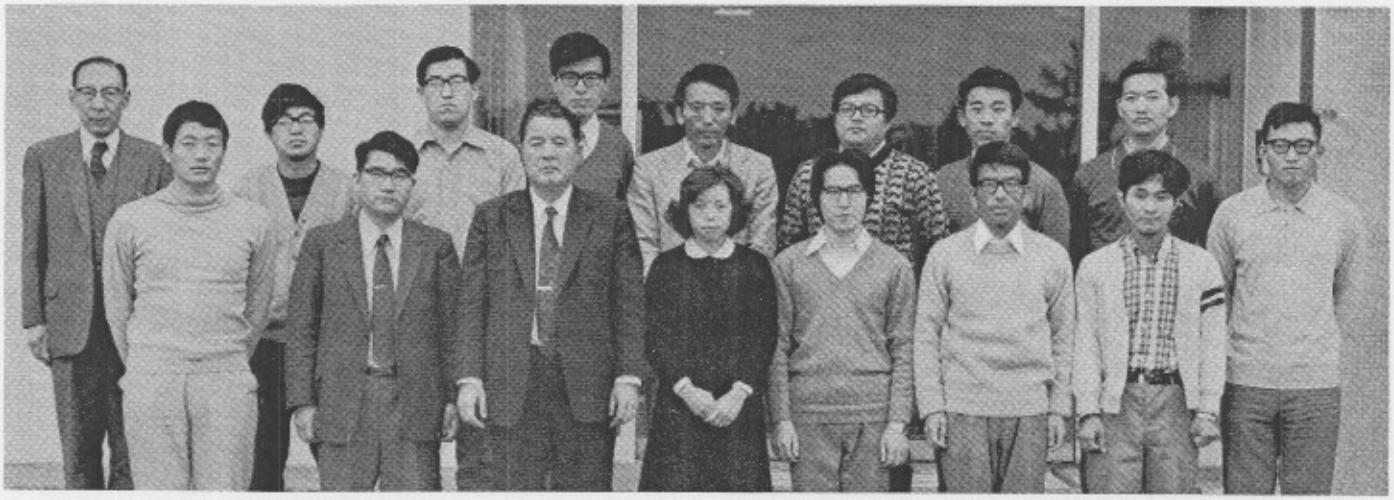
RARE-EARTH INFORMATION CENTER NEWS

ENERGY AND MINERAL RESOURCES RESEARCH INSTITUTE
IOWA STATE UNIVERSITY / AMES, IOWA

Volume X | March 1, 1975 | No. 1



TOHOKU UNIVERSITY Rare Earth Group in the back row from left are K. Matsuyama, H. Toma, T. Amano, K. Okamura, J. Hayashi, M. Hasegawa, T. Matsuzawa and T. Kenjo. In the front row from left are M. Hamano, H. Kayano, S. Yajima, J. Ueda, T. Shishido, M. Omori, S. Tokutomi and Y. Higashiguchi.

Tohoku University—

Synthesizes Rare Earth Compounds

Rare earth research under Prof. S. Yajima, director of the Oarai Branch of The Research Institute for Iron, Steel and Other Metals, Tohoku University, Japan, is mainly concerned with the synthesis of new rare earth compounds. This group carries out both developmental and fundamental research.

1. Many new rare earth compounds are being prepared by solid state reaction and arc melting. Compounds which have been prepared in the laboratory are RCo_2B_2 (tetragonal, $ThCr_2Si_2$ type structure, R = lanthanide element), RCo_3B_2 (hexagonal), RCo_4B_4 (tetragonal), $RCo_{12}B_6$ (rhombohedral), RNi_4B (hexagonal), RNi_2B_2 (tetragonal) and $R_4O_3F_6$ (tetragonal) by Dr. K. Niihara and Mr. T. Shishido; $RR'F_3$ (orthorhombic YF_3 type structure) and $RKCuF_3$ (tetragonal) by Dr. K. Okamura. Current research is focused on the synthesis of amorphous materials which contain rare earth oxides such as the R-Al-O, R-Nb-O, R-Ta-O, R-Ti-O and R-Fe-O systems. These amorphous materials are prepared by heating in a laser beam or a plasma flame followed by rapid quenching (Dr. K. Okamura, Mr. T. Matsuzawa and Mr. T. Shishido). Semiconductive and magnetic properties of the amorphous materials have been investigated.

2. Dr. T. Kenjo is investigating the relation between the radiation sensitivity and the electronegativity of rare earth niobates (Fergusonite, $RNbO_4$) and their related compounds which have been irradiated in the Japan Material Testing Reactor (JMTR).

3. Both practical and basic aspects of magnetic materials are being studied by Mr. M. Hamano who is working on the magnetic anisotropy of rare earth-transition metal 2:17 intermetallics, especially $Y_2(Co_{1-x}M_x)_{17}$ compounds (M = Fe, Al and Cu), using single crystals or oriented powders. The potential of 2:17 type compounds for permanent magnet materials is being examined as well.

4. New refractory alloys containing rare earths such as Ce and Y are being prepared by Mr. T. Amano. Ni-Cr and Fe-Cr alloys containing Ce or Y are found to remarkably improve in oxidation resistance.

5. Mr. H. Toma has found that 1 molecule of La_2Mg_{17} alloy absorbs 12 atoms of hydrogen. The amount of hydrogen absorbed by the La_2Mg_{17} alloy is about twice that of $LaNi_5$ and $SmCo_5$ alloys.

(Continued on page 3.)

Longtime Rare-Earther Dies

Word has been received at RIC of the death of Dr. Eng. Egon Ihwe. A former Director of Th. Goldschmidt AG, Dr. Ihwe was largely responsible for the development of Goldschmidt's rare earth production after World War II.

A major portion of Dr. Ihwe's professional life was devoted to the rare earths. He was born February 18, 1897 in Brandenburg/Havel. In 1919 Dr. Ihwe began chemistry studies at Berlin and later graduated from Darmstadt.

From 1926 to 1938, Dr. Ihwe was concerned with procedural and technical aspects of development and production at the E. Merck firm. He moved to the Auer company in 1938 as director of the rare earth manufacturing division at Oranienburg and became a member of its governing board in 1944.

After World War II, Dr. Ihwe remained active in the management of the Auer company until he moved to Th. Goldschmidt AG in 1953. Rare earth and zirconium chemical production had already begun at Goldschmidt AG and Dr. Ihwe vigorously developed this highly specialized branch of inorganic chemistry.

Dr. Ihwe resided in Ahrensburg after his retirement in late 1962.

RIC DOCUMENTS AVAILABLE

IS-RIC-4 *Rare Earth Metals in Steels*, Nancy Kippenhan, Karl A. Gschneidner, Jr., March 1970.

IS-RIC-5 *Thermochemistry of the Rare Earth Carbides, Nitrides and Sulfides for Steelmaking*, Karl A. Gschneidner, Jr., Nancy Kippenhan, August 1971.

IS-RIC-6 *Thermochemistry of the Rare Earths, Part 1. Rare Earth Oxides, Part 2. Rare Earth Oxysulfides, Part 3. Rare Earth Compounds with B, Sn, Pb, P, As, Sb, Bi, Cu and Ag*, Karl A. Gschneidner, Jr., Nancy Kippenhan and O. Dale McMasters, August 1973.

IS-RIC-7 *Selected Cerium Phase Diagrams*, Karl A. Gschneidner, Jr., Mary E. Verkade, September 1974.

Reports listed above are available without charge from the Rare-Earth Information Center, Energy and Mineral Resources Research Institute, Iowa State University, Ames, IA 50010 or from Molycorp, Inc., Metallurgical Sales, No. 4 Gateway Center, Pittsburgh, PA 15222.

Improved Corrosion Resistance

Increased corrosion resistance in metals irradiated with helium ions is the subject of a paper by Yu. M. Khirnyi and A.P. Solodovnikov [*Dokl. Akad. Nauk SSSR*, **214**, 82-3 (1974), English transl., *Sov. Phys. - Doklady* **19**, 31 (1974)].

Several metals including cerium were used to test the hypothesis that irradiation of a metal with helium ions creates a barrier of helium atoms on the metal surface. This barrier is thought to hinder adsorption of other gases onto the surface of the metal and thereby reduce the corrosion resulting from these adsorbed gases.

The authors' experiments revealed that cerium resistance to hydrogen corrosion more than doubled after irradiation in a 20 keV helium ion beam. Furthermore, the helium surface layer remained stable after two years of exposure to normal atmospheric conditions.

Low-level Tritium Detector

A low-level tritium detection system has been developed by C. Colmenares, E. G. Shapiro, P. E. Barry and C.T. Prevo [*Nucl. Inst. Meth.* **114**, 277-89 (1974)] employing an Eu-doped CaF_2 scintillator-photomultiplier. Calibrated over a range of tritium concentration from 0.35 nCi/cm^3 (STP) to 0.68 μCi/cm^3 (STP), the minimum detectable level was 48 pCi/cm^3 (STP).

The system successfully overcomes limitations of other solid scintillators, both inorganic and organic, for low level tritium detection, but at concentrations above 3.27 μCi/cm^3 (STP) severe contamination by traces of tritiated water nullifies the usefulness of the CaF_2 crystal. To overcome this problem, the authors are experimenting with thin film coatings for the crystal and the walls of the sample cavity.

Designed to monitor and automatically control tritium contaminated gas effluent by means of 30 computerized detection stations, the system is said to be less expensive and more compact than others currently available.

Rare Earth-Treated Steels

The need for low sulfur steels in modern technology, and the procedures, economics and limitations of desulfurization processes were among the topics examined at the Iron and Steel International Congress, Paris, France, October 1973. High strength structural steels have been growing in demand for several years and are expected to account for an increasingly larger share of production.

In published proceedings [*Rev. Metallurgie* (April 1974)] metallurgists from Great Britain (pp. 333-44), Germany (pp. 369-75), France (pp. 377-82) and Japan (pp. 395-405) all described the adoption of cerium mischmetal additions to achieve superior mechanical performance at relatively low cost, especially in high strength structural steels such as those used in large diameter pipe.

It was generally noted that conventional desulfurizing processes reduce the sulfur content to only about 0.005%. The remaining inclusions are primarily sulfides of Al and Mn which deform on rolling, lower the ductility of the steel and may cause lamellar tearing during welding.

Because rare earth metals have a greater affinity for sulfur than do Al and Mn and because their sulfides have a higher specific gravity, they are able to precipitate 50% of the remaining sulfur before solidification. The residual 50% occurs mainly as rare earth oxysulfides which are not deformed during rolling. Rare earth-treated steels thus exhibit greatly increased strength with no effect on yield point.

RIC News
Vol. X, No. 1 March 1, 1975
published in
March, June, September and December
by
Rare-Earth Information Center
Energy and Mineral Resources Research Institute
Iowa State University
• • • •
Second-Class postage paid at Ames, Iowa 50010
• • • •
Telephone: Area Code 515 294-2272
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Airborne Rare Earths

Citing the lack of data, M.J. Potts, C.W. Lee and J.R. Cadieux have undertaken the analysis of rare earth compositions in atmospheric particles [*Environ. Sci. & Tech.* 8, 585-7 (1974)]. Samples were taken from three different locations in the St. Louis metropolitan area. Rare earths were found in nanogram per cubic meter quantities.

The researchers hope to correlate rare earth distributions in atmospheric particles in much the same way that geologists use the rare earths as geological indicators. Relative fractionations within the rare earths or anomalous quantities of certain elements of the group provide the most useful information since these abundances correlate directly to the particle formation processes and sources. In this case the investigators hope to solve the problem of distinguishing the natural sources of air pollutants from man-made sources.

New Soviet Volume

Our latest Russian acquisition is a 142-page paperback, *Soedineniya Dvoinykh Okislov Redkozemel'nye Elementov* [*Binary Oxide Compounds of the Rare Earth Elements*]. The book was written by Ya. S. Rubinchik and published by Izdatel'stvo Nauka i Tekhnika, Minsk (1974).

Permanent Magnet Workshop

The International Workshop on Rare Earth-Cobalt Magnets, held October 13-16, 1974 at the University of Dayton, drew 138 people representing the U.S. and 10 foreign countries. One of the interesting facts brought to light was that there are now 17 companies who produce up to six different types of rare earth-cobalt permanent magnets with the emphasis on $SmCo_5$.

The number of applications for these materials is also growing and includes use in DC motors, wristwatches, clocks, klystron amplifiers, microwave devices and magnetic bearings. Weight savings in these applications were reported to range from ten to thirty times that of conventional magnets.

Grace Honored

J. Peter Grace, president and chief executive officer of W.R. Grace & Co., has received the 1974 International Palladium Medal of the Societe de Chimie Industrielle (SCI) for his outstanding contributions to the chemical industry. In naming Grace, SCI cited his contributions to international friendship, understanding and good will as a leader in the international chemical industry.

Improved Coating

R.H. Long, M.C. Sze acd H. Unger have demonstrated increased corrosion resistance of alloy steel when coated with an aluminum - 4% mischmetal (MM) alloy [*Metal Progress* **107**, No. 2, 52-3 (1975)]. Tests involved sulfur-containing or carburizing gaseous environments which occur in high temperature petrochemical and metallurgical operations.

At temperatures greater than 1000°C the Al-MM coating proved substantially better at limiting corrosion than conventional Al coatings. After 2200+ hours at 1040°C carbon penetration was only 0.4 mm; there was no evidence of spalling, and aluminum diffusion was minimal. Sulfide penetration was not measurable after 2300+ hours. The Al-MM coating almost doubled the service life of alloy steel parts operating at high temperature in corrosive atmospheres.

Pressure Calibration

O. Alm, P. Andersson and G. Bäckström have prepared a coaxial wire containing cerium, bismuth and thallium or barium which has application to the calibration of high pressure devices [*Rev. Sci. Instrum.* **45**, 594-5 (1974)]. Calibration is made by recording the change in electrical resistance due to polymorphic transition in metal wires. To obtain more than one signal several different metals were used in a series or parallel connection. This method was limited by available space and the difficulty in soldering various metals together. Using extrusion, these researchers have accomplished the parallel connection of three metal resistances

(Continued on page 4.)

Contributors

Contributions have been received from Asarco Mexicana, S.A., Mexico, Colt Industries, Crucible Inc., U.S.A., and Ohio Ferro-Alloys Corp., U.S.A., all three contributing to the Center for the first time; from Allied Chemical Corp., U.S.A. and British Flint and Cerium Manufacturers, England, both three-time contributors; and from Santoku Metal Industry Co., Ltd., Japan, who has contributed five years. Center supporters now number 31.

Tohoku University

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In addition to the above researches, the synthesis of polymers of rare earth and transition metal organometallic compounds has been studied. A challenge to prepare Fe^+ salt has been accepted by Mr. M. Omori, and the preparation of SiC fiber is being attempted by Dr. J. Hayashi, who is using dodecamethylsilacyclohexane as a starting material. Radiation effects on metals and alloys are being studied by Assoc. Prof. H. Kayano, Mr. Y. Higashiguchi and Mr. S. Tokutomi, while Mr. M. Hasegawa is studying positron annihilation in long period ordered alloys and compounds of Cu.

Cool Catalyst

$LaCoO_3$ is included in a new family of catalysts which promise more efficient removal of unwanted organic waste products in certain chemical reactions and at a much lower temperature [*Industrial Research* **17**, No. 1, 15 (1975)].

University of Southern California researchers report that replacing a fraction of lanthanum with tin, zirconium or thorium changes the type of predominant defect in the compound. Modifying the compounds in this way allows a study of the effect on catalytic properties that defects have.

The authors believe that these new catalysts, in the form of bricks or coarse mesh, might be able to replace afterburners for the removal of organic waste emissions. With improved fabrication technology, application to automotive exhaust catalytic converters is possible.

Sputtered Amorphous Magnetic Materials

Amorphous Gd-Co magnetic films offer many advantages over crystalline materials, according to J.J. Cuomo, P. Chaudhari and R. J. Gambino [*J. Elect. Mat.* **3**, 517-27 (1974)]. Since the sputtered films are substrate independent, one is able to prepare large surface area magnetic materials and thus allow for a wide variation of substrate compositions including flexible heat-stable polymers.

The authors report that it is possible to maintain magnetic behavior and vary the magnetization (from 10^2 to 10^3 Oe) and the coercivity (from < 0.50 Oe to > 5000 Oe) over a wide range of compositions (from ~ 50 to 95 at. % Co). These properties suggest applications to both bubble domain and magneto-optic technologies.

Additional advantages include a room temperature compensation point at about 79 at. % Co, unhindered mobility of domains at surface indentations, and high bubble propagation velocities.

Atomic Parameters Updated

Spectroscopically-determined ground level designations for neutral through triply ionized lanthanide and actinide species and the first four ionization potentials of these elements have been compiled and updated by W.C. Martin, L. Hagan, J. Reader and J. Sugar [*J. Phys. Chem. Ref. Data* **3**, 771-80 (1974)].

New or improved values based on results published from 1970 through 1974 account for approximately two-thirds of the ionization potentials reported in this review. More than 70 literature sources are cited for the lanthanides alone in addition to 18 general references to earlier reviews and bibliographic outlines.

Reprints of this article are available for $3.00 from:

American Chemical Society
Subscription Services Department
1155 Sixteenth Street, N.W.
Washington, DC 20036, U.S.A.

Gadolinium-153 is used in industrial x-ray fluorescence.

New Brochure

The Santoku Metal Industry Co., Ltd., has published a short brochure on the rare earths. In addition to answering a few historical questions about the rare earths the brochure pictorially displays the kaleidoscope of rare earth applications.

Copies of this attractive publication are available free by writing to:

Santoku Metal Industry Co., Ltd.
No. 14-34, 4 - Chome
Fukae-Kitamachi,
Higashinada-ku
Kobe, Japan

High Pressure Data Reviewed

J. F. Cannon has compiled and analyzed the high pressure data available for all the chemical elements, with the exception of those which are gases at room temperature and pressure, with special emphasis on pressures > 1 kbar [*J. Phys. Chem. Ref. Data* **3**, 781-824 (1974)]. Of the 68 elements surveyed 15 are rare earths. No phase equilibria data at high pressure have been reported for Sc and Pm.

Pressure-temperature phase diagrams are presented for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Yb. Also included are lattice parameters for both normal and high pressure polymorphs. The review is based on 431 references of which 76 are related to the rare earths.

Reprints of this article are available for $4.50 from:

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Bivalent Holmium

Holmium, long considered to be one of the few members of the 4*f* group which display only the 3+ oxidation state, may also be bivalent according to D.J. Apers, R. DeBlock and P.C. Capron [*J. Inorg. Nucl. Chem.* **36**, 1441-5 (1974)]. Though chemical means continue to be inadequate, the potent punch of gamma radiation appears able to overcome the exceptionally strong reduction potential ($\sim$2 V) of Ho^{2+}.

First alerted to the possibility of a new Ho species by anomalous behavior of irradiated Ho_2O_3 samples, the authors examined 10 M rad irradiated oxide samples by means of electrophoretic analysis, chronopotentiometry, polarography, titration, annealing, and differential thermal analysis. Each investigation confirmed the existence of a relatively stable bivalent holmium ion with a maximum yield of $\sim 5\%$ when oxygen was excluded from the system. Similar results were obtained from examinations of irradiated Tm_2O_3, heretofore only considered to contain trivalent Tm, and Sm_2O_3 for which the bivalent state of Sm was already established.

Pressure Calibration
(Continued from page 3.)

in a single wire. The central wire consists of cerium; the intermediate layer is either thallium or barium and bismuth forms the outer layer. Two additional advantages of this arrangement are the ease with which bismuth can be soldered and the protection from oxidation of the inner metals afforded by the bismuth sheath.

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