CONF-800609--13

MICROCHEMICAL EVOLUTION OF
NEUTRON-IRRADIATED STAINLESS STEEL

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H. R. Brager and F. A. Garner

April 1980

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Paper to be presented at the ASTM 10th International Symposium on Effects of Radiation on Materials, to be held in Savannah, Georgia, June 3-5, 1980.

HANFORD ENGINEERING DEVELOPMENT LABORATORY
Operated by Westinghouse Hanford Company, a subsidiary of
Westinghouse Electric Corporation, under the Department of
Energy Contract No. EY-76-C-14-2170

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ABSTRACT

The precipitates that develop in AISI 316 stainless steel during irradiation play a dominant role in determining the dimensional and mechanical property changes of this alloy. This role is expressed primarily in a large change in matrix composition that alters the diffusional properties of the alloy matrix and also appears to alter the rate of acceptance of point defects at dislocations and voids. The major elemental participants in the evolution have been identified as nickel, silicon, and carbon. The exceptional sensitivity of this evolution to many variables accounts for much of the variability of response exhibited by this alloy in nominally similar irradiations.

MICROCHEMICAL EVOLUTION OF NEUTRON-IRRADIATED STAINLESS STEELS

H. R. Brager and F. A. Garner

INTRODUCTION

Although several countries are using AISI 316 as the major structural material for core components in near-term breeder and fusion reactors, it might be inferred from the accumulating data base on radiation-induced swelling of this alloy that each country has been using steels of different composition. Microscopy and energy dispersive X-ray studies have now provided a basis for understanding that the variability in swelling behavior arises from the inherent metastability of this steel, a condition which is substantially altered and accentuated by irradiation.

The magnitude of this metastability and its consequences on alloy behavior during irradiation previously have not been fully appreciated, particularly in theoretical descriptions. In the modeling of radiation-induced dimensional and mechanical property changes an implicit assumption is often made that the property change of interest can be described in terms of a microstructural scenario in which precipitates are assigned relatively minor roles such as sites for nucleation or reservoirs for minor solute atoms. The major components of the microstructure (voids, Frank loops, dislocations) are also assumed to have preferences or "biases" for point defects which are not strong functions of alloy matrix composition; nor are the concentrations of the major elements in the matrix assumed to change during irradiation. In this scenario the diffusional properties of the matrix are thought to be influenced only by irradiation temperature, displacement rate and the level of minor solute atoms which act as traps for point defects.

It is the purpose of this paper to show that the precipitates that develop in AISI 316 during irradiation play a dominant role in the alloy response. This role is expressed primarily in a large change in matrix composition that alters not only the diffusional properties of point defects

but also appears to substantially alter the rate of acceptance of point defects at dislocations and voids.

This conclusion arises from the results of an extensive investigation of the microstructural evolution of AISI 316 and its dependence on environmental, compositional and metallurgical variables. The original intent of this investigation was to provide a comprehensive description of the parametric dependence of void, loop and dislocation evolution and then to correlate the densities and actions of these microstructural components to the various radiation-induced property changes.

As the data were accumulated it became obvious, however, that descriptions based on such microstructural considerations alone could not possibly explain the influence on swelling of variables such as the cold worked level, preirradiation aging and temperature history. In an attempt to reconcile these differences it was noted that there was almost always a correlation between the onset of swelling and the development of precipitate particles.^(1,2) Figure 1 shows a typical example of this correlated microstructural development. As shown in the inset, two adjacent points along a fuel pin clad tube suffered a large difference in swelling over a 25°C temperature interval. The neutron fluxes and fluences were essentially identical but the large amount of swelling was accompanied by a substantial amount of precipitates of the γ' phase. The low swelling region had just begun to develop precipitates.

As the role of the precipitates was studied it became clear that there were two concurrent and interactive evolutions proceeding in the alloy. The first concerned the microstructural components usually assumed to be important in the creep and swelling phenomena, and the second involved a prolonged and extensive evolution of the composition of the alloy matrix.

The full details of this latter evolution are presented in other papers⁽¹⁻⁹⁾ and are summarized here along with recent data that support the earlier interpretation. The major elemental participants in this evolution have been identified and their action will be discussed in some detail. A summary will then be presented of the consequences of this evolution on the dimensional and mechanical properties of this steel.

PHASE STABILITY

20% CW 316
PNL -11-9R

2770

$\phi t \sim 9.8 \times 10^{22} \text{ n/cm}^2$ $T \sim 455^\circ\text{C}$

4498 2741

$\phi t \sim 10.0 \times 10^{22} \text{ n/cm}^2$ $T \sim 480^\circ\text{C}$

6264

HEDL 7805-148.10

FIGURE 1. Correlated Development of Voids and γ' Precipitates (shown in dark field) Observed in Cladding of the PNL-11-9R Fuel Pin.

OVERVIEW OF THE MICROSTRUCTURAL/MICROCHEMICAL EVOLUTION PROCESS

It appears that in the 300 series alloys the development of dislocation and loop microstructure (and to a lesser extent voids) proceeds toward a saturation state, comprised of number densities and component identities which eventually become independent of starting microstructure.⁽³⁾ The microchemical evolution induced by radiation also appears to proceed toward a saturation state but at a much more sluggish pace,^(1,2) although certain temperature paths or preirradiation treatments can short-circuit the sluggishness.^(1,4)

The various microstructural components interact with the defect fluxes and lead to point defect gradients which function as the driving force for the segregation process. The element nickel seems particularly prone to concentrate at the bottom of such gradients in response to the inverse Kirkendall effect and perhaps other mechanisms. The matrix nickel content is then reduced, although not by much unless solutes such as silicon and carbon are present. These elements coprecipitate with nickel at microstructural sinks and form a microchemical reservoir capable of removing from the matrix approximately three atoms of nickel for each silicon (and possibly carbon) atom. In AISI 316 with a nominal silicon level of 0.5 weight percent this leads to a reduction in matrix nickel content from 13.5 to 9 weight percent.

The most interesting feature of the precipitate-related segregation process is that the path by which the segregation proceeds does not appear to influence the final outcome in the matrix. A large variety of phases can develop, depending strongly on irradiation temperature and history, minor variations in composition and preirradiation thermomechanical treatment.⁽⁶⁾ The precipitate types formed during irradiation can be summarized into four classes. These are precipitates which are progressively changed in composition by the infiltration-exchange process, such as $M_{23}C_6$ and Laves phase; precipitates which are naturally rich in nickel and silicon, such as η -carbide; precipitates which are induced by irradiation, such as γ' and G-phase (Mn-Ni silicide); and precipitates which appear to result from the transformation of $M_{23}C_6$ particles whose composition has been changed by irradiation, such as M_6C . But all such phases either form as nickel

and silicon-rich phases or become progressively richer in these elements as a result of the infiltration-exchange process. At fluences approaching 100 dpa even the Laves (Fe_2Mo) phase approaches a composition of essentially Ni_3Si .⁽⁵⁾ If no other phase forms in the intermediate temperature range centered at about 500°C, the "phase of last resort" forms eventually. This is the γ' phase (nominally Ni_3Si) which not only requires irradiation to form but once formed will dissolve in the absence of displacive irradiation.⁽¹⁾

The consequences of the nickel segregation process on phase stability can be rather large. If the solute content is increased over the nominal specification for AISI 316, the matrix nickel content can be driven so low as to initiate the transformation of substantial amounts of matrix austenite to ferrite.⁽⁷⁾ In AISI 304 the initial nickel level is only 9 weight percent and the specified 0.5 weight percent silicon is sufficient to cause the austenite to ferrite transformation.⁽⁸⁾

THE MICROCHEMICAL ROLE OF CARBON, SILICON AND NICKEL

Although the swelling of AISI 316 has been found to be sensitive to the concentration of many elements^(10,11) it appears that the microchemical evolution primarily involves the action of carbon, silicon and nickel. It has been shown that even in Fe-Ni-Cr alloys without other solute atoms the swelling is critically dependent on the nickel concentration at levels below ~30%.⁽¹²⁾ This suggests that the nickel level strongly affects either the diffusional properties of the matrix or the capture efficiencies of each microstructural component. The former possibility has been discussed by Venker and Erlich⁽¹³⁾ but experiments directed toward this proposal do not support the concept of a substantial modification of diffusional properties with nickel content.^(14,15) A large dependence of the irradiation-induced dislocation density on nickel content has also not been observed. Since many properties of Fe-Ni-Cr alloys (stacking fault energy, modulus, magnetic properties, etc.) show a pronounced sensitivity to the nickel content it appears that the capture efficiencies of dislocations and voids may depend on the nickel content.

As shown in Figure 2 it appears that a parallel can be drawn between

FIGURE 2. Schematic Representation of the Parallel Observed Between Swelling and the Original Nickel Content and Swelling Vs. Instantaneous Nickel Content in AISI 316.

the dependence of swelling on initial nickel content and the acceleration of swelling with declining nickel content. Just as the initial nickel content C_{Ni}^0 has been shown to be the major factor determining the magnitude of swelling,⁽¹²⁾ the declining instantaneous nickel content in a specific alloy has been correlated with the acceleration of the swelling rate.^(1,7) When the average matrix nickel content reaches the level $C_{Ni}^* \approx C_{Ni}^0 - 3(C_{Si} + C_C)$, then the steady state swelling is established. The correlation between the onset of void growth and the local nickel content has been demonstrated quite clearly in studies where the nickel concentration of irradiated AISI 316 was sampled by energy dispersive X-ray analysis in many small volumes throughout the matrix. In Figure 3 the distribution of matrix nickel contents is presented for two AISI 316 specimens of different starting conditions which were exposed to identical irradiation conditions. The solution annealed specimen has been found to contain Laves precipitates which were substantially enriched in nickel and silicon, with some indication that the mean levels of these elements in the precipitates were higher than that of the 20% cold worked specimen. Note that the average nickel level

LOCAL NICKEL CONCENTRATIONS

AISI 316, $1.0 \times 10^{23} \text{ n/cm}^2$, 650°C

HEDL 7904-083.3

FIGURE 3. Distribution of Nickel Content in Many Small Matrix Locations in Irradiated AISI 316 Specimens Irradiated at 650°C to a Fluence of $1.0 \times 10^{23} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$).

of the matrix of the annealed specimen has been lowered from the original 13.5% level to about 9%. The cold worked specimen at these conditions has a matrix nickel content that has been lowered to an average of 10.4% and the distribution is much broader. The void swelling of the annealed specimen was about 8% and quite homogeneously distributed, while the void swelling of the cold worked specimen was only 0.6% and quite nonuniformly distributed. In almost all cases, however, large area analyses (about $0.5 \mu\text{m}$ in diameter) of voided regions showed the nickel content to be in the $<10\%$ range while regions containing $>11\%$ nickel had not yet begun to swell.

The role of silicon appears to be two-fold as shown in Figure 4a. While in solution the silicon causes a suppression of void nucleation.⁽¹¹⁾ As the matrix silicon level is increased the void incubation period is extended. This behavior has been explained in terms of silicon's simultaneous role in interstitial-solute binding⁽¹⁰⁾ and enhanced vacancy mobility.⁽¹⁷⁾ When the silicon leaves solution, however, it coprecipitates with nickel and leads to a substantial reduction in the matrix nickel content. This

HEDL 7903-231.3

FIGURE 4. Schematic Representations of the Dual Role of Silicon in Void Swelling of AISI 316. The addition of silicon leads to an extension of the incubation period but a later increase in the swelling rate.

causes an increased swelling rate at higher fluence.⁽¹¹⁾ Therefore any short-term benefit of reduced swelling with additional silicon is lost at higher fluences. The simultaneous removal of nickel and silicon can also be observed on a microscopic level as shown in Figure 5.

Figure 4b also shows a comparison between the observed swelling behavior of two nominally similar steels, both with the same major element composition, but one without solutes (carbon and silicon). The "pure" 316 alloy exhibits a very short incubation period and a swelling rate of only $2\%/10^{22} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$) which was essentially independent of irradiation temperature.⁽¹⁸⁾ The "commercial" 316 alloy on the other hand exhibits the expected long incubation and a swelling rate that was 50% higher. Figure 6 shows that additions of silicon to both annealed or cold worked AISI 316 at several temperatures leads first to a suppression of swelling as the incubation period is increased. At higher silicon levels the swelling increases, however, as the higher swelling rate overcomes the influence of the longer incubation period. If the silicon level is increased to even larger levels the nickel concentration of the matrix is drawn down to levels at which the austenite is unstable and a transformation of the matrix to ferrite occurs.⁽¹⁹⁾ The transition is resisted near pre-existing voids which concentrate nickel to their surfaces by way of the inverse Kirkendall effect. Since ferrite swells less than austenite the swelling behavior with additional silicon exhibits a peak as shown in Figure 6.

The role of carbon appears to shift with temperature. At low temperatures the addition of carbon depresses swelling⁽¹⁰⁾ primarily by extending the incubation period.⁽²⁰⁾ At higher temperatures the addition of carbon accelerates swelling.⁽¹¹⁾ The mechanisms proposed to explain this behavior are still somewhat speculative⁽²¹⁾ but it appears that carbon interferes with the development of the radiation-stable G-phase that forms at low temperature (Figure 7). At higher temperatures however, carbides function as precursors to the formation of intermetallic phases such as Laves. It is the infiltration of these phases by nickel and silicon that controls the swelling rate at temperatures above $\sim 550^\circ\text{C}$. Thus adding carbon accelerates the microchemical evolution by accelerating the development of

HEDL 7901-129.1

(a)

HEDL 7901-129.8

(b)

Fig. 5 - Simultaneous determinations of elemental compositions at many areas in 20% cold worked AISI 316 irradiated at 650°C to a fluence of 1.0×10^{22} n/cm² ($E > 0.1$ MeV). Note that nickel and silicon tend to be high together while molybdenum is not. This indicates that nickel and silicon flow together and against the flow of molybdenum. There are large local variations in all elements, however.

HEDL 7810-056.14

FIGURE 6. Effect of Silicon Level on Swelling of AISI 316. (1,11)

G PHASE

FIGURE 7. Determination of Composition and Crystal Structure of G-Phase Found in Irradiated 20% Cold Worked AISI 316 Using the Edge-Foil Analysis. The adjacent matrix composition is also shown.

the Laves phase.

It is important to note that the actions of nickel, silicon and carbon are all highly interactive with each other. One example will suffice to show that ignorance of the synergism between these elements caused many of the earlier conflicting conclusions concerning the role of these elements.

Recently comparative irradiation data on various British steels has shown that during irradiation at 425°C, the role of carbon is clearly to extend the incubation period of swelling (see Figure 8).⁽²¹⁾ In the interpretation of these data, however, the British authors inadvertently spotlighted one of the apparent inconsistencies which arise as a result of the Ni-C-Si synergism. Although two of the steels have essentially identical

HEDL 7909-074.4

FIGURE 8. Effect of Carbon Content on the Swelling of Four U.K. 316 Stainless Steels Irradiated at 425°C.(20)

carbon levels and exhibit identical swelling behavior, the silicon levels are substantially different (0.32 vs 0.63 weight percent). This forced the authors of that report to conclude that silicon plays no great role at that temperature. This conclusion is not only inconsistent with all other British data but also with all relevant US and European data. As shown below, however, the low silicon steel was also low in nickel relative to that of the high silicon steel. Using the previous definition for the coprecipitation relationship and a factor of two to convert silicon weight percentages to atomic percentages, the saturation nickel content for the two steels can be defined.

Springfields VA 408A

$$C_{Ni}^* = (13.7) - (3)(0.63)(2) = 9.9\%$$

Harwell VR 906A

$$C_{Ni}^* = (11.4) - (3)(0.32)(2) = 9.5\%.$$

Therefore the effect of silicon in each alloy is to reduce the matrix nickel content to almost identical saturation levels. The influence of silicon in this experiment was therefore obscured by the nickel variations and the apparent inconsistency concerning the role of silicon has been resolved.

CONSEQUENCES OF THE MICROCHEMICAL EVOLUTION

It is now obvious that the large variation in swelling behavior observed for AISI 316 arises from the exceptional sensitivity of the early phase evolution that develops in this alloy. Each of the phases exhibits a different sensitivity to the large number of participating variables. The radiation-stable phases are very sensitive to displacement rate and one would anticipate that at higher fluxes this would lead to a shorter incubation period at low temperatures. As shown in Figure 9, this behavior has been observed in comparative irradiations in two French fast reactors.⁽²²⁾ One would also expect that the intermetallic phases would be very sensitive to time at temperature. Therefore in higher flux reactors a component would spend less time in reactor to reach a given fluence. As a consequence, the high temperature swelling peak would recede somewhat. This behavior has also been observed in comparative Phenix/Rapsodie irradiations.

The low temperature phases have been found to be insensitive to applied stress but the intermetallics have exhibited such a sensitivity.⁽²³⁾ The radiation-stable phases are also very sensitive to in-reactor temperature history and this leads to unexpected behavior for both swelling and creep.⁽⁴⁾ The phase evolution also has consequences that are expressed in mechanical properties such as the yield stress.⁽²⁴⁾

CONCLUSIONS

It appears that future attempts to model the radiation-induced dimensional and mechanical property changes must include the large and possibly dominant impact of the microchemical evolution. The sensitivity of this evolution to a large number of variables means that property-change correlations developed in one reactor environment may not necessarily predict the behavior in another environment.

HEDL 7909-074.11

Figure 9. Flux-dependent Swelling Behavior Observed in Irradiation of French Solution-annealed Cladding and CW 316L Duct Steels.(22)

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