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<Technical Note>

Estimation of Thermal Aging Embrittlement of LWR Primary Pressure Boundary Components

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Abstract

Cast duplex stainless steels are extensively used for primary pressure boundary components. These components are, however, embrittled due to the precipitation of α' phase by spinodal decomposition and other processes when exposed to reactor operating temperature for a design lifetime or life extension conditions. This report presents a procedure for estimating the current condition and the residual life of safety-related stainless steel components by using ANL database and correlations. The database of Charpy impact energy suggests that CF-8M grade is the most susceptible to thermal aging and CF-3 grade is the least. Thus, the integrity of CF-8M alloys may be degraded seriously and the degree of deterioration may exceed acceptance limit after several years of service in the nuclear reactors.

1. Introduction

Cast duplex stainless steels, composed of austenite and ferrite phases, are extensively used for primary pressure boundary components such as primary coolant pipe, valves, and pump casings and weld filler metal in LWRs. The ferrite phase in the duplex structure increases tensile strength and improves weldability, resistance to stress corrosion cracking, and soundness of castings. Superior properties of the cast stainless steels result primarily from the presence of the ferrite phase in the duplex structure. On the other hand, it is known that the ferritic phases become brittle owing to the precipitation of the Cr-rich α' phase when exposed to temperatures in the range of 300~500℃ for a long time [1-3]. This thermal aging of the cast stainless steels at these temperatures increases hardness and tensile strength while it decreases ductility, impact strength, and fracture toughness of the materials.

It was reported that primary pressure boundary components such as hot leg elbow, main valve, and recirculation pump cover decommissioned from Ringhals Unit 2, Shippingport PWR, and KRB BWR had suffered serious degradation of impact property [4,5]. The embrittlement due to aging at temperatures of 300~450℃ has been confirmed by recent studies [6,7]. Although it is crucial to validate that the two processes are mechanistically identical, accelerated aging at 400 ℃ is, in general, taken in the laboratory since real

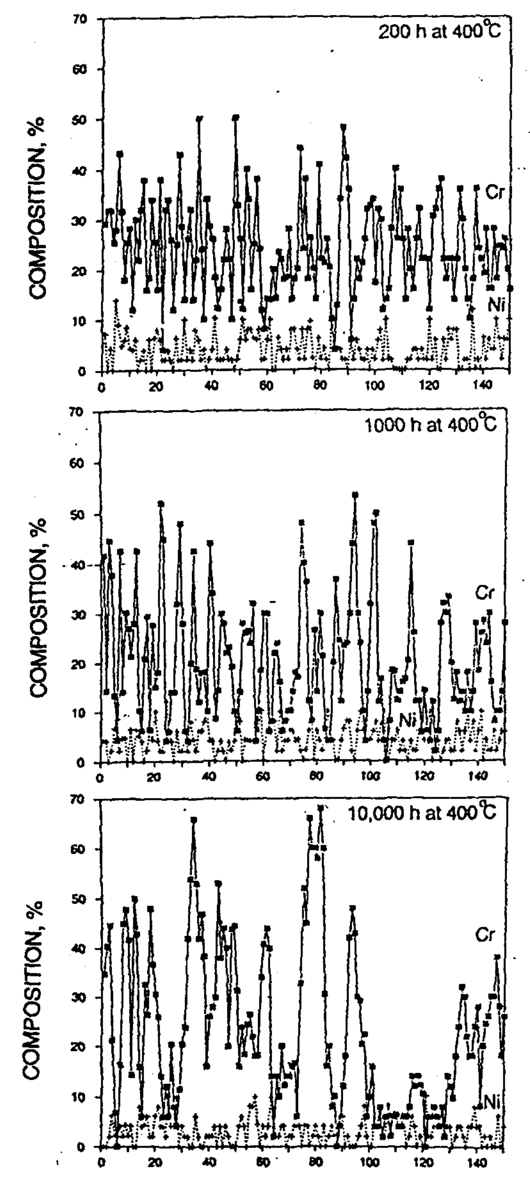

Fig. 1. APFM Composition Profiles of 15% Ferrite CF-3 Stainless Steels Aged for 200, 1,000, and 10,000 Hours at 400℃

reactor temperature aging of the components at the end of lifetime or life extension conditions cannot be reproduced. Fortunately, it has been demonstrated that they are similar and the embrittlement is attributed primarily to Cr-rich α' precipitation by spinodal decomposition [7,8].

Recently, non-destructive methods such as magnetic properties analysis by Mössbauer spectrometer, electro-chemical properties analysis, and measurement of dissolution rate in chemical solution as a function of aging time are applicated to estimate the degree of thermal aging embrittlement of duplex stainless steels, where good correlations with the changes in mechanical properties such as microhardness, USE, and DBTT [9-11].

This paper presents a procedure for estimating the current condition and residual life of safety-related cast stainless steel components that are being used in LWRs. Available information on thermal embrittlement of the cast stainless steels and a method for assessing the degree of embrittlement of in-service cast stainless steel components are reviewed. The cast stainless steels of interest for the evaluation in this paper are confined in ASTM A351 grade CF-3, CF-8, and CF-8M.

2. Mechanism of Thermal Aging Embrittlement

Earlier investigations using transmission electron microscopy (TEM), small angle neutron scattering (SANS), and atom probe field ion microscopy (APFIM) results have shown that several metallurgical processes such as the precipitation of G phase, γ_2 phase, α' phase by spinodal decomposition, and $M_{23}C_6$ can be the causes of aging embrittlement in the duplex stainless steel [6-8]. The embrittlement or the loss of impact toughness due to thermal aging was believed to be related to the formation of Cr-rich α' phase and Ni- and Si-rich G phase in the ferrite and to the precipitation of carbides at the ferrite-austenite phase boundaries. However, it was not understood which one is dominant process between α' phase precipitation by spinodal decomposition and G phase precipitation. Recently, microhardness analysis, toughness recovery, and microstructural evolution of aged specimens following annealing treatments at 550℃ showed that the precipitation of α' phase in ferrite by spinodal decomposition is primary cause of thermal aging embrittlement [12]. It is known that α' phase typically forms by the process of spinodal decomposition in the LWR conditions [13,14]. This process occurs at very fine scale (a few nm) in the ferrite regions of duplex stainless steel and the atom probe field ion microscopic technique (APFIM) is required to resolve the presence of the α' phase. The examples of APFIM analysis of CF-3 stainless steel are shown in Figure 1, which shows that the fluctuation of Cr composition increases with aging time, that is, the degree of phase separation into the Cr-rich α' phase and Fe-rich α phase increases with aging time [12]. G phase forms in the ferrite by nucleation and growth process and it is known that the formation rate of G phase is enhanced by increased levels of carbon and molybdenum [14].

In many previous studies, several metallurgical processes have been identified in association with thermal aging embrittlement of grade CF-3, CF-8, and CF-8M stainless steels at the temperature at 280~400℃. Six processes have been identified in the ferrite phase, precipitation of α' via spinodal decomposition, G phase, γ_2, $M_{23}C_6$, niobium carbide, and plate-like α' phase via nucleation and growth. Two processes, $M_{23}C_6$ and Cr_2N precipitation, take place at the ferrite-autenite boundaries and other two processes have been identified to occur in austenite of some of the aged specimens, spinodal-like decomposition (involving Fe and Ni segregation) and σ phase precipitation on stacking faults and slip band [7]. These processes are summarized in Table 1.

Table 1. Metallurgical Processes Identified in Thermally-aged Duplex Stainless Steel

Phase	Process
Ferrite Phase	· precipitation of α' phase via spinodal decomposition · precipitation of G phase · precipitation of γ_2 · precipitation of $M_{23}C_6$ · precipitation of niobium carbide · precipitation of plate-like α' phase via nucleation and growth
Austenite Phase	· spinodal-like decomposition · precipitation of σ phase
Ferrite/Austenite Boundary	· precipitation of $M_{23}C_6$ · precipitation of Cr_2N

3. Estimation of Thermal Aging Embrittlement Based on Database

Following procedure and correlations have been developed at Argonne National Laboratory (ANL)[15] for mechanical properties of cast stainless steel components under LWR operating conditions from material information in Certified Material Test Records (CMTRs). The correlations are based on the extensive data base (~80 compositions of cast stainless steel) of the mechanical property changes resulting from aging up to ~58,000 hours at 290~350℃. Mechanical properties of a specific cast stainless steel are estimated from the extent and kinetics of thermal embrittlement.

3.1. Determination of Ferrite Content

The amount of ferrite in an aged cast stainless steel directly influences the degree of impact and fracture toughness loss of the steel because only

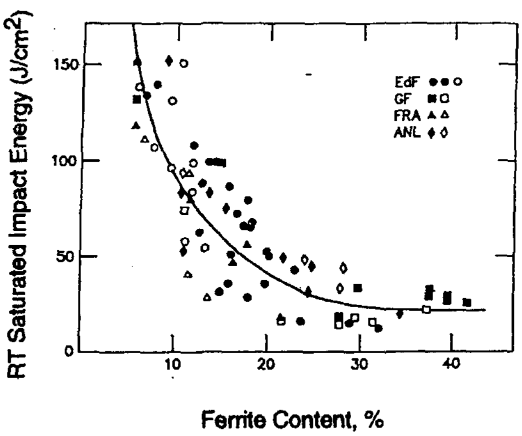

Fig. 2. RT Minimum Saturated Impact Energy vs. Ferrite Content

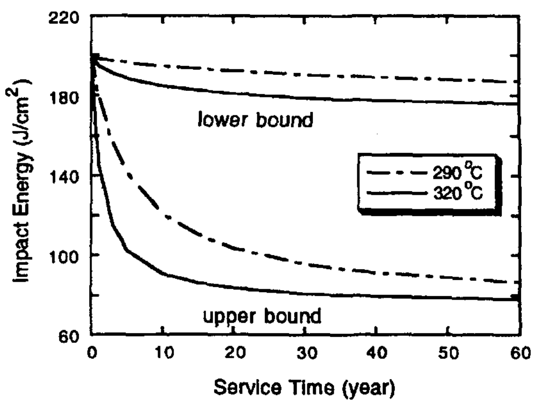

Fig. 3. Predicted RT Charpy V-notch Impact Energy for CF-3 Stainless Steel as a Function of Ractor Service Time

the ferrite phase, not the austenite phase, is embrittled by thermal aging. Thus, it is important to know the amount of ferrite present in the duplex stainless steel that has been exposed during extended time to temperatures in the range where aging embrittlement can occur. The relationship of saturated minimum impact energy data with ferrite content is shown in Figure 2 [16]. From the figure, it is seen that saturated minimum impact energy decreases with increasing ferrite content and reaches saturated value of 25 J/cm^2 at 30 % of ferrite content.

The primary factor controlling the ferrite-austenite balance is bulk chemical composition. Procedures for estimating ferrite content from chemical composition have been reviewed by Leger [17] and Aubrey et al. [18]. All of these procedures for computation a volume percent of ferrite content are based on the calculation of a chromium equivalent value, Cr_{eq}, and a nickel equivalent value, Ni_{eq}. Elements that contribute to the chromium equivalent content promote the formation of ferrite, whereas those that contribute to the nickel equivalent promote the formation of austenite. Empirical formulas for computing the chromium and nickel equivalents have been developed from correlations of experimental data. Aubrey et al. [18] analyzed an extensive database on CF-3, CF-8, and CF-8M stainless steel by linear regression technique to derive four different ferrite estimation formulas and found that following relationship gives the best fitting:

$$\delta = 100.30(Creq/Nieq)^2 - 170.72(Creq/Nieq) + 74.22 \quad (1)$$

where, $Cr_{eq} = Cr + 1.21(Mo) + 0.48(Si) - 4.99$, and
$Ni_{eq} = Ni + 0.11(Mn) - 0.0086(Mn)^2 + 18.4(N) + 24.5(C) + 2.77$.

Thus, if bulk chemical composition of an aged cast stainless steel component is known or measured, above equations can be used to estimate its ferrite content. The standard deviation of this correlation was calculated to be 3.03 by Aubrey et al.. Since only ferrite phase is embrittled by long-term service at LWR operating temperatures, overall thermal embrittlement depends on not only the amount but also the morphology of the ferrite.

For LWR applications, low temperature

embrittlement is of major concern only when the volume fraction of ferrite exceeds a level of approximately 15 % [19] because the ferrite phase tends to form in the isolated pools within austenite at about the level. In the case, overall toughness is not greatly affected even if the ferrite is embrittled. For ferrite levels greater than 15 %, there is a tendency networking embrittled region through the thickness, which greatly reduces its toughness. There is a recent evidence that thick-walled (typically greater than 100 mm) stainless steel castings may subject to low temperature embrittlement in the ferrite levels of 10 to 15 % [20].

In heavy-section castings, grain size tends to be large and the ferrite spacing (average distance between ferrite islands) increases. With the distance increase at a constant ferrite content, the degree of thermal embrittlement increases [20].

3.2. Determination of Activation Energy

Current best estimates of the degree of embrittlement at reactor operating temperatures are based on the Arrhenius extrapolations of laboratory data obtained at higher temperatures, e.g., 400℃.

$$\frac{t_2}{t_1} = \exp\left[\frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right], \qquad (2)$$

where, t_1 and t_2 are aging times to reach equivalent material toughness at absolute aging temperatures of T_1 and T_2, respectively, Q is activation energy of this thermal aging processes, and R is gas constant. In most investigations the activation energy, usually defined for aging temperatures between 300 and 400℃, has been derived on the basis of aging embrittlement measurement by room-temperature Charpy impact tests.

Aging parameter, P, is defined such that it is equivalent to the logarithm of the number of hours of aging at 400℃. For example, a value of p=4 is equivalent to aging for 10,000 hours at 400℃.

$$P = \log_{10}\{t/\exp[(Q/R)(1/T - 1/673)]\}, \qquad (3)$$

where t is reactor service time(hour), Q is activation energy, R is gas constant, and T is service temperature(K). Activation energy, Q, is given in terms of both chemical composition and constant θ which will be discussed in the following section.

$$Q = 10[74.52 - 7.20\theta - 3.46Si - 1.78Cr - 4.35I_1Mn + (148 - 125I_1)N - 61I_2C], \qquad (4)$$

where the indicators I_1 and I_2 are set to be 0 and 1, respectively for CF-3 or CF-8 steels and they are 1 and 0, respectively, for CF-8M steels. Above equation is applicable to the compositions within ASTM Specification A 351, with up to 1.2 wt.% Mn content. That is, actual Mn content is used when it is lower than 1.2 wt.% Mn whereas 1.2 wt.% is taken when greater than 1.2 wt.%. The predicted activation energy from the equation is valid in between 65 kJ/mol minimum and 250 kJ/mol maximum. Q is assumed to be 65 kJ/mol and 250 kJ/mol if the predicted one is lower than 65 kJ/mol and if higher than 250 kJ/mol, respectively. Aging kinetics are strongly influenced by synergistic effects of other metallurgical reactions that occur in parallel with the spinodal decomposition, i.e. clustering of Ni, Mo, and Si and G phase precipitation in ferrite [21].

3.3. Estimation of Charpy Impact Energy with Reactor Service Time

Charpy impact energy as a function of reactor service time and temperature is estimated from the kinetics of thermal aging embrittlement, which can also be determined from the chemical composition as mentioned in the previous section.

The embrittlement of cast stainless steel is characterized by room temperature(RT) Charpy impact energy, which is determined as a function of aging time and temperature by its estimated RT saturation impact energy, Cv_{sat}, and the kinetics of embrittlement. The decrease of RT Charpy impact energy, Cv, with aging time can be expressed as:

$$\log_{10} Cv = \log_{10} Cv_{sat} + \beta\{1 - \tanh [(p - \theta)/\alpha]\}. \quad (5)$$

The constants α and β are determined from RT initial Charpy impact energy and RT saturation Charpy impact energy as follow:

$$\alpha = -0.585 + 0.795\log_{10}Cv_{sat} \quad (6)$$

and

$$\beta = (\log_{10}Cv_{int} - \log_{10}Cv_{sat})/2. \quad (7)$$

The value of θ varies with service temperature, which is 3.3 for<280℃, 2.9 for 280~330℃, and 2.5 for 330~360℃. These values are best-fitted constants with extensive data base of ~80 compositions of cast stainless steels. The value of p is aging parameter as discussed.

4. Results of Database Analysis and Discussion

Activation energies for thermal aging embrittlement of the steels derived on the basis of the correlation are as follow:

- CF-3 : 32.10~49.11 (kcal/mol),
- CF-8 : 24.81~37.57 (kcal/mol), and
- CF-8M : 16.18~28.94(kcal/mol), respectively.

Chemical compositions of ASTM A351 grade stainless steels of interest, CF-3, CF-8, and CF-8M

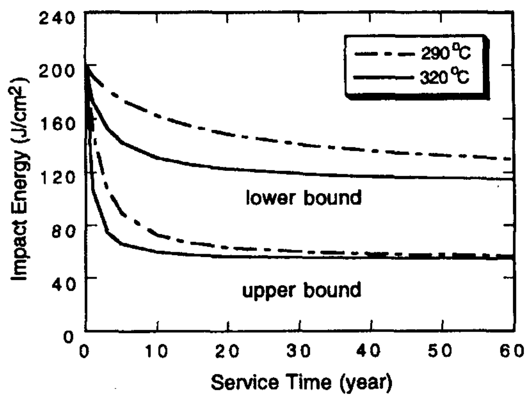

Fig. 4. Predicted RT Charpy V-notch Impact Energy for CF-8 Stainless Steel as a Function of Ractor Service Time.

are given in Table 2. Minimum and maximum values of the activation energies correspond to upper and lower composition limit of ASTM specification, respectively. Thus, the actual activation energy under reactor operation condition lies in the range. This suggests that the activation energy is sensitive to chemical composition of duplex stainless steel.

Earlier investigators have reported that the embrittlement of thermally aged duplex stainless steels is attributed only to the precipitation of Cr-rich α' phase in ferrite, whose mechanism is essentially identical to the '475℃ embrittlement' of ferrite stainless steels. In the mechanism, the activation energy of the process is expected to be similar to the activation energy of Cr diffusion in the ferrite phase (i.e. ~50 kcal/mol). This discrepancy indicates that the mechanism of thermal aging embrittlement is not merely phase separation into Fe-rich and Cr-rich region by means of Cr diffusion, but complex processes containing metallurgical processes summarized in Table 1.

Based on the correlations, variations in RT Charpy impact energy for grade CF-3, CF-8, and

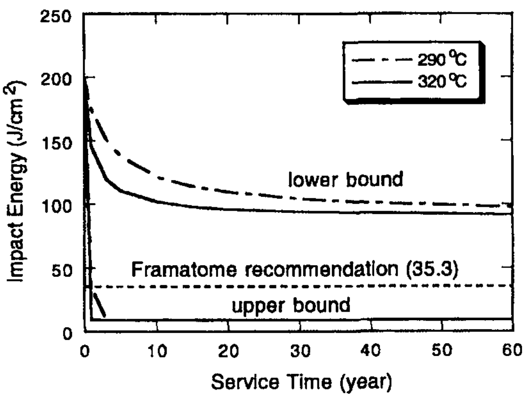

Fig. 5. Predicted RT Charpy V-notch Impact Energy for CF-8M Stainless Steel as a Function of Ractor Service Time

CF-8M during reactor service time are plotted in Figure 3 through 5 respectively. The temperatures of 290℃ and 320℃ were taken to estimate the degree of embrittlement in cold leg and hot leg under reactor operating condition, respectively. Lower bound and upper bound correspond to minimum and maximum composition limit of ASTM specification, respectively. From the figures, it is seen that the degree of embrittlement is more serious in hot leg than in cold leg, but temperature dependence is not significant, compared with chemical composition dependence of duplex stainless steel in ASTM specification.

Based on the figures CF-8M shows the widest spread in predicted Charpy impact energy data and it is most affected by thermal aging. CF-3 is found to be the least affected by thermal aging. CF-8 falls in between them. If grade CF-3 is used as the hot leg material, impact toughness can decrease down to 40% of initial impact toughness after design lifetime of 40 years. In cases of grade CF-8 and CF-8M, the impact toughnesses can decrease down to 27% and 5% of initial impact toughnesses, respectively. The horizontal dotted line in Figure 5 corresponds to the lower bound RT Charpy impact energy of 35.3 J/cm^2 recommended by Framatome [20]. After a 40-year service, the toughnesses of CF-3 and CF-8 are predicted to fall above the recommended lower bound energy, but that of CF-8M steels can fall below the recommended lower bound. Based on this model and Framatome recommendation, CF-3 and CF-8 alloys are predicted to provide acceptable service for extended lifetime of 60 years. However, CF-8M may be degraded and the deterioration exceeds the acceptance limit after several years of service, depending on its composition.

5. Conclusions

Phase separation by so-called spinodal decomposition into Fe-rich and Cr-rich phase is the primary cause of the embrittlement in primary pressure boundary components at LWR operating temperatures. The degree of embrittlement is significantly affected by chemical composition of the steels, but less affected by operating temperature. CF-3 and CF-8 alloys are predicted to provide safe performance during extended lifetime of 60 years as well as designed lifetime of 40 years, but database demonstrates that the loss of impact toughness of CF-8M steels can be potential problems after several years of service. Considering most of primary coolant piping materials in domestic nuclear power plants are grade CF-8M, tight in-service inspection (ISI) of CF-8M alloys may be required to secure the integrity of primary pressure boundary components during the service time or extended lifetime.

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