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RADIATION DAMAGE CONSIDERATIONS

By

B.R.T. Frost

Presentation at the Battelle Colloquium
Fundamental Aspects of Structural Alloy Design
Battelle Memorial Institute
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ABSTRACT

The designs of nuclear fission and fusion power plants do not, in general, appear to make unusual demands on materials in terms of mechanical-property requirements. Superficially, the needs of the designer can be met by commercially available alloys. However, the radiation environment produces unique effects on the composition, microstructure, and defect population of these alloys, resulting in time-dependent and time-independent changes in mechanical properties. These changes must be quantified for the designer.

To illustrate these problems, the materials needs of the core of a Liquid-Metal Fast-Breeder Reactor (LMFBR) and of the first wall of a fusion reactor are discussed. In the case of the LMFBR core, the phenomenon of void swelling causes serious design problems, and a search is being made for a low-swelling alloy that has adequate mechanical properties. The fusion reactor poses different problems because the neutron energy is high (14 MeV) and is accompanied by a high flux of charged particles. The long-term choices for a wall material have been narrowed to vanadium and niobium alloys.

*Work supported by the U.S. Energy Research and Development Administration.

In the search for low-swelling alloys, it has become clear that minor elements play an important role in determining the nature of the radiation effects. The segregation of minor elements to void surfaces and the dispersion and reformation of second-phase precipitates are two important radiation-induced phenomena that require additional study in view of their influence on void swelling and high-temperature properties.

INTRODUCTION

The mechanical properties required of alloys for use in nuclear plants are basically similar to those required in any power plant. In water-moderated fission reactors operating at temperatures below 800°F (430°C), the materials generally deform elastically, and design emphasis is placed on mechanisms of crack initiation and propagation. In gas-cooled and sodium-cooled fission reactors and in fusion reactors, materials are generally operating above 400°C. In this case, the design emphasis is on high creep strength and ductility and on creep-fatigue interactions (cumulative damage), i.e., on time-dependent properties. However, the temperatures and stresses involved are within the ranges encountered in modern steam and gas turbine systems.

To meet these requirements and to have the capability of withstanding the generally corrosive environments of these reactors, conventional austenitic and ferritic steels have been used, together with zirconium alloys that were specially developed for use in water reactors. For the future, increasing emphasis will be given to precipitation-hardened

alloys and to the bcc metals and alloys. This will permit increased operating temperatures and thermal efficiencies.

The unique feature of fission and fusion reactors is the radiation environment. Energetic neutrons, gamma rays, and charged particles produce radiation damage and localized heating within the bulk of the alloys. Radiation damage, for the purposes of this discussion, involves the production of lattice defects and transmutation products. The production of defects may lead to enhanced diffusion (including enhanced creep), defect cluster formation, and void formation. The dispersion of precipitates into the lattice under energetic particle bombardment is a special case; a dynamic, flux-dependent equilibrium is established between dispersion and reprecipitation, which is enhanced by radiation. Transmutations can produce hydrogen and helium gases and other metallic species, e.g., niobium becomes transmuted to zirconium, so that the pure niobium wall of a fusion power reactor would become a Nb-10% Zr alloy after ~20 years. Thus, although conventional alloys have often been selected for nuclear applications, their long-term behavior in service is quite different from that in a nonnuclear plant.

A basic, and as yet only partially solved, problem is to understand the special effects of the radiation environment on alloy structures and properties. The problem is complex because two types of processes occur simultaneously: (1) flux-dependent processes, which include diffusion (atomic transport), diffusion creep, and stress-relaxation, and (2) dose- or fluence-dependent processes, which produce changes in chemical composition and microstructure. These two types of processes are interactive, i.e., the radiation-enhanced creep rate will change with time,

even when all other factors are held constant, because the microstructure changes. Hence, it is difficult to select or design alloys for nuclear applications because we do not adequately understand these time-dependent and time-independent processes and their interrelationships. In the current research approach, an attempt is made to isolate the important radiation-induced phenomena and to test the effects of different initial microstructures and compositions on these in a systematic manner.

In an effort to give more physical meaning to the present discussion, two examples of the importance of considering radiation effects in the selection of alloys will be cited from nuclear systems currently under development. The first is the Liquid-Metal Fast-Breeder Reactor (LMFBR). The core of this reactor is a compact heat source, which is assembled from a number of closely packed hexagonal subassemblies, as illustrated in Fig. 1, each of which contains hundreds of small diameter, metal-clad fuel elements (Fig. 2). The temperature range to which the fuel assemblies and rods are exposed is ~ 400 - 650°C .

The neutron flux is energetic and of high intensity; typically in the range of from 10^{15} to 10^{16} n/cm²/sec. The fuel-element tubes are required to resist the internal pressure that arises from fuel swelling and fission-gas release. A universal choice for these tubes has been 20% cold-worked Type 316 stainless steel, because of its good creep strength, reasonable ductility, ease of fabrication and manipulation, and resistance to hot sodium. During its lifetime exposure to the neutron flux, the stainless steel swells, because of the formation of voids, in the manner shown graphically in Fig. 3. It also loses

nonuniform ductility as a result of combination of interior hardening of the grains and grain-boundary weakening. The neutron flux is non-uniform across the reactor core; hence, nonuniform swelling of fuel assemblies will occur, leading to distortion.⁽¹⁾ Figure 4 shows the manner in which the subassemblies are held in the core, whereas Fig. 5 shows the direction of distortion due to swelling. The distortion could make the unloading of the core impossible. This problem cannot be solved by spacing the hexagonal cans further apart, since that will lead to an unacceptably high loss of neutrons that are needed to breed new fuel. Some relief is afforded by radiation-induced stress relaxation or creep; the magnitude of radiation-induced creep is illustrated by results of a uniaxial creep test conducted on Type 316 stainless steel in the core of the EBR-II fast reactor, shown in Fig. 6. The creep may be sufficient to relax the interference stresses caused by bowing, but it is difficult to strike the correct balance between the two processes. Hence, a search is being made for a swelling-resistant alloy that also has adequate strength and residual ductility.

Void swelling, the microstructural form of which is illustrated in Fig. 7, is caused by the biased flow of interstitials to dislocations and other sinks, leaving a net excess of vacancies that cluster in association with helium produced by (n,α) transmutations in, for example, iron, chromium, and nickel.^(2,3) An increase in the number of sinks for the vacancies should reduce swelling; this has been sought through the use of two-phase alloys such as γ' in a nickel matrix (e.g., PE16), by a change in stacking-fault energy, and by changes in minor alloying elements that alter the void-nucleation process.

This is essentially a "biological" approach in which many alloys are being tested. Hence a rapid screening method is required. In current fast reactors, several years are required to attain an adequate neutron dose, which is unacceptable. To overcome this problem, energetic charged particles (typically 4 MeV) are used to produce intense but localized damage in alloy samples; void formation is analyzed by transmission-electron microscopy, which also permits interrogation of other microstructural changes. This screening process has yielded valuable indications of the compositional factors that produce alloys with low swelling rates. Figures 8a and 8b show the results of tests on a range of commercial and synthetic Fe-Cr-Ni alloys, some of which contain other elements such as Al and Mo. It should be noted that the swelling rate becomes low at nickel contents in excess of 40 wt %. In Fig. 9, the swelling rate of an Fe-15Cr-20Ni alloy is plotted as a function of minor alloy additions. The effectiveness of Ti and Si additions is significant; a combination of these two elements at approximately the 1 wt % level of each has been shown to reduce drastically the swelling of Type 316 stainless steel. These results show that several low-swelling alloys are available which fall within the allowed composition limits for existing commercial alloys. This is important because of the long time required for code acceptance of new alloys.

To date, fusion reactors have not demonstrated scientific feasibility, and they probably will not be in commercial service before the year 2000 A.D. However, because of the optimism generated by recent plasma physics experiments, considerable thought has been given to the probable materials requirements of such reactors and to the peculiar environment

to which the materials will be subjected. The most popular reactor concept at this time is the Tokamak, shown schematically in Figs. 10 and 11.

The most probable reaction for early fusion reactors is

Deuterium and tritium are ionized in the vacuum chamber of the Tokamak, compressed magnetically, and heated ohmically to an energy in excess of ~ 10 keV. The break-even point (or scientific feasibility) will be demonstrated when $n\tau > 10^{14}$, where n is the number of ions/cm³, and τ is the confinement time in seconds. As shown in Fig. 12, the first wall will be subjected to bombardment by 14-MeV neutrons, charged and neutron particles, and short-wavelength radiation (Bremsstrahlung). The neutrons will cause damage, including surface sputtering, displacements, voids, gas bubbles, and metal atom transmutations.⁽⁴⁾ They will pass into the lithium blanket where most will be captured to produce tritium, but some will be slowed down and will diffuse back into the metal wall and cause some damage and transmutations. The charged and neutral particles and energetic neutrons will cause sputtering from the inner wall.⁽⁵⁾ Since plasma energy losses vary with Z^4 , where Z is the atomic number of the sputtered wall atom, the wall must be made of (or coated with) a low Z material.

The radiation-damage processes in the fusion reactor first wall will include void swelling, radiation creep, and helium-induced loss of ductility. Thus, the selection of a suitable alloy for this application has some of the same elements of choice as the LMFBR fuel tube. However, other factors are different, e.g., the displacement damage produced by 14-MeV neutrons versus fission neutrons, the transmutation rates, and the

surface effects. The magnitude of these differences is indicated in tabular form in Fig. 13, where the damage and transmutation rates in the niobium wall of a fusion reactor are compared with these rates for stainless steel in a fast fission reactor. Although the damage or displacement rates differ by only a factor of two, the transmutation rates differ by much greater factors. The latter will cause large changes in mechanical and physical properties.

From a design viewpoint, the fusion reactor first wall will be subjected to high thermal stresses but not high loading stresses. Design tolerances can be fairly loose, but differential swelling and excessive radiation-creep rates are to be avoided. The outer surface of the wall may be in contact with liquid lithium, which is used to generate tritium fuel.

In early experimental fusion reactors, wall temperatures may be as low as 400°C, so that ferritic or austenitic steels could be used (although data on 14-MeV neutron effects in these materials will be needed). More efficient reactors will have higher wall temperatures, possibly as high as 1000°C and certainly in excess of 600°C. Since lithium is known to corrode nickel-base alloys and even stainless steels at these temperatures, the only materials with an adequate combination of properties are the refractory metals niobium, molybdenum, vanadium, and their alloys. Nuclear considerations, such as the level of induced radioactivity (which is important from the standpoint of maintenance and ultimate disposal), favor vanadium and its alloys as a long-term choice for first-wall material, with niobium as a second choice. Fission reactor and ion bombardment irradiations have been conducted on vanadium,⁽⁶⁾ niobium,⁽⁷⁾ and

their alloys. The pure metals have high swelling rates, but small alloying additions (e.g., 1% Ti or Zr) reduce these considerably. No measurements of irradiation creep have been made, although it has been shown that realistic levels of helium reduce the ductility markedly at temperatures above 700°C (Fig. 14).

These two examples of design problems illustrate the ways in which the radiation environment increases the difficulty of the task of alloy selection for nuclear reactors. In the course of the work outlined above, additional complicating factors have become apparent. One has been mentioned, i.e., the development of a different size and spacing of precipitates⁽⁸⁾ in two-phase alloys, which will obviously influence the high-temperature mechanical properties. This is evident from the microstructural changes shown in a Ni-Al alloy during irradiation (Fig. 15). Closely related to this effect is the promotion of diffusion-controlled phase transformations by irradiation. An alloy that normally is thermally stable may become unstable in a fast-neutron flux.

Minor alloying elements (or impurities) have been shown to exert a major influence on radiation processes. First, it has been shown that the size and number density of dislocation loops in the bcc metals is strongly influenced by the level of the interstitial elements in solution.⁽⁹⁾ Second, the void-swelling behavior of niobium and vanadium is strongly influenced by the oxygen content of the metal.⁽¹⁰⁾ For example, niobium forms an ordered void lattice at ~780°C when it contains oxygen in excess of ~250 ppm, but it does not form an ordered lattice at 10 ppm; larger, randomly arranged voids are formed that produce a considerably higher swelling rate (Fig. 16). It is speculated that a very fine ordered

precipitate of NbO may be formed at the higher oxygen levels, which provides nucleation sites for voids. As shown in Fig. 16, an ordered lattice of voids is not observed at 828°C but the influence of oxygen content on void size is evident.

Careful transmission-electron microscopy has shown that solutes with negative size factors segregate toward void surfaces.⁽¹¹⁾ A particular case is an Fe-18Cr-8Ni-1Si alloy in which the silicon clearly segregated at the void surfaces during electron irradiation (Figs. 17a and 17b). It has been shown theoretically that this can lead to a reduction in void growth,⁽¹²⁾ and a kinetic model of the segregation process has been developed.⁽¹³⁾ Possibly related to this effect is the empirical finding (mentioned earlier) that the addition of ~1 wt % Ti and 1 wt % Si to Type 316 stainless steel markedly reduces the swelling rate.⁽¹⁴⁾

A general conclusion from the findings on minor element effects is that the specifications normally used for alloys, such as ASME Type 316, have limits that are too broad for nuclear applications. To optimize between adequate mechanical properties and minimum radiation effects, it is generally necessary to specify narrow composition ranges (especially of the minor elements) and to use special processing methods such as double vacuum melting. Some indications have been found that special thermomechanical working processes may be beneficial, e.g., a process that produces fairly large carbide precipitates crossing grain boundaries results in less deterioration in ductility during service.⁽¹⁵⁾ This area has not been well explored, and caution must be exercised in proceeding without taking into account the possible effects of radiation in modifying thermally stable microstructures.

In summary, the designer of nuclear plants generally works within stress and temperature ranges that appear to be capable of being met by commercially available alloys. However, the radiation environment produces unusual effects on these alloys; one is the change of microstructure by void and cluster formation together with precipitate modification, and the other is the change in diffusion rates or the "effective temperature." The former is time dependent, the latter is time independent and both affect mechanical properties. Hence, the nuclear designer must be provided with data such as creep rates and ductility limits for given stress levels as functions of neutron dose, dose rate, and spectrum as well as temperature. This makes alloy improvement and optimization a slow and expensive process. Not surprisingly, the designer often attempts to by-pass this process by using safety factors of large magnitude or by attempting to design around the problems. However, the economic incentives to develop new alloys are sufficiently strong to provide convincing arguments for following this lengthy and difficult process.⁽¹⁾ Consequently, sizeable alloy development programs in support of advanced nuclear reactors are under way in most of the major industrialized countries.

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FIGURES

1. Plan view of a fast-breeder reactor (EBR-II) showing the packing of hexagonal assemblies.
2. Cross section of a typical LMFBR fuel subassembly showing the regular close packing of many small fuel elements.
3. Approximate curves of void swelling versus irradiation temperature in stainless steel at three fluence levels.
4. Vertical section of an LMFBR core showing the points of support for the subassemblies.
5. Schematic representation of the deflection of subassemblies due to differential swelling and compensation by creep.
6. Radiation-creep curve for Type 316 stainless steel in the core of the EBR-II reactor.
7. Transmission-electron micrograph of irradiated stainless steel showing voids.
- 8a. Fe-Cr-Ni phase diagram at the 625°C isotherm showing swelling behavior as a function of composition.
- 8b. The same data plotted in the form of swelling versus nickel content of commercial synthetic or pure alloys.
9. Swelling of an Fe-15Cr-20Ni alloy at 675°C and 140 dpa as a function of various minor alloy additions.
10. Schematic representation of a Tokamak fusion device.
11. Cross section of a fusion reactor.
12. Possible radiation processes that occur in the first wall of a fusion reactor.
13. Neutron effects in fusion- and fission-reactor materials.
14. Ductility as a function of temperature in vanadium containing 0 and 25 ppm of injected helium.
15. The change in Ni_3Al precipitate size and density in a nickel-aluminum alloy as a function of charged-particle irradiation dose at 550°C.
16. Void size and number density in niobium containing various levels of oxygen after nickel ion bombardment.

FIGURES (Contd.)

- 17a. Transmission-electron micrographs of electron-irradiated 18/8/Si stainless steel. Silicon has segregated to the void surfaces--note the circled regions.
- 17b. Auger spectroscopy of surfaces in 18/8/Si stainless steel showing silicon segregation after irradiation.

Fig. 1. Plan view of a fast-breeder reactor (EBR-II) showing the packing of hexagonal assemblies.

Fig. 2. Cross section of a typical LMFBF fuel subassembly showing the regular close packing of many small fuel elements.

Fig. 3. Approximate curves of void swelling versus irradiation temperature in stainless steel at three fluence levels.

Typical LMFBK core-support concept.

Fig. 5. Schematic representation of the deflection of subassemblies due to differential swelling and compensation by creep.

Fig. 4. Vertical section of an LMFBK core showing the points of support for the subassemblies.

Fig. 6. Radiation-creep curve for Type 316 stainless steel in the core of the EBR-II reactor.

Fig. 7. Transmission-electron micrograph of irradiated stainless steel showing voids.

Fig. 8a. Fe-Cr-Ni phase diagram at the 625°C isotherm showing swelling behavior as a function of composition.

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Fig. 9. Swelling of an Fe-15Cr-20Ni alloy at 675°C and 140 dpa as a function of various minor alloy additions.

Fig. 10. Schematic representation of a Tokamak fusion device.

Fig. 11. Cross section of a fusion reactor.

Fig. 12. Possible radiation processes that occur in the first wall of a fusion reactor.

NEUTRON-RADIATION DAMAGE

	FUSION REACTOR NIOBIUM WALL	EBR II FISSION REACTOR STAINLESS STEEL CLADDING
NEUTRON FLUX	$4 \times 10^{15} \text{ n/cm}^2 \text{ sec}$	$4 \times 10^{15} \text{ n/cm}^2 \text{ sec}$
NEUTRON ENERGY	14.1 mev	1 mev
DISPLACEMENT RATE	200 atoms/year	100 atoms/year
HYDROGEN PRODUCTION	900 ppm/year	300 pp/year
HELIUM PRODUCTION	300 ppm/year	20 ppm/year
ZIRCONIUM PRODUCTION	10^4 ppm/year	—
VOLUME SWELLING	(1%/year??)	3%
OPERATING TEMPERATURE	600°- 1000°C	470°C

Fig. 13. Neutron effects in fusion- and fission-reactor materials.

Fig. 14. Ductility as a function of temperature in vanadium containing 0 and 25 ppm of injected helium.

Fig. 15. The change in Ni_3Al precipitate size and density in a nickel-aluminum alloy as a function of charged-particle irradiation dose at 550°C .

Fig. 16. Void size and number density in niobium containing various levels of oxygen after nickel ion bombardment.

1 Mev Electron Irradiated 18/8/Si Austenitic Steel
Temperature = 500 C

Fig. 17a. Transmission-electron micrographs of electron-irradiated 18/8/Si stainless steel. Silicon has segregated to the void surfaces--note the circled regions.

Fig. 17b. Auger spectroscopy of surfaces in 18/8/Si stainless steel showing silicon segregation after irradiation.