obtained while working at the Stanford Research Institute. He stated, "Virtually complete breakdown of extra-neous gasoline was achieved, and catalysts were not poisoned by the lead component of the exhaust gases."

Rare Earthers are Promoted

Two rare earthers have recently been promoted at their respective institutions. At Iowa State University, Ames, Ia., Dr. Richard G. Barnes has been named chairman of the department of physics and chief of the physics division of the AEC's Ames Laboratory, effective July 1. He has been active in NMR studies of the rare earths. At Molycorp, Gordon A. Barlow has been appointed sales manager of the chemicals and rare earths division. He will supervise sales and market development for the rare earth-based firm.

(Continued from page 1)

Italian Rare Earth Research Group

4. Investigation on the valency behavior of Ce in its intermetallic compounds by structural and magnetic properties determinations. The electronic configuration of Ce has been investigated in its elemental state at room temperature and at high pressures (up to 100 kbars), and in 21 intermetallic binary compounds. Work in progress concerns the rare earth-rich side of the binary systems between La, Ce and Pr with the Group VIII metals.

C. V. Banks is Dead

Charles V. Banks, professor of chemistry and section chief in the chemistry division of the AEC's Ames Laboratory at Iowa State University, died Feb. 26, 1971, following a lengthy illness. Dr. Banks, 52, a 30-year staff member at Iowa State, was probably best known to rare earthers for his work in developing wet analytical methods for determining rare earths and the common impurities in them.

Yttrium Corrosion

Corrosion of Yttrium, by R. M. Al'tovskii, D. S. Gornyi, A. A. Eremin and A. S. Panov is a summary of the data published from 1958 to 1968 and of the results of the authors' own studies on the corrosion and compatibility of yttrium. This summary of the properties of yttrium and some of its compounds was written primarily for nuclear engineers.

Among the topics discussed are the corrosion resistance of yttrium in both aqueous and gaseous media, the influence of yttrium on the heat resistance of metals and alloys, the compatibility of yttrium with uranium and uranium alloys and the interaction of yttrium with refractory structural materials.

Corrosion of Yttrium (AEC-tr-7176) 87 pages, 160 references, is available as an English translation for \$3.00 from the National Technical Information Service, Department A, Springfield, VA 22151 USA.

RE: RE MAGNETS

SmCo_5 devices are now undergoing trial on patients who have been unable to adequately open or close their eyes as a result of muscle or nerve injury or disease. Severe ptosis (eyelid drooping) which obstructs vision and orbicularis oculi weakness (the inability to close eyes) are relieved by these devices, according to D. Grob and P. Stein, *J. Appl. Phys.* 42, 1318-1319 (1971).

The magnetic prosthesis developed to relieve ptosis consists of 5 to 7 SmCo_5 magnets attached below the eyebrow and a strip of ferrous magnetic material which, when attached to the eyelid, elevates the eyelid. Lid closure can be achieved by blinking or winking. To relieve orbicularis oculi weakness, the SmCo_5 magnets are placed on the inferior eyelid, permitting normal eye closure. The SmCo_5 magnets are imbedded in polyurethane in the shape of an arc. The over-all weight of the device is less than 1 gram.

RE Intra-alloys

Late in 1970 C. C. Koch reviewed the alloying behavior and structure of intra-rare earth alloys (*J. Less-Common Metals*, 22, 149-173). In his review he divided these alloys into three groups depending upon the nature of phases formed between any two members. These groups are based on systems which exhibit: (1) complete solid solubility, (2) low temperature phase separation, and (3) a sequence of close-packed phases based on different stacking variations.

The major portion of the review is concerned with the third group of alloys. In it, Koch discusses the experimental results and examines the various models and explanations proposed for the stacking sequences of close-packed planes in the intra-rare earth alloys. This excellent review collates the considerable amount of work (67 references) done on these alloys in the last 10 years.

Hasler Award to Fassel

The 1971 Maurice F. Hasler Award to "recognize notable achievement in spectroscopy which has resulted in significant applications of broad utility"



V. A. Fassel

has been won by Velmer A. Fassel, deputy director of the AEC's Ames Laboratory, Ames, Iowa. Dr. Fassel will receive the award at the 1971 St. Louis Meeting of the Society for Applied Spectroscopy (SAS) which administers the award.

A rare earther of long standing, Fassel's studies have contributed greatly to the development of modern spectroscopic techniques. He is a past winner of the SAS Annual Medal Award and in 1969 received the Spectroscopy Society of Pittsburgh Award.

Lanthanides in Ferns

Ferns can be used as geobotanical indicators when prospecting for rare earths, noted O. Erämetsä and M. Haukka in their study of the occurrence of lanthanides in ferns, *Suomen Kemist* 43, 189-193 (1970).

An analysis of 56 samples of the fern species *Lastrea dryopteris* gathered around the pegmatites of Varala and Pyörinmaa in southwestern Finland showed that the lanthanide distribution is different in the vicinity of the pegmatites and therefore, that the ferns could be used as geobotanical indicators.

The authors also investigated the seasonal variation of lanthanides in fern samples taken from a three-square-meter area in Helsinki and found that the lanthanide content increased during the summer and decreased slightly at the end of the growth season. It was also found that the fern ash contained about three times the amount of lanthanides as the underlying soil.

The analyses were made by x-ray fluorescence and mass spectrometric methods.

Rare Earths In the News

ELECTRO-OPTIC CERAMICS

Sandia Laboratories, Albuquerque, N.M., has developed an improved process for making lanthanum-modified lead zirconate/lead titanate. This ferroelectric electro-optic ceramic is characterized by "whiter whites" and "blackier blacks." Its greater degree of black-white contrast (4000:1 compared to 1000:1) should make the materials useful in optical memory devices, as well as in display devices, say the developers.

GLOWING GREEN

Rare earths and the color television industry seem on the way to becoming inseparable. Now that europium is firmly ensconced as the red emitting phosphor, Westinghouse Research Laboratories reports the development of a green emitting CaS:Ce³⁺ phosphor. Westinghouse says that the green emitted by their new phosphor corresponds closely to that of the (Zn,Cd)S:Ag (P-22) phosphor now being used in color TV tubes. This Ce-doped phosphor rivals the best green ZnS-type phosphor at low beam current and is superior to ZnS phosphor at high current.

FUSION INITIATOR

A neodymium-glass laser was used in the first nuclear fusion reaction initiated by a laser beam. Temperatures in excess of 10 million °C were produced by the fusion of deuterium in an experiment conducted at the Centre d'Etudes Atomiques de Limeil, France.

FREE

Copies of *Rare Metals* by O. A. Songina and of *Rare-Earth Metals in Steels*, IS-RIC-4, are still available from RIC.

RE Spectrometry

Atomic emission and absorption spectrometry of the rare earth elements has been reviewed by R. N. Kniseley, V. A. Fassel and C. C. Butler in a chapter in *Analytical Flame Spectroscopy*, R. Mavrodineanu, ed. (Philips Technical Library, Eindhoven, The Netherlands, 1970).

One of the most useful applications of flame atomic spectra is the analysis of rare earth mixtures. The simplicity of the spectra produced by the fuel-rich oxyacetylene flame compared to arc or spark spectra makes possible adequate spectral resolution with small table-model spectrometers. All of the rare earths have line spectra sufficiently intense for analytical utility; moreover, in the analysis of mixtures no inter-element effects are seen. The detection limits of each of the rare earth elements by both flame emission and flame absorption techniques are summarized in a table. Analytical lines for flame emission analysis of the rare earth mixtures are also summarized in a table, and the complete emission spectra of the rare earth elements are contained in an appendix to the chapter.

Other topics discussed in the review include an introduction to atomic and molecular emission spectra, and the production of free atoms in both flame and atomic absorption spectrometry.

Some reprints of this review are available from RIC.

RIC News

Vol. VI, No. 2

June 1, 1971

published in
March, June, September and December
by
Rare-Earth Information Center
Institute for Atomic Research
Iowa State University

Second-Class postage
paid at Ames, Iowa

Telephone: Area Code 515 294-2272
K. A. Gschneidner, Jr. Editor
Nancy Kippenhan and W. H. Smith
Staff Writers

Biological Probes

Lanthanide cations have been shown to be excellent NMR probes of the environment around their bindingsites in proteins, according to K. G. Morallee and co-workers, *J. Chem. Soc. D* 1970, 1132-1133.

Eu(III), Ho(III) and Gd(III) were used as proton NMR shift and shift broadening agents in the spectral study of the protein lysozyme. The binding sites of distant molecules within the protein, but outside the coordination sphere of the lanthanide cation, were determined from dipolar paramagnetic shifts. These values were in good agreement with those determined in previous x-ray studies.

The full potential of this method is still under study. It should be easily applicable to the study of metallo-enzymes. Since the lanthanide cations are close to the size of the calcium ion, it is hoped that the method also will be useful for the study of calcium containing biological substances.

Materials Survey

The Rare-Earth Elements, Yttrium and Thorium. A Materials Survey, J. G. Parker and C. T. Baroch, has been recently published as an information circular in the materials survey series by the U.S. Bureau of Mines.

The 92-page report is a comprehensive compilation of fundamental information on the rare earths and their minerals. Statistics are presented for the supply, production, consumption, and trade of these materials for both the United States and the world. The report contains an excellent discussion of the geology and mineralogy of the rare earths as well as the structure of the industry and the technology of rare earth production. The various uses of mixed and individual rare earths are also briefly presented.

This circular, U.S. Bureau of Mines IC-8476, is available for \$1.00 from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, USA.

PATENT REFERENCE

A new patent reference has recently come to our attention. *Mineral Exploration, Mining and Processing Patents 1969* by O. S. North contains about 18 patent citations relating to rare earth ores and metals. The volume is fully indexed and contains abstracts of the 1969 patent literature. The U.S., Canadian and British patents are covered as well as selected German, French, Japanese and Russian patents.

A volume in this series is issued yearly, and the 1970 edition is in press. The price of the 260-page 1969 issue is \$25. Current and past volumes may be ordered from O. S. North, 812 S. Ode St., Arlington, VA 22204, USA.

Help Needed on RE Coordination Chemistry

Reprints and preprints of recent research on the structural aspects of rare earth coordination chemistry are being sought by R. E. Sievers and M. F. Richardson who are writing a review on the topic for *Chemical Reviews*. The authors are particularly interested in x-ray structural studies and in NMR shift reagent work. If you can help, please contact the authors at the Aerospace Research Laboratories, ARL/LJ, Wright-Patterson AFB, OH 45433 USA.

Rare-Earth Information Center
Institute for Atomic Research
Iowa State University
Ames, Iowa 50010

JOINS RIC CONTRIBUTERS

Bulldog Chemical Company, Laramie, Wyoming, has joined the ranks of industrial concerns which provide financial support for RIC. This brings to 27 the number of firms throughout the world which contribute to the Center.

Geothermometers

The distribution of rare earth elements between coexisting minerals is a fairly effective indicator of the relative temperature at which equilibria is attained in rocks, since it is known that a decrease in temperature leads to the fractionation of rare earths.

A. P. Khomyakov, *Doklady Akad. Nauk SSSR* 191, 440-442 (1970); Engl. transl., *Doklady Earth Sci. Sec.* 191, 182-183 (1970), arranged a series of 18 minerals in decreasing order of their affinity for La and Ce. The position of minerals in this series determines the sign and relative magnitude of the heats of reactions in which the individual lanthanides are exchanged between minerals. The analyses of several mineral pairs from rocks known to have formed at different temperature were found to fit the series.

The author states that it should be possible to compare the modes of origin of various igneous, metamorphic and metasomatic rocks by means of only one of two rare earth mineral geothermometers.