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ALLOYS IN ENERGY DEVELOPMENT*

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G. V. Raynor Memorial Conference

Alloys in Energy Development B. R. T. Frost

Introduction

The Industrial Revolution triggered the process of alloy development in support of increasingly efficient and complex energy systems. Starting with wrought iron, more complex iron alloys or steels were developed that led to the introduction of high-pressure steam boilers and turbines which were subsequently linked to alternators to produce electricity on a large scale. Over the past century these systems have become more efficient through the refinement of the austenitic stainless steels and nickel-base alloys until we are close to the thermodynamic limits of the systems.

The refining of oil to produce highly volatile fuels, beginning around the beginning of this century - with the concomitant provision of suitable steels with which to build these refineries - led to increasingly efficient internal combustion engines and to the gas turbine. The latter required blade materials that operate at temperatures up to, and now beyond, 1000°C. The nickel and cobalt base Superalloys were developed, starting with the Nimonic series developed in Birmingham shortly after World War II. Subsequent developments included sophisticated precipitation hardened alloys followed by amorphous alloys and ceramics. The availability of efficient engines spurred the advance of aviation which in turn demanded light alloys for airframes, skins and other components resulting in the development of a large range of aluminum alloys and subsequently titanium alloys and fibre-reinforced composites.

The discovery of Nuclear Power during World War II and its subsequent peaceful applications made severe demands on the ingenuity of the materials scientist but also gave the world a series of new elements with very

interesting properties, the scientific study of which has advanced to a very sophisticated state.

As the commercialization of nuclear power around the world was becoming a reality in the early 1970's an unexpected crisis arose in 1973 when the developing countries which control most of the world's oil supply formed a cartel (OPEC), raised oil prices and threatened to limit supplies to the developed countries. The reaction to this crisis was the study of a number of alternative energy supply systems, coupled with a drive towards energy conservation measures. Some examples are the development of advanced coal combustion and conversion systems; solar energy systems including concentrators, photovoltaic and ocean thermal conversion; conservation through off-peak storage batteries which could be used to power vehicles, and more effective heat recuperation systems, Fig. 1. All of these required special materials in order to work effectively. Some of these could be adapted from existing alloys and compounds but they often required new processing or fabrication methods.

With the example of OPEC in full view, concerns surfaced around the beginning of this decade that many of the key elements that were essential ingredients of alloys used in energy (and defense) systems were concentrated in overseas countries whose long-term political stabilities were questionable. In particular the guarantees of supply of chromium and manganese from southern Africa and cobalt from Zaire were questioned, Fig.2. Among the proposed solutions to this dilemma were the development of substitute alloys and increased recycling of scrap.

Thus, alloy development for energy systems is not simply a scientific and technological endeavor, it also has to take into account economics and

geopolitics. Nevertheless, it still holds many challenges for the materials scientist.

Nuclear Power

Considerable emphasis in this review will be given to the role of alloys in the development of nuclear power because it has more dimensions than other energy systems. The fuel is often an alloy; if not, it is a compound. The environment includes radiation as well as temperature, pressure and chemistry. Most important, the reliability required of a nuclear power plant is greater than in other power sources: components must not fail.

We will deal first with the Actinide Elements. The naturally occurring nuclear fuels are uranium and thorium. Irradiation of these elements produces a family of transuranic elements: plutonium, neptunium, americium, etc., the scientific study of which started around 1945. Only thorium, uranium and plutonium are useful fuels or precursors of fuels. In the early days of nuclear power emphasis was placed on the metallic form of these elements because this produces the most dense packing of heavy atoms. Uranium and plutonium have respectively three and six phases, most of which are noncubic and hence have anisotropic properties, Fig. 3. This anisotropy can produce undesirable effects such as thermal cycling growth and fracture. Hence, an intense study of the binary and ternary alloys of these two elements was embarked on in the 1940's and 1950's, primarily for technological reasons. Early fuels derived from these studies include U-Mo in which the cubic gamma phase is stabilized on quenching and UAl_3 in Al which is still the standard "dispersion" fuel for research reactors, Fig. 4. However, in the late 1970's an alternative to the latter was developed in order to increase the uranium loading and decrease its enrichment to a level where diversion to weapons use

became very difficult. This involved a dispersion of U_3Si in Al, requiring further studies of the U-Si-Al phase diagram.

The 1950's was era of exploration of new reactor systems. The plutonium-iron eutectic melts at $413^\circ C$ and seemed to be an attractive fuel for a fast reactor. The LAMPRE project, on which this was based, found that the only container for this fuel was specially fabricated tantalum alloy which had undesirable nuclear properties. Uranium dissolves in liquid bismuth to a limit of 0.6 w/o at $500^\circ C$; this was sufficient to form the basis of a Liquid Metal Fuel Reactor (LMFR) which was developed at Brookhaven and Harwell in parallel. This was overtaken by the more conventional reactors being developed at that time: the Light Water Reactors in the USA which use UO_2 as the fuel, and the Magnox and AGR reactors in the UK which use metallic uranium and UO_2 respectively. Thus, from about 1965 onward the most used fuel forms were uranium metal and UO_2 , with $(U,Pu)O_2$ as a variant for fast reactors.

The performance of uranium metallic fuel was markedly improved by a process called "adjustment," invented by Jepson and Slattery in the UK, in which small quantities of iron (400 ppm) and aluminium (1000 ppm) are added and the cast fuel is quenched from the beta phase to refine its grain size. This results in a fuel which performs well to acceptable burn-up limits. The exact influence of the small alloying additions has not been satisfactorily explained although the fine precipitates of UAl_2 seen in this fuel clearly strengthen the grains.

Uranium dioxide is a compound rather than an alloy; nevertheless the U-O phase diagram is of considerable interest because UO_{2+x} exists over a range of values of x varying from 0 to 0.25, Fig. 5. Its properties are strongly influenced by departure from stoichiometry. When plutonium is added the compound exhibits oxygen deficiency, i.e., it exists down to an oxygen: metal

ratio of 1.7. The effects of fission product elements on these ranges of composition have been studied intensively; for example, it has been shown that zirconium and the rare earths dissolve in UO_2 to produce a lattice contraction which helps to offset the swelling due to dissolved and undissolved noble metals and the volatile and gaseous elements.

Nuclear fuels are well understood after thirty-five years of development and have changed from being the greatest concern in nuclear power development to one of the least. The scientific understanding of the actinide elements and their alloys is less well advanced because it is a more diverse and complex field of study.

The electronic structure of the actinide atoms consists of a radon core (with 86 electrons), a partially filled 5f shell (0 in Th, 3 in U, 6 in Pu, 7 each in Am and Cm, and 8 in Bk) and 2 to 4 valence electrons in the atomic 6d and 7s states, Figs. 6 and 7. Theory and related experiments have been aimed at understanding the nature and role of the open shell of 5f electrons and their influence on electrical and magnetic properties. Parallels have been drawn with the rare earths with their open shell of localized 4f electrons, although in general the rare earths are easier to understand and certainly are better suited for experimental studies. Today it is possible to calculate band structures for the lighter actinides and their compounds that correspond well with band structures derived from experiments, many of which are concerned with magnetic properties.

While the width of the 5f band precludes U, Np and Pu from being magnetic, long-range magnetically ordered structures occur in many of their compounds, especially the AnX_2 Laves phases and the AnX_3 AuCu_3 -type compounds (An = Actinide). Neutrons interact with atomic magnetic moments and provide a powerful tool for measuring magnetic moments, especially when single crystals

are available. The successful efforts in Switzerland and Germany to make single crystals of actinide compounds, combined with the availability of intense neutron sources at the reactors at Grenoble, Brookhaven and Oak Ridge have provided much valuable information on which to build a better understanding of the magnetic and electronic characteristics of the actinides, Fig. 8. The intense ultraviolet and x-ray beams available at modern synchrotron sources make possible sophisticated photo-electron spectroscopy and EXAFS (extended x-ray absorption fine structure) studies on the necessarily small actinide samples to throw additional light on the relationships between electronic properties and crystal structures. A dedicated facility for studying actinides is being set up at the University of Wisconsin Center for Synchrotron Studies. With these powerful new tools it is expected that a better understanding of the electronic properties of the actinide alloys phases will develop over the next decade.

Turning now to Structural Materials in nuclear power plants, these include the core structure (other than the fuel), the reactor vessel, coolant piping, valves and pumps. The most commonly used material is austenitic stainless steel with zirconium alloys (Zircaloy) being used as fuel cladding in light water and heavy water reactors, and as pressure tubes in the latter.

The majority of the problems concerned with structural alloys in reactors involve alloys that are not at equilibrium. When the alloy is in the core of a reactor it is exposed to a high neutron flux, as well as to high temperature and pressure. Fast neutrons, with energies above 0.1 MeV, produce a number of effects:

1. Atomic defects, i.e., vacancies and interstitials, which may annihilate one another or cluster and collapse into loops. Vacancy clusters may be

stabilized as voids or low pressure bubbles by helium that is generated by (n, α) reactions. These phenomena have a large effect on mechanical properties and dimensional stability.

2. Transmutation products, which are usually of little consequence. However, in the special case of a fusion reactor first wall, an initially pure niobium wall becomes a Nb-10 at/o Zr alloy after several years.
3. The vacancy flux adds to the thermal vacancy population and leads to enhanced diffusion.
4. Vacancy migration to sinks, such as surfaces, grain boundaries and voids, carries along solute elements in a manner that is related to the size factor of the solute. A nickel-silicon alloy under irradiation will result in a silicon-rich layer at surfaces, disturbing the overall solute distribution.
5. Neutron damage cascades may disperse precipitates of a second phase into the matrix.

These processes occur simultaneously: all are flux-dependent except 2, which is fluence (time) dependent. To predict the state of an alloy after a given residence time in a neutron flux is extremely difficult. Fig. 9 lists six major phases which are found in stainless steels after neutron irradiation; the understanding of the factors affecting their development and stabilities are far from complete.

Outside the reactor core one expects components to last the lifetime of the reactor, i.e., 30 years or more. Two kinds of problem may exist, one being the consequence of short-term heating and the other of long-term heating. Stress-corrosion cracking is a common phenomenon in water-cooled reactors, Fig. 10. An important factor is the sensitization of stainless steels in the heat-affected zone near a weld. The chromium in the Fe-Cr-Ni steel reacts with the carbon to form Cr_{23}C_6 and in doing so denudes the grain boundaries of chromium, making them more susceptible to corrosion by anions in the water when high stresses exist. While one can reduce sensitization by reducing the carbon content of the steel (and thereby weakening it) it may be more difficult to counter long-term effects that result from the steel remaining at about 400°C for many years. Sensitization will occur more slowly but it becomes a problem after some years. Furthermore, if one uses cast stainless steels (as is common practice for some components such as elbows) some of the brittle sigma and chi phases may appear and reduce ductility to unacceptable levels after long time exposures.

In nuclear power plants one is faced on the one hand by departures from alloy equilibrium due to radiation effects and on the other hand to an approach to equilibrium due to long-term aging effects. Some of these effects are on a very small scale: on the order of a few hundred Angstroms in diameter. They require high voltage electron microscopy and small angle diffraction techniques with x-rays or neutrons to measure their size and distribution and this is not easy with highly irradiated samples.

Non-Nuclear Power

Coal and oil fired power plants often operate at temperatures above those of the water-cooled nuclear plants: up to and beyond 600°C . However, similar

stainless steels are generally used and the problems of nuclear plants cited above, such as long-term aging and embrittlement, occur but without the complications caused by radiation fields.

Plants for the conversion of coal to oil or gas operate at higher temperatures and pressures than power plants and with more aggressive environments. Two approaches are taken to materials selection. For the large reaction vessels low alloy pressure vessel steels are used whose creep strength falls rapidly above $\sim 400^{\circ}\text{C}$. The alloy is maintained at or below that temperature through the use of refractory brick linings just as in a blast furnace. For more specialized components such as transfer lines and valves another approach is used in which high temperature alloys are selected for their strength properties. These may then be protected against oxidation and sulphidation by coatings or by an alloy modification that influences the nature of the protective surface scale. For example, a Type 310 (Fe-25% Cr-20% Ni) steel, exposed to a CO , CO_2 , CH_4 , H_2S and H_2 mixture at 1000°C degraded rapidly, while the same alloy with additions of 3% of zirconium or niobium degraded much more slowly, Fig. 11. The solubilities of zirconium and niobium in the steel are very low so that their addition results in nickel-rich precipitates containing Zr or Nb which lead to a fine grain size and good mechanical properties in addition to improved protective oxide scale.

In a different approach, workers at the Oak Ridge National Laboratory developed long-range ordered alloys in the $(\text{Ni}, \text{Co}, \text{Fe})_3\text{V}$ systems for practical use. Generally these phases possess low ductility but it is found that if they are cubic and remain below the order-disorder transition temperature they have good ductility. The trick is to optimize the Fe, Co and Ni contents to produce a high transition temperature in the cubic phase and it is found that this can be done at an electron to atom ratio between that of Fe_3V (7.25) and

Co_3V (8.00). Fig. 12 shows this graphically and Fig. 13 compares the ductilities of the hexagonal and cubic ordered alloys. Several of these alloys have high temperature creep strength, high resistance to oxidation and a very low neutron-induced swelling rate. They are being developed for use in steam power plants, advanced heat engines (Stirling engines) and for fission and fusion reactors.

In another approach to the development of high temperature, corrosion-resistant alloys extensive research is being conducted on amorphous and rapidly solidified alloys. There are several different approaches to making such alloys: 1) following the elegant work of Pol Duwez, who developed "splat" cooling to a fine art, is the rapid cooling of a eutectic alloy such as $\text{Fe-Fe}_2\text{B}$. This is often carried out by jet casting a ribbon onto a cooled cylinder and is being commercialized to produce transformer materials, 2) the production of powders (RSP) by flinging molten drops of metal off a rapidly rotating rod or disc, and 3) solid state reactions e.g. interdiffusing co-deposited films of two metals that have a large negative heat of mixing. Whatever the fabrication route, the result is either an amorphous alloy or a very fine-grained material. In terms of alloy theory they are far from equilibrium and there is considerable interest in the kinetics of crystallization which may be represented by a C-shaped curve, as shown in Fig. 14. The position of the nose of the curve is typically $\sim 10^{-5}$ to 10^{-6} sec which defines the required cooling rate. In fabrication and in service the temperature must be below the lower flat position of the C curve. Despite these restrictions it is confidently expected that turbine blades made from rapidly solidified materials will be in service by the end of this decade.

In the quest for greater thermal efficiency the engineer has reached temperatures where the more sophisticated alloys are becoming too weak for

prolonged use and ceramics are being used to an increasing extent. Ceramics are, of course, brittle below $\sim 1100^{\circ}\text{C}$ and are of limited use. Above 1100°C they become more ductile while retaining acceptable creep strength. Special emphasis is placed on the fabrication of sintered or hot pressed solids that contain no flaws above the critical crack size. This places emphasis on powder production and characterization and on non-destructive testing. Silicon carbide and silicon nitride have been studied extensively for gas-turbine components and for adiabatic diesel engines. However, for the latter application partially-stabilized zirconia (PSZ) has emerged as the favored material. Zirconia (ZrO_2) exists in three crystalline forms. The monoclinic to tetragonal martensitic transformation is accompanied by a 3.25% volume change which can have undesirable effects on properties. Small additions of MgO , CaO or Y_2O_3 followed by a controlled firing cycle produces a partially stabilized structure, i.e., part monoclinic and part tetragonal. During load and temperature cycles the microstructure changes in a manner similar to the TRIP steels, resulting in the dissipation of elastic energy and a reduction in crack growth. This sophisticated approach to tough ceramics has resulted in a commercial product which is being successfully used in experimental engines.

Conclusion: The development of new and advanced energy systems often requires the tailoring of new alloys or alloy combinations to meet the novel and often stringent requirements of those systems. Longer life at higher temperatures and stresses in aggressive environments is the most common goal. Alloy theory helps in achieving this goal by suggesting uses of multi-phase systems and intermediate phases, where solid solutions were traditionally used. However, the use of materials under non-equilibrium conditions is now quite common -- as with rapidly solidified metals -- and the application of alloy theory must be modified accordingly. Under certain

conditions, as in a reactor core, the rate of approach to equilibrium will be modified; sometimes a quasi-equilibrium is established. Thus an alloy may exhibit enhanced general diffusion at the same time as precipitate particles are being dispersed and solute atoms are being carried to vacancy sinks. We are approaching an understanding of these processes and can begin to model these complex systems. The models may, in turn, allow us to design alloy systems with greater confidence.