

MATERIALS FOR NUCLEAR ENGINEERING

THE summer meeting of the Physical Society took the form of a two-day conference on "Materials for Nuclear Engineering". It was organized with the help of Associated Electrical Industries Ltd., and was held at the Associated Electrical Industries Research Laboratory, Aldermaston, during July 11-12.

Dr. T. E. Allibone (director of the Research Laboratory, Associated Electrical Industries Ltd.) opened the conference with a general review of the problems encountered in finding suitable materials for nuclear engineering and their importance in the future development of nuclear energy. He considered it very appropriate for the Physical Society to arrange a conference to discuss the physical properties of materials rather than their technology, for the technological questions would no doubt be answered when the underlying physics was better understood.

The papers delivered at the Conference could be classified into four groups: irradiation effects, physical properties of particular metals, liquid metals and the structure of materials.

Irradiation effects were discussed in four of the papers. Dr. A. H. Cottrell (Atomic Energy Research Establishment, Harwell) considered the effect of irradiation on creep. The importance of this problem was due to the fact that materials, although not subject to movement, had to withstand stresses at fairly high temperatures. The main effects of irradiation were the production of vacancies and interstitials, structure changes, radiation hardening, and the generation of internal stresses. Since the movement of vacancies was the vital factor affecting the creep-rate, it might be expected that if the coefficient of self-diffusion was high, poor creep properties would result, and he suggested that it was a good idea to use materials for which the diffusion coefficient is less than 10^{-15} cm.²/sec. Cottrell calculated that the effect of irradiation on the diffusion coefficient kept its value less than the critical 10^{-15} , and thus there was no significant change in creep properties due to this cause, as was in fact found in the early experiments. Structure changes could be caused by irradiation; for example in the uranium/molybdenum system, irradiation changes the structure from α -uranium + ϵ to γ -uranium in the quenched alloy at 400° C. Radiation hardening helped creep properties, but usually this occurs at temperatures lower than those where creep is important. Internal stresses can cause creep when they arise in a non-Newtonian body, and may be caused by thermal gradients, growth strains, thermal cycling strains and swelling. Growth strains are caused by a non-cubic crystal changing its shape, and in α -uranium this change is an expansion in two directions plus contraction in a third; the increased creep-rate has been observed experimentally.

Irradiation effects in insulating crystals were considered by Prof. R. W. Ditchburn (University of Reading). In order to understand the effects of pile neutrons it is desirable to study the displacement of single atoms to form vacancy interstitial pairs. This can also be done by using electrons of controlled energy (about 0.5 MeV.), but local heating must be

reduced in order to avoid partial annealing. The damage produced is studied by measuring the change of some physical property, and optical absorption is a particularly powerful method of investigation for it gives the energy-levels and the relative numbers of displaced atoms. For diamond, it is possible to investigate the displacement of single atoms. Experiments showed that heating at 450° C. causes some annealing; at 600° C. it causes the formation of pairs of defects and at 900° C., after prolonged heating, agglomerations of defects occur. Another valuable technique for the understanding of irradiation damage is the study of the polarization of irradiation-induced fluorescence, and by this means it is possible to deduce the orientations of defect systems.

Dr. G. B. Greenough (U.K. Atomic Energy Authority, Windscale) discussed irradiation effects in graphite. When it is exposed to neutrons with energies greater than 100 eV. at temperatures below 150° C., vacancies and interstitials are created, which cause changes in the physical properties. Thus the thermal and electrical conductivities decrease by factors of thirty and three respectively, and Young's modulus and the breaking strength increase by a factor of two. Changes in the external dimensions of a block of graphite also occur due to the fact that the *c* and *a* interatomic spacings increase and decrease respectively. Annealing the graphite restores its physical properties, but temperatures in excess of 1500° C. are required for full restoration. The annealing process, which causes the return of interstitials to vacant lattice sites, is accompanied by a high energy release. Dr. Greenough stressed the fact that experimental work is somewhat difficult because the properties of unirradiated graphite depend on its method of manufacture, and thus many samples must be investigated.

Dr. R. S. Barnes (Atomic Energy Research Establishment, Harwell) and Dr. A. T. Churchman (Associated Electrical Industries Ltd.) considered the structural effects in solids of nuclear-induced gases. These, which are generally of the rare-gas type, result from nuclear reactions caused by neutron irradiation, and can cause drastic structural changes in the material which is used. For example, boron and boron carbide, both of which are brittle, fragment upon irradiation with thermal neutrons, there being a helium-producing reaction in boron. It is believed that in each of these materials, the included gas diffuses to flaws, so creating a gas pressure which causes crack propagation resulting in fragmentation. The behaviour of deformable materials containing gas is quite different from that of brittle materials. From experiments on irradiation of beryllium by 40 MeV. α -particles producing helium, and of uranium by thermal neutrons, when the rare gases xenon and krypton are among the gaseous products, it was concluded that at low temperatures large quantities of the inert gases can exist in materials without causing an appreciable increase in volume. Heating permits the precipitation of the gas into bubbles if the material is ductile, or it cracks if it is brittle. The size and number of bubbles or cracks are determined by the presence of nuclei, the diffusion coefficient and the solubility of the gas. It was found that

the increase in volume caused by bubble formation depended upon the distribution of the gas, and that if the bubbles were small and numerous the gas was contained at a very high pressure and the resulting increase in volume was small. But if the same amount of gas was distributed in a few large bubbles, a large volume increase resulted. Such increases in volume could be troublesome in a reactor since, for example, it may cause splitting of the fuel can, allowing corrosion, or impeding the flow of coolant.

The physical properties of particular metals were dealt with in two papers. Mr. G. C. Ellis (Atomic Weapons Research Establishment, Aldermaston) delivered a paper on beryllium and in particular discussed the problem of its brittleness. This metal has attractive nuclear and high-temperature properties, but the main difficulty in its use is its relatively low ductility. Mr. Ellis reviewed the metallurgy of beryllium and considered the methods of producing the ductile metal by controlling the grain orientation. He considered that a considerable improvement might be obtained by removing interstitial solute impurities. However, the problem of purification, especially on a large scale, was likely to prove very difficult, but he suggested that there was sufficient justification to make the necessary effort.

The physical properties and alloying behaviour of plutonium were discussed by Dr. M. B. Waldron (Atomic Energy Research Establishment, Harwell). He stressed that the two most distinctive features of plutonium were its radioactive toxicity, which with its inherent difficulties slowed up the progress of research with the metal, and its allotropic behaviour, for six different forms of the metal have been identified. The relative stabilities of the various forms are of particular interest. Although certain similarities existed between plutonium and uranium phase diagrams, to assume direct analogies between the two was very dangerous. Dr. Waldron produced data on the specific heat at low temperatures and on dilatometric studies. Of particular interest was the negative coefficient of thermal expansion of the face-centred cubic δ -phase. This is unique for a metal with an isotropic crystal structure and emphasized the abnormal behaviour of the plutonium atom. In the discussion on the paper, Dr. E. Dempsey (Atomic Weapons Research Establishment, Aldermaston) contributed data on the Young's modulus and oxidation properties of the metal.

During the course of the conference it was evident that the subject of liquid metals was very important, and three papers were read on various aspects of it. Dr. B. R. T. Frost (Atomic Energy Research Establishment, Harwell) delivered a paper on the wetting of solids by liquid metals. He outlined the role taken by liquid metals in reactor technology, and stressed that in all the fields of use, wetting problems arise. This usually means that it is necessary to know the condition at the interface between the liquid metal and the solid metal under consideration. Definitions of wetting are usually given in terms of the contact angle θ , and for metallurgical application it is convenient to use $\theta=90^\circ$ as the dividing line between 'wetting' and 'non-wetting'. It depends on the balance of solid and liquid surface tensions, or in other words on the degree to which the solid and liquid interact. For a quantitative understanding of the process of wetting it is necessary to measure the surface tensions of the solid and liquid, and also their interfacial tension, and Dr. Frost gave an account

of the various methods of measuring these quantities. He discussed the inducement of wetting by the addition of elements (wetting agents) to the liquid metal, and mentioned the part that fluxes can play. As particular examples of the problems encountered, he mentioned the wetting of particles in slurries where the liquid metal acts as a fuel carrier, the wetting of surfaces in an electromagnetic pump, wetting during brazing, and also the problem of corrosion.

A special type of corrosion is mass transfer, which was discussed in a paper by Dr. A. K. Covington, Dr. G. A. Geach and Dr. A. A. Woolf (Associated Electrical Industries Ltd.). It is a process whereby a liquid or vapour takes up a solid at one point by chemical reaction or solution, transfers it by mass flow to a point where conditions differ and there allows it to be re-deposited. This deposition may be a consequence of change in temperature or it may be due to chemical reaction with another material. Mass transfer can be one of two types. Thermal gradient mass transfer arises when a liquid metal is confined in a solid metal system subjected to a temperature gradient. The difference in solubility of the container material in the liquid metal at different temperatures results in solution in the hotter portions and precipitation in the colder portions, with subsequent rapid blockage of the system. Ways of reducing such transfer were discussed with particular reference to the formation of inhibiting layers of zirconium nitride on steels. Isothermal mass transfer can occur when two dissimilar metals are placed in a liquid metal. Some affinity between a metal soluble in the liquid metal and one less soluble can lead to the formation of a layer of an intermetallic compound or solid solution on the less soluble metal. For example, aluminium has been observed to transfer on to the surface of pure iron, causing the formation of Fe_3Al_2 . As in the inhibition of thermal mass transfer by zirconium nitride, the presence of free nitrogen in the iron may prevent transfer of aluminium probably by the formation of an aluminium nitride film.

The third paper connected with liquid metals was that by Mr. J. S. Hilditch (British Thomson-Houston, Rugby) on the electromagnetic pumping of liquid metals. The great advantage of the electromagnetic pump over its mechanical counterpart is that it allows liquid metals to be circulated at high temperatures without glands, seals or moving parts. Principles upon which such pumps operated were described, and the performance figures given for some d.c. and a.c. conduction pumps. Alternating current induction pumps of the spiral, flat, annular and re-entrant types were also explained. The future of electromagnetic pumps appeared to be in their large-scale application to power reactors, and for bismuth the choice lay between the d.c. conduction pump with homopolar generator and the low-frequency a.c. conduction pump with separate transformer, or possibly the rotating-magnet induction pump. However, for sodium and sodium potassium alloys, where the resistivity was lower, the flat or re-entrant annular type of linear induction pump was favoured.

The structure of materials was dealt with in two papers. Dr. J. Friedel (Ecoles des Mines, Paris) discussed possible causes for allotropic transformations in the heavier elements. He first compared the behaviour of these elements with those of the first

period transitional metals. In the period commencing with francium and extending to americium, a big drop in the melting point occurred at uranium, while very complicated crystal structures existed for those elements showing allotropy. This was due to the presence of homopolar unsymmetrical binding caused by the filling of the *f*-shells as well as the *d*- and *s*-shells. In uranium, this operation of both *d*- and *f*-states gave rise to an unsymmetrical crystal structure, while on heating the *d*-bonds were broken, causing anomalies in the linear expansion, abnormally small electrical resistivity and, at higher temperatures, a change in crystal structure to β - and γ -uranium. Americium existed in only one form with a peculiar double hexagonal close-packed crystal structure, indicating the beginning of a rare-earth behaviour with the electrons not forming bonds but existing in independent shells. Thus Dr. Friedel considered that the elements of low atomic number in the range had a structure similar to the transition metals, with a mixture of *d*- and *f*-orbitals giving rise to directional homopolar bonding, while for plutonium and americium the structures were more analagous to the rare earths, with the electrons in the *f*-shells predominating over those in the *d*-shells.

Some aspects of structure and solid solution were considered by Dr. G. K. Williamson (Atomic Energy Research Establishment, Harwell). The alloying behaviour of uranium was discussed with the view of determining its behaviour empirically. There was negligible solubility in the complex α - and β -structures and in the body-centred cubic γ -structure; it was restricted to the transition elements (Group IVA onwards). The Hume-Rothery size factor rule was obeyed for the elements of the first two long periods, but this is not so for elements of the third long period, and the reason for this is not yet understood. Uranium forms a large number of compounds, but it seems remarkable that, apart from those with a special

size factor, no compounds are formed with elements of lower electronegativity. The compounds formed cannot be accounted for on the basis of electron compounds, for the effective valency of uranium is uncertain.

The conference was concluded with a talk by Sir John Cockcroft (Atomic Energy Research Establishment, Harwell) on the place of metallurgical development in the atomic programme. Future reactors would require fuel elements operating at higher temperatures, with higher heat ratings and burn-ups than those at present in use. Ratings could be increased in two ways. The surface area to volume ratio of the fuel element could be increased by using clusters of thin rods or plate fuel elements, but these were limited by fabrication problems or by the increase in the ratio of casing material to fuel. Again, the fuel element temperature could be increased, but this causes swelling in metallic uranium at 550–600° C. This difficulty could be overcome by using a 14 per cent molybdenum alloy, but such a degree of alloying is too high for thermal reactors, although it may be applicable for use in fast reactors. At temperatures above 600° C., it is necessary to use ceramic materials, uranium oxide or uranium carbide, as fuel, but these have their difficulties. With such high operating temperatures, beryllium cans are required and experiments have been carried out to test their ability to withstand such temperatures. By a combination of methods, it is hoped to increase the rating to 5–10 MW. per ton compared with 1.3 MW. per ton for the Calder Hall reactor. Sir John mentioned the more advanced reactor types—the Dounreay fast reactor, the high-temperature gas-cooled reactor and the liquid fuel reactor—and concluded with a consideration of other problems, including those of irradiation damage of the steel pressure vessels, and stress corrosion difficulties.

T. E. ALLIBONE

THE CHEMISTRY OF TERPENOID COMPOUNDS

A SYMPOSIUM on recent advances in the chemistry of terpenoid compounds, organized by the Chemical Society, was held in the Chemistry Department, University of Glasgow, during July 11–12. A marked feature of this symposium was the emphasis placed on ideas and methods which had scarcely entered the field even as late as 1950. Terpene chemistry was the first chemistry of natural products in which a wide range of related substances was examined, and the emphasis for many years was on structures. The first great generalization was the 'isoprene rule', which has recently been expanded into the 'biogenetic isoprene rule', and nowadays it is evident from the conference that chemists are not content merely to determine structures but wish to correlate these structures with those of the isoprenoid compounds in general. The term 'biogenesis' was mentioned in some connexion in almost every paper. Another feature was the universal dependence on physical methods for suggesting probable structures: infra-red and ultra-violet spectra and optical rotatory determinations are some of the chief tools used. Attempts at total synthesis of terpenoid compounds were described in only two papers.

The attendance at the symposium was international, with representatives from several countries including Australia, Canada, France, Great Britain, New Zealand, Switzerland and the United States.

The first paper, on the structure of the sesquiterpene ketone zierone (Prof. A. J. Birch, D. J. Collins, R. P. Hildebrand, A. R. Penfold and M. D. Sutherland), is an example of the use of newer methods based largely on absorption spectra. The substance is a derivative of a new natural azulene, and the chief method of structure determination was by dehydrogenation, by methylation at the carbonyl group and adjacent to it, and dehydrogenation, and then a study of the spectra of the resulting azulones. Some probable conclusions can even be reached as to the stereochemistry of the whole molecule by a study of the spectra of dihydrozierone diol produced by osmic acid oxidation. Zierone is chiefly notable in that although it is isoprenoid one of the units is reversed from the normal head-to-tail linkage. In this connexion also Prof. F. Sörm discussed the structure of acorone and laserpitine, both rather remarkable ketonic sesquiterpenes. The latter is an isocadalene derivative with one reversed unit, the former a