

Radiation Damage at High Temperatures

A new and important problem in radiation damage
may require development of new materials.

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Interest in the effects of neutrons from nuclear reactors on the properties of metals and alloys was first generated by the work of Wigner (1) and others during World War II. Since then we have seen the rapid development of power-producing nuclear reactors and an attendant increase in the study of radiation damage in the structural materials used in them.

Most solid-state physicists and metallurgists think of radiation damage in structural materials or metals in terms of the changes in properties produced by the atoms displaced by elastic collisions between high-energy particles and the atoms of the metal. The nature of the alterations in the properties of materials produced by the atoms dislodged from their normal sites in crystalline materials might be termed classical radiation damage or displacement damage (2).

In 1963 Hinkle (3) published some experimental results that indicated rather severe effects of neutron irradiation on the properties of some alloys of nickel and iron at high temperatures. The temperatures were well above those at which classical radiation damage would be expected to disappear as a result of thermal rearrangement of the displaced atoms. Hinkel's results and those of Robertshaw *et al.* (4) showed that the ductility of a number of iron-base and nickel-

base alloys was significantly reduced by exposure to high-intensity radiation. Prior to 1965 there was considerable speculation among workers at Oak Ridge National Laboratory, at General Electric's Nuclear Materials and Propulsion Operation, and at the United Kingdom's Atomic Energy Authority laboratory at Harwell concerning the cause of this radiation-induced embrittlement of materials at high temperatures. The evidence suggested that the mechanism was possibly associated with helium bubbles produced in the grain boundaries of materials, the source of which could be the alpha particles (helium nuclei) produced by the thermal neutron reaction with the boron impurity in the alloys. Further results supporting this general mechanism were published by Harries and Roberts (5) and by Martin *et al.* (6, 7). Work in our laboratory gave further support.

The Environment

Before discussing this discovery in detail I shall describe the features of the reactor environment that are important as regards the structural materials, as well as the structural materials themselves.

The reactor itself is merely a source of heat. This heat is transported by some liquid or gas coolant to a steam

generator or boiler where steam is produced and used in essentially a conventional way to produce electrical power. The uranium-containing fuel is generally housed in several thousand metal tubes that are affixed in an array that allows the coolant to extract the heat. This array of fuel elements is, in turn, contained in an appropriate metal container, usually called the pressure vessel. The fuel container and pressure vessel are exposed to the high temperatures and the neutrons generated by the fissioning uranium. These two structures must withstand the stresses generated by the pressure of the coolant and the gaseous products of fissioning and must withstand the small strains generated by variations in thermal expansion in the system. Thus, the structural material used must be reasonably strong and ductile (that is, able to sustain small deformations without fracturing). Further, these properties must not be significantly reduced by exposure to high temperatures and neutron bombardment.

The Structural Material

The high strength of the structural alloys used in the reactor results from several factors. The alloy base, usually iron or nickel, is mixed in the molten state with elements that dissolve in the base. This solid solution is stronger than any of the pure elements used in the alloy. Other elements are added that form compounds within the solid solution and thus further strengthen the alloy.

If we examine a structural alloy such as type-304 stainless steel (chromium, 19 percent; nickel, 10 percent; carbon, 0.06 percent; iron, remainder) with the microscope (see Fig. 1), we find that it consists of crystals (or grains) of the solid solution of iron, chromium, and nickel, separated by grain boundaries. Interspersed throughout the alloy are chromium carbide particles. In addition, this alloy and

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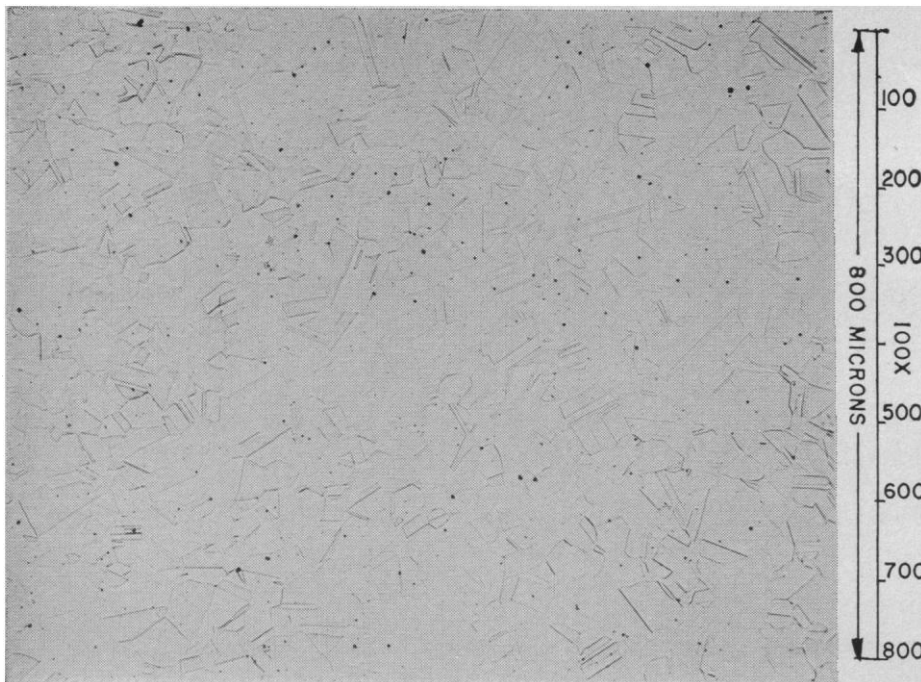


Fig. 1. Microstructure of type-304 stainless steel. The straight dark lines are called "twin" boundaries, separating areas of the crystals having mirror-image differences in crystallographic orientation.

most others contain a large number of impurities in concentrations up to a few hundred parts per million, some of which affect the properties of the alloy.

In a reactor, the alloy must sustain stresses at temperatures up to about

700°C. At such temperatures these alloys deform under stress; the grains become longer in some directions and contract in the others in such a way as to remain contiguous with neighboring grains. The initiation of fracture in the material is a result of the

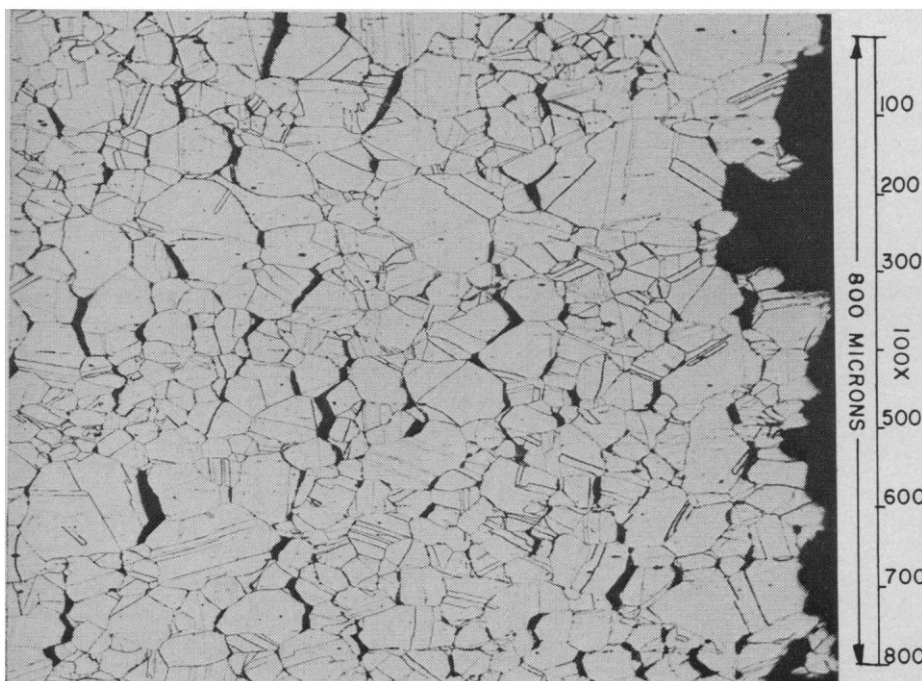


Fig. 2. Photomicrograph showing a typical high-temperature fracture in type-304 stainless steel. The stress was applied in the horizontal direction, and the separation (the complete fracture) is at the right of the photograph. Note that the incipient fractures throughout the material are in the grain boundaries and appear to start at the triple junctions.

local internal stresses that build up across the grain boundaries during deformation (Fig. 2). These fractures tend to originate at the junctions of three grains (triple junctions).

To estimate the stress, σ , necessary to create cracks of this kind, one assumes that the work necessary to start the crack equals the energy required to form the two new surfaces of the crack:

$$\sigma = 2\gamma/R \quad (1)$$

where γ is the surface energy and R is the interatomic spacing. Reasonable values for γ and R are 10^3 ergs per square centimeter, and 3×10^{-8} centimeter, respectively; thus, the stress required is roughly 7×10^4 kilograms per square centimeter. Experimentally we observe that applied stresses of the order of 10^2 to 10^3 kilograms per square centimeter produce intergranular fractures, indicating that the deformation itself concentrates the applied stress, by a few orders of magnitude, in local areas in the material.

Zener (8) suggests a mechanism whereby the applied stress may be concentrated at triple junctions. If the boundaries are assumed to have shearing stresses across them, as shown in Fig. 3, then the stress in the vicinity of the triple junction is

$$\sigma_c = (L/2\rho)^{1/2} \tau \quad (2)$$

The distance, L , between triple junctions is much larger than the radius of curvature, ρ , at the triple junction, and the shear stress, τ , is of the order of σ , the applied stress. Therefore, the stress at the triple junction may be larger than the applied stress by a few orders of magnitude. Not all experimental results are in detailed agreement with this proposed mechanism; however, Eq. 2 is a useful qualitative relationship.

Evolution of the Discovery

The experimental results of Hinkle (3) and Robertshaw *et al.* (4) showed that the ductility of a number of iron- and nickel-base alloys was significantly reduced by exposure to bombardment of approximately 10^{20} neutrons per square centimeter. For example, stainless steels at temperature of 700°C and under stress conditions that normally produce fracture only after strain of 10 to 20 percent (the material stretched to the extent of 10 to 20

percent of its original length) were found to fracture after strain of 2 to 6 percent, after exposure to neutron bombardment in a reactor. Robertshaw's results on three other alloys showed qualitatively similar behavior even after the temperature of the alloys had been raised, after irradiation, to around 1175°C (above 0.8 times the melting temperature expressed in degrees Kelvin); clearly, at 1175°C any trace of the effects of classical displacement damage should have disappeared. Many investigators (9) have shown that the defects produced by displaced atoms are removed rapidly by diffusional processes at temperatures above about the midpoint between 0° and the melting point of the metal or alloy.

Systematic studies (10) of the effects of irradiation temperature on the mechanical properties of type-304 stainless steel at room temperature showed that, at irradiation temperatures above about 450°C, displacement damage did not accumulate in the alloy. However, when the material was deformed at higher temperatures, the ductility (or elongation before fracture) was significantly reduced (see Fig. 4). At testing temperatures above about 600°C, the ductility was reduced by the irradiation to half the value for the unirradiated material; the ratio continued to decrease as the testing temperature was further increased. We also found that reducing the rate of deformation during testing (over the range of 0.1 to 100 percent per minute) at high temperatures tends to enhance the effect produced by the neutron irradiation.

As mentioned above, results obtained before 1965 had suggested that the mechanism was associated with helium bubbles produced in the grain boundaries, and that the source of the helium could be the helium nuclei produced by the thermal neutron reaction with the ^{10}B impurity in the alloys. Small amounts of inert gases formed by other mechanisms in other materials (11) were known to produce effects having characteristics somewhat similar to those observed in these materials. However we needed some more direct evidence that the problem was a result of the presence of helium.

Harries and Roberts (5) then showed that the embrittlement was predominantly a function of thermal-neutron exposure at low doses of fast neutrons. Martin *et al.* (6, 7) showed that

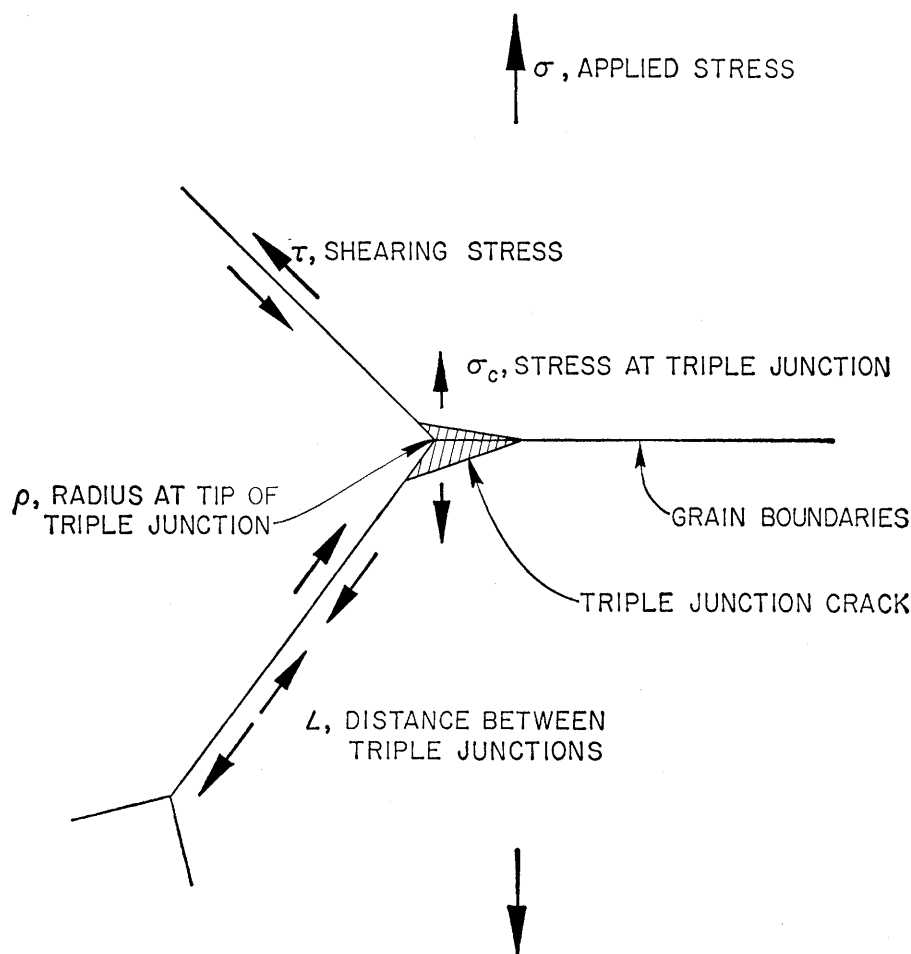


Fig. 3. The model proposed by Zener (8) to account for high stresses at triple junctions. The applied stress may be resolved into shearing stresses across those boundaries which are at angles other than 90 degrees to the direction of the applied stress. The shearing itself then produces a stress at the triple junction that may be significantly greater than the applied stress in that vicinity.

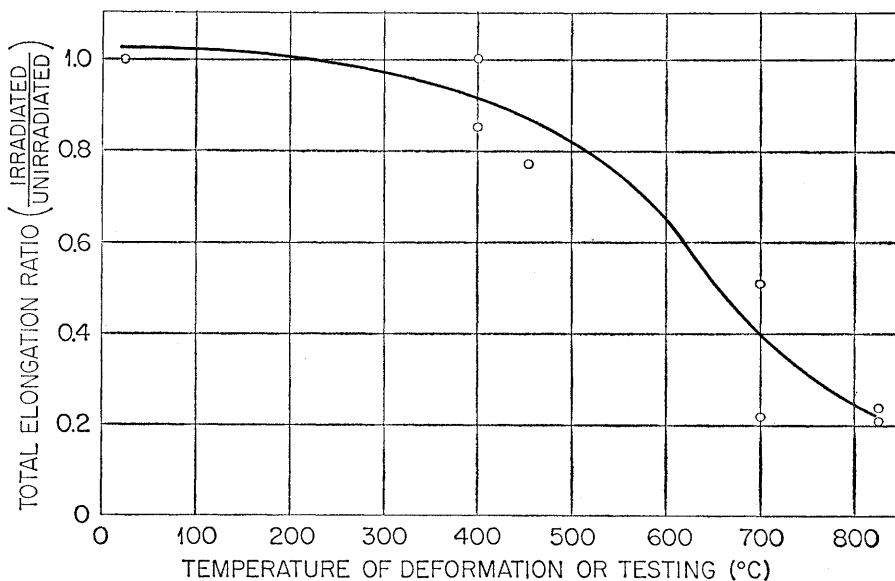


Fig. 4. Deformation in samples of type-304 stainless steel tested at various temperatures in both the irradiated and unirradiated conditions. The effect of the irradiation is described in terms of the ratio of the fracture elongations in the irradiated samples to those in the unirradiated samples. The irradiated samples were exposed to doses of 7×10^{20} neutrons per square centimeter at temperatures between 450° and 600°C.

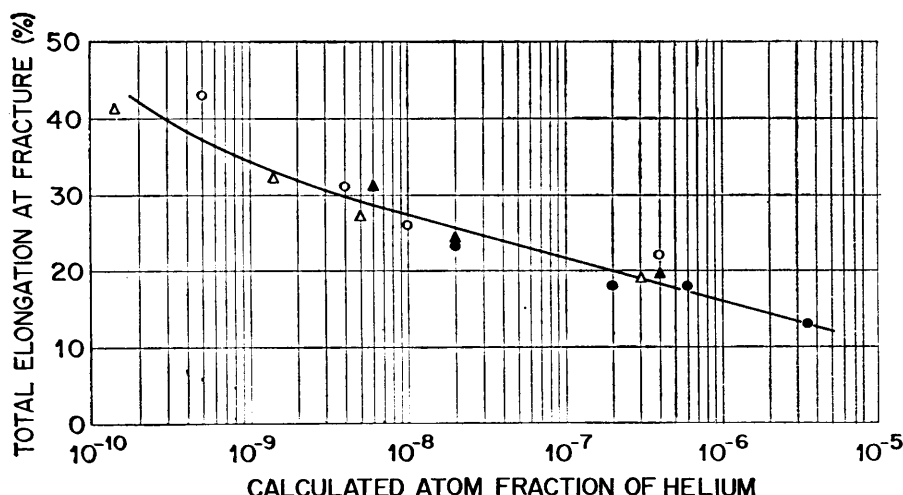


Fig. 5. The elongation at fracture of type-304 stainless steel containing various amounts of boron and exposed to four radiation doses, ranging from 1×10^{18} to 5×10^{20} neutrons per square centimeter. The elongation is shown to be a function of total concentration of helium produced by both high-energy and thermal neutrons. The specimens were tested at 700°C after irradiation at 50°C in the Oak Ridge research reactor. Boron concentrations (in parts per million): open triangle, 0.015; open circle, 0.11; solid triangle, 0.15; solid circle, 3.9.

the embrittlement was related to the helium generated by the thermal-neutron $^{10}\text{B}(n,\alpha)$ reaction, and that at very low concentrations of boron in type-304 stainless steel the contribution of helium from (n,α) reactions between high-energy neutrons (fast neutrons) and iron, nickel, and other constituents in the alloy was also important. Figure 5 shows that the ductility, after irradiation, of type-304 stainless steel containing various amounts of boron and subjected to various doses of irradiation is a function of the total helium content from both the thermal $^{10}\text{B}(n,\alpha)$ reaction and the high-energy (n,α) reactions. Higgins and Roberts (12) reported that the ductility of an alloy at high temperatures was reduced through the injection of helium by means of cyclotron bombardment with alpha particles.

That helium, or any other atomic species, at a concentration of 10^{-9} (see Fig. 5), could produce a pronounced effect on the mechanical properties of a metal is difficult to imagine. However, the noble gases are probably very insoluble in metal. Rimmer and Cottrell (13) have estimated the energies required for solution of the inert gases in copper. The least energy is required when the gas atom is in a vacant lattice site of the metal; for helium, the value is about 1 electron volt. Cottrell (14) indicates that the equilibrium concentration C of gas in solution is

$$C = P/NkT \exp(-F/kT), \quad (3)$$

where P is pressure, N is the number of solvent atoms per unit volume, T is temperature, k is Boltzmann's constant, and F is the energy of solution.

At temperatures of 700°C the concentration of helium is less than 10^{-9} at a pressure of 1 atmosphere. If there are not enough vacant lattice sites for

the helium atoms, then the energy of solution is approximately 2.5 electron volts and the solubility is less than 10^{-15} at a pressure of 1 atmosphere.

Therefore, if helium is produced in a material, we should expect to find bubbles of gas when the concentration exceeds about 10^{-9} . Vela and Russell (15) observed bubbles in large numbers in neutron-irradiated copper-boron alloys containing helium at a concentration of 5×10^{-4} . The bubbles, observed by means of the electron microscope, had diameters of the order of 10^{-6} centimeter. Conclusive identification of bubbles in stainless steels containing helium in low concentrations is difficult, particularly because of artifacts produced during preparation of the thin sample (10^{-5} centimeter thick) for electron-microscope examination. However, small voids having the characteristics of bubbles are found, after neutron irradiation, in stainless steels having helium concentrations in the neighborhood of 10^{-7} (16). Figure 6 is a photomicrograph of type-304 stainless steel containing bubbles. Substituting, in Eq. 1, the bubble diameter (10^{-6} centimeter) for R , the interatomic spacing (10^{-8} centimeter), reduces, by 2 orders of magnitude, the stress necessary to form a crack.

Let me summarize the problem of embrittlement at high temperatures and speculate on the potential seriousness of the problem relative to development of the nuclear power reactors of the future.

Basically, the embrittlement appears to be related to the helium generated in thermal and fast-neutron (n,α) reactions. The ductility of the alloys is affected only at temperatures where they tend to fracture under stress, through processes that produce intergranular cracks. The helium probably forms into bubbles in the grain boundaries of the alloys, and these bubbles grow in size under the stresses in their vicinity until they link together to form large cracks that lead to fracture. These fractures occur at deformations that are significantly smaller than those the material would be capable of sustaining in the absence of the helium. Helium concentrations of the order of 10^{-7} reduce the ductility of type-304 stainless steel at 700°C to half its normal value.

The nuclear power reactors of the future will be those that not only produce electrical power in an economical way but also produce (or breed) new

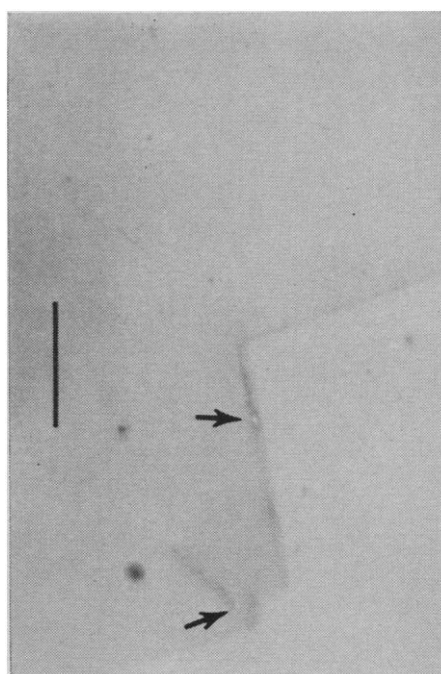


Fig. 6. Photomicrograph, obtained with the electron microscope, showing a portion of a grain boundary (straight dark bands) in an irradiated stainless steel. The two light spots in the grain boundaries (see arrows) are interpreted as helium bubbles. The vertical scale represents 5×10^{-5} centimeter.

fuel from uranium-238 or thorium-232. Breeder reactors typically must operate at temperatures in the 500° to 700°C range and, more significant, generate neutron fluxes, in the vicinity of the fuel, which are greater by 2 orders of magnitude than the fluxes generated by today's power reactors. Alter and Weber (17) have estimated that the fuel cladding in a fast-neutron breeder reactor will contain helium in a concentration higher than 10^{-4} after a 2-year residence in the reactor. Extrapolation of our data in Fig. 5 to helium concentrations of 10^{-4} leads to the conclusion that the ductility of normal type-304 stainless steel at 700°C will approach zero at these helium concentrations.

Approaches and Possible Solutions

Provided our understanding of the mechanism of radiation-induced embrittlement at high temperatures is qualitatively correct, there are several approaches to the problem that, in principle, should reduce the sensitivity of the alloys to the radiation damage.

First, it is rather obvious that reducing the amount of helium generated in the materials should reduce the embrittlement. This may be accomplished by reducing the boron content in some materials used predominantly in a thermal-neutron flux. However, in the fast-neutron reactors and in the high-power-density thermal-neutron reactors, the number of neutrons having energies above 10^6 electron volts is sufficient to produce significant amounts of helium in *any* material. Thus, we will have to deal with the helium.

The second approach is that of decreasing L in Eq. 2. This may be accomplished by reducing the grain size and, therefore, the distance between triple junctions, and possibly by introducing hard-precipitate particles in the boundaries, which would impede the shearing at the grain boundaries. Reducing the grain size may also reduce the concentration of helium at the grain boundaries through the concomitant increase in grain-boundary area per unit volume of alloy (or per helium atom).

The third potential solution would be the introduction, into the grains of the alloy, of precipitate particles that would tend to gather the helium atoms or bubbles and keep them from diffusing to the grain boundaries.

Martin and Weir (18) investigated

the effect of grain size in type-304 stainless steel on embrittlement of the steel at high temperatures under conditions where the helium produced was primarily due to the $^{10}\text{B}(n,\alpha)$ reaction. Some of these results are shown in Fig. 7. Detailed interpretation of these data must be based on several speculative factors. However, it is important to observe that the postirradiation ductility is a sensitive function of grain size; the fine-grained material exhibits from two to four times as much ductility as the coarser-grained material.

The minimum that appears in Fig. 7a may result from two kinds of effects. The smaller amount of damage (the larger ratio) in the finer-grained material probably results from the relationship shown in Eq. 2 and the larger grain-boundary area discussed above. At the other end of the grain-size scale, we must consider the probable distribution of boron in the alloy, as influenced by the high annealing temperature and the variation in cooling rate. The higher annealing temperature and higher cooling rate should pro-

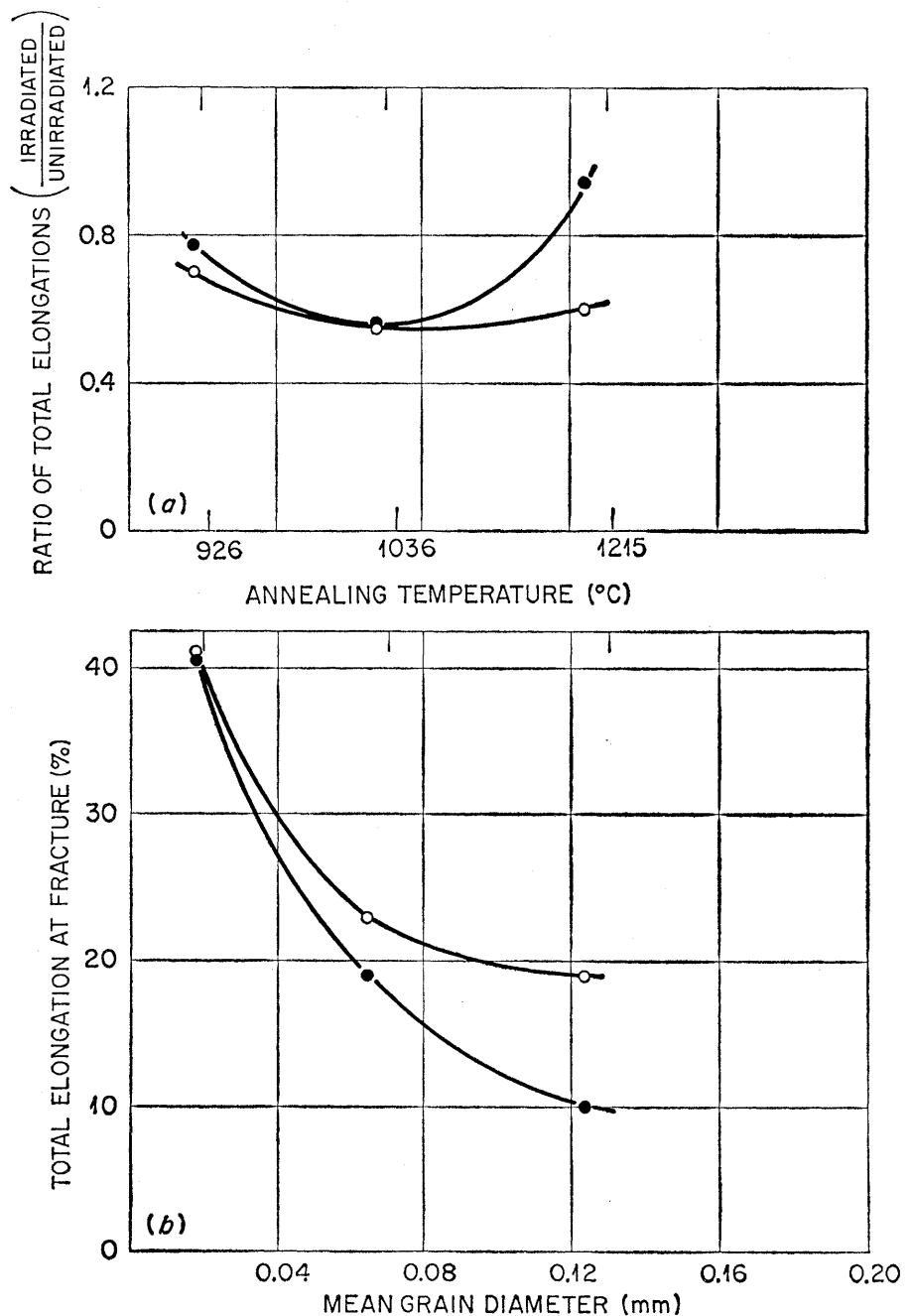


Fig. 7. (a) Ratio of elongations at fracture as a function of grain size for type-304 stainless steel specimens cooled slowly (open circles) and rapidly (solid circles) from the annealing temperature indicated. (b) Elongations of the irradiated samples. Irradiation temperature, 50°C; dose, up to 2×10^{20} neutrons per square centimeter. The samples were tested at 700°C at a strain rate of 0.2 percent per minute.

Table 1. Effect of aging, prior to irradiation, on the postirradiation ductility of type-304 stainless steel. The alloy was solution-annealed at 1038°C ("annealed material" refers to this stage), solution-annealed at 1038°C, then aged at 800°C for 100 hours ("aged material" refers to this stage) prior to irradiation. The samples were then irradiated, at 50°C, at doses up to 9×10^{20} thermal neutrons per square centimeter, in the Oak Ridge research reactor and subsequently tested.

Test conditions	Total elongation (%)	
	Annealed material	Aged material
Tensile test at a strain rate 0.2%/min at 704°C	20.5	30.5
Tested at a stress of 14 kg/mm ² at 650°C until fracture occurred, in several hundred hours	4.0	14.0

duce a more homogeneous boron distribution (hence, helium distribution) in the alloy than a lower annealing temperature and slower cooling rate. The lower temperature and slower rate should allow the boron to segregate to the grain boundaries; thus, on irradiation, the helium would be produced in the vicinity of the grain boundaries. Thus, we speculate that, after irradiation, more helium is available to the grain boundaries in the material annealed at low temperature and slowly cooled than in the alloy annealed at high temperature and rapidly cooled.

We may introduce chromium car-

bide particles into the grain boundaries of type-304 stainless steel by first heating the alloy to a temperature above 1000°C, the point where the carbides dissolve into the solid solution, and then heating the alloy at about 800°C, the point where the chromium carbides are insoluble in the solid solution and precipitate as irregularly shaped, discontinuous particles in the grain boundaries. The first of these treatments is called "solution annealing," and the second is commonly called "aging" the alloy. Our data of Table 1 (see 11) show that aging the alloy prior to irradiation increases the postirradiation ductility of type-304 stainless steel tested at high temperatures. The steel is tested both by conventional tensile testing and by application of a constant stress which allows the material to deform very slowly until it fractures. Levy *et al.* (19) have performed similar experiments on Hastelloy X, an alloy of nickel, molybdenum, and chromium, with resulting increase in ductility of the alloy.

Arranging for small, stable precipitate particles within the grains of the alloy to trap the helium and keep it from collecting in the grain boundaries is a bit more complex than one might at first imagine. Our approach has been to alloy type-304 stainless steel with elements which would be expected, from thermodynamic considerations, to form stable compounds with both carbon and boron. In this manner we hoped to produce a precipitate that

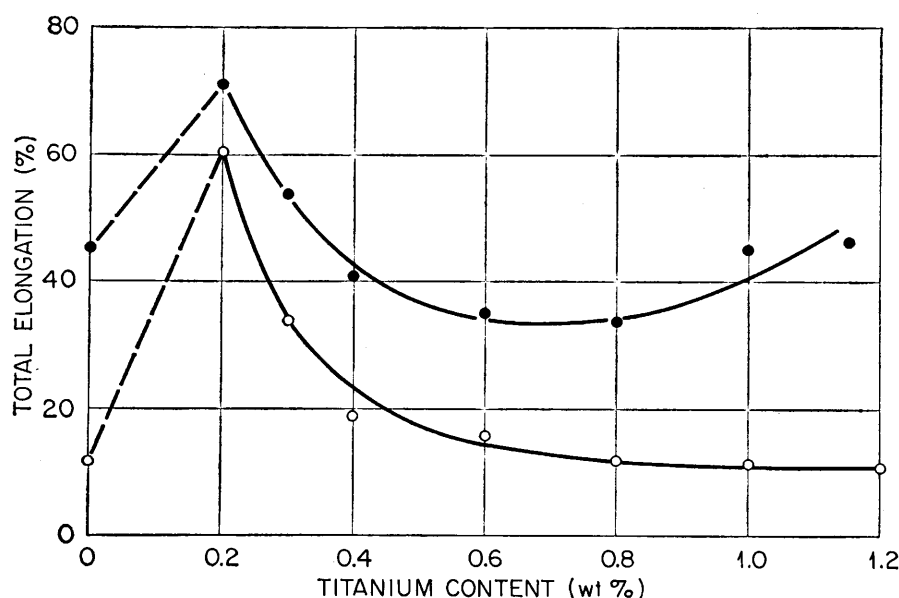


Fig. 8. Fracture elongations for specimens of type-304 stainless steel alloyed with titanium, tested (at 842°C) before irradiation (solid circles) and after irradiation (open circles). Irradiation temperature, 50°C; dose, up to 1×10^{20} neutrons per square centimeter. Both the nonirradiated and the irradiated specimens are significantly influenced by the titanium content of the stainless steel.

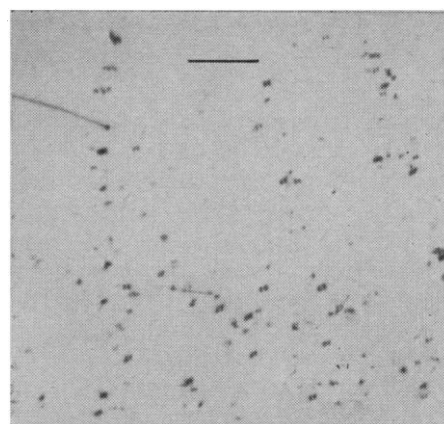


Fig. 9. Electron transmission photomicrograph of a specimen of stainless steel containing titanium (0.15 percent) and annealed at 900°C for 1 hour. The dark images result from electron diffraction effects produced by the elastic-strain fields around the smaller precipitate particles. The horizontal scale represents 5×10^{-5} centimeter.

would attract not only helium but also boron from the grain boundaries, so that, upon irradiation, the helium would not be generated preferentially near the grain boundaries. These and other metallurgical considerations led us to select titanium as an alloying element to be added to the basic type-304 stainless steel. A set of small laboratory batches of type-304 stainless steel alloyed with titanium in various concentrations was produced, irradiated, and tested. The results (see 11) are shown in Fig. 8. We see that both curves—that for ductility before irradiation and that for ductility after irradiation—have a maximum near titanium content of 0.2 percent. This set of data may appear surprising in that one would expect, all other things being constant, the effect of irradiation on the elongation to decrease in some continuous manner with increasing concentration of titanium. Clearly this is not the case. However, as the titanium concentration is increased, solid phases other than titanium carbides begin to appear in the material, as viewed with the microscope. The potential side effects of these phases have not been examined in detail and may account for the anomaly.

The precipitate that forms in the stainless steel with titanium concentration of 0.2 percent is shown in Fig. 9. The actual particles are somewhat smaller than the black images of Fig. 9, appearing to be of the order of 10^{-6} centimeter or less in diameter. The mean spacing between particles is of the order of 5×10^{-5} centimeter. The distance between grain boundaries in

the steel is roughly 10^{-3} centimeter. If we assume that the helium is produced uniformly in the alloy and that the precipitate as well as the grain boundary acts as a trap for the gas, then we may calculate the amount of gas that can get to the grain boundary, on the basis of the model chosen for the motion of the gas atoms or bubbles.

The picture I have presented is that of radiation damage, at high temperatures, that involves predominantly the effects of helium produced by (n,α) reactions. This damage appears to be quite general; that is, it occurs in a large number of metals and alloys. However, other mechanisms of radiation damage are known in some alloys in the temperature range from 400° to 650°C . Some workers (20) have observed precipitation of compounds in alloys that occurs only in irradiated material. It is possible that, with certain alloys and under certain conditions of irradiation, these precipitates may produce large changes in the properties of the alloy, in addition to the changes due to the helium.

Summary

The successful development of nuclear power reactors that are economically competitive with other sources of energy has led us to believe

that more economical reactors will be developed. But, in developing the next generation of reactors, a new set of problems must be overcome. One of the most important of these is that of the embrittlement of the structural materials at high temperatures as a result of the intense neutron fields in these advanced systems.

The radiation-induced embrittlement at high temperatures is probably associated with helium produced in the materials due to (n,α) reactions with the metal, and in some alloys radiation-induced precipitation of compounds within the alloy may also play a role. We believe that the most serious long-term problem is the generation of helium. Our current understanding of the mechanism by which this radiation damage is produced has allowed us to effect some improvement in the behavior of conventionally produced structural alloys, through minor modifications of the normal working and annealing processes used in their manufacture. However, we may find that new alloys will have to be developed to withstand the service conditions in future nuclear power reactors.

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Evolutionary Significance of Metabolic Control Systems

The β -ketoadipate pathway provides a case history in bacteria.

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When a metabolic pathway of considerable complexity occurs in several different groups of organisms, biologists are sometimes tempted to assume without further evidence that the pathway in question has had a single evolutionary origin and can thus serve as a marker of evolutionary affinities. A characteristic example of such reason-

ing can be found in Vogel's review of the biological distribution of the diaminopimelic and α -amino adipic pathways for lysine biosynthesis (1). This class of assumptions about evolutionary origin could be rigorously tested by ascertaining whether the enzymes of a pathway which have the same catalytic function in different organisms show

extensive homologous amino acid sequences. However, relatively few proteins have been systematically compared in this fashion; cytochrome *c* (2) and hemoglobin (3) are the most carefully studied examples. For the most part, attempts to distinguish between analogous and homologous enzymes have been less direct and have involved comparisons of molecular weight, amino acid composition, catalytic behavior, or immunological properties (4). We believe that the evolutionary significance of the presence of a given biochemical pathway in representatives of several different biological groups can be assessed by means of a somewhat different kind of analysis—comparison of control mechanisms.

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