RARE-EARTH INFORMATION CENTER NEWS

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1977 IR-100

Phosphors and magnets constitute the two rare earth products that placed in *Industrial Research's* IR-100 list for 1977 [*Industrial Research* **19,** (10) 60-4 (1977)]. The IR-100 represent the top 100 products of 1977 as rated by *Industrial Research.* Brief descriptions of this year's place winners are given below.

The rare earth-containing phosphors strontium chlorapatite doped with europium (+2) and yttrium oxide doped with europium (+3) represent two of the three phosphors present in a new fluorescent lamp which is energy efficient and provides better "seeability". Research has shown that the human eye responds more to three colors (wavelengths): blue-violet (450 nm), green (540 nm) and orange-red (610 nm). When combined, a very efficient white light results because of the reduced ultra violet and infrared radiation. Strontium chlorapatite: Eu^{2+} provides the blue-violet and yttrium oxide: Eu^{3+} provides the orange-red coloration.

Rare earth magnets have replaced the solenoid in control valve drivers which electromechanically drive control valves on hydraulic power actuators like those used in aircraft hydraulic systems. The new drivers require less power to operate and eliminate the need for a secondary hydraulic power system resulting in an order of magnitude cost savings.

RE's Used in Contact Printing

The use of amorphous GdFe, TbFe and DyFe alloy films for contact printing without a bias field or thermal transfer contact printing has been studied by N. Imamura, Y. Mimura and T. Kobayashi [*J. Appl. Phys.* **48,** 2634-7 (1977) and *Japan J. Appl. Phys.* **15,** 715-6 (1976)]. The films contained 15 to 30% rare earth, the compensation composition at which the easy axis of magnetization is perpendicular to the film plane. The stray magnetic fields from the magnetic tape or card are large enough to "write" information into the amorphous alloy films. This information can then be magneto-optically read out using the polar Kerr effect. The quality of a printed pattern was found to decrease with increasing film thickness. The low coercivity of the GdFe films allows contact printing with no bias field. The coercivities of TbFe and DyFe are too high for them to be of any use in the same manner as the GdFe film. However, the Curie temperature of the DyFe alloy is low (60° C) and its coercivity decreases with increasing temperature to the extent that near 60° C the stray fields from the magnetic tape or card are large enough to "write" information on the DyFe film. Therefore the DyFe alloy is suitable for contact printing if a thermal transfer is used.

Unusual Isotope Effect

H. Kruger, O. Lutz and H. Oehler have used NMR spectroscopy in aqueous solution to determine the nuclear magnetic moments and ratios of quadrupole moments for ^{138}La and ^{139}La [*Phys. Letters* **62A,** 131-2 (1977)]. While measuring the dependence of the Larmor frequencies and linewidths as a function of concentration of various lanthanum salts in H_2O and D_2O, the lanthanum solvent isotope effect was determined. The value obtained indicates that the solvent isotope effect anomalously decreases with increasing atomic number of the IIIb elements.

CONTRIBUTORS

Five companies renewed their support of RIC in the third quarter of fiscal year 1978, bringing the total number of benefactors to 35 so far. Contributions were received from Apache Chemicals, Inc. USA for the second year, British Flint and Cerium Manufacturers, England, and Companhia Industrial Fluminense, Brazil, both six year contributors, Colt Industries-Crucible Inc., USA, for the fourth year and Santoku Metal Industry Co. Ltd., Japan, an eight year supporter of the Center. Response has been slow in the third quarter following a record breaking first half year, however we look for a strong finish in 1978.

Deformation Mechanism

Using X-ray diffraction, optical and scanning electron microscopy and high and low field magnetic measurements, H. H. Liebermann and C. D. Graham, Jr., attempt to determine the mechanism of plastic deformation in dysprosium single crystals [*Acta Metallurgica* **25,** 715-20 (1977)]. They found the mechanism to be $\{10\bar{1}2\}\ <10\bar{1}\bar{1}>$ mechanical twinning and that it was a primary twinning system. The lowering of the magnetostatic and magnetocrystalline anisotropy energies resulting from twin formation is thought to be the driving force for the deformation. Simplified energy considerations support this explanation. Other possible causes for deformation include the magnetostrictive strains in high fields exceeding the elastic limit of the sample or the mechanical torque forces acting on the sample due to misalignment of the hard axis with the applied field exceeding the sample yield stress.

Separation, Preparation Application, Toxicology

Book number B2 of *System 39, Rare Earth Elements, the Gmelin Handbuch der Anorganischen Chemie* has been published by Springer-Verlag in 1976. This volume is 283 pages in length and costs DM 585, - (~$239.90). This book features English table of contents, preface and margin notes.

The four topics covered in Book B2 are separation of the rare earths, preparation of rare earth metals, application of the metals and toxicology. Types of separations discussed include fractional precipitation, crystallization, hydrolysis and decomposition; selective dissolution, oxidation and reduction; electrolysis, amalgam extraction, ion exchange and solvent extraction. The chapter on metal preparation covers metallothermic, electrolytic and other reduction methods; preparation of special forms, i.e. thin film, flake, single crystal; refining processes; purity testing; storage, shaping and handling. Rare earth applications reported include use in pyrophoric alloys, cast iron, steel, non-ferrous alloys, welding, solder, brazing alloys, magnets, X-ray filters, cathodes, getters, nuclear technology, catalysts and hydrogen storage. Last is the chapter concerning the toxicology of the rare earths.

R_2O_3 + Ti ?

Citing the fact that there are no commercially available titanium alloys which contain insoluble dispersed particles for improved high temperature mechanical properties, R. C. Waugh has undertaken research to determine the high temperature compatability of 16 oxides, which included 14 rare earth oxides, with titanium [*Int. J. Pwdr. Met. Pwdr. Tech.* **12,** 85-9 (1976)]. Titanium—10% oxide compacts containing Dy_2O_3, Er_2O_3, Eu_2O_3, Gd_2O_3, Ho_2O_3, La_2O_3, Lu_2O_3, Nd_2O_3, Pr_6O_{11}, Sc_2O_3, Sm_2O_3, Tb_2O_3, Y_2O_3 and Yb_2O_3 were subjected to differential thermal analysis (DTA), electron microscopy and electron microprobe analysis. DTA revealed a definite exothermic reaction between Pr_6O_{11} and Tb_2O_3 [Editor's note: The Tb_2O_3 probably contained some Tb_4O_7 to give this exothermic reaction.] and the titanium matrix thereby excluding these oxides from further consideration. The remaining compacts were vacuum sintered for 4 hours at 1066° C. Electron microprobe analysis showed that Gd_2O_3, Sm_2O_3, La_2O_3, Y_2O_3, Ho_2O_3, Sc_2O_3, Yb_2O_3, Er_2O_3 and Eu_2O_3 reacted with the titanium matrix at a slower rate. Unfortunately any reaction is unsatisfactory and so these oxides are also eliminated as dispersants. Only Lu_2O_3, Nd_2O_3 and Dy_2O_3 displayed no evidence of reaction with the titanium matrix, which makes them promising candidates for dispersion strengthening of titanium alloys.

Physical Properties of Chalcogenides

The Russian book *Fizicheskie Svoistva Khal'kogenidov Redkozemel'nykh Elementov (Physical Properties of the Chalcogenides of Rare Earth Elements),* V. P. Zhuze, Ed., Nauka Publishers, Leningrad (1973) has been translated to English and is available from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161 as report number DOE-tr-6 (December 1977). The translation is 526 pages in length. The cost of a paper copy is $15.50 and microfiche is $3.00.

The authors attempt to systematize and collate the huge volume of theoretical and experimental data that has been generated due to the many interesting properties and possible applications inherent in the chalcogenides of the rare earths. Physical and physico-chemical properties discussed include phase diagrams; crystal structures; valence states; methods of preparation; single crystal growth and identification; temperature, pressure, thermomagnetic and electromagnetic effects on the electrical conductivity; superconductivity; heat capacity; thermal expansion; thermal conductivity; magnetic properties and magnetic ordering; exchange interactions and optical properties. Applications include thermo-electric and magneto-hydrodynamic transducers, nuclear cooling, superconductors, reflective coatings, phosphors, lasers, magneto-optical storage, optical communications, magnetic materials and semiconductor devices. This review includes 719 references.

Lasers Initiate New Series

Lasers and Excited States of Rare Earths by R. Reisfeld and C. K. Jørgensen is the title of volume one of a new series entitled *Inorganic Chemistry Concepts,* edited by C. K. Jørgensen and published by Springer-Verlag, Heidelberg (1977). This clothbound volume contains 226 pages and costs $29.50 (DM 64,-).

In chapter one, analogies and differences are drawn between monatomic entities and condensed matter with respect to spherical symmetry, minor deviations from spherical symmetry, intershell transitions and electron transfer bands.

Chapter two discusses various aspects of rare earth lasers including spontaneous and stimulated emission, three- and four-level laser systems, oscillation modes, optical pumping threshold and laser output. Examples are given of various rare earth gaseous, liquid and solid state lasers in general and neodymium-doped crystal, glass and glass ceramic lasers, in particular.

The discussion of chemical bonding and lanthanide spectra in chapter three covers the nephelauxetic effect, photo-electron spectra, hypersensitive pseudoquadrupolar transitions and the Judd-Ofelt parametrization.

Chapter four deals with energy transfer. Transfer probabilities, migration of excitation, inhomogeneous broadening and phonon-assisted energy transfer are discussed and examples are given.

Applications and suggestions constitute chapter five. Among the applications the most notable possibilities are induced thermonuclear reactions and advanced communication systems.

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Possible $LaNi_5$ Substitute

C. E. Lundin and F. E. Lynch of the Denver Research Institute have developed a new intermetallic nickel compound which appears to be a viable alternative to most of the other hydrogen storage materials under consideration—including $LaNi_5$ [*E/MJ* **178,** [7] 43, 47 (1977)]. Their compound, $(La_{0.67}Nd_{0.25}Pr_{0.08})$ Ni_5, has the advantages of being less costly, having abundant raw materials, does not contain co-occurring metals (e.g. Ce) which inhibit hydrogen absorption or desorption, absorbs six hydrogen atoms per molecule, is not contaminated in air as much as other alloys under consideration and requires pressures only slightly higher than $LaNi_5$. Another advantage is safety, since cryogenics and extreme pressures are not used, and container puncture or ignition is much less of a hazard.

Applications of (La, Nd, Pr) Ni_5 could include solar heating and cooling of homes, leveling of peak load demands at electric utility companies, a nonpolluting combustion engine, hydrogen gas purification, compression and storage, and utilization of natural heat sinks.

Ce Aids Holograms

High optical sensitivity has been observed in cerium-doped strontium barium niobate (SBN:Ce) crystals by K. Megumi, H. Kozuka, M. Kobayashi and Y. Furuhata [*Appl. Phys. Letters* **30,** 631-3 (1977)]. Introduction of cerium gave rise to a four order of magnitude increase in recording sensitivity and an approximately eightfold enhancement in saturation efficiency. The increased sensitivity is thought to be due to the high quantum yield for carrier generation processes. Another advantage is the symmetrical behavior of the storage and erasure cycles. When kept in darkness at room temperature, the decay time constant of holograms stored in SBN:Ce was found to be one month. A longer decay time could be expected if the crystal were treated under higher oxidation conditions to reduce any oxygen deficiencies formed during crystal growth. The authors feel that holographic storage in SBN:Ce is feasible. *According to the authors it is the most sensitive electro-optic crystal to date and has great potential for high speed rewritable optical memory applications.*

Hume-Rothery Award

K. A. Gschneidner, Jr.

K. A. Gschneidner, Jr. has been named the recipient of the 1978 William Hume-Rothery Award. This annual award was created in 1972 by the Metallurgical Society of AIME to honor an outstanding scientific leader in recognition of scholarly contributions to the science of alloys.

Educated at the University of Detroit and Iowa State University (Ph.D. 1957) Gschneidner conducted research at the Los Alamos Scientific Laboratory and then at the University of Illinois before joining the Ames Laboratory and Iowa State University in 1963. He is currently the Assistant Program Director for Metallurgy and Ceramics at Ames Laboratory-DOE, Professor of Materials Science and Engineering and Director of the Rare-Earth Information Center, Iowa State University. Current research interests include the alloy theory of metallic systems, preparation of high purity rare earth metals and single crystals of both metals and intermetallic compounds, low temperature heat capacity, magnetic susceptibility and electrical resistivity of rare earth solid solution alloys.

Mg Alloy Phase Diagrams

G. V. Raynor has critically summarized the available knowledge on the constitutions of a number of potentially important magnesium-based alloy systems, many of which contain one or more rare earths [*International Metals Reviews,* No. 216, 65-96 (June 1977)]. Citing renewed interest in the development of high strength lightweight magnesium alloys and the varying degree of completeness and accuracy of available constitutional studies the present review was aimed at those systems with a high potential for application. Ternary phase diagrams are discussed for the alloys of magnesium and yttrium with manganese or zinc; magnesium and neodymium with manganese, nickel, yttrium or zinc; and, magnesium and cerium with aluminum, lanthanum, silicon, manganese, calcium or nickel. The quaternary systems covered which included rare earths are magnesium-neodymium-yttrium-zinc, magnesium-neodymium-manganese-nickel and magnesium-cerium-cobalt-manganese.

Amorphous Materials Surveyed

Recent research concerning amorphous magnetically ordered metals and alloys which can be prepared by evaporation or sputtering and chemical or electrodeposition has been surveyed by G. Dietz, in order to obtain information about the atomic ordering in amorphous materials, the influence of structural disorder on magnetic properties and possible applications as soft magnetic materials, bubble materials and for magneto-optical writing and erasing [*J. Magnetism and Mag. Mater.* **6,** 47-51 (1977)]. The 131 references include articles on binary alloys of Gd, Ho, Tb, Dy, Y, Lu, Er, Tm and Yb with Co, Fe, Ni and Cu and ternary alloys of Gd and Dy with Co, Mo, Cu, Au, Cr, Fe and Ni. In addition, the studies on the uniaxial magnetic anisotropy of these alloys were summarized. The author concludes that the main cause of the observed uniaxial anisotropy should be short range atomic ordering.

CF in RE Compounds

Crystal field effects in rare earth intermetallic compounds is the subject of a recent review by W. E. Wallace, S. G. Sankar and V. U. S. Rao [*Structure and Bonding* **33,** 1-55 (1977)]. In updating an earlier summary made in 1973 the authors briefly review the nature of exchange interactions and crystal field effects and the mathematical treatment of a single J state, the effects of J mixing and the effect of an external or exchange field. This approach is then related to experimental evidence obtained from magnetic susceptibility, heat capacity and free energy, neutron inelastic scattering, spin disorder resistivity and magnetic anisotropy. Experimental data for specific families of rare earth intermetallic compounds including $RA1_2$, $RA1_3$, RNi_2, RNi_3, RNi_5, RCo_2, RCo_5, R_2Co_{17}, RFe_2 and RH_2 are examined. Special mention is given to the crystal field effects in samarium compounds, i.e. spin reorientation in $SmFe_2$ and the magnetocrystalline anisotropy of $SmCo_5$. 167 references are included.

Superalloy Metallurgy

Powder metallurgy techniques as applied to superalloys is the subject of a review by J. S. Benjamin and J. M. Larson [*J. Aircraft* **14,** 613-23 (1977)]. At present superalloy powder metallurgy can be divided into three catagories. These are conventional techniques, thermoplastic processing and mechanical alloying. The development of mechanical alloying is of the most interest to rare earthers, since this process has made possible the production of rare earth oxide-dispersion strengthened superalloys unattainable by other techniques. The mechanism of the oxide dispersion is briefly reviewed. Three commercially-produced, mechanically-alloyed, nickel-based superalloys which contain Y_2O_3 for dispersion hardening are discussed with respect to structural characteristics, physical properties, chemical properties and mechanical properties. These increasingly complex alloys offer possible advantages in aircraft turbine vanes, burner cans and turbine blading applications.

$YFeO_3$ Zaps Water

The possibility of photoelectrolyzing water with illuminated semiconducting electrodes as a means of solar energy conversion has caused M. A. Butler, D. S. Ginley and M. Eibschutz to study the use of $YFeO_3$ electrodes for photoelectrolysis [*J. Appl. Phys.* **48,** 3070-2 (1977)]. A model has related the hydrogen production to the electronegativities of the electrodes and predicted that rare earth orthoferrites would have improved zero bias operation characteristics over currently used materials. The photoresponse was observed only when $YFeO_3$ was positively biased, however because of its improved flatband potential $YFeO_3$ required less bias for operation. The electrode showed no sign of deterioration although the long term stability was not specifically studied. Low quantum efficiency in $YFeO_3$ can be modified by improving its purity and/or optimizing dopant levels to enhance the carrier concentration. This study indicates $YFeO_3$ to be a promising candidate as a photoanode for the practical conversion of solar energy to chemical energy by the photoelectrolysis of water.

Room Temperature Blue Light Laser

L. Esterowitz, R. Allen, M. Kruer, F. Bartoli, L. S. Goldberg, H. P. Jenssen, A. Linz and V. O. Nicolai believe they are the first to report room temperature operation of a solid state laser in the blue region [*J. Appl. Phys.* **48,** 650-2 (1977)]. A 0.2% Pr-doped $LiYF_4$ crystal was longitudinally pumped using a pulsed dye laser. Laser emission occurred at 479 nm and required a threshold energy density of 8 J/cm^2. The authors plan to measure the conversion efficiency once the experimental parameters have been optimized. Possible applications include the conversion of long-pulse dye laser excitation to Q-switch output in the blue spectral region.

Russian RE Semiconductor Bibliographies

In the past few months RIC has received *Redkozemel'nye Poluprovodniki. Tekuschchaya Bibliograficheskaya Informatsiya 6* [*Rare Earth Semiconductors. Current Bibliographic Information, No. 6*] V. P. Zhuze, editor, Fiziko-Tekhnicheskii Institut im. A. F. Ioffe, Akademii Nauk SSSR, Leningrad (1977), and also No. 7, which carries the same title, editor and publisher as No. 6. The sixth bibliography on semiconductors has 774 citations while the seventh has 632. The references are printed in their original language—English, Russian, French, etc. A brief subject index (20 entries) is also included in each volume.

RE's in the News

World's Most Powerful Laser

A neodymium-doped glass laser, called Shiva, has been constructed at the Lawrence Livermore Laboratory (LLL) and initial tests have revealed it to be the world's most powerful laser. 10,200 joules of laser light energy was produced in a 10^{-9} second pulse almost tripling the output of LLL's Argus laser. The Shiva laser is to be used in inertial confinement fusion experiments in which scientists hope to demonstrate a significant thermonuclear burn using deuterium and tritium targets.

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, Iowa 50011 or from Molycorp, Inc., Metallurgical Sales, No. 4 Gateway Center, Pittsburgh, PA 15222.

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