HEDL-6929

MASTER

DAFS CONTRIBUTION
THE INFLUENCE OF DISLOCATION DENSITY
AND RADIATION ON CARBON ACTIVITY AND PHASE
DEVELOPMENT IN AISI 316

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Operated by Westinghouse Hanford Company
P.O. Box 1970 Richland, WA 99352
A Subsidiary of Westinghouse Electric Corporation
Prepared for the U.S. Department of Energy
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I. PROGRAM

Title: Irradiation Effects Analysis (AKJ)

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II. OBJECTIVE

The objective of this effort is to identify the role of each major element in the microchemical evolution of AISI 316 and the dependence of that role on preirradiation treatment and parameters such as neutron energy and flux, temperature and stress.

III. RELEVANT DAFS PROGRAM PLAN TASK/SUBTASK

Task II.C.2.4 Modeling

IV. SUMMARY

It is proposed that the primary role of cold work on the swelling of AISI 316 is to distribute the element carbon throughout the alloy matrix and increase the apparent solubility of carbon by binding it in the stress-field of the dislocation core. The resultant decrease in supersaturation and activity of carbon leads to a decrease in the rate of phase formation which preceeds swelling. A model developed to describe this phenomenon predicts that all carbon present in 20% cold-worked AISI 316 of nominal specification will be initially in bound-solution at all irradiation temperatures.

V. ACCOMPLISHMENTS AND STATUS

A. The Influence of Dislocation Density and Radiation on Carbon Activity and Phase Development in AISI 316 - F. A. Garner (HEDL) and W. G. Wolfer (U. of Wisc.)

1. Introduction

In a recent paper it was noted that the roles of carbon and cold-work appear to be interrelated.⁽¹⁾ The available data indicate that cold-work suppresses swelling at all temperatures in AISI 316^(2,3) and that the role of cold-work lies in the retardation of radiation-induced precipitation and microchemical evolution. Out-of-reactor the normal role of cold-work in this steel is to accelerate the phase evolution rather than to retard it, however.⁽⁴⁾ Any model developed to explain the role of cold-work must successfully address this apparent contradiction.

The model must also explain the role of carbon on the swelling of this alloy. Even though cold-work retards swelling at all temperatures, carbon reverses its role with temperature. At low temperatures the addition of carbon depresses swelling in AISI 316,^(5,6,7) primarily by extending the incubation period as shown in Figure 1. At temperatures between 500 and 550°C, however, carbon begins to increase swelling as shown in Figure 2. As Figure 3 shows, the effect of carbon in increasing swelling at high temperature is visible in a variety of thermal-mechanical starting conditions and exhibits a synergism with other interstitial solutes such as nitrogen.⁽⁸⁾ The role of carbon on phase development appears to be different in the low and high temperature regimes⁽¹⁾ and is currently being investigated in more depth. One expression of the changing role of carbon with temperature is its role in determining the relative height of the two swelling peaks usually observed in annealed 316. This is schematically illustrated in Figure 4.

In this report the relationship of cold-work and carbon solubility during irradiation will be addressed. The additional influence of radiation-produced vacancies on carbon activity will also be considered. The role of carbon on phase stability will be addressed in later work.

2. Solubility of Carbon in Austenitic Stainless Steels

AISI 316 contains about 0.04 weight percent of carbon. This amount of carbon is soluble in the austenitic phase above a temperature of about 1100°C, and its presence reflects the high solubility in the liquid phase. At lower temperatures, however, this amount of carbon is in supersaturation,

and it tends to precipitate in the form of carbides such as $M_{23}C_6$ and M_7C_3 . The rate of precipitation in the absence of irradiation depends on the time, the temperature, and the level of cold-work, according to the familiar T-T-P plots. One role of cold-work is to provide favorable nucleation sites for the carbide precipitates. This leads to a reduction in the incubation time for carbide precipitation compared to that of the annealed material.

As mentioned previously, cold-work appears to retard phase evolution during irradiation. It is proposed here that the dense, dynamic and mobile dislocation network maintained by irradiation leads to a reduction in the driving force for precipitation. This occurs as a result of the binding of carbon atoms in the stress-field of dislocations, as described below.

3. Solute Adsorption in Dislocation Fields

The mechanical interaction energy $U(r,\phi)$ between a misfitting solute atom and a dislocation results in a non-uniform solute distribution given by

$$C(r,\phi) = C_0 \exp(U/kT) \quad (1)$$

Here, C_0 and C are the atom fractions of solute in equilibrium far and close to the dislocation, respectively. The interaction energy for an isotropic solute inclusion is given by

$$U = \frac{A \sin(\phi)}{r} \quad (2)$$

in a linear isotropic elastic medium. The dependence on ϕ reflects the fact that carbon tends to be attracted only to the tensile side of the dislocation core.

$$A = \frac{Gb}{3\pi} \frac{1+\nu}{1-\nu} v, \quad (3)$$

where G is the shear modulus, b the Burger vector, ν is Poisson's ratio, and v the relaxation volume or the partial molar volume of the solute.

Equation (1) is valid as long as the local solute concentration $C(r, \phi)$, does not exceed the number of available solute sites in the host lattice. If we assume that carbon occupies the octahedral interstitial sites in the fcc structure of austenitic steel, then there is one solute site per host atom. Accordingly, C can not exceed the value of one. The region of complete occupation of all available solute sites can be determined from Equation (1) by setting $C = 1$. This defines the radial distance $r_o(\phi)$ from the dislocation which marks the boundary of the fully occupied solute region. With Equation (2) we find

$$r_o(\phi) = \frac{A/kT}{\ln(1/C_o)} \sin \phi \quad \text{for } 0 < \phi < \pi \quad (4)$$

if $A > 0$.

The total atom fraction of solutes trapped in the saturated region of dislocations is then given by

$$\begin{aligned} N_o &= \rho \int_0^\pi d\phi \int_0^{r_o(\phi)} r dr \\ &= 1/4 \pi \rho [A/kT \cdot \ln(1/C_o)]^2 \end{aligned} \quad (5)$$

where ρ is the dislocation density.

To evaluate Equation (5), the relaxation volume of carbon in the austenitic matrix is needed. This can be obtained from lattice parameter measurements on austenites with varying carbon content. According to Hume-Rothery,⁽⁹⁾ the lattice parameter is given by

$$a = (0.3564 + 0.076 C) \quad \text{in nm.} \quad (6)$$

In order to determine the relaxation volume v one can relate it to the change in lattice constant with carbon addition according to the relationship

$$\frac{v}{\Omega} \equiv 3 \frac{1}{a} \frac{da}{dC}. \quad (7)$$

Therefore from Equations (6) and (7) we obtain

$$v/\Omega = 0.64$$

where $\Omega = 1.132 \times 10^{-29} \text{ m}^3$ is the atomic volume of the solvent atoms.

Using the values $v = 0.3$, $\mu = 10 \text{ Mpa}$, we obtain

$$N_o = 5.11 \times 10^{-16} \rho [1000/T \ln (1/C_o)]^2 \quad (8)$$

for the atom fraction of carbon atoms bound in the dislocation cores.

Beyond the saturated region, carbon atoms are still attracted to the dislocation region, but the concentration remains below saturation. This additional trapping in the remote stress field has been evaluated by Hirth and Carnahan⁽¹⁰⁾ for the case of hydrogen as an interstitial solute in bcc iron. They concluded that the enhancement of the hydrogen concentration in the remote stress field is only significant for dislocation densities above 10^{15} m^{-2} and for very low hydrogen contents of the order of 10^{-8} atomic fraction. For the present analysis, we assume that we may therefore neglect this additional contribution for the case of carbon.

4. Effect of Dislocations on Carbon Solubility

The solubility of carbon in austenite has been determined experimentally by Rosenberg and Irish⁽¹¹⁾ and by Tuma et al.^(12,13) It is defined as the carbon concentration at which the chemical potential of carbon in solution becomes equal to the chemical potential of carbon in $M_{23}C_6$. Tuma et al. have developed the following equation to fit the experimental results. If N_C and N_{Ni} are the atomic fractions of carbon and nickel, the maximum atom fraction of carbon in solution is given by

$$\log N_C = 2.93 - 4.0 N_{Ni} + (4500 N_{Ni} - 6800)/T \quad (9)$$

where T is the absolute temperature. The form of this equation is suggested by thermodynamic considerations. As a result, it can be extrapolated beyond the temperature range of 700°C to 1200°C where the data were obtained. Figure

5 shows the predictions of Equation (9) for the solubility of carbon as a function of temperature and nickel content of the matrix. The horizontal dashed line represents the actual carbon concentration (0.04 wt%) in AISI 316 stainless steel prototypic of that used in U. S. Fast Flux Test Reactor. It is evident that in the 300-700°C temperature range for breeder reactor operation, the carbon supersaturation is very high and provides a strong driving force for carbide precipitation.

The effect of a high dislocation density on the solubility can now be determined with Equation (8) when $N_c(T)$ is substituted for C_0 . The results are given in Table 1 together with the matrix solubility N_c for a ternary alloy comparable in composition to that of AISI 316.

Table 1
Solubility of Carbon in Fe - 18% Cr - 14% Ni (in Atom Fractions)
With Different Dislocation Densities

$T, ^\circ\text{C}$	N_c	$\rho = 10^{12} \text{ m}^{-2}$	$\frac{N_0}{\rho = 10^{14} \text{ m}^{-2}}$
300	4.0×10^{-9}	4.2×10^{-6}	4.2×10^{-4}
400	1.6×10^{-7}	4.6×10^{-6}	4.6×10^{-4}
500	2.4×10^{-6}	5.1×10^{-6}	5.1×10^{-4}
600	2.0×10^{-5}	5.7×10^{-6}	5.7×10^{-4}
700	1.1×10^{-4}	6.5×10^{-6}	6.5×10^{-4}
800	4.2×10^{-4}	7.3×10^{-6}	7.3×10^{-4}

It is seen that the apparent carbon solubility in heavily cold-worked materials is substantially higher than the solubility of the undislocated matrix. It should be noted that the network dislocation density of AISI 316 has been found to be $\geq 3 \times 10^{15} \text{ m}^{-2}$ prior to irradiation and $6 \pm 3 \times 10^{14} \text{ m}^{-2}$ after irradiation at all temperatures in the breeder reactor regime. At temperatures below $\sim 500^\circ\text{C}$ the Frank loop contribution to the dislocation density is on the same order or larger than that of the network dislocations. Therefore it can be seen that the initial bound carbon concentration in irradiated cold-worked AISI 316 is essentially that of the base alloy at all temperatures.

5. Discussion

Carbide precipitation depends critically on the supersaturation ratio. Based on the enhanced carbon solubility in cold-worked material one could conclude that precipitation is delayed by cold-working rather than accelerated as observed out-of-reactor. However, there are two mitigating factors. First, carbon is locally enriched near dislocation cores. Second, the strain field provides a preferred nucleation site where the nucleation barrier energy is substantially reduced. Readily available carbon in close vicinity to a favorable nucleation site is the reason why carbide precipitation commences earlier in cold worked materials compared to annealed materials.

However, for nucleation of carbides to take place near a dislocation it must be sessile for the period of the incubation. Under irradiation, the dislocations continue to climb, dragging along the carbon atmosphere. Under these dynamic conditions, formation of carbide precipitates is impaired, and precipitation at static sites becomes the controlling mechanism.

Under these conditions, the supersaturation formed by the ratio of actual carbon content divided by the apparent solubility is the driving force for carbide nucleation. This ratio is substantially less than the supersaturation ratio formed with the solubility N_c of Equation (9).

There is one test that can be made of the hypothesis underlying this model. Such a mechanism would cease to produce increases in the incubation period of swelling with increasing cold-work if the starting dislocation density saturated. As shown in Figure 6, swelling is not influenced by cold-work levels above 30% in AISI 316⁽¹⁴⁾ and the dislocation density of AISI 316 also saturates at this cold-work level.⁽¹⁵⁾

If the primary role of cold-work on swelling is to redistribute the small carbon clusters that form upon cooling of annealed steel and then to decrease carbon's tendency to precipitate, what about other elements? The lesser interstitial elements such as phosphorus and nitrogen are known to affect carbon activity⁽¹⁾ and may also be adsorbed on dislocations. The substitutional element silicon is also known to strongly affect swelling but it has recently been shown that the effect of cold-work on swelling occurs in alloys bearing carbon but not silicon.⁽¹⁶⁾ Silicon acts on swelling

primarily through its influence on the diffusion on vacancies and interstitials.^(16,17)

If this model is correct, it is fair to ask in what manner will the carbon-dislocation interaction be observed in the swelling behavior? It is anticipated that the interaction will serve primarily to delay the phase evolution and therefore to delay the swelling as shown in Figures 1 and 7.

An additional effect of radiation is the change of the carbon diffusivity. Without radiation carbon diffuses interstitially, and therefore at a much faster rate than vacancies. In the presence of the radiation-produced vacancies, however, carbon diffusion is reduced because of trapping in the vacancies. This mechanism has been proposed by Damask and coworkers^(18,19) to explain the results of low-temperature irradiations in iron.

The reduction of carbon diffusivity thus depends on the vacancy concentration. Figure 8 shows the calculated vacancy concentration for fast reactor irradiations as a function of temperature for two dislocation densities. It is seen that the vacancy concentration is very high at low irradiation temperatures, and independent of the dislocation density. The vacancy concentration decreases rapidly with temperature, and becomes equal to the thermal vacancy concentration above 700°C.

Based on this behavior, it is expected that radiation strongly reduces carbon mobility through the matrix at low irradiation temperatures. However, this phenomenon decreases rapidly with increasing temperature, and the effect becomes negligible above 500°C. A more quantitative assessment requires a mechanistic model of carbon trapping in mobile vacancies.

6. Conclusions

It is proposed that the primary role of cold-work on the swelling of AISI 316 is to distribute the element carbon throughout the alloy matrix and increase its apparent solubility by binding it in the stress-field of the dislocation core. The resultant decrease in supersaturation and activity of carbon leads to a decrease in the rate of phase formation. Such phase formation has been shown to be the necessary precursor to swelling. A model developed to describe this phenomenon predicts that all carbon present

in AISI 316 of nominal specification will initially be in bound-solution at all irradiation temperatures.

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VII. FUTURE WORK

The model will be expanded to cover the influence of Frank loops and also carbon levels higher than 0.04 weight percent. An experimental program involving alloys already irradiated in EBR-II or ORR will be defined and initiated to provide input to the modeling effort.

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FIGURE 1. Carbon Prolongs the Incubation Period of Swelling at Low Temperatures.(5)

FIGURE 2. The Role of Carbon Shifts with Increasing Temperature, as Observed in Both Cold-Worked and Annealed Steel.(7) The numbers in parentheses are the fluence levels of each datum in 10^{22} n/cm² (E > 0.1 MeV).

FIGURE 3. Swelling Increases with Carbon Level at High Temperatures for all Thermal-Mechanical Starting Conditions and Nitrogen Levels Tested.(8)

FIGURE 4. Schematic Representation of Dependency of Swelling in Annealed Fuel Pins on Free Carbon Level.(1)

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FIGURE 5. Effect of Nickel Level and Dislocation Density on the Temperature-Dependent Solubility of Carbon in Austenite. The horizontal line at 0.178 is the total atomic carbon level at 0.04 weight percent.

FIGURE 6. The Dependence of Swelling(14) and Dislocation Density(15) (Measured by Root Mean Strain) in AISI 316.

FIGURE 7. The Effect of Solute on Swelling of AISI 316 Observed in 5 MeV Ni^+ Ion Irradiation (Step-Height Measurements). The high purity steel has very small levels of carbon, nitrogen and silicon compared to the commercial steel.

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FIGURE 8. The Calculated Dependence of the Vacancy Concentration on Temperature and Dislocation Density.