OVERVIEW

Recent Progress in Fusion Reactor Materials Studies: Focus on Transmutation and Radioactivation Aspects

F. A. Garner and L. R. Greenwood

Pacific Northwest Laboratory, Richland, WA 99352, USA

A review is presented of recent progress attained in the understanding of the influence of transmutation on the development of fusion-relevant property change data. It is shown that early experiments on helium effects on void swelling, irradiation creep and tensile properties of austenitic stainless steels were often misleading, and the influence of helium is much smaller than originally expected. Similar definitive conclusions concerning the role of helium in ferritic steels, copper alloys, and vanadium alloys cannot be drawn at this time. It is also shown, however, that the formation of solid transmutants can be very important in a number of alloy systems, especially for some of those proposed as reduced radioactivation candidates.

(Received June 30, 1993)

Keywords: *neutron irradiation, helium, solid transmutation, radioactivation, fission-fusion correlation, void swelling, irradiation creep, embrittlement*

I. Introduction

It is well known that the properties of most materials of interest to fusion power application will change as a result of neutron irradiation. Most of the changes arise from atomic displacements and the subsequent diffusion, interaction, and segregation of point defects, as well as from the interaction of these point defects with the various elemental constituents. In some materials, however, the changes can be strongly influenced or even dominated by processes associated with nuclear transmutation to new elements. Whereas most previous research concentrated on the gaseous transmutants (helium and sometimes hydrogen), increasing emphasis has been placed recently on the influence of solid transmutation products.

Associated with transmutation is also radioactivation, a process that does not necessarily require the formation of a new element. Radioactivation is important for both personnel and public safety concerns and for engineering issues such as afterheat removal. The recent focus of the fusion materials community on employment of low activation materials has accelerated the interest in developing new materials for fusion applications that address this concern⁽¹⁾. Some of the new material paths now being explored involve the use of manganese, tungsten, and vanadium, elements whose nuclear characteristics have reactivated interest in the solid transmutation area. A number of elements that are not considered to be low activation in nature are still under consideration for fusion application, however, and some of these also undergo strong transmutation.

Transmutation, radioactivation, and atomic displacement rate are very sensitive to the neutron spectrum, however. This requires that data developed in one neutron spectrum be evaluated for its spectral sensitivity and then be "translated" prior to application in another spectral environment⁽²⁾. This translation process is often referred to as "fission-fusion correlation". In some materials, the translation may require either no change or only a minimal change in the data-based property change correlation. However, for other materials, the spectral dependence of the property change under study may totally dominate the evolution of that property. In such cases, the data cannot be directly applied to fusion design, and any data-based prediction may require very large changes to incorporate the spectral dependence of that property.

For example, the translation process for solid transmutation concerns may require that separate experiments be conducted to determine the sensitivity of the material to starting variations in the element being formed or removed by transmutation. Where two spectrally-related parameters both exert separate and possibly synergistic influences, it is necessary to separate and quantify the effect of both variables. As discussed in Ref. (2), the often large differences in displacement rate that accompany spectrum differences in various reactors can exert a larger effect on the translation process than is caused by other direct consequences of the spectral difference.

As the understanding of the radiation damage community has evolved and matured, it has become obvious that some of the early experiments on helium's influence yielded misleading results, primarily because the ex-

periments were strongly affected by the operation and influence of other unrecognized, but nevertheless very important, variables. This paper will review some of the new spectrally-related insights developed by the fusion materials community in the past decade, concentrating first on the effects of helium and then on the effects of solid transmutants. Hydrogen as a transmutation product has not received very much attention recently, since the common perception is that, unlike helium, hydrogen is very mobile in most metals and, therefore, does not concentrate in them. It is anticipated, however, that future studies may lead to a reassessment of hydrogen's influence in metals and possibly in other materials.

II. Review of Neutron Experiments on Helium's Influence

In the early stages of both the liquid metal fast breeder and fusion reactor programs, it was usually assumed that helium would play a very large role in the evolution of almost all properties of engineering interest. This assumption was based on several major perceptions. First, voids were known to require helium or other gases to nucleate, and therefore the onset of swelling should be strongly affected by the rate of helium production. Second, it was also thought that the post-transient swelling rate would be sensitive to the helium generation rate. Third, helium-induced changes in swelling would probably also be mirrored in the creep and creep rupture behavior. Fourth, since relatively small amounts of helium were known to cause helium embrittlement at relatively high irradiation temperatures, then much larger amounts of helium should cause proportionally more embrittlement. Implicit in this latter perception was that such embrittlement at higher helium levels should extend over a wider range of temperature.

In one series of papers in the early 1980's, however, Brager and Garner showed that, contrary to the then-prevailing perception, the post-transient swelling rates developed in the high helium generation environment of HFIR (High Flux Isotope Reactor) were actually quite similar to those developed at much lower helium generation rates in EBR-II (Experimental Breeder Reactor II), even though the voidage was often distributed on a much finer scale for HFIR irradiation⁽³⁾⁻⁽⁶⁾. It was also shown that differences in the duration of the transient regime of swelling were much more sensitive to displacement rate and temperature history than to the helium generation rate or to the details of the void sizes and number densities. Thus, it was not possible to compare HFIR and EBR-II data directly and confidently ascribe any differences in the incubation behavior of swelling to helium differences alone. No conclusive contradictory data have appeared in the last decade to contest these conclusions concerning the relatively small effect of helium on swelling in austenitic stainless steels.

The early perception that large helium levels would lead to a significant alteration of all mechanical properties of stainless steels at all relevant temperatures was

Fig. 1 An early estimate by Bloom and Wiffen of the effect of helium/dpa ratio on irradiation-induced changes in tensile properties of annealed AISI 316 irradiated in the Dounreay Fast Reactor (DFR) and HFIR⁽⁷⁾. The quoted temperatures for the HFIR data are much too low, and the displacement levels for both reactors require significant revision⁽²⁾, thus invalidating the conclusion drawn in the original paper concerning the strong influence of helium generation rate. The shaded area above 600°C represents the temperature regime traditionally associated with helium embrittlement.

also eventually found to be largely incorrect, but the misperception persisted much longer. Figure 1 shows an early and often quoted comparison of U.S. and U.K. data on neutron-induced changes in total elongation of annealed 316 stainless, showing an apparently very large effect of the helium/dpa ratio across the full temperature range of interest to fast reactors and fusion reactors⁽⁷⁾. For many years, these results strongly influenced the perception of the fusion materials community concerning the potential strength of helium's influence, especially at lower temperatures (< 600°C) where helium embrittlement is normally not a major concern. Garner and coworkers later demonstrated that the data shown in Fig. 1 were actually quite inconclusive with respect to any conclusions concerning the influence of helium below 600°C⁽²⁾. This original misinterpretation of the data arose primarily from an unrecognized but substantial underestimate of the gamma heating levels and temperatures in early HFIR experiments, and secondarily from changes later found to be required in the displacement levels specified for each of the several data sets. These data only support the well-known effect of helium embrittlement in its traditional high temperature range.

More recent studies of this type conducted at Oak Ridge National Laboratory (ORNL) involved a similar comparative irradiation in HFIR and EBR-II of cold worked titanium-modified 316 steels. These studies used updated gamma heating rates and better defined displace-

Fig. 2 Hardening and ductility loss observed in stainless steels during neutron irradiation in the HFIR, HFR and R2 reactors, with helium generation rates spanning the range from ~ 10 to 35 appm/dpa⁽⁹⁾. Note that cold working has a larger consequence on ductility loss than does the helium.

ment levels, but showed that the influence of the large differences in helium generation rate on mechanical property changes was not significant⁽⁸⁾. The authors of this second study, however, did not attribute the unresponsiveness to helium/dpa ratio of cold worked steels (compared to that of annealed steels) to a better definition of irradiation temperatures and displacement levels, but ascribed it only to improvements in the steels themselves. This conclusion has not been supported by any other evidence gathered in the last decade, however.

A similar insensitivity of tensile properties to helium generation rate was observed in the range ~ 10 to ~ 35 appm/dpa for both annealed and cold worked stainless steels by Elen and Fenici⁽⁹⁾ in comparative irradiations conducted at $\sim 250^\circ\text{C}$ in HFIR, HFR (High Flux Reactor at Petten) and the R2 reactor in Studsvik, Sweden, as shown in Fig. 2. Note that the nil ductility values found at this temperature arise primarily from cold working and irradiation, rather than from the helium generation rate alone.

Another series of experiments that addressed the possible influence of helium generation rate were conducted in the ORR (Oak Ridge Research) Reactor in a series of spectrally-tailored experiments. These experiments reduced the number of thermal neutrons at some point in the experiment to control the subsequent helium generation rate produced by the $^{58}\text{Ni}(n, \gamma)^{59}\text{Ni}(n, \alpha)^{56}\text{Fe}$ sequential reactions⁽¹⁰⁾. In these experiments, the microstructures of stainless steels⁽¹¹⁾, as well as those of simple Fe-Cr-Ni ternary austenitic alloys⁽¹²⁾, were found to be dominated by an unprecedented refinement of cavity microstructure. As shown in Fig. 3, this refinement caused large increases in strength compared to those developed in comparable irradiations conducted in EBR-II⁽¹³⁾. Some differences in

swelling and irradiation creep behavior shown in Fig. 4 were also attributed to this refinement⁽¹⁰⁾⁽¹²⁾⁽¹³⁾. Early interpretations of these data attributed the higher strength, as well as the differences in swelling and creep levels, only to the higher rates of helium production in ORR.

It was later found, however, that the microstructural

Fig. 3 Irradiation-induced changes in yield strength of Fe-Cr-Ni ternary alloys as a function of irradiation temperature for the MFE-4 experiment conducted in ORR and the AD-1 experiment conducted in EBR-II⁽¹³⁾. The large difference observed between the two sets of results is primarily a consequence of the very different temperature history in the two experiments⁽¹²⁾⁽¹⁴⁾.

Fig. 4 Published comparisons of the behavior observed for creep and swelling of 25% cold worked PCA in ORR, FFTF and HFIR⁽¹⁰⁾⁽¹⁹⁾. Originally explained in terms of differences in helium generation rate, the differences observed following irradiation are thought by the authors of this review to be dominated by the large differences in displacement rate and temperature history in ORR as compared to that of the other two reactors.

refinement and associated additional hardening observed in ORR were primarily a consequence of the very atypical temperature history experienced during irradiation in these spectrally-tailored experiments⁽¹²⁾⁽¹⁴⁾. Substantial set-backs in temperature occurred almost daily in ORR and caused a periodic and profuse nucleation of fine dislocation loops that served as excellent nucleation sites for helium bubbles. Once formed, these bubbles were sessile, and helium could not easily migrate and aggregate to form the lower densities of larger cavities that usually develop during isothermal irradiation. The differences observed in swelling and creep may also have been influenced somewhat by this atypical temperature history during irradiation, but were probably more strongly influenced by the difference in displacement rate, with the ORR irradiation proceeding at one order of magnitude lower displacement rate than those of HFIR and FFTF (Fast Flux Test Facility). The incubation period of swelling in typical stainless steels has been shown to be sensitive to differences in displacement rate, decreasing strongly in duration with decreasing displacement rate⁽²⁾. Thus, on the basis of displacement rates

alone, earlier and larger swelling would be expected in the specimens irradiated in ORR.

The irradiation creep rate has also been shown to increase with decreasing displacement rate in the absence of swelling⁽¹⁵⁾, and then to accelerate even more strongly with the onset of void swelling, such that the total creep rate per unit stress and dpa is the sum of two terms, B_0 and $D\dot{S}$, where B_0 and D are the creep compliance and swelling-creep coupling coefficients, respectively, and $\dot{S}$ is the swelling rate⁽¹⁶⁾⁻⁽¹⁸⁾. Thus, it is not surprising that irradiation creep would accelerate concurrently with the earlier swelling observed in the ORR experiment.

There are additional complexities required for the analysis of irradiation creep data taken from such diverse spectral environments. These complexities are related to the definition of displacement levels, separation of the various creep regimes, the impact of precipitate-related strains, and the inclusion of differences in displacement rate on the various strain contributions.

In the original interpretation, the densification measured in the stress-free tubes was not taken into

Fig. 5 Comparison of (a) published⁽¹⁹⁾ and (b) revised data analysis⁽²⁰⁾ on irradiation creep at 400°C in 20% cold worked PCA irradiated in ORR and FFTF, illustrating that the difference in behavior previously attributed only to differences in helium generation rate actually arises primarily from differences in displacement rate. A similar conclusion was also reached for irradiations conducted at 500 and 600°C.

account. The B_0 creep contribution shown in Fig. 5 for ORR is that measured by Grossbeck and Horak for the stressed tubes. The B_0 contribution for FFTF is also a measured value. Figure 5 shows the change in interpretation that results when the original creep data from such comparative irradiations⁽¹⁹⁾ are reanalyzed in light of these considerations⁽²⁰⁾. Note that in the reinterpretation, it is not necessary to invoke a major role for helium. The differences are largely explained only by the difference in displacement rate and by the separation of the creep compliance and swelling-enhanced creep regimes.

It thus appears that some of the early and most influential neutron irradiation experiments on the impact of the helium generation rate very strongly overemphasized the

role of helium. This overemphasis occurred as a result of not recognizing the strong influence on the experiments of other important variables such as gamma heating rate, irradiation temperature, temperature history, and displacement rate.

Until recently, it has been impossible to conduct experiments in which spectrum-related parameters such as helium/dpa ratio could be varied without also accepting variations in other important parameters. A technique currently being used, however, allows the study of the influence of helium alone on density change, microstructural evolution and mechanical properties of nickel-bearing alloys. This technique uses isotopic tailoring to vary the helium production rate without introducing changes

Fig. 6 Influence of thermomechanical starting state and helium generation rate on yield strength and elongation of three Fe-Cr-Ni model alloys irradiated in three segments at 365°C in the ^{59}Ni isotopic tailoring experiment⁽²⁴⁾⁽²⁵⁾. The He/dpa ratio of the doped specimens was fixed to be almost independent of alloy content, allowing separation of the separate effects of nickel and the helium generation rate on alloy behavior. Filled and open symbols denote annealed and cold worked specimens, respectively, in this and the following figure. The average helium generation rates for undoped and ^{59}Ni doped specimens in the first two irradiation segments are shown in both figures. The influence of helium is shown to be smaller than the effect of all other variables studied.

in neutron spectrum, temperature, or significant changes in displacement rate⁽²¹⁾⁽²²⁾. By producing alloys whose only difference is the presence or absence of ^{59}Ni , an isotope that does not occur naturally, and irradiating doped and undoped specimens side-by-side in the appropriate regions of FFTF, it is possible to produce substantial variations in helium/dpa ratio without varying any other important parameter. The ^{59}Ni isotope produces helium by the $^{59}\text{Ni}(n, \alpha)^{56}\text{Fe}$ reaction whose cross section increases with decreasing neutron energy and which exhibits a strong resonance at 203 eV⁽²³⁾. The recoil of the ^{56}Fe is quite energetic, however, and leads to a maximum increase of several percent in the displacement rate of the doped specimens during irradiation in the FFTF experiments.

A particular advantage of these experiments is that one need not be as concerned about details of the tempera-

ture history, since both doped and undoped specimens experience exactly the same history. As shown in Figs. 6 and 7, large differences in helium/dpa ratio have been found not to lead to significant differences in tensile properties of FeCrNi ternary alloys during irradiation in FFTF under either isothermal or non-isothermal conditions⁽²⁴⁾⁽²⁵⁾. The influence of high helium levels on the microstructural evolution of these alloys has also been studied in this experimental series^{(26)–(28)}. While high levels of helium have been found to alter the various microstructural densities somewhat, it does not do so to an extent that produces significant macroscopic consequences on either the swelling or the mechanical properties of these alloys.

An interesting byproduct of the ^{59}Ni isotopic tailoring experiments has been the realization that the values usually quoted for helium production rates for nickel-bearing

Fig. 7 Influence of the helium generation rate and temperature history on the yield strength and elongation of annealed Fe-Cr-Ni model alloys following irradiation in the ^{59}Ni experiment at a target temperature of 495°C ⁽²⁴⁾⁽²⁵⁾. The solid line corresponds to the original non-isothermal temperature history experiment described in the text and the dotted line corresponds to a nominally similar isothermal experiment.

Fig. 8 Helium generation rates measured in undoped Fe-15Cr-25Ni irradiated at various positions and temperatures in FFTF, averaged at a given displacement level over the full prior duration of the experiment. Thus, the instantaneous rates are larger than those shown on the graph⁽²⁹⁾.

ing alloys irradiated in fast breeder reactors (0.2–0.3 appm/dpa) are only correct at the very beginning of the experiment. The ^{59}Ni isotope is also formed slowly in fast reactors, and, as shown in Fig. 8, the helium production rate increased substantially and continuously in the undoped alloys during the isotopic tailoring experiment⁽²⁹⁾. Thus, the gap in helium generation rates between fission experiments and fusion-relevant studies was being reduced throughout the irradiation.

While it appears that helium at fusion-relevant generation rates may not significantly influence the neutron-induced evolution of properties in austenitic steels, a similar conclusion cannot be drawn at this time for some other materials of interest, such as ferritic/martensitic steels, vanadium-base and copper-base alloys. Various experiments are in progress to determine whether helium plays a large role in the evolution of these materials. The experiments on ferritic steels are being conducted in HFIR and use variations in the $^{58}\text{Ni}/^{60}\text{Ni}$ ratio to control the helium production rate⁽²²⁾ rather than doping with ^{59}Ni . The Dynamic Helium Charging Experiment on vanadium alloys utilizes pre-doping with tritium as well as continuous generation of tritium in the ^6Li -enriched lithium coolant surrounding the specimens⁽³⁰⁾. This produces fusion-relevant helium generation rates in the vanadium alloys via infiltration of tritium and its subsequent decay to ^3He .

No truly satisfactory method has yet been developed to study helium effects in copper alloys. One possibility to explore helium's influence in copper alloys involves either elemental or isotopic tailoring, but it is more difficult than the techniques used for nickel-bearing alloys. The proposed technique is based on the fact that in mixed-spectrum reactors, helium production in copper is slowly enhanced by the sequential reactions

$^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}(\beta^-)^{64}\text{Zn}(n, \gamma)^{65}\text{Zn}(n, \alpha)^{62}\text{Ni}^{(31)}$. However, since two thermal neutron capture reactions are needed to produce ^{65}Zn , the net helium generation rate is much smaller initially than for the corresponding reactions in nickel. Nevertheless, fusion-like helium levels will be produced in pure copper after about 1.5 years in HFIR. Unfortunately, this will be accompanied by large amounts of solid transmutation in HFIR that are very atypical of that produced in fusion spectra, as discussed in the next section.

Helium production in copper could be greatly enhanced by the addition of natural zinc, and a further factor of two could be obtained by isotopic tailoring with ^{64}Zn . Isotopic tailoring with ^{65}Zn is impractical due to its relatively short half-life (244 days) and its high radioactivity level. Zinc additions will change the starting alloy composition, however. Since both Ni and Zn are natural transmutants of copper, it is probably possible to design a reasonable gaseous/solid transmutation experiment involving Cu-Ni-Zn alloys if spectral tailoring is also used to reduce the overall level of solid transmutation. In such an experiment, the helium generation rate produced by zinc and nickel additions to copper could be directly comparable to that produced by nickel additions in ferritic steels⁽²²⁾.

Boron-doping to produce helium in copper via the $^{10}\text{B}(n, \alpha)^7\text{Li}$ reaction has been used to study swelling, as shown in Fig. 9, but it is sometimes difficult to identify the separate effects of boron, helium, and the lithium that also forms in equal amounts⁽³²⁾⁽³³⁾. Similar studies have been conducted on vanadium^{(34)–(36)} and nickel alloys⁽³⁷⁾⁽³⁸⁾. A recent example of the results of such an experiment is shown in Fig. 10 and illustrates the complexity of the swelling response to B, He, and Li at various irradiation temperatures and alloy compositions.

One unresolved area still exists where helium's in-

Fig. 9 Influence on swelling of using boron-doping to produce helium and lithium in pure copper irradiated in ORR to 1.2–1.5 dpa⁽³²⁾⁽³³⁾. The boron content was ~ 116 appm, enriched with 92% ^{10}B , which transmuted at an initial rate of 500 appm/dpa. Most of the helium and lithium generation thus occurred very early in the experiment.

Fig. 10 Influence on swelling of using boron-doping to produce helium and lithium in pure vanadium and V-5Cr irradiated in FFTF⁽³⁶⁾. The data shown in the top right figure were derived from a companion experiment to that at 427°C (shown at top left), but which was conducted at one-third the displacement rate. This comparison indicates that displacement rate also plays a strong role in determining the swelling.

fluence may be significant in stainless steels. As summarized by Mansur and Grossbeck, ion bombardment experiments indicate that large helium levels may influence the creep rupture life, especially during very slow strain rate tests⁽⁸⁾. Additional tests are required to confirm this possibility.

III. Solid Transmutation and Its Consequences

When typical iron-based alloys are irradiated in fast reactors, the composition is not changed significantly even after irradiation to very high exposures⁽³⁹⁾⁻⁽⁴¹⁾. When these same steels are irradiated in a mixed spectrum reactor such as HFIR, however, significant changes in some minor elemental components can occur. Vanadium, not normally present at high levels in austenitic stainless steels, can form from the $^{50}\text{Cr}(n, \gamma)^{51}\text{Cr} \rightarrow ^{51}\text{V}$ reaction and approach levels on the order of 1% in 316 stainless steel by ~60 dpa. Manganese, on the other hand, is normally present at 1 to 3% in many austenitic steels and can transmute almost completely in HFIR to iron (~50%

loss at ~40 dpa). In the FeCrMn-base steels explored over the last decade as potential low activation substitutes for FeCrNi-base alloys, however, the large or near total loss of manganese in HFIR at high dpa levels would severely impact the metallurgical stability of the steel and would produce data of little value for fusion application⁽¹⁾. With this one exception, however, neither the V nor the Mn reactions are thought to significantly influence the response of typical lower-manganese austenitic steels to neutron radiation. The vanadium transmutant formed in HFIR appears to become concentrated into various naturally-occurring precipitates as it forms, thus yielding no net effect on the alloy matrix⁽⁴⁾⁽⁵⁾, and the influence of manganese on swelling in typical stainless steels has been found to be weak, even in the absence of transmutation⁽³⁹⁾. Neither element has been shown to play a large role in the post-irradiation mechanical properties of these steels.

Manganese-stabilized (15-30% Mn) austenitic stainless steels are not really low activation in nature, however. In this case, "low activation" is a misnomer. Reduced

long term radioactivity is purchased at the expense of a greatly enhanced short-term radioactivity. The afterheat associated with the high short-term decay rate of manganese, combined with its high volatility in stainless steels at elevated temperatures, has recently led the fusion materials community to abandon this alloy concept. The phase stability of manganese-stabilized alloys has also been found to be inherently lower under irradiation than that of nickel-stabilized alloys^{(42)–(44)}.

In fusion spectra, the behavior of vanadium and manganese are different from that in fission reactors. Vanadium forms at a somewhat lower rate than in HFIR via the $^{52}\text{Cr}(n, 2n)^{51}\text{Cr} \rightarrow ^{51}\text{V}$ reaction, and the manganese level increases slowly, rather than decreases, as a consequence of a variety of (n, p) and $(n, 2n)$ reactions involving Fe and Mn isotopes. In general, however, most studies have indicated that these and other solid transmutants will be of little consequence for most austenitic and ferritic/martensitic steels irradiated in fusion spectra. As will be shown later, the on-going development and testing of low activation ferritic/martensitic steels using tungsten additions for strengthening should take into account the effects of transmutation upon this element.

Copper and its alloys are currently being considered for high heat flux applications such as the divertor, even though copper is not low-activation in nature⁽⁴⁵⁾. During either fission or fusion neutron irradiation, transmutation produces moderately large levels of nickel and zinc and relatively small levels of cobalt. Nickel additions, in particular, strongly degrade the thermal and electrical conductivities of copper alloys, especially when combined with the reduction of conductivity associated with void swelling. As shown in Fig. 11⁽⁴⁶⁾, nickel additions themselves do not appear to affect void swelling significantly. Zinc has a lesser effect per atom on conductivity degradation but zinc's impact can not be ignored since in fast reactors, it forms at almost the same rate as nickel. Zinc's influence on void swelling has not yet been determined, but experiments on this subject are currently being conducted in joint Japan/U.S. studies.

Figure 12 shows the calculated production of the major nickel and zinc isotopes during a three-cycle irradiation of pure copper in FFTF⁽⁴⁷⁾. The validity of these calculations has been confirmed by back-calculating the concentrations necessary to reasonably produce the observed decreases in electrical conductivity⁽⁴⁸⁾ and by direct measurement using energy-dispersive X-ray analysis⁽⁴⁹⁾.

The conductivity data shown in Fig. 11 cannot be applied directly to fusion design without some translation⁽²⁾. While void swelling may not be very sensitive to spectra related differences in nickel (and possibly zinc) production, the total transmutant level per dpa not only increases significantly in fusion spectra, but the partition of transmutants shifts from Ni/Zn=1.1 in FFTF to 2.2 in the STARFIRE first wall spectrum⁽⁴⁷⁾. Thus, the conductivity loss per dpa will be significantly larger in the STARFIRE spectrum and other fusion spectra.

Fig. 11 Swelling and electrical conductivity changes observed in pure copper (411–430°C and 539°C) and Cu–5 mass%Ni (430°C) after irradiation in FFTF⁽⁴⁶⁾.

Fig. 12 Predicted transmutation of pure copper to nickel and zinc in an FFTF irradiation cycle for the MOTA 2A experiment just below the core centerline⁽⁴⁷⁾. The steps correspond to reactor downtimes between typical irradiation subcycles.

The nickel formed during irradiation of copper is known to segregate to void surfaces⁽⁴⁹⁾ but this segregation does not appear to limit the further growth of voids. This behavior is contrary to the segregation behavior observed for transmutant silicon formed in pure aluminum⁽⁵⁰⁾⁽⁵¹⁾ and that proposed for technetium formed in pure molybdenum⁽⁵²⁾.

The neutron-induced conductivity loss in copper can be diminished first by reducing or avoiding swelling altogether⁽⁵³⁾, and secondly by providing some sink that removes transmutants from the matrix. While segregation of nickel to void surfaces does not accomplish this goal, HfO_2 dispersoids in copper appear to remove nickel

from solution⁽⁵⁴⁾. This reduction in conductivity loss is obtained at the expense of a substantial hafnium-induced increase in the residual radioactivity of the alloy, however.

The formation of transmutants in copper will be even more pronounced in a mixed spectrum reactor such as HFIR, where approximately one half of the copper will be transformed in a few years⁽²⁾. Spectral tailoring in such reactors to strongly reduce the number of thermal neutrons is required for irradiation of copper to simulate a fusion neutron irradiation. This limitation also applies to vanadium, tungsten and molybdenum-rhenium alloys. Each of these materials has been proposed for applica-

Fig. 13 Influence of chromium and other solutes on the swelling of vanadium irradiated in FFTF, as observed in two separate experiments⁽⁵⁶⁾. The first experiment (top) shows the strong temperature sensitivity of the swelling of some binary alloys and the second (bottom) shows that the swelling rate of the alloys at 600°C may peak at intermediate chromium levels not yet irradiated.

tions in fusion design.

Vanadium is a bcc metal whose alloys are truly low activation in nature and are known to resist swelling, especially when alloyed with titanium, which also is low activation⁽⁵⁵⁾. Pure vanadium also swells very slowly, but when vanadium binary alloys based on silicon, iron, chromium, and possibly nickel additions are irradiated with neutrons, very large swelling rates are attained, as shown in Fig. 13^{(55)–(59)}. While pure vanadium and some of its alloys may not swell significantly during fast reactor irradiation, the very large transmutation of vanadium to chromium that can occur in HFIR (10–15% in one year) may yield a very high swelling behavior that is atypical of both fast reactor and fusion irradiations. Since the ductility of irradiated V–Cr–Ti alloys is also very sensitive to the Ti+Cr content, these alloys may also exhibit atypical ductility losses⁽⁶⁰⁾.

Molybdenum and molybdenum-rhenium alloys have also been considered as possible candidates for fusion reactor application⁽⁶¹⁾⁽⁶²⁾. Recent experimental studies conducted in FFTF show that some of the strong response of Mo–Re alloys to neutron irradiation can be traced primarily to the strong transmutation of rhenium to

osmium, and secondarily to the transmutation of molybdenum to technetium and ruthenium⁽⁶³⁾. As shown in Figs. 14–16, each of these processes is very spectral-sen-

Fig. 15 Predictions of osmium formation in pure rhenium during irradiation in FFTF⁽⁶³⁾.

Fig. 14 Predictions of technetium and ruthenium formation in pure molybdenum during irradiation in several spectra. (a) Two FFTF positions at core midplane and the middle of the below core basket position. The displacement level is given for pure iron. (b) The first wall position of STARFIRE at 3.8 MW/m^2 ⁽⁶³⁾.

Fig. 16 Prediction of osmium formation in rhenium during irradiation in (a) the PTP position of HFIR at 85 MW and (b) the first wall position of STARFIRE at 3.8 MW/m^2 ⁽⁶³⁾.

Fig. 17 Predicted formation of rhenium and osmium from pure tungsten irradiated in FFTF at both the core midplane and below core positions⁽⁶⁴⁾.

sitive, even for various locations within a given reactor system. It is not surprising, therefore, that vastly different rates of transmutation for Mo-Re alloys will occur in fusion devices⁽⁶³⁾. The use of mixed spectrum reactors is not recommended for rhenium-containing alloys, however, as demonstrated by the near total burn-out of rhenium in HFIR in less than one year. The initial burn-out rate is $\sim 2\%$ per day. This probably explains why Mo-Re alloys lost a large fraction of their electrical conductivity after irradiation in the Russian SM-2 reactor⁽⁶¹⁾, which is similar to HFIR in its neutron spectrum.

Tungsten has been used in a variety of low activation ferritic alloys and also in copper-composite alloys, both currently being irradiated in various U.S. and Japanese fusion materials experiments. It has also been proposed to serve as an armor material in fusion devices. Unfortunately, however, tungsten transmutes strongly to rhenium and then to osmium in a manner that is strongly dependent on neutron spectra⁽⁶³⁾. Figures 17 and 18 demonstrate this sensitivity for irradiations conducted in FFTF, HFIR, and STARFIRE. This strong response adds significant complexity to the interpretation of data developed in one spectral environment, but intended for application to another environment. It also complicates

Fig. 18 Predicted formation of rhenium and osmium irradiated in (a) the PTP position of HFIR at 85 MW, and (b) the first wall position of STARFIRE at 3.8 MW/m^2 ⁽⁶⁴⁾. Note that the relative amounts of osmium and rhenium are reversed in the two reactors after 100 days.

the comparison of helium effects experiments conducted in FFTF and HFIR on tungsten-containing alloys such as HT9⁽⁶³⁾. The small amount of nickel in HT9 is used to provide different helium generation rates in the two reactors, but the effects of osmium production may overshadow the influence of helium. More detailed comparisons of transmutation rates for a variety of refractory alloys are contained in Ref. (65).

While general comments can be made concerning the relative transmutation rates in fission reactors and fusion reactors, there is actually a wide variation of neutron spectra from one proposed fusion device to another, and from one position in a given device to another. At this time there is no typical fusion spectrum on which to draw detailed conclusions.

IV. Conclusions

While the influence of fusion-relevant helium levels on neutron-induced changes in the properties of ferritic-martensitic, vanadium-base, and copper-base alloys has yet to be definitively determined, it appears that austenitic stainless steels are much less sensitive to helium than previously anticipated. Solid transmutants, however, can exert a very large influence on some properties of a number of materials proposed for fusion applica-

tion. In most cases, it is possible to conduct tests in a fission neutron spectrum and then translate the data for application to fusion neutron spectra. In other cases, however, the spectral dependency of some properties overwhelms the translation and precludes application of the fission data to fusion spectra. Many of the solid transmutation issues discussed in this paper involve materials that were chosen as low activation candidates for fusion application.

Acknowledgments

This work is supported by the U.S. Department of Energy under contract DE-AC06-76RLO with Battelle Memorial Institute, which operates Pacific Northwest Laboratory.

REFERENCES

- (1) *Reduced Activation Materials for Fusion Reactors*, ASTM STP 1047, Ed. by R. L. Klueh, D. S. Gelles, M. Okada and N. H. Packan, Amer. Soc. for Testing and Materials, Philadelphia, (1990).
- (2) F. A. Garner, H. L. Heinisch, R. L. Simons and F. M. Mann: *Radiation Effects and Defects in Solids*, **113** (1990), 229.
- (3) H. R. Brager and F. A. Garner: *J. Nucl. Mater.*, **103 & 104** (1981), 993.
- (4) H. R. Brager and F. A. Garner: *J. Nucl. Mater.*, **108 & 109** (1982), 347.
- (5) H. R. Brager and F. A. Garner: *J. Nucl. Mater.*, **117** (1983), 159.
- (6) H. R. Brager and F. A. Garner: *Dimensional Stability and Mechanical Behavior of Irradiated Metals and Alloys*, British Nuclear Energy Society, London, (1984) p. 1.
- (7) E. E. Bloom and F. W. Wiffen: *J. Nucl. Mater.*, **58** (1975), 171.
- (8) L. K. Mansur and M. L. Grossbeck: *J. Nucl. Mater.*, **155-157** (1988), 130.
- (9) J. D. Elen and P. Fenici: *J. Nucl. Mater.*, **191-194** (1992), 766.
- (10) A. F. Rowcliffe, A. Hishinuma, M. L. Grossbeck and S. Jitsukawa: *J. Nucl. Mater.*, **179-181** (1991), 125.
- (11) T. Sawai, P. J. Maziasz and A. Hishinuma: *J. Nucl. Mater.*, **179-181** (1991), 519.
- (12) N. Sekimura, F. A. Garner and R. D. Griffin: *J. Nucl. Mater.*, **191-194** (1992), 1234.
- (13) M. L. Hamilton, A. Okada and F. A. Garner: *J. Nucl. Mater.*, **179-181** (1991), 588.
- (14) F. A. Garner, N. Sekimura, M. L. Grossbeck, A. M. Ermi, J. W. Newkirk, H. Watanabe and M. Kiritani: *J. Nucl. Mater.*, **205** (1993), 206.
- (15) G. W. Lewthwaite and D. Mosedale: *J. Nucl. Mater.*, **90** (1980), 205.
- (16) K. Ehrlich: *J. Nucl. Mater.*, **100** (1981), 149.
- (17) F. A. Garner and D. L. Porter: *J. Nucl. Mater.*, **155-157** (1988), 1006.
- (18) M. B. Toloczko, F. A. Garner and C. R. Eiholzer: *J. Nucl. Mater.*, **191-194** (1992), 803.
- (19) M. L. Grossbeck and J. A. Horak: *J. Nucl. Mater.*, **155-157** (1988), 1001.
- (20) F. A. Garner and M. L. Grossbeck: *Fusion Reactor Materials Semiannual Progress Report*, DOE/ER-0313/15, (1993), in press.
- (21) R. L. Simons, H. R. Brager and W. Y. Matsumoto: *J. Nucl. Mater.*, **141-143** (1986) 1057.
- (22) G. R. Odette: *J. Nucl. Mater.*, **141-143** (1986), 1011.
- (23) C. H. De Raedt: *Proc. Conf. on Fast, Thermal and Fusion Reactor Experiments*, Amer. Nucl. Soc., La Grange Park, (1982), p. 226.
- (24) M. L. Hamilton and F. A. Garner: *J. Nucl. Mater.*, **191-194** (1992), 1239.
- (25) F. A. Garner, M. L. Hamilton, L. R. Greenwood, J. F. Stubbins and B. M. Oliver: *Effects of Radiation on Materials*, 16th International Symposium, ASTM STP 1175, Ed. by A. S. Kumar, D. S. Gelles, R. K. Nanstad and E. A. Little, Amer. Soc. for Testing and Materials, Philadelphia, (1993), p. 921.
- (26) J. F. Stubbins and F. A. Garner: *J. Nucl. Mater.*, **179-181** (1991), 573.
- (27) H. Kawanishi, F. A. Garner and R. L. Simons: *J. Nucl. Mater.*, **179-181** (1991), 511.
- (28) J. F. Stubbins and F. A. Garner: *J. Nucl. Mater.*, **191-194** (1992), 1300.
- (29) F. A. Garner and B. M. Oliver: *Fusion Reactor Materials Semiannual Progress Report*, DOE/ER-0313/14, (1993), p. 47.
- (30) D. L. Smith, H. Matsui, L. Greenwood and B. Loomis: *J. Nucl. Mater.*, **155-157** (1988), 1359.
- (31) D. W. Kneff, L. R. Greenwood, B. M. Oliver, S. P. Skoronski and E. L. Callis: *Radiation Effects*, **92-96** (1985), 553.
- (32) S. J. Zinkle and K. Farrell: *J. Nucl. Mater.*, **168** (1989), 262.
- (33) S. J. Zinkle, K. Farrell and H. Kanazawa: *J. Nucl. Mater.*, **179-181** (1991), 994.
- (34) H. Kawanishi, S. Ishino and E. Kuramoto: *J. Nucl. Mater.*, **141-143** (1986), 899.
- (35) H. Kawanishi and S. Ishino: *J. Nucl. Mater.*, **155-157** (1988), 940.
- (36) N. Sekimura and F. A. Garner: *Fusion Reactor Materials Semiannual Progress Report*, DOE/ER-0313/13, (1993), p. 235.
- (37) T. Muroga and N. Yoshida: *J. Nucl. Mater.*, **191-194** (1992), 1254.
- (38) T. Muroga: *Effects of Radiation on Materials*, 16th Inter. Symp., ASTM STP 1175, Ed. by A. S. Kumar, D. S. Gelles, R. K. Nanstad and E. A. Little, Amer. Soc. for Testing and Materials, Philadelphia, (1993), in press.
- (39) J. F. Bates, F. A. Garner and F. M. Mann: *J. Nucl. Mater.*, **103 & 104** (1981), 999.
- (40) F. M. Mann: *Transmutation of Alloys in MFE Facilities as Calculated by REAC (A Computer Code System for Activation and Transmutation)*, HEDL-TME-81-37, Westinghouse Hanford Company, (1981).
- (41) F. M. Mann: *Damage Analysis and Fundamental Studies Quarterly Progress Report*, DOE/ER-0046/24, U.S. Department of Energy, (1986), p. 10.
- (42) F. A. Garner, H. R. Brager, D. S. Gelles and J. M. McCarthy: *J. Nucl. Mater.*, **148** (1987), 294.
- (43) J. M. McCarthy and F. A. Garner: *J. Nucl. Mater.*, **155-157** (1988), 877.
- (44) J. M. McCarthy: *J. Nucl. Mater.*, **179** (1991), 626.
- (45) R. W. Conn, V. A. Chuyanov, H. Inoue and D. R. Sweetman: *Scientific American*, April (1992), p. 103.
- (46) F. A. Garner, M. L. Hamilton, T. Shikama, D. J. Edwards and J. W. Newkirk: *J. Nucl. Mater.*, **191-194** (1992), 386.
- (47) F. A. Garner, L. R. Greenwood and F. M. Mann: *Fusion Reactor Materials Semiannual Progress Report*, DOE/ER-0313/13, (1992), p. 42.
- (48) D. J. Edwards and F. A. Garner: *Fusion Reactor Materials Semiannual Progress Report*, DOE/ER-0313/13, (1992), p. 258.
- (49) T. Muroga and F. A. Garner: *Fusion Reactor Materials Semiannual Progress Report*, DOE/ER-0313/15, (1993), in press.
- (50) K. Farrell: *Proceedings of Conference on Dimensional Stability and Mechanical Behavior of Irradiated Metals and Alloys*, British Nuclear Energy Society, London, (1983), p. 73.
- (51) K. Farrell, J. Bentley and D. N. Braski: *Scripta Met.*, **11** (1977), 243.
- (52) J. H. Evans: *J. Nucl. Mater.*, **88** (1980), 31.
- (53) D. J. Edwards, K. R. Anderson, F. A. Garner, M. L. Hamilton, J. F. Stubbins and A. S. Kumar: *J. Nucl. Mater.*, **191-194** (1992), 416.
- (54) D. J. Edwards: *The Properties and Microstructure of Neutron-Irradiated Oxide Dispersion Strengthened Copper Alloys*, Doctoral Dissertation, University of Missouri, Rolla, MO, (1993).
- (55) B. A. Loomis, D. L. Smith and F. A. Garner: *J. Nucl. Mater.*, **179-181** (1991), 771.
- (56) F. A. Garner, D. S. Gelles, H. Takahashi, S. Ohnuki, H. Kinoshita and B. A. Loomis: *J. Nucl. Mater.*, **191-194** (1992), 948.
- (57) H. Matsui, D. S. Gelles and Y. Kohno: *Effects of Radiation on*

- Materials*, 15th Intern. Symp., ASTM STP 1125, Ed. by R. E. Stoller, A. S. Kumar and D. S. Gelles, Amer. Soc. for Testing and Materials, Philadelphia, (1992) p. 928.
- (58) J. Nakajima, S. Yoshida, Y. Kohno and H. Matsui: *J. Nucl. Mater.*, **191-194** (1992), 952.
- (59) S. Ohnuki, D. S. Gelles, B. A. Loomis, F. A. Garner and H. Takahashi: *J. Nucl. Mater.*, **179-181** (1991), 775.
- (60) B. A. Loomis, H. M. Chung, L. J. Nowicki and D. L. Smith: *Proceedings of ICFRM-6*, Stresa, Italy, Sept. 1993, *J. Nucl. Mater.*, in press.
- (61) S. A. Fabritsiev, V. A. Gosudarenkova, V. A. Potapova, V. V. Rybin, L. S. Kosachev, V. P. Chakin, A. S. Pokrovsky and V. R. Barabash: *J. Nucl. Mater.*, **191-194** (1992), 426.
- (62) I. V. Gorynin, V. A. Ignatov, V. V. Rybin, S. A. Fabritsiev, V. A. Kazakov, V. P. Chakin, V. A. Tsykanov, V. R. Barabash and Y. G. Prokofyev: *J. Nucl. Mater.*, **191-194** (1992), 421.
- (63) F. A. Garner and L. R. Greenwood: "Density Changes Observed in Pure Molybdenum and Mo-41Re after Irradiation in FFTF-MOTA", *Fusion Reactor Structural Materials Semiannual Progress Report*, DOE/ER-0313/14, (1993), p. 205.
- (64) F. A. Garner and L. R. Greenwood: "Transmutation of Tungsten in FFTF, HFIR, and STARFIRE", *Fusion Reactor Structural Materials Semiannual Progress Report*, DOE/ER-0313/14, (1993), p. 7.
- (65) L. R. Greenwood and F. A. Garner: *Proceedings of ICFRM-6*, Stresa, Italy, Sept. 1993, *J. Nucl. Mater.*, in press.