Rare-Earth Information Center NEWS

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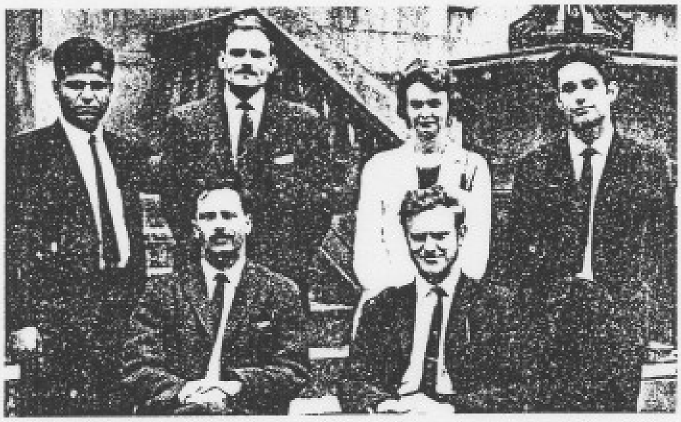
CHEMISTRY GROUP —

University of Dundee



DUNDEE GROUP — Standing from left are Said Malik, Hugh Pincott, Christine Duncan and Phil Bristow. Seated are Tim J. R. Weakley, left, and John C. Barnes.

On August 1, 1967, the University of St. Andrews relinquished its northern constituent college and the University of Dundee was created as Britain's newest University, with a student enrollment of 2200 and a faculty of about 400. A small but intrepid group of rare-earth chemists have infiltrated the new organization.

The faculty members involved are John C. Barnes and Tim J. R. Weakley. The first Ph.D. candidate from the group is Hugh Pincott, an ebullient Welshman, who is currently writing a thesis describing his studies of the ligand to metal electron transfer spectra of trivalent rare-earth compounds. He has also been working on some compounds of Tb(IV) and Pr(IV). Next in line is Phil Bristow who has been studying carboxylate complexes of divalent and trivalent ions in solution, and who will now move on to decompose the solid complexes in our new Perkin Elmer DSC 1B calorimeter.

Said Malik and Bob Peacock are studying the composition and structure of heteropoly-molybdates and tungstates with Tim Weakley. Using lanthanides as hetero-atoms will keep them busy for a long time to come; there are some very curious reports in the early literature about these compounds.

Miss Christine Duncan finds time from her duties as technician in

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FUEL CELL

O. Erämetsä and A. Johansson describe in *Suom. Kemist. 40*, 93 (1967) the results of a preliminary investigation of praseodymium oxide as a solid electrolyte for fuel cells.

A cell which consisted of a Pr_6O_{11} layer between two platinum electrodes was constructed so that one platinum electrode was exposed to air (oxidizing atmosphere), and the other electrode to ammonia gas (reducing atmosphere). When heated to 750 °C the cell generated a voltage of about 410 millivolts.

RIC Closes

The cessation of agency funding for the Rare-Earth Information Center has made it necessary to discontinue RIC operations.

This means that the publication of *RIC News* will be suspended indefinitely with the distribution of this final issue. Also, information requests can no longer be handled in the manner established during the two years of RIC's operation.

Discontinuance of the center, however, does not indicate any change in the Ames Laboratory's status as a center for rare-earth research. Ames Laboratory researchers will continue, as they have always done, to actively exchange ideas and information with others on a scientist to scientist basis. RIC subscribers are encouraged to initiate and maintain contacts of this type with the Ames Laboratory staff.

There are still some copies of RIC publications available; IS-RIC-1, catalog of rare-earth producers, and the color chart of the rare-earth compounds. Copies of the AEC

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GREINACHER TO GOLDSCHMIDT BOARD

Dr. Ekkehard Greinacher has been named to the Board of Directors of Th. Goldschmidt A.G., Essen, West Germany. Dr. Greinacher's appointment was effective Jan. 1. He had previously been in charge of technical activities in Goldschmidt's rare-earth and zirconium departments.

Reports, Brochures, Booklets

RARE EARTHS IN INDUSTRY

A new book, *The Industrial Chemistry of the Lanthanons, Yttrium, Thorium and Uranium* by R. J. Callow, (Pergamon Press, Inc., New York, 1967) 248 pp., $9.50, is an historical and descriptive review of solution chemistry, ore treatment processes, purification and preparation of commercial products, principal sources, separation methods, uses and the industrial significance of these elements.

The book is enhanced by considerable experience of the author which is included and by references to other definitive works covering many aspects of chemistry of interest to industrialists and chemists.

YTTRIUM

A new book on yttrium metal has been written by V. F. Terekhova and E. M. Savitskii (*Ittrii*, Izdatelstov Nauk, Moscow, 1967). The book is divided into three sections, which deal with (1) the production and properties, (2) the constitutional diagram and properties of alloys, and (3) utilization in technology. This volume contains 280 references.

ADVANCES IN CHEMISTRY

The American Chemical Society has released a new Advances in Chemistry Series book, *Lanthanide/Actinide Chemistry* by P. R. Fields and T. Moeller (American Chemical Society, Washington, D.C., 1967) 359 p., $11.00.

Thirteen chapters are devoted to the lanthanides and the remaining twelve to the actinides. Chemistries of the two groups are compared, particularly in areas of oxidation states, bonding, and complex-ion formations.

The rare-earth chapters review recent advances in new complexes of rare earths, chemical thermodynamics, preparation and identification of rare-earth diiodides, absorption and electronic spectra, europium chelates as lasers, and properties of tetravalent praseodymium compounds.

Inhaled Europium

The distribution and elimination of europium isotopes were studied in a man who inhaled them. The study was reported by C. E. Miller, Argonne National Laboratory, in *Radiation Research 31*, 541 (1967). Lengthwise distribution and selected points of the body were measured with a whole body counter using the 7-crystal-position technique, a slit collimated crystal and a collimated crystal.

Results of the three techniques agreed and showed the following: (1) 46% of the total Eu inhaled remained in the lungs after 393 days, (2) Eu from the lungs migrated to the lower limbs, (3) biological half-time of Eu in the lungs is 360 days and two years in the skull, and (4) over-all biological half-time between the 130th and the 393rd day is three years.

Letters

In a letter we received from the Radiation Shielding Information Center, Oak Ridge National Laboratory, Oak Ridge, Tenn., the value of adding rare earths to shielding material was seriously questioned.

The rationale for adding rare earths to shielding is, of course, that with the large cross sections available thermal neutron flux density can be suppressed. This is of little value, the writer points out, if capture gamma-rays are increased as so often happens with the rare earths.

If any of our readers have made a careful analysis and can provide justification for adding rare earths to shielding, the Oak Ridge center would like to know about it.

X-RAY FLUORESCENCE –

RE Isotopes Used As Analytical Tool

Sm^{145}, Eu^{155} and Gd^{153} are suitable radioisotope sources in x-ray fluorescent techniques for analyzing alloys, ore slurries, and determining coating weights, reports J. S. Watt in *Intern. J. Appl. Radiation Isotopes 18*, 383 (1967). The advantages of radioisotope units over conventional x-ray tube devices are high sensitivity, low cost and simplicity.

To determine suitable applications, comparisons were made of geometrical arrangements of source, sample and detector in relation to radioisotopes used. A high sensitivity of analysis resulted from using greater non-energetic x-rays than the K-shell adsorption edge of the sample. The energy was chosen by the appropriate atomic number target cone of the γ-ray source. For example, Am^{241} was used instead of Gd^{153} for analyzing Sn in Pb since the back-scattered component from Gd^{153} is enough to excite Pb K x-rays and reduce sensitivity.

γ-ray purity is important for more sensitive analyses. A ratio of low energy to high energy purity of 10,000 or greater is desirable. Gd^{153} meets the specification, but Sm^{145} falls short of this value and must be chemically processed to remove Eu^{152} and Eu^{154} impurities. Because of radioisotope impurities Eu^{155} is a less desirable source.

A lower limit of 150 ppm sample detection and coatings of several $\mu g/cm^2$ were found in eleven applications studied.

RIC CLOSES

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booklet *The Fraternal Fifteen* are also plentiful.

Subscribers can obtain copies of these publications by addressing their requests to the Information and Security Department of the Ames Laboratory.

Liquid Lasers

In a recent article Dr. Adam Heller (*Physics Today 20*, 35, Nov., 1967) reviewed the history, difficulties, newly developed solvents, performances and advantages of liquid lasers. He noted interest in liquid lasers lagged behind that of solid and gas lasers primarily because of their low power and energy outputs.

It was not until studies were initiated to find the underlying causes of these deficiencies that real progress was made in producing usable liquid lasers. As Heller points out, the low outputs are due to radiationless relaxation processes in the liquid solvents. These processes are generally due to transfer of electronic energy to high-energy vibrations of C-H, O-H and N-H bonds.

Armed with this knowledge scientists developed two kinds of liquid solvents. One consisted of an inorganic solvent which did not have any high-energy vibrational modes, e.g., selenium oxychloride (see *RIC News 1* [4] 7, 1966). The second type of solvent, which did not totally eliminate high-energy vibrational groups, relied on the exclusion of such vibrations from the immediate proximity of the laser ion or atom by incorporating the active ion in a molecular complex.

By employing these two kinds of solvents, higher outputs have been obtained in liquid lasers than in solid lasers containing the same active ion. Neodymium has been the most actively investigated laser ion, but some research has also involved samarium, europium and terbium.

The advantages of liquid lasers over solid lasers are these: they can be made into a variety of shapes (bulbs, spiral and straight tubes), cannot be permanently damaged at high power levels (10^{10} W), can be circulated and cooled in heat exchangers, and can be prepared at low cost.

MEETING

CALL FOR ABSTRACTS

The Seventh Rare Earth Research Conference Committee has issued a call for abstracts from those intending to present papers at this year's conference; Oct. 28-30. Abstracts should be submitted no later than May 1 to J. F. Nachman, Research Laboratories (R-1), Solar Division of International Harvester Company, 2200 Pacific Highway, San Diego, California 92112.

New to the rare-earth conference this year is a session on the geochemistry, geology, and mineralogy of the rare earths. This is in addition to sessions on ceramics, chemistry, metallurgy, and physics of rare-earth elements, compounds, and alloys which are an established part of rare-earth research conferences.

Fermi Surface Measurements

In the November 1967 issue of *Physics Letters* (*25A*, p. 669) Tanuma, Ishizawa, Nagasawa and Sugawara report that they have measde Haas-van Alphen oscillations in ytterbium metal. To our knowledge these are the first experimental results of Fermi surface measurements obtained on a rare-earth metal. The big difficulty is that very high purity metals are required to make de Haas-van Alphen or other Fermi surface measurements.

The authors started with 99.9% pure ytterbium which was purified to a claimed five nines purity by vacuum distillation. A single crystal 1.5 x 1.5 x 2.5 mm was used in the measurements. Periods of the order of 6×10^{-6} Oe^{-1} were found in the [110] and [112] directions and a shorter period of about 6.5×10^{-7} Oe^{-1} was found in the [111] direction. The authors, however, have not yet determined the Fermi surface from these results. Further work is in progress.

Mechanical Metallurgy

The recrystallization and work-hardening behaviors of most of the rare-earths metals have been discussed by I. N. Ross in *J. Inst. Metals 95*, 337 (1967). It was found that most metals could be cold worked to about a 50% reduction in area before the metals had to be annealed. Exceptions are Er and Y which developed cracks at 25% reduction, and Sm and Lu at 10% reduction. Whether the cracking phenomenon is inherent in the metals or resulted from large amounts of unfavorable impurities in the samples Ross examined is not known.

Recrystallization temperatures of the lanthanides did not follow any logical relationship with the atomic number or size.

Copper impurities were found to be very detrimental in cold-working these metals. This is due to the formation of brittle, low-melting copper phases which agglomerate in the grain boundaries.

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EUROPIUM, atomic number 63, was discovered in 1889 by Sir William Crookes and named after the continent Europe.

Rare Earths In the News

MERGER APPROVED

American Potash & Chemical Corp., and Kerr-McGee Corp. stockholders have approved the merger of Potash into Kerr-McGee. Potash is a manufacturer and distributor of chemicals for industry and agriculture. The stock exchange agreement called for in the merger will cost Kerr-McGee about $130 million.

COLOR TV OUTLOOK, ROSY

Although estimates vary somewhat, there is general agreement that the sales of color TV sets will climb to record highs in 1968. Estimates are that sales will climb 14 to 17% with total sets sold in excess of 6 million.

MOLYCORP ACQUIRES YTTRIUM CORP.

Molybdenum Corp. of America has acquired the 49% interest in Yttrium Corp. of America, which was formerly held by Pyrites Co., Inc., to gain full control of the firm. Yttrium Corp.'s plant is at Louviers, Colo., where Molycorp maintains rare-earth products manufacturing facilities.

TO RELEASE STOCKPILES

Upon the recommendation of its Armed Services Committee, the U.S. Senate approved bills to release scarce materials from Government stockpiles. Included among the materials which are to be sold immediately are 7640 short tons of rare-earth materials (rare-earth oxide content).

CHEMISTRY GROUP

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charge of the Inorganic Teaching Laboratory to do some research work. A number of senior year undergraduates have also worked on related problems for short periods during the last four years.

For a small group we are very well equipped and most of the measurements we need can be obtained within the chemistry department.

Alloy Thermionic Emitters Described

The development of alloy thermionic emitters for use in thermionic energy converters has been described by M. J. Albert and M. A. Atta, *Metals and Materials* 1, 43-9 (1967). These thermionic emitters consist of a refractory metal matrix (W, Ta or Mo), an activator (Ca, Y, La, Ce, Gd or Th) and a mobilizer (many different transition metals including La). Since these thermionic emitters operate at 1200-2000 ° C, the refractory metals are needed for their high temperature strength. The refractory metals alone have high work functions ~4.5eV and low emission levels $\sim 0.5 A/cm^2$.

The rare-earth activator metals lower the work functions by about 2eV and increase the emission levels by a factor of about two. The mobilizer metals have little effect on the work function but increase the electron emission tenfold. The mobilizer metals are thought to increase the surface coverage and life time of the activator metal monolayer on the emitter surface.

The alloy emitters investigated so far are much better than the oxide or compound emitters which are commonly used as cathodes. The advantages of the alloy emitters are higher emission levels with no significant increase of the work function, resistance to poisoning and ruggedness.

Aluminum Eutectics

In recent years controlled solidification of eutectic alloys to form lamellar or fiber-like structures have been used to improve the mechanical strength of one of the eutectic components (usually the phase which forms the major portion of the eutectic). The effect of rare-earth metals on the aluminum-rich eutectic has been reported by Street, St. John and Piatti (*J. Inst. Metals*, 95, 326 [1967]).

They found that the Al-Al_4Ce and Al-Al_3Y eutectics, when unidirectionally solidified at 2 to 20 cm/hr, have a fiber-like micromorphology. At rates greater than 20 cm/hr the eutectics become rod-like. The interphase spacing of these eutectics naturally increases as the solidification rate decreases, reaching values of about 8μ at a rate of 1 cm/hr.

The rare earths may be important in strengthening aluminum by forming fiber-like eutectics since the melting point of aluminum is only slightly lowered (20°C for Ce and 10°C for Y) and the aluminum intermetallic compound of the eutectic reaction is quite refractory ($CeAl_4$ or Ce_3Al_{11} melts at 1235 ° C and YAl_3 at 1355 ° C). Futher development work, however, is required before a useful composite is available.

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