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ABSTRACT

Microstructures of cast-duplex stainless steels subjected to long-term aging either in the laboratory or during in-reactor service have been characterized and compared by TEM, SEM, and optical microscopy. The microstructural characteristics have been correlated with the impact failure behavior of the material. G-phase, α', and an unidentified Type X precipitate were responsible for the ferrite-phase embrittlement. Precipitation of $M_{23}C_6$ carbides on austenite-ferrite boundaries further degraded the reactor-aged material.

INTRODUCTION

Cast-duplex stainless steels are used extensively in nuclear power plants. The ferritic phase in the duplex structure of austenitic-ferritic stainless steels increases the tensile strength and improves weldability, resistance to stress corrosion, and soundness of the casting of these steels. However, various carbide phases, intermetallic compounds such as sigma and chi phases, and the chromium-rich bcc phase (α') can precipitate in the ferrite phase during service at elevated temperatures and lead to substantial degradation in mechanical properties. Unfortunately, the bulk of previous work has been carried out at temperatures above 400°C, and it is not clear whether extrapolation of the results to light-water reactor operating temperatures (i.e., 280-320°C) would be valid. It is the purpose of this paper to report the results of microstructural characterization of several heats of cast-duplex stainless steel either after long-term aging at 300-400°C in the laboratory or after long-term service in a power reactor. The microstructural characteristics, determined from scanning and transmission electron microscopy (SEM and TEM), were then correlated with fracture properties of the material, which were assessed by Charpy-impact tests at room temperature. Chemical composition and ferrite contents of the duplex steels are given in Table I.

DEGRADATION OF RESISTANCE TO IMPACT FAILURE

Long-term aged CF-8 cast-duplex stainless steels containing 10 to 40% ferrite were obtained from the Georg Fischer Co. of Switzerland. Aging was conducted at 300, 350, and 400°C for up to 8 yr. A cover plate assembly of cast-duplex stainless steel has been also obtained from the recirculation pump of a boiling-water reactor (KRB) after a nominal service period of ~12 yr. Charpy-impact tests were conducted at room temperature for the laboratory-aged and reactor-component materials. Figure 1 shows the failure impact energies of the materials plotted as a function of aging or service time. A significant degradation of the resistance to impact failure is evident from Fig. 1. After the impact tests, microstructures of the specimens have been characterized by TEM, SEM, and optical microscopy and correlated with the failure behavior. The results showed that three types of precipitates were responsible for embrittlement of the ferrite phase. Precipitation of a grain-boundary phase may be responsible for the weakening of the ferrite-austenite grain boundary.

FERRITE EMBRITTLEMENT

G-Phase

Figure 2 shows the characteristic morphology and selected area diffraction (SAD) patterns of the G-phase observed in the G. Fischer Co. CF-8 material after aging at 400°C for 7.6 yr.[2] The precipitates were also observed in the reactor-aged pump cover material, which was exposed to the coolant at ~274°C. Although the 400°C aging produced precipitates of the G-phase in the ferrite grains as well as on the grain boundaries [Fig. 2(A)], no grain boundary precipitation was observed after aging at ≲300°C. During lower temperature aging, the precipitates were observed primarily in association with dislocations in the ferrite; this observation indicated

TABLE I. Chemical Compositions of CF-8 Grade Cast Stainless Steels Used for Microstructural Evaluation

Heat No.	Composition (wt %)									Ferrite Content (%)
	Mn	Si	Mo	Cr	Ni	P	S	N	C	
280	0.28	1.00	0.13	20.20	8.27	0.008	0.019	0.027	0.038	38
278	0.50	1.37	0.25	21.60	8.00	0.015	0.006	0.029	0.028	15
60	0.71	1.01	0.26	21.02	8.07	-	-	0.050	0.070	21
KRB Reactor	0.31	1.17	0.17	21.99	8.03	-	-	0.038	0.062	34

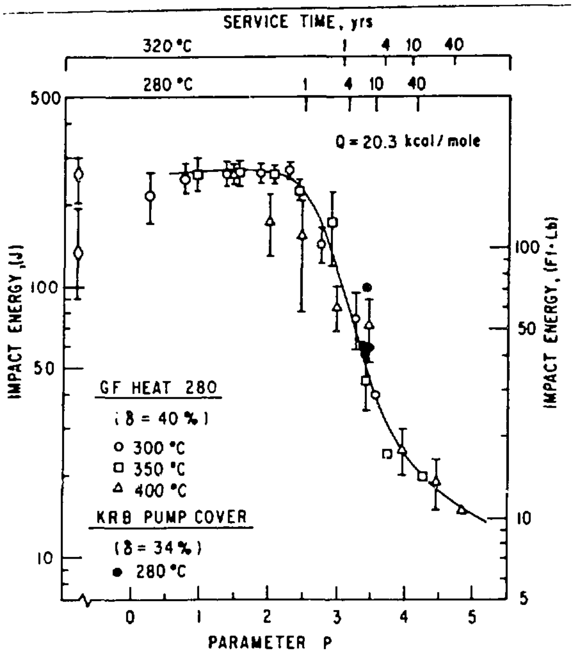

Fig. 1. Effect of Thermal Aging on the Room-Temperature Impact Energy of CF-8 Cast-Duplex Stainless Steels Containing >30% Ferrite. The aging parameter P is related to time (t) by the equation $t = 10^P \exp\left[\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{673}\right)\right]$, where R is the gas constant, T is the absolute temperature, and Q(kJ/mole) = -182.6 + 19.9 (% Si) + 11.08 (% Cr) + 14.4 (% Mo).[1]

a dislocation pinning effect. The nearly spherical precipitate is ~10 nm in size. The diffraction patterns are similar to those of the $M_{23}C_6$ phase, but with a slightly larger lattice parameter. The precipitates also had a cube-on-cube orientation relative to the bcc ferrite matrix, which would be unusual for the $M_{23}C_6$ phase. (400) reflections were characteristically weak or absent in the diffraction patterns [Fig. 2(C))]. Energy-dispersive x-ray analysis showed an enrichment of Ni and Si in the precipitates. From these results, the precipitates were tentatively identified as the G-phase (a phase rich in Ni and Si), which has been observed in an Fe-12Cr-4Ni alloy after aging at 450°C[3] and in commercial EM-12 (9Cr-2Mo), HT-9 (12Cr-1Mo), and AISI 416 (13Cr) ferritic steels after irradiation at temperatures <425°C.[4]

Type X Precipitates

In both the laboratory- and reactor-aged materials, the unidentified (Type X) precipitate was always observed on dislocations. Figure 3 shows the morphology of the precipitates that are interwoven with the dislocations. Apparently, the precipitates were very effective in pinning dislocation motion in the material aged for a long time near 300°C. The precipitate reflections in the SAD patterns were weak, diffuse, and streaked, owing to a low volume fraction and small particle size. In typical SAD patterns containing the Type X precipitates, only extremely weak precipitate reflections with a d-spacing of 0.218 nm were detected. The weak reflections could not be detected on the microscope screen. No cross-grid patterns could be obtained.

α' Precipitate

Chromium-rich α' precipitates in the ferrite were observed in KRB boiling-water-reactor pump cover material, Fig. 4(A). The extremely small (1-2 nm) α' precipitates could not be resolved by TEM either under a strong bright-field or under a dark-field imaging condition. The precipitates could be resolved only under weak beam bright-field imaging condition. The mottled morphology characteristic of the α' was difficult to resolve in the G. Fischer material after aging at 300°C for

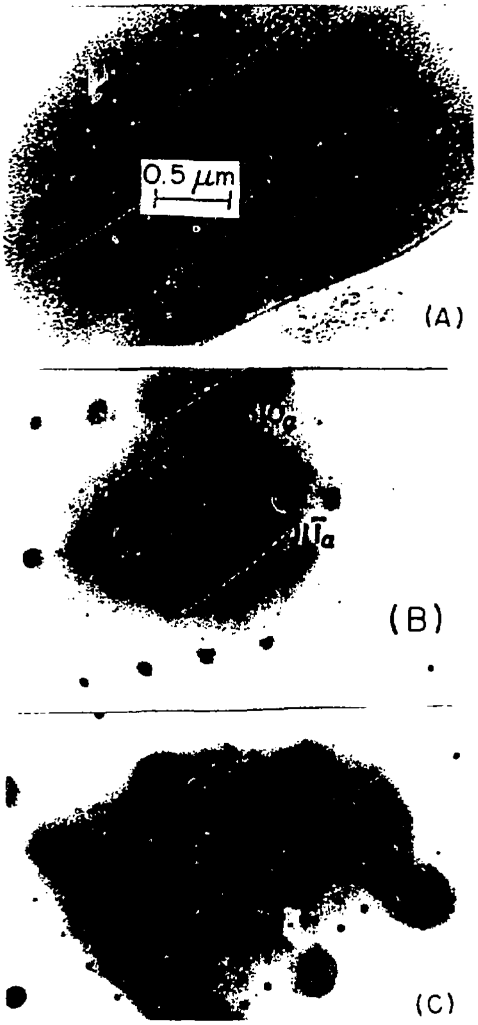

Fig. 2. Dark-Field Morphology (A) and Characteristic SAD Patterns (B and C) of the Ni- and Si-rich G-Phase Observed in CF-8 Cast-Duplex Stainless Steel afte. Aging at 400°C for 7.6 yr.

8 yr. However, optimum weak-beam imaging[5] at a magnification of 20-40 thousand times revealed α' precipitates 1-1.5 nm in size when the negatives were developed and examined on a lighted table with a magnifying glass. Negatives taken under normal bright- or dark-field imaging condition did not reveal any α' precipitates in the G. Fischer materials. Figure 4(B) shows the α' in the ferrite of Heat 60 alloy after aging at 400°C for 1.2 yr. The α' size and morphology are similar to those of the KRB reactor-aged material.

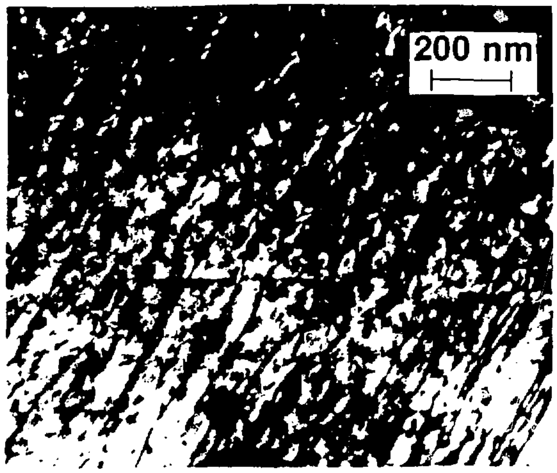

Fig. 3. Dark-Field Image Showing Light Type X Precipitates Interwoven with Dislocations in the Ferrite Phase of the Reactor Pump Cover Material.

GRAIN BOUNDARY PRECIPITATE

A distinct difference between the microstructures of the laboratory-aged G. Fischer material and the reactor pump cover materials involved precipitation of a grain boundary phase in the latter. Bright- and dark-field morphologies and an SAD pattern of the grain boundary phase are shown in Fig. 5. The phase was observed on the boundary between the austenite and ferrite grains, examples of which appear as the dark and light areas, respectively, in Fig. 5(A). Several different zone axes similar to that of the SAD pattern in Fig. 5(C) were obtained. Indexing of the diffraction patterns showed that the grain boundary precipitates were $M_{23}C_6$ carbides, which were of cube-on-cube orientation relative to austenite. The overall distribution of the grain boundary phase could be more clearly observed in low-magnification optical micrographs. For example, in Fig. 5(D), ~60% of the austenite-ferrite grain boundaries are decorated by the unknown phase; this observation indicates a possible weakening of the grain boundaries. The lacy morphology of the ferrite is evident from Fig. 5(D). Aging of the Heat 60 alloy, of which chemical composition is similar to that of the reactor pump material (Table I), also resulted in the grain boundary precipitation of the $M_{23}C_6$ carbide, Fig. 4(B). The absence of the grain boundary carbide precipitates in the G. Fischer materials, Heats 280 and 278, is probably related to their low carbon contents (Table I) compared to the high carbon contents of the reactor pump and Heat 60 materials.

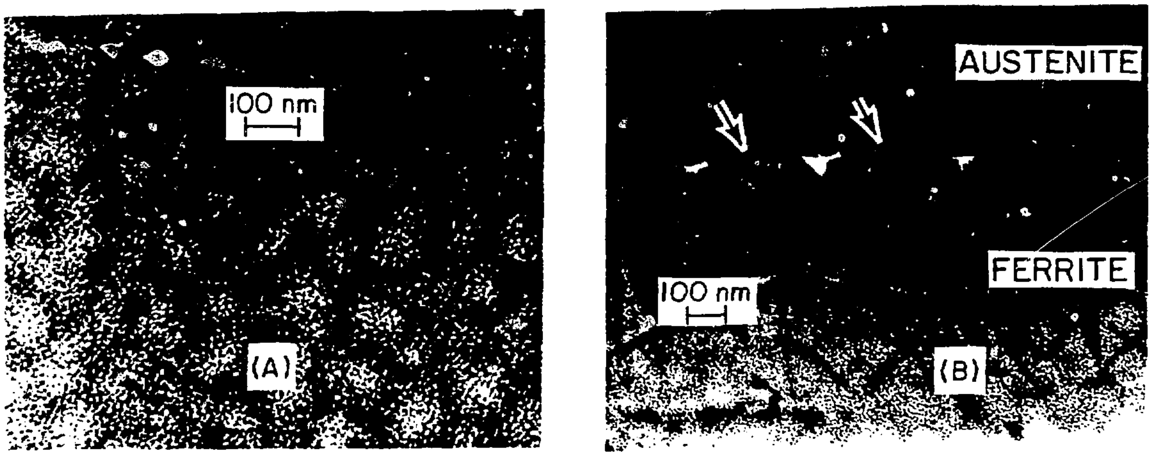

Fig. 4. Morphologies of α' Observed in the Ferrite Phase of the Reactor Pump Cover (A) and Heat 60 Cast-Duplex Stainless Steel after Aging at 400°C for 10,000 h (B). $M_{23}C_6$ precipitates on the phase boundary are denoted by arrows in (B).

SEM FRACTOGRAPHY

Fracture surface morphologies of the laboratory-aged G. Fischer materials and the reactor pump cover material were evaluated by SEM after room-temperature impact tests. The fracture surface morphology of the ferrite phase of the reactor pump cover and the G. Fischer material aged at 300°C for 8 yr or at 400°C for 1.2 yr was invariably cleavage-type (Fig. 6), which means negligible ductility of the phase. Undoubtedly, the ferrite was generally embrittled by one or combinations of the above-mentioned precipitates, i.e., G-phase, Type X, and α'. It was, in fact, possible to map the cleavage-ferrite and ductile-austenite portions of a given fracture surface. The cleavage map of the reactor pump cover indicated that ~50-60% of the overall fracture surface was ferrite, although the ferrite volume fraction was only ~30%. Although not conclusive, this finding indicates preferential crack propagation along the ferrite phase under the impact condition. There was also some indication of decohesion along the grain boundary of the reactor pump cover material, as shown in Fig. 6(B). The relatively smooth morphology shown in Fig. 6(B) appears to correspond to grain boundaries that are partly covered by ductile tears. This observation is consistent with the microstructures of Fig. 5, in which a significant fraction of the grain boundaries was covered by the carbide precipitates. However, for the laboratory-aged G. Fischer materials, the austenite fracture surface morphology invariably showed transgranular ductile failures, as in Fig. 6(A).

SUMMARY AND CONCLUSION

Microstructures of cast-duplex stainless steels were evaluated after long-term aging in the laboratory at 300-400°C or after in-reactor service for 12 yr. The ferrite phase of the duplex steel was embrittled by precipitation of G-phase, unidentified Type X, or Cr-rich α'. Precipitation of the $M_{23}C_6$ phase on the austenite-ferrite grain boundary was observed in the reactor-aged material and in a laboratory-aged heat, both of which contained a relatively high-level of carbon. It appears that the aging behavior of the cast-duplex stainless steel in reactor could be assessed on the basis of the characteristics of similar heat obtained after long-term aging in the laboratory.

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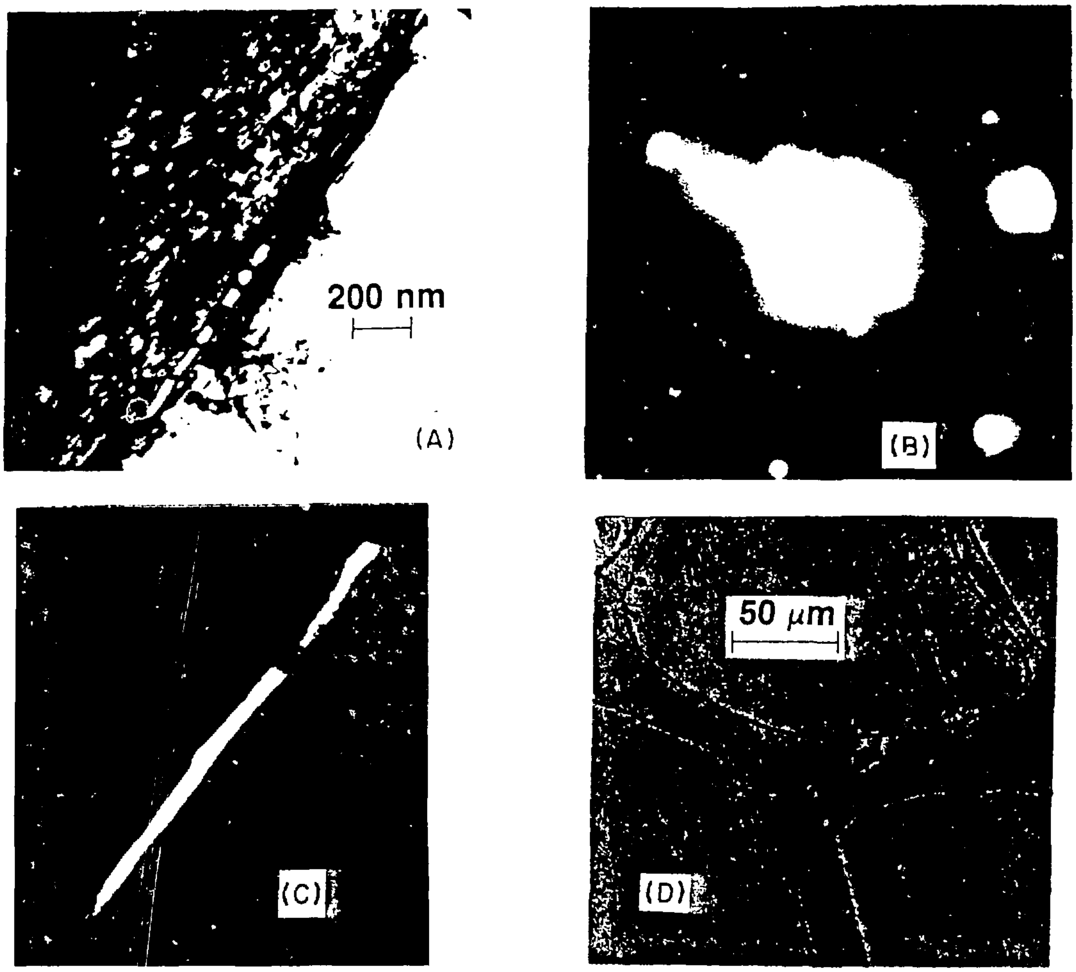

Fig. 5. Bright-Field (A) and Dark-Field (B) Images, SAD Pattern (C), and an Optical Micrograph (D) of $M_{23}C_6$ Grain Boundary Precipitates Observed in the Reactor Pump Cover Material.

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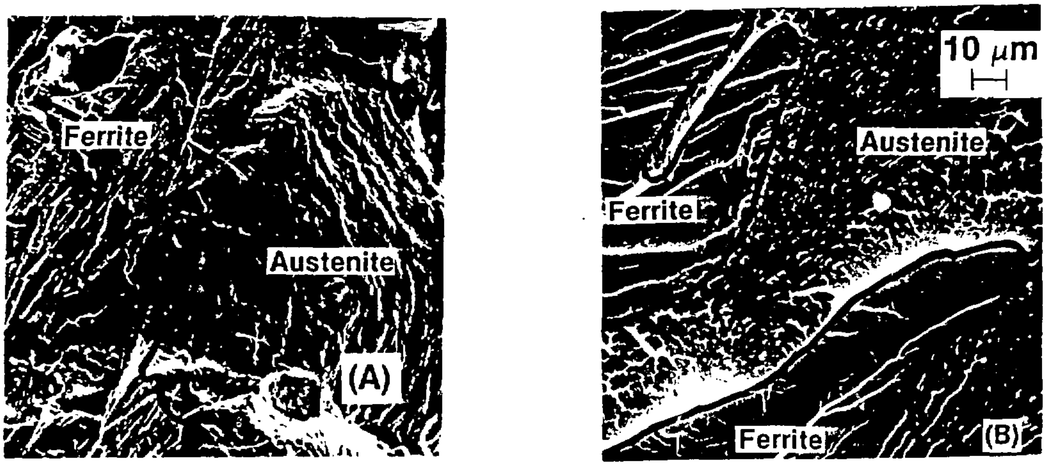

Fig. 6. Fracture Surface Morphologies of the Room-Temperature Impact-tested Specimens of the G. Fischer Material Aged at 300°C for 8 yr (A) and the Reactor Pump Cover Material after 12 yr of Service in a Boiling-Water Reactor (B).