B.4 "Thermal Aging and Embrittlement of Cast Stainless Steels," by Peter M. Scott

Introduction

Cast stainless steels (CASS) are used for many components in Light Water Reactors including piping, elbows and T's, and particularly those components with complex shapes such as pump and valve bodies. They are not normally subject to high neutron fluxes although some CASS components on the edges of PWR cores may reach fast neutron fluences on the order of 10^{20} n/cm^2 at end of life (for 40 years initial licensing period).

The most commonly used CASS materials are SA-351 grades CF-3, CF-3A, CF-8, CF-8A and CF-8M, the specifications of which are shown in Table B.4.1. They have a duplex (γ) austenite / δ ferrite microstructure and are susceptible to thermal aging embrittlement of the δ ferrite phase at typical PWR and BWR operating temperatures. The volume fraction of ferrite is typically 10 to 20% but may attain 25%; only the lower limit is imposed by the ASME code. Stainless steel weld deposits, typically Type 308 and 309, have a similar duplex microstructure but with a lower volume fraction of ferrite typically in the range 5 to 10% and notably lower Cr contents.

Embrittlement of the δ ferrite phase results in an increase in hardness and loss of ductility and of fracture toughness. The mechanisms of thermal aging have been extensively studied from the point of view of microstructural changes resulting in the formation of nanometer-scale embrittling phases. Predictive, albeit empirical, equations have been developed for the purpose of forecasting the deterioration in mechanical properties over typical reactor lifetimes.

The purpose of this appendix is to provide a summary of current understanding of the thermal aging mechanism of CASS and the application of that knowledge currently proposed in the United States for predicting changes in mechanical properties and loss of fracture toughness in PWR and BWR components [1,2,3]. There are no known published studies of the stress corrosion resistance of these materials in the aged and embrittled condition when exposed to PWR or BWR primary coolants although there are some instances of stress corrosion cracks propagating into stainless steel weld metals in BWRs, apparently along the δ ferrite, after long periods of service. There are also no known published studies of the influence of these aqueous environments compared to air on fracture resistance.

Mechanism of thermal aging

Thermal aging embrittlement of CASS at temperatures below about 400°C arises primarily as a consequence of a thermally activated separation of chromium by diffusion in the Fe-Cr solid solution of the δ ferrite phase resulting in the formation of an iron rich α phase and a chromium rich α' phase. This process is called 'spinodal decomposition' and occurs mainly at the higher chromium contents greater than ~23% in the δ ferrite (for temperatures <400°C). The α' phase may also form by precipitate germination and growth, particularly at temperatures >400°C, but can also contribute at lower temperatures depending on the precise combination of chromium content and temperature e.g. <~26%Cr at 400°C and <~23%Cr at 300°C. The austenite phase of CASS is unaffected by thermal aging in the same temperature range.

The formation of α' during thermal aging can affect all Fe-Cr solid solutions with Cr contents in solution >10%. An "oscillation" in the resulting Cr distribution is observed by high resolution microscopic techniques with "wavelength" (measured in nanometers) and amplitude increasing with aging time and temperature. The effect increases notably with the Cr and Mo content of

the ferrite phase and consequently CF-8M is less resistant to aging than CF-8 or CF-3 without Mo. The formation of embrittling α' phase from δ ferrite is enhanced by other alloying elements such as silicon which together with Cr and Mo can be represented by the chrome equivalent. The presence of the adjacent austenite phase in CASS appears to exert a detrimental influence relative to purely ferritic alloys of similar composition.

Other precipitation phenomena occur in the δ ferrite phase and at the ferrite-austenite interfaces above about 350°C, particularly the formation of the fcc Ni,Si,Mo rich G phase which can reach up to 12% by volume in Mo containing CASS. Carbon also enhances G phase precipitation. Nevertheless, G phase does not appear to contribute significantly to hardening and loss of toughness. At higher temperatures between 400 and 500°C other intermetallic phases precipitate but to a much lesser extent than G phase. However, extensive carbide (and sometimes nitride) precipitation, particularly at austenite-ferrite interfaces, occurs in the Mo-free CASS.

Although the microstructural evolution of CASS during thermal aging is fundamentally driven by solid-state diffusion processes, the complexity and changing nature of the phenomena with temperature is such that extrapolation over large temperature ranges using Arrhenius type relations is very difficult. Accelerated thermal aging for PWR and BWR applications is generally only carried out up to 400°C where hardening of the δ ferrite by α' formation is the predominant aging process. Even with this restriction, the apparent activation energy observed for changes in mechanical properties such as hardness and toughness (see next section) can be very variable and sometimes significantly below the activation energies of 210 to 260 kJ/mole associated with diffusion of metallic species, particularly Cr, in ferrite.

Mechanical properties of thermally aged CASS

The complexity of the microstructural changes associated with thermal aging of CASS gives rise to very strong material and heat dependencies for the extent and kinetics of evolution of mechanical properties. Consequently, very careful studies have been necessary to determine the range of temperature, composition etc for which mechanical properties data obtained from accelerated aging tests can be applied to service conditions.

The overall degree of embrittlement depends strongly on the amount, composition and distribution of the ferrite phase. The increase in hardness and decrease of ductility of the ferrite phase due to thermal aging promotes premature cleavage in this phase that can extend preferentially through it if there is a continuous ferrite network. Even if the fracture path intersects the austenite, deformation induced martensitic transformation can allow the brittle fracture to extend beyond the embrittled ferrite.

The main parameter used for characterizing the evolution of mechanical properties due to thermal aging has been the Charpy impact energy. Measurements of tensile properties, hardness, microhardness of the ferrite phase and J-R fracture resistance curves have also been made.

Thermal aging of CASS at BWR and PWR operating temperatures is characterized by an increase in hardness and tensile strength and a decrease in ductility, impact strength and toughness. In addition, the "brittle-ductile" transition temperature increases and the upper shelf decreases. Examples of Charpy impact energy measurements at room temperature on many heats of CASS are shown in Figure B.4.1. Although the dispersion in the results is large, all heats show a clear trend to a saturation of the aging effect (lower plateau value of Charpy

impact energy) that is independent of aging temperature, at least up to 400°C. The main trends in the data are with chemical composition, the plateau Charpy impact energy decreasing with increasing ferrite and chrome equivalent.

A procedure proposed in the United States for estimating the toughness of CASS components in service is based on empirical equations relating Charpy impact energy to the chemical composition, notably Cr, Mo, Si and C (i.e. Cr_{eq}), and time and temperature, including accelerated aging data at temperatures up to 400°C. The kinetics of aging are based on Arrhenius type correlations in which the apparent activation energy also depends on the concentrations of the aforementioned elements. The toughness ($J_{0.2}$) and J-R curve are then estimated from empirically established correlations with the Charpy impact energy from room temperature to normal operating temperatures. Lower bound estimates of end-of-life toughness are made based only on the chemical composition and lower bound correlations if no further details of the microstructure are available. The procedure can be refined if the initial Charpy impact energy and/or ferrite content are known, for example by classifying the material into three groups defined for <10%, 10 to 15%, and >15% ferrite.

A method proposed in the United States for screening CASS components for their potential susceptibility to thermal aging embrittlement is to divide all such components into six categories as shown in Table B.4.2. The indicated ferrite levels may be calculated or measured. All components identified as having a potentially significant reduction in fracture toughness due to thermal aging are then placed in an aging management program. The NRC staff position is described in a letter dated May 19, 2000 from C.I. Grimes (NRC) to D. J. Walters (NEI). A corollary of this classification is that no significant thermal aging is anticipated for stainless steel weld deposits because of the low ferrite contents relative to CASS. However, studies of the fracture properties of weld heat affected zones in aged CASS do not appear to have been published.

It is important to note that there is significant variability internationally in approaches used to estimate the degradation in CASS toughness that can lead to differing judgments of the significance and extent of thermal aging embrittlement. In particular, the US approach eliminates from consideration all heats known or believed to contain niobium on the grounds that these are out of specification in the USA. The counter argument is that niobium precipitates as niobium carbide very quickly and in any case has no significant effect on toughness in either the as-received or thermally aged condition. An even greater dispersion in possible toughness levels and a significantly reduced lower bound compared to that adopted in the US have been measured [1,4], i.e., significantly lower than the saturation room temperature impact energy of ~25 J/cm^2 seen in Figure B.4.1. It is acknowledged, however, that the very low toughness heats in the international population of CASS heats is strongly influenced by heats from a particular foundry that has not supplied the US market. Nevertheless, the range of ferrite contents and chrome equivalents are not considered to be unrepresentative of the range encountered in CASS used in US plants.

Other possible degradation phenomena

As mentioned in the Introduction, some CASS components below or above the core can be irradiated possibly up to ~10^{20} n/cm^2 at the end of a 40 year licensing period. Since the fracture resistance of fully thermally aged CASS is essentially that of the network of austenite (because the fully thermally aged ferrite is so brittle and hardly contributes at all to remaining fracture toughness), the effect of irradiation damage will only be significant if the austenite is embrittled by neutron irradiation. At a neutron fluence of ~10^{20} n/cm^2 the mechanical properties of

austenitic stainless steels are scarcely affected. It follows, therefore, that no significant effect of irradiation damage on fracture resistance of CASS is anticipated in the fully thermally aged condition. Of course, at intermediate stages of thermal embrittlement of the ferrite phase, the effect of irradiation damage on fracture toughness could be more marked. The industry is currently investigating the mechanical and fracture of irradiated CASS to check the anticipated behavior described.

It is well known that fracture resistance can be affected by the environment in which the fracture events occur. For example, the fracture resistance of nickel base weld metals appears to be significantly reduced in a PWR primary water environment compared to air at temperatures below about 150°C, probably due to hydrogen embrittlement (See Paper B.13 N° 13). Given the nature of the embrittlement of the ferrite phase in CASS, it is reasonable to suppose that some effects of hydrogen embrittlement may also combine with thermal aging embrittlement in this case. However, there are no known published studies of the effects of aqueous environments on fracture resistance of CASS although certain electrochemical non-destructive tests proposed for the detection of thermal aging embrittlement of CASS depend on different dissolution response between aged and non-aged material[5,6]. In oxidizing environments such as BWR normal (oxygenated) water chemistry, this could result in preferential dissolution/oxidation at the γ-ferrite interface. Such differences would be less likely in hydrogenated BWR hydrogen water chemistry or PWR primary water chemistry. On the other hand, hydrogen entry into the aged duplex stainless steels, especially into the hardened ferrite phase, may raise some concerns.

An ancillary question to the one posed above concerns the stress corrosion/hydrogen embrittlement behavior of thermally aged CASS but again there are no known published studies other than the (unexpected) observations of stress corrosion cracks propagating into stainless steel weld metals mentioned in the Introduction.

Some effort has been devoted to examining fatigue and corrosion fatigue S-N and fatigue crack propagation behavior of CASS. The corrosion fatigue data for de-oxygenated PWR environments appear to present similar environmental effects as wrought stainless steels. Given the unresolved controversy regarding how to incorporate such environmental effects in fatigue evaluations no further discussion is given here. The extent to which these corrosion fatigue studies extend to thermally aged material is not known.

References for B.4

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[2] O. K. Chopra, "Estimation of fracture toughness of cast stainless steels during thermal aging in LWR systems – Revision 1," NUREG Report CR-4513-Rev1, August 1994.

[3] License Renewal Issue No. 98-0030, "Thermal aging embrittlement of cast austenitic stainless steel components," NRC, May 19, 2000.

[4] A. Bache, M. Akamatsu, P. Ould, P. Thibaut, H. Churier-Bossenec, G. Bezdikian, "Contribution de l'expertise des coudes déposés lors de RGV à la validation des méthodes de caractérisation et la justification de la tenue en service des produits moulés" (Translated: "Contribution of experimental investigations on cast elbows removed from service during steam generator replacement and validation of the methods used for characterizing and justifying the in-service behavior of CASS"), pp

967-976, Proceedings of International Symposium Fontevraud V, 23-27 September 2002.

[5] Y. S. Yi and T. Shoji, "Detection and Evaluation of Material Degradation of Thermally Aged Duplex Stainless Steel: Electrochemical Polarization Test and AFM Surface Analysis". Journal of Nuclear Materials, 231, (1996), 20-28.

[6] Y. S. Yi and T. Shoji, "Quantitative Evaluation of Material Degradation of Thermally Aged Duplex Stainless Steels Using Chemical Immersion Test ". Journal of Nuclear Materials, 240, (1996), 62-69.

Table B.4.1 ASME Specifications for CASS Grades Commonly Used in PWR and BWR

	CF-3	CF-3A	CF-8	CF-8A	CF-8M
Carbon %max	0.03	0.03	0.08	0.08	0.08
Manganese %max	1.50	1.50	1.50	1.50	1.50
Silicon %max	2.00	2.00	2.00	2.00	1.50
Sulfur %max	0.040	0.040	0.040	0.040	0.040
Phosphorus %max	0.040	0.040	0.040	0.040	0.040
Chromium	17.0-21.0	17.0-21.0	18.0-21.0	18.0-21.0	18.0-21.0
Nickel	8.0-12.0	8.0-12.0	8.0-11.0	8.0-11.0	9.0-12.0
Molybdenum %max	0.50	0.50	0.50	0.50	2.0-3.0
Tensile strength Min Ksi (MPa)	70 (485)	77 (530)	70 (485)	77 (530)	70 (485)
Yield strength Min Ksi (MPa)	30 (205)	35 (240)	30 (205)	35 (240)	30 (205)
Elongation Min %	35.0	35.0	35.0	35.0	30.0

Table B.4.2 Proposed Thermal Aging Screening Criteria in EPRI TR 106092

Mo Content (Wt. %)	Casting Method	Ferrite Content	Significance of Thermal Aging
High (2.0 – 3.0	Static	All	Potentially significant
	Centrifugal	>20%	Potentially significant
		<20%	Non-significant
Low (0.50 max.)	Static	> 20%	Potentially significant
		<20%	Non-significant
	Centrifugal	All	Non-significant

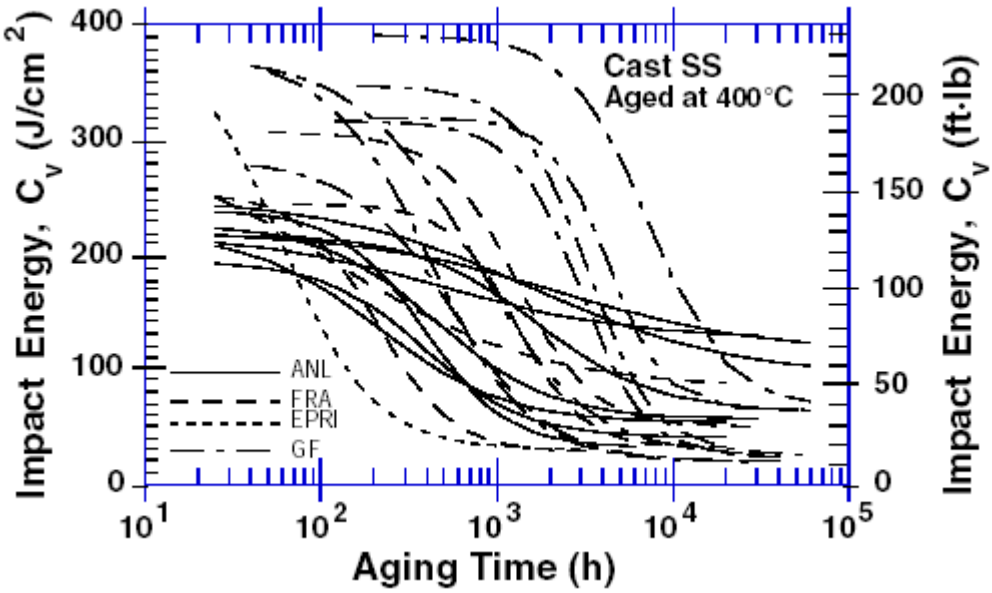

Figure B.4.1 Decrease in Charpy impact energy for various heats of cast stainless steels aged at 400℃ (2).