



RARE-EARTH INFORMATION CENTER NEWS

SUPPORTED BY INSTITUTE FOR ATOMIC RESEARCH
IOWA STATE UNIVERSITY / AMES, IOWA

Volume IV

March 1, 1969

No. 1

Spectral Behavior of Lanthanides

During the past few months several interesting papers have come to our attention dealing with the spectral properties of the lanthanide elements and some of their potential applications.

DISPEL MISCONCEPTIONS

The cathodoluminescent properties of the trivalent lanthanides in Y_2O_3 were studied by Buchanan and co-workers, *J. Appl. Phys.* 39, 4342 (1968). They noted that their results indicate, contrary to extensive prejudices, that optimum activator concentrations in Y_2O_3 are quite large (1 to 10%). The reasons for these past prejudices and the advantages of Y_2O_3 as a host over other materials are discussed.

Buchanan and co-workers also show that ions at the beginning and end of the lanthanide series contrary to accepted opinions have luminescent efficiencies equal or greater than those for the ions in the middle of the series.

INFRARED QUANTUM COUNTER

An infrared quantum counter, as noted by Esterowitz and co-workers [*Appl. Optics* 7, 2053 (1968)], is the only quantum amplifier with photon gain that can approach a noise temperature of 0°K. These researchers have investigated 165 different combinations of trivalent lanthanide ions in a variety of inorganic single crystal lattices.

Some of the best combinations of lanthanide ions and host crystal, and their output wavelengths were found to be: Pr^{+3} in $LaCl_3$ (0.645 μ), Er^{+3} in CdF_2 (0.668 μ), Tm^{+3} in $CaWO_4$ (0.385 μ), Ho^{+3} in LaF_3 (0.538 μ) and Er^{+3} in LaF_3 (0.546 μ).

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Diffusion

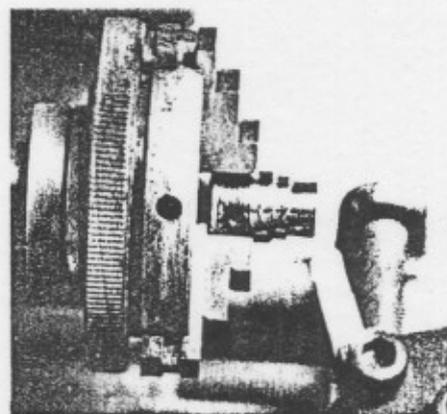
In two different papers Russian scientists have reported on the self-diffusion of yttrium and the chemical diffusion of zirconium in yttrium.

The self-diffusion results by Maskalets and co-workers [*Met. Metalloved. Chist. Metal.*, No. 6, p. 189, Atomizdat, Moscow (1967); *Metal Abstracts* 1, No. 13-0770 (1968)] are the first such values reported for any rare-earth metals, as far as *RIC News* is aware. The temperature dependence of self-diffusion was given as $D = 5.5 \times 10^{-6} \exp(-30800/RT)$ for the temperature range 1000-1175°C. The authors noted that in this temperature range volume diffusion is the dominant mechanism for transport of material and its activation energy is 25-30 kcal/g-at.

The chemical diffusion of zirconium in yttrium was measured from 1000 to 1300°C, and the temperature dependence was determined to be $D = 4 \times 10^{-3} \exp(-38000/RT)$. These studies were reported by Rogozin, Gert and Babad-Zakhryapin in *Izv. Akad. Nauk SSSR, Metall* 1968 [3] 228. These authors also determined the chemical diffusion coefficients of molybdenum and niobium in yttrium at 1300°C to be $\leq 1.8 \times 10^{-8}$ and $\leq 1.4 \times 10^{-8}$ cm²/sec, respectively.

Rare Earths In the News

Pm METAL'S METTLE



Shown ready for machining is the ^{147}Pm ingot weighing about 100 g which was produced at Battelle-Northwest. It is the largest known amount of promethium metal ever made.

Photo courtesy of Pacific Northwest Laboratory operated by Battelle Memorial Institute for the U.S. Atomic Energy Commission.

E.J. Wheelwright at Battelle-Northwest reports that he and his associates have produced the largest amount of ^{147}Pm metal ever made — more than 100 g (see figure). Wheelwright reports a density of 7.2 g/cc of the metal, and a melting point at $1168 \pm 6^\circ C$, considerably higher than the $1080 \pm 10^\circ C$ reported by F. Weigel, *Angew. Chem.* 75, 451 (1963).

HEAT RESISTANT ALLOY

A cobalt-base alloy containing yttrium may contribute to increased service temperatures of high temperature alloys. Yttrium's affinity for sulfur is said to make such

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Lanthanum Compound As Electrode Material

Considerable attention has been given in recent years to solid electrode voltammetry for use in electrochemical applications. Curran and Fletcher, *Anal. Chem.* 40, pp. 78, 180 and 1809 (1968), have used LaB_6 as an indicator electrode for anodic oxidation instead of mercury which is hampered by oxide formation. LaB_6 has high cathodic and anodic over-potential in aqueous solutions although the potential span is very short.

In the first study, a procedure was found for determining cathodic limit of the electrodes by reduction of water at high pH or reduction of hydrogen ion at low pH, and for the anodic limit by gross oxidation of LaB_6 . The potential range was found to be 1 V. The second study involved application of LaB_6 as an indicator-electrode for acid-base titrations in aqueous solutions by using constant current potentiometry. The study demonstrated precision of a few parts per thousand of a hydrochloric acid with potassium hydroxide titration.

In the third study LaB_6 was used as an electrochemical generant of La(III) for titrations in determining Ni(II), Cu(II) and Zn(II). Constant current electro-oxidation of LaB_6 in pH-controlled solutions allows generation of known amounts of La^{+3} , where EDTA can be used for determining these three metal ions with excellent accuracy.

Friction

The influence of crystal structure and other properties on the friction and adhesion of some hexagonal metals have been studied by Buckley and Johnson, *Wear* 11, 405 (1968). A number of the hexagonal rare-earth metals were included in this study.

These authors found that the coefficient of friction was inversely proportional to the ratio of the interbasal planar spacing to the a lattice parameter. Thus the heavy lanthanide and yttrium metals

which have the small ratios (~ 1.57) have coefficients of friction of about 0.7, while the light lanthanides which have large ratios (~ 1.61) have values of about 0.35 for this coefficient. Most of the other hexagonal metals have coefficients of friction between 0.35 and 0.7; titanium, however, is a notable exception with a coefficient of 1.2.

Buckley and Johnson also point out that in general body-centered and face-centered cubic metals have higher coefficients of friction than the hexagonal metals.

THERMIONIC CONVERTERS

Interest in high-heat-resistant materials for use in thermionic converters led to the investigation of Y_2O_3 . E. S. Keddy reports that 98.7% pure Y_2O_3 withstood 1000°C in vacuo, but disintegrated at 2000°C [U.S. Atomic Energy Comm. Report LA-3822-MS (1968)]. A similarly pure Y_2O_3 sample failed at 1000°C after immersion in molten barium or lithium. Higher purity Y_2O_3 (99.5%) withstood all the above tests, although there was some surface attack by barium and lithium.

Impurities in Y_2O_3 affect heat resistance considerably and indicate that high-purity yttria must be used in high-temperature thermionic converters.

Rare Earths Common in Body

Since 1945, the determination of rare earths in the human body has been conducted by a team at the Technical University, Otaniemi, Finland. Results were negative until recent use of x-ray emission spectroscopy has proved their presence to be surprisingly common.

Yttrium was found (0.003% of the ash) in 61 out of 236 organ specimens of patients who died in Helsinki hospitals reports Erämetsä, Sihvonen and Forssén, *Ann. Med. Biol. Fenniae* 46, 179 (1968). Distribution varied and was high at 0.670% yttrium in one specimen.

Describe Rare-Earth Metal Production

The industrial methods used to produce rare-earth metals have been described in two articles during the past year. The fused salt electrolysis method was described by I. S. Hirschhorn, *J. Metals* 20, 19 (Mar. 1968), and the metallothermic method was discussed by J. L. Moriarty, Jr. *J. Metals* 20, 41 (Nov. 1968).

Moriarty is primarily concerned with the preparation of high purity rare-earth metals, whereas Hirschhorn emphasizes mischmetal and commercial grade metals.

La Improves Ti

The effect of lanthanum additions on the strength and plasticity of titanium between -196 to 800°C has been reported by Ul'yanov and Kovtun in *Izv. Akad. Nauk SSSR Metallurgiya* 1967, [4] 117 (English translations - *Russ. Metallurgy* 1967, [4] 59). Alloys containing between 0.4 and 2.2 wt % La were examined. Ul'yanov and Kovtun found that 1.8 wt % La was optimum with respect to the tensile strength; a 50% increase in strength was obtained for this addition.

Lanthanum additions also improved the ductility, especially below room temperature. A 1.0 wt % addition was found to be optimum with respect to the ductility. At -196°C the ductility of the 1.0 wt % La alloy was increased by 100% over that of pure Ti.

It would appear that lanthanum is a beneficial alloying additive for titanium especially for low temperature service applications.

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alloys nearly impervious to sulfur's corrosive effects.

COOL CONTROL RODS

A Dy_2O_3 -Ni cermet developed at Douglas United Nuclear, Inc., may eliminate the need for water to cool nuclear reactor control rods. The cermet can withstand the heat of a reactor core, absorbs neutrons readily, and neither swells nor contracts under prolonged neutron bombardment.

Cobalt-RE Alloys By Electrolysis

A method for producing cobalt-rare earth alloys by electrolysis has been developed at the Reno Metallurgy Research Center of the U. S. Bureau of Mines. Morrice and co-workers reported on their process in *J. Metals* 21, 34 (Jan. 1969).

The method utilizes rare-earth oxides as feed materials to produce alloy products rich in rare-earth metals. Desired compositions can then be achieved by the addition of more cobalt.

The thermal-gradient cells used in the preparation of the alloys consisted of a graphite crucible to contain the electrolyte (usually LiF and the respective rare-earth fluoride), a graphite anode and a cobalt cathode. The authors report that, in general, all the alloy products were relatively low in impurities.

Cobalt alloys containing, individually La, Ce, Pr, Nd, Sm, Gd, Dy, Y, didymium mixture, and mixed yttrium - and cerium-group metals have been produced.

Lab Safety

Several recent studies have dealt with the biochemical hazards and exposure to radioactive ^{147}Pm and neodymium lasers.

A report by C. V. Durham, U.S. Air Force Report APGC-TR-68-53 (June 1968) contains a brief discussion of laser systems and a more detailed review of the Nd-doped laser. More specifically, this report makes recommendations for safe operation of the laser. For example, special safety goggles with an optical density of over 16 at the Nd wavelength are required for all personnel within range of the laser. Serious corneal injury to the eye can occur from infrared and ultraviolet radiation.

Exposure to ^{147}Pm has recently been of great concern. Studies have been primarily focused on the distribution in the body after expo-

sure, ingestion, or inhalation of the isotope. Comer and Knapton, *Health Physics* 15, 166 (1968), studied the leaching effect that gastric juice has on ^{147}Pm .

Howell and King, *ibid.*, p. 174, described radiation protection problems encountered during preparation of ^{147}Pm capsules. Both Bremsstrahlung energy spectra and β -energy require strict contamination control such as inspection of rubber gloves damaged from ozone or high temperatures.

Palmer and co-workers, *ibid.* p.187, were called upon to establish realistic exposure limits and to determine the dose from accidental exposures, uptake, retention and localization of ^{147}Pm . Internally deposited ^{147}Pm was evaluated by using urinary and fecal excretion data.

The above studies with ^{147}Pm resulted from investigation of potential accidental acute intakes and recognized safety hazards of the workers at Battelle-Northwest.

LaB₆-MHD Generator

The use of lanthanum hexaboride to increase the conductivity of the working fluid in a magneto-hydrodynamic (MHD) generator was discussed by Honma and Nomura, *Denki Shikensho Iho* 32, 507 (1968); *Nucl. Sci. Abstracts* 22, No. 47877 (1968). The increased conductivity of the gas is due to the favorable thermionic emission properties of LaB₆. The authors found that an electron density of 10^{14} cm^{-3} is obtained with a powder density of 10^{13} cm^{-3} for LaB₆ solid particles of 10^{-5} cm radius. (Note solid LaB₆ contains 10^{21} formula units/cm³). The maximum conductivity was calculated to be 0.1 mho/cm for these conditions at 2300°K with nitrogen gas.

The other transport values, *e.g.* viscosity and thermal conductivity, were also calculated, and it was found that these properties were not appreciably affected by the LaB₆ powder suspension in the gas.

NEW ARC LIGHT

During the past few years Sylvania has developed a new high pressure discharge light which is claimed to be the closest anyone has ever come to duplicating natural sunlight. This light, called *Metalarc*, contains primarily mercury, and scandium and sodium oxides. The mercury lines in the discharge give rise to blue and green light and the oxides to red, orange and yellow.

The lines in the spectrum are generally less than 20Å apart and when thorium is included the spacing between lines becomes less than 5Å. Minor amounts of other rare earths are added to improve the spectral characteristics of the light.

Metalarc is presently being used in several sports stadiums and indoor coliseums in the United States, including Charger Stadium in San Diego. The basic ideas of Metalarc are covered by United States patents 3,334,261 and 3,407,327.

TRANSMUTATION

A novel use of lanthanum has been developed by J. W. Denison, Jr. of Trak Microwave Corp., Tampa, Fla. The lanthanum is alloyed with nickel which is used as cathodes in vacuum radio tubes.

After the tube is manufactured it is irradiated by neutrons in an atomic pile, which transmutes the lanthanum to barium. When the new tube is used the barium, which

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RIC News

Vol. IV, No. 1

March 1, 1969

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

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Second-Class postage
paid at Ames, Iowa.

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Telephone: Area Code 515 294-2272
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TUNABLE PHONON DETECTOR

A tunable, acoustical phonon detector has been demonstrated by Sabisky and Anderson, *Appl. Phys. Letters* 13, 214 (1968), by using Tm^{+2} ions in a CaF_2 host. The phonon detector is based on the optical detection of the spin population difference of an impurity ion (Tm^{+2}) through the spin-phonon interaction. The phonons were generated at $1.4^\circ K$ by a transducer using a few milliwatts of radio frequency power at 9.5×10^9 Hertz (cycles per second).

PHOSPHORS AND SCINTILLATORS

The application of lanthanide ions for radiation detection and measurement was discussed by Buchanan and Wickersheim, *IEEE Trans. Nucl. Sci.* NS-15, [3] 95 (1968). The luminescent properties of lanthanide phosphors fall into two groups: those which exhibit sharp line spectra due to $4f \rightarrow 4f$ transitions and those which exhibit broad-band spectra due to $5d \rightarrow 4f$ transitions of the activator ion or from emission of the host itself.

In the first category the efficiencies of the phosphors are high, but decay times range from micro- to milli-seconds. Materials which have these characteristics are being studied for imaging and energy conversion applications.

In the second category phosphors have decay times in the nano- to micro-seconds range, and thus these materials look quite attractive for scintillation counting applications. The stopping power of the host material is quite important in this application. Y_2O_3 , a common host material, is too light but Gd_2O_3 and/or Lu_2O_3 should be effective hosts since their stopping powers are significantly higher than that of Y_2O_3 .

PHOTOSENSITIVITY

Eu^{+3} and Tb^{+3} in fluid solutions emit fluorescence which in turn is absorbed by organic sensitizers present as non-associated solutes and can be measured quantitatively. These rare-earth ion probes were one of the topics presented by N.

Filipescu at the 156th American Chemical Society Meeting in Atlantic City, N. J.

Rate constants for the transfer process in several organic carbonyl compounds were taken at varying lanthanide concentrations, viscosities and temperatures. Then treatment was extended to photochemical reactions. The photokinetic data were consistent with an inter-molecular (collisional) transfer.

RE-OPEN AUSTRALIAN TREATMENT PLANT

The South Australian Government's uranium treatment plant at Port Pirie, closed since 1962, will be re-opened as a result of the merger of two Australian firms which have purchased the plant from the Government.



Australian Ceramic Industries Pty. Ltd. and Field Group Research Pty. Ltd. will process both uranium and rare-earth oxides at the Port Pirie plant. Re-opening of the plant

is expected to boost Australia's annual export earnings by millions of dollars.

The site taken over by the new company covers 80 acres including 70 acres of residue dams left over from previous operations. South Australian Minister of Mines R. C. DeGaris said the dams contain the world's largest known supply of scandium which has potential for a new type of light. (see story on page 3).

RE'S IN TOP 100

When Industrial Research Inc. named the 100 innovations it considered the most significant technical products for 1968, the rare-earth industry took a giant step forward.

Four of the 100 products named by Industrial Research Inc. were developed around the rare earths. The four products named which employed rare earths in their manufacture included three lasers, all of which employed Nd - one of which also utilized YAG as the host material - and a solid state lamp which converts infrared radiation to visible green light by means of a LaF_3 phosphor.

Rare Earthers, hold your heads high!

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is much less soluble in nickel than lanthanum, diffuses to the surface, thereby increasing the thermionic properties of the cathode.

The advantage of these tubes is that they operate at low temperatures increasing the lifetime and reducing internal contamination.

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