Alloy Additions for Improved Creep-Rupture Properties of a Cast Austenitic Alloy

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Abstract

A new cast austenitic alloy, CF8C-Plus, has been developed by Oak Ridge National Laboratory (ORNL) and Caterpillar for a wide range of high temperature applications including diesel exhaust components and turbine casings. The creep strength of CF8C-Plus is much greater than that of the standard cast CF8C and comparable to the highest strength wrought commercial stainless steel alloys. Further alloy modifications typical in some commercial wrought stainless steel alloys are being pursued for increased creep strength, high-temperature stability, and corrosion resistance. The effect of these alloy additions, namely B, W, Cu, and Al, on tensile and creep strength are discussed in terms of the observed microstructural changes. The addition of Cu was found to be beneficial to the creep strength of the alloy while the addition of W had little effect on either tensile and creep properties. The addition of Al, and to a lesser degree B, decreased the tensile and creep strength of the alloy.

Introduction

Advanced heavy truck diesel engines must continue to have higher fuel efficiency as well as reduced exhaust emissions, without sacrificing durability and reliability. More demanding normal duty cycles require exhaust manifolds and turbocharger housing materials to withstand temperatures ranging from 70 to above 750°C [1]. Such materials must withstand both prolonged, steady high-temperature exposure as well as more rapid and severe thermal cycling. New emissions reduction technology and transient power excursions can push temperatures in these critical components even higher. Additionally, turbine manufacturers are considering lower-cost alternatives to nickel-based superalloy castings for casings and large structural components, as temperatures are pushed beyond the limits of current cast ferritic materials [2]. These needs lead to a cooperative research and development agreement (CRADA) between the Caterpillar (CAT) Technical Center and Oak Ridge National Laboratory (ORNL) to investigate various cast stainless steel materials for advanced diesel engine components. One development of this work was a new cast austenitic stainless steel, CF8C-Plus, which showed dramatic improvements compared to typical diesel exhaust alloys and standard CF8C steel in creep, thermal fatigue, high-temperature tensile strength, and aging response (impact toughness) [3]. Small alloying additions, typical in the most recently developed wrought stainless steels, may provide increased creep strength, high-temperature stability, and corrosion resistance for the most demanding high-temperature applications targeted, such as steam turbines. In this paper we investigate the effects of minor alloying additions of B, W, Cu, and Al on tensile and creep strength compared to the base CF8C-Plus steel composition.

Background

CF8C steel is the casting equivalent of grade 347 stainless steel. The typical composition of CF8C steel is given in Table 1 with the compositions of CF8C-Plus steels used in this study. CF8C steel is nominally a 10Ni-20Cr precipitation strengthened stainless steel. Precipitation strengthening is primarily due to the presence of NbC. Standard CF8C steel is an overstabilized stainless steel, which guarantees the formation of $M_{23}C_6$ and that sensitization does not occur. This results in the as-cast microstructure containing 15% delta-ferrite, typically found in the interdendritic regions [3]. The general assumption is that the delta-ferrite improves weldability and is beneficial for some mechanical properties.

The alloy design methodology used to modify the CF8C steel for improved high-temperature mechanical properties is described in detail elsewhere [3,4]. Commercial heats of the new steel, CF8C-Plus, show large improvements in creep strength compared to the CF8C. Figure 1 is a Larson-Miller Parameter (LMP) plot for creep-rupture testing of several identical commercially cast (both sand and centrifugally cast) CF8C and CF8C-Plus steels. The plot (taken from ref. [3]) is updated with the most recently available creep data produced at ORNL. Extrapolation of the average rupture data from the LMP plot shows that CF8C-Plus steel has a 35X improvement in rupture life at 700°C or a 60°C improvement in temperature for equivalent rupture life at 100,000 hours compared to CF8C steel.

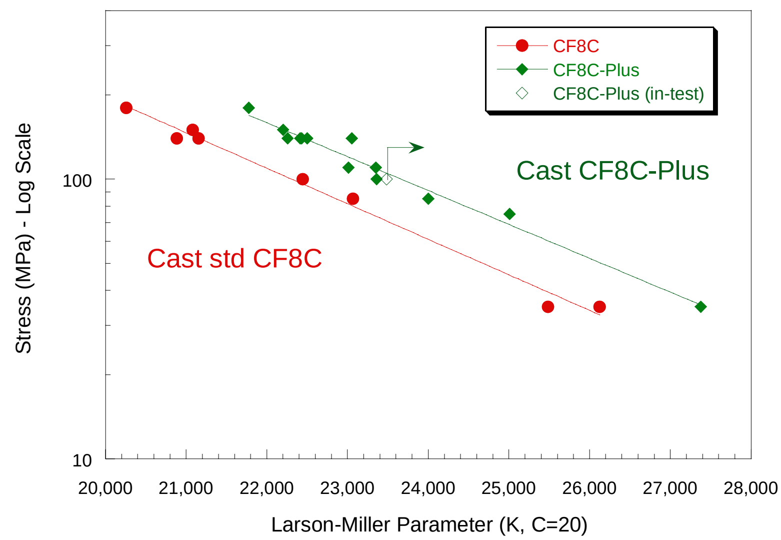


Figure 1. LMP plot for CF8C and CF8C-Plus steel commercial castings creep tested between 650 and 850°C for times up to 24,000 hours (arrow indicates test in progress)

Three main microstructural differences contribute to the improved mechanical properties of the new CF8C-Plus steel compared to standard CF8C steel. First, the additions of Mn, N, and Ni stabilize the austenite matrix and eliminate delta-ferrite, which forms sigma phase during high-temperature aging. The interdendritic regions in the CF8C-Plus steel contain only $M_{23}C_6$ and NbC. Second, the addition of Mn increases the solubility of N in the austenite. Mn and N in the austenite both provide increased strength and strain-hardening behavior. Third, the presence of a dense, uniform, and stable nano-scale (less than 50nm diameter) dispersion of NbC in the CF8C-Plus, that forms rapidly at high temperatures, is the origin for the excellent creep strength. These fine carbides do not show significant coarsening after exposure at 850°C for over 20,000 hours. Several theories have been presented to explain the presence of these fine carbides in an as-cast and aged or creep tested microstructure [3], but more detailed analytical electron microscopy data on the CF8C-Plus steel in various material conditions is still needed to clarify the mechanistic behavior.

Austenitic Stainless Steel Alloy Additions

Four separate alloying additions, B, W, Cu, and Al, were chosen for evaluation on CF8C-Plus steel. The choice of these elements was based upon the current knowledge of modification to enhance creep-resistance of wrought stainless steel alloys. A comprehensive review of the historical evolution of creep resistant wrought austenitic stainless steels and alloys (mainly boiler superheater tubing) has been produced by Masuyama [5]. By tracking the changes in chemistry and 100,000 hour creep strength at 600ºC, some major alloy effects are clearly seen. For the under-stabilized H grade stainless steels (nominally 18C-10Ni), the strongest alloy in the group is Super 304H, which is a typical 304H composition with the addition of Nb, N and Cu. For the class of more robust stabilized austenitic stainless steels, the highest creep strength has been reported for SAVE25 which is a nominally 22.5Cr-18.5Ni stainless with additions of Nb, N, Cu, and W. The additions of W and Cu have also been used on a number of new alloys. Sanicro 25, which was developed for the AD700 program goals of an austenitic alloy having a 100,000 hour creep strength of 100MPa at 700ºC, has a composition similar to SAVE25 containing both W and Cu [6]. To improve the creep properties of Esshete 1250, which is a lower Ni and higher Mn stainless steel, a current research project in Europe is evaluating the effects of adding Cu and W [7]. The addition of 2 to 5% Cu has long been known to improve the creep properties of stainless steels [8], and this was the basis for the particular addition of Cu made to the CF8C-Plus steel. The W added in many of the new steels is thought to improve the creep strength of these alloys either by solid solution strengthening or by stabilization of the $M_{23}C_6$ carbides. For this reason W was chosen. Small quantities of B have been found to be beneficial for creep strength in ferritic and martensitic steels [9,10], austenitic alloys [11], and nickel-based alloys [12]. In general, B is considered a 'surface active element' that may retard the coarsening of grain boundary $M_{23}C_6$ carbides in ferritic steels and refine carbide structures in austenitic steels. It was not clear whether or not a B addition would have a beneficial effect on a stainless steel casting, so it was added as well. The addition of Al to improve the high-temperature oxidation resistance has long been a goal of austenitic alloy development; so, Al was added for this reason.

Experimental Procedure

Five 15lbs lab-scale heats of CF8C-Plus with minor alloy additions were produced by induction melting with an Argon cover gas and cast into graphite blocks (152mm X 102mm X 25.4mm). The measured compositions of the five castings (wt%) are given in Table 1. One heat was cast to the CF8C-Plus composition, 19Cr-10Ni-0.1C-4Mn-0.5Si-0.25Mo-0.8Nb-0.25N. This is the 'base' composition. The four other heats contained a single alloy addition each. These will be identified throughout the rest of the paper as 'base+alloying addition.' The desired amounts for the B, W, Cu, and Al additions were 0.005, 0.5, 2.5, and 1.5 wt%, respectively, and these target additions were obtained with good accuracy.

Table I. Average and Measured Composition of CF8C and CF8C-Plus Alloys

Measured Composition (wt%) for CF8C-Plus Castings

Alloy	C	Mn	Si	Ni	Cr	Mo	V	Nb	N	Additions
Std. CF8C*	0.08	0.50	1.5	10.0	19.5			0.85		
CF8C-Plus	0.10	4.20	0.5	12.7	19.3	0.25	0.008	0.78	0.28	
Mod. CF8C-Plus	0.10	4.25	0.5	12.7	19.4	0.25	0.010	0.79	0.22	0.005 B
Mod. CF8C-Plus	0.10	4.16	0.5	12.6	18.9	0.25	0.008	0.75	0.26	0.45 W
Mod. CF8C-Plus	0.09	4.26	0.5	12.9	19.1	0.25	0.008	0.77	0.25	2.5 Cu
Mod. CF8C-Plus	0.01	4.44	0.6	12.3	19.2	0.26	0.008	0.80	0.26	1.3 Al

*Typical Composition

No post-casting stress-relief or solution annealing treatment was given to these castings. Tensile bars were machined from the casting blocks and room temperature and elevated temperature tensile tests were performed. Short-term creep-rupture testing was performed in air on a lever-arm creep testing machines with an extensometer attached to the shoulders of the specimen to continuously measure creep deformation. The test condition chosen to screen all the specimens was 850ºC and 75MPa. Samples that had rupture lives comparable to the base compositions were then tested at 750ºC and 140MPa. As-cast material and creep-tested specimens were sectioned, mounted, and polished for microstructural evaluation (unetched) in the SEM using BSE imaging. Energy dispersive X-ray spectrometry (EDS) was performed on areas, phases, and constituents of interest.

Results

The tensile results for the base and modified CF8C-Plus steel castings are given in Table 2. At room temperature, the yield strength (YS) of the base+W and base+Cu was comparable with the base, while the base+B was 8% lower and the base+Al was 22% lower. For room temperature ultimate tensile strength (UTS), the base+Cu was comparable to the base, while the base+B and base+W were lower by about 8% and the base+Al was lower by 15%. At 850ºC, the YS and UTS trend was similar, with both the base+W and base+Cu modified steels being similar to the base, while the base+B was reduced by 6 and 5%, respectively, and the base+Al was 19 and 24% lower, respectively.

Table II. Tensile Properties of Modified CF8C-Plus Alloys

	25ºC			850ºC		
	YS (MPa)	UTS (MPa)	Elong. (%)	YS (MPa)	UTS (MPa)	Elong. (%)
Base	291	655	44.0	151	231	25.5
+B	267	608	34.9	145	220	29.7
+W	298	604	28.0	153	233	29.0
+Cu	283	667	43.3	153	231	25.7
+Al	227	555	40.4	123	176	24.2

Figure 2 shows the creep strain versus time curves for creep tests performed on all heats at 850ºC and 75MPa. The rupture life of base CF8C-Plus composition was 185.0 hours. Differences in creep strength were observed that closely matched the trends in the tensile results at 850ºC. The base+W lasted 181.3 hours and the base+Cu lasted 192.8 hours. However, the base+B had a life of 84.1 hours (45% of base) and the base+Al had a life of 34.7 hours (19% of base). Figure 3 shows the creep curves for the base, base+Cu, and base+W for 140MPa and 750ºC. Here the base and base+W have comparable lives (342 and 342.4 hours respectively) while the Cu shows a small increase (471.8 hours) in creep-rupture life. For both creep tests, it appears the base+Cu showed an increase in creep strength, an improvement in creep resistance (lower creep-rate), and a small decrease in ductility compared to the base and base+W.

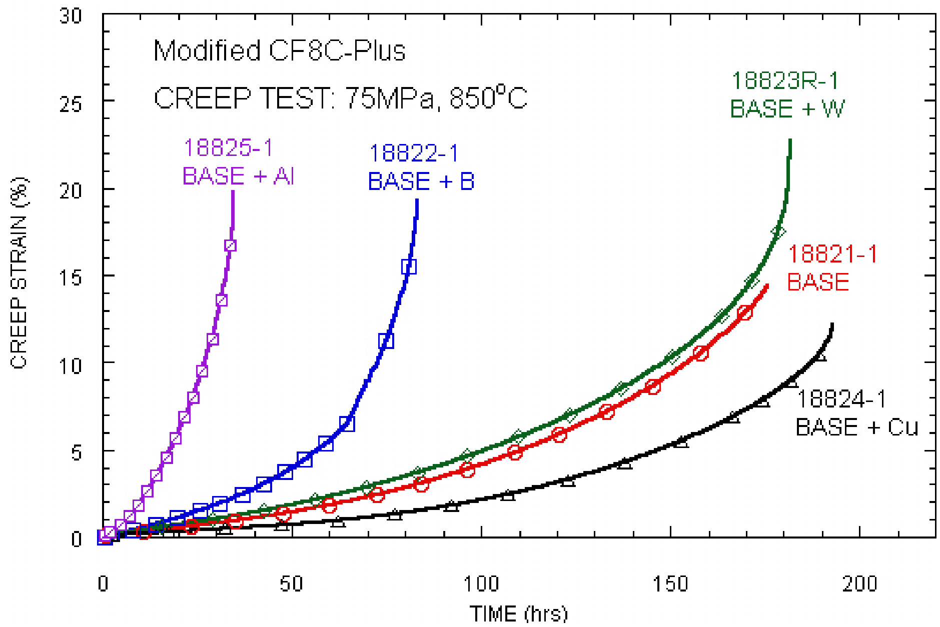


Figure 2. Creep strain vs. time curves for modified CF8C-Plus castings compared to CF8C-Plus alloy (base composition) tested at 850ºC and 75MPa

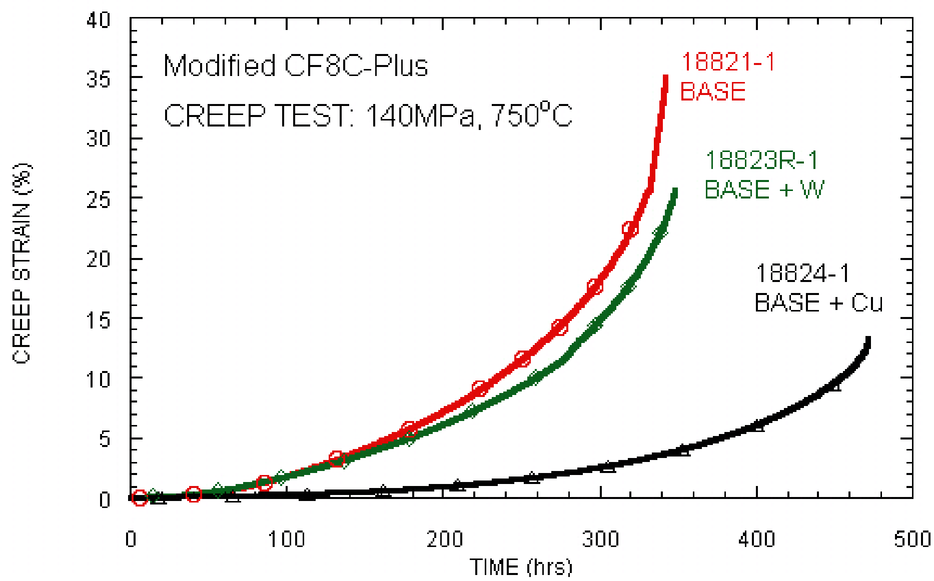
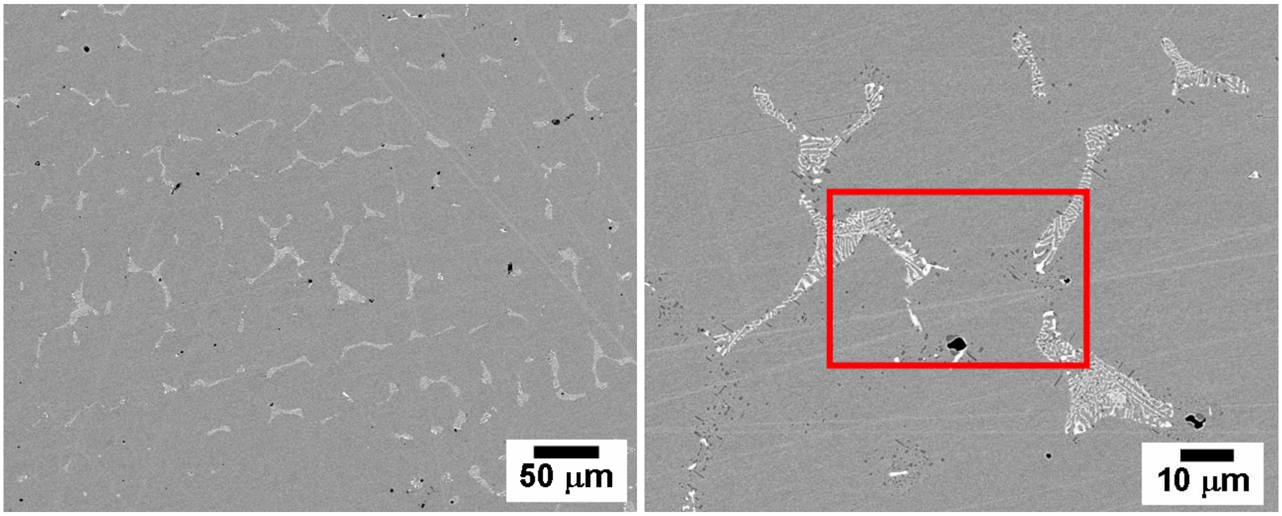


Figure 3. Creep strain vs. time curves for the alloys tested at 750ºC and 140MPa

The general microstructure of the base CF8C-Plus is shown in the BSE images in figure 4. The as-cast structure has a dendrite spacing on the order of 50µm, figure 4 (a), with a small number of inclusions well less than 5µm in diameter dispersed in some of the interdendritic regions. After creep testing at 850ºC and 85MPa, three different microconstituents have been identified in the interdendritic regions. These are shown in figure 5. The high Z-contrast (white) phase is NbC, the gray precipitates are $M_{23}C_6$ carbides, and the black inclusions are MnS. This microstructure was consistent for all the different casting with the exception of the base+Al alloy. In general, no large differences were quantified for the overall dendrite spacing in the different castings.



(a) (b)

Figure 4. SEM BSE image of CF8C-Plus base composition after creep testing at 850ºC and 75MPa.

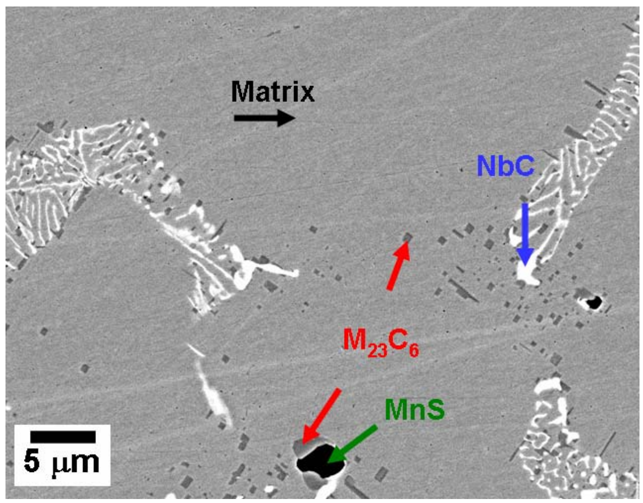


Figure 5. SEM BSE image from figure 4 (b) of CF8C-Plus base composition after creep testing at 850ºC and 75MPa. Interdendritic microconstituents and inclusions are identified by EDS.

A BSE image of the base+Al after creep testing at 850ºC and 75MPa is shown in figure 6. As evident in image (a), a large number of larger inclusions are observed throughout the steel matrix. These are shown more clearly in (b) where the size is on the order of 10 to 15μm. Small MnS inclusions are still present, but as identified in (c), these large inclusions are AlN particles. The interdendritic regions also show a change in structure. These regions are smaller compared to the other castings and, although they contain the same carbides, the carbide structures are different.

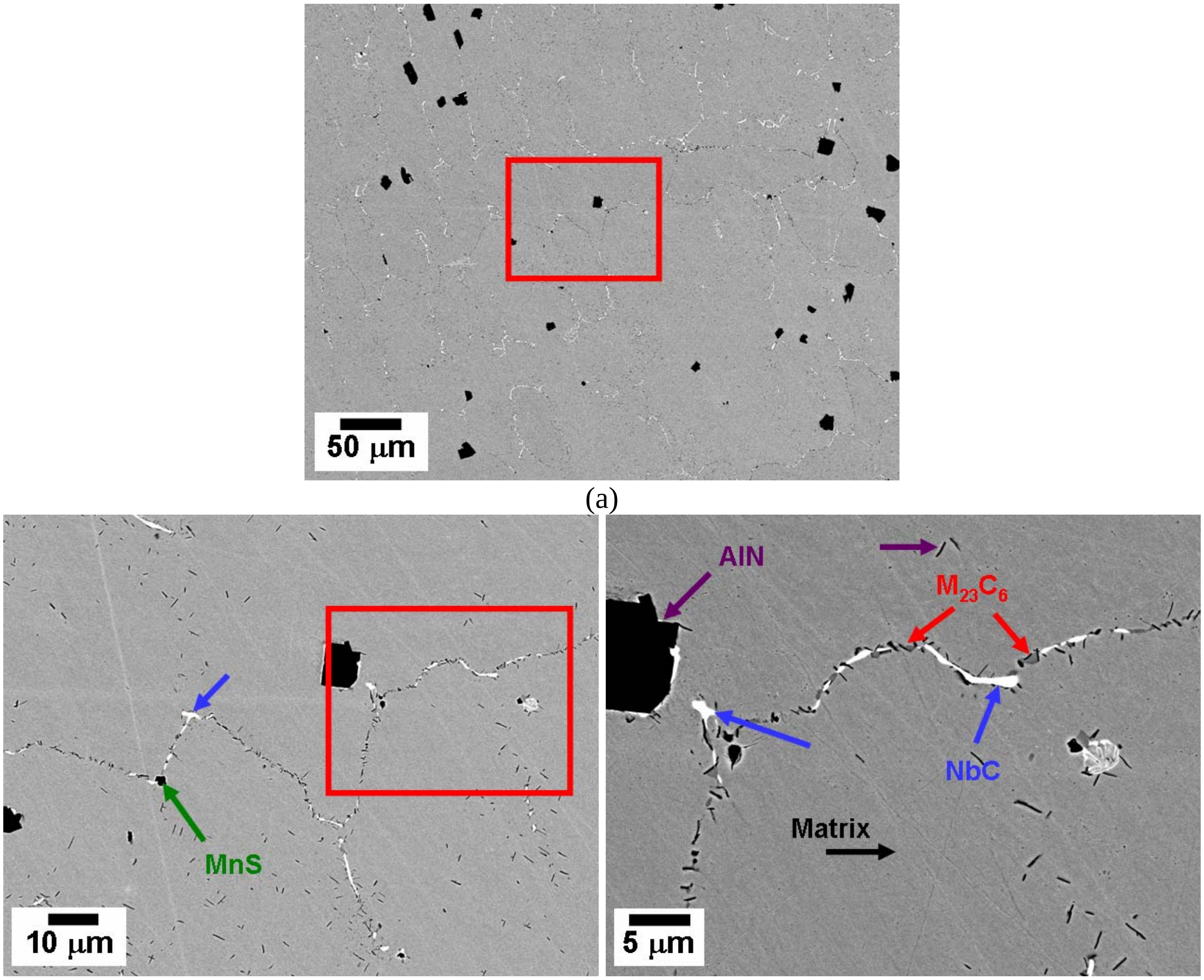


Figure 6. SEM BSE Images of base+Al after creep testing at 850ºC and 75MPa. Figure (a) shows the general microstructure including 10 to 25 μm inclusions, (b) is a high-magnification image of the region identified in (a), and (c) is a high-magnification image of the region in (b). The large inclusions are identified as AlN by EDS analysis.

A summary of the EDS analyses done on the alloys after creep testing at 850ºC and 75MPa is given in Table III. For the matrix and the different microconstitiuents, each element identified in the EDS spectra is listed. For all alloys: Fe, Ni, Cr, and Mn are present in the matrix, Cr, Fe, and Mn are in the $M_{23}C_6$ carbides, Nb is the only element identified in the NbC, and Mn and S are identified in the MnS. For the base+B, the X-ray EDS spectra for some of the MnS inclusions also contained Si. For the base+W, W was associated with the $M_{23}C_6$ carbides, and not with the overall matrix. By contrast, Cu was only identified in the matrix of the base+Cu. Finally, Al and N were identified in the AlN inclusions in the base+Al. N is not easily detected in the matrix using X-ray EDS, even with a windowless detector, but the identification of N in the AlN particles is clear because the concentration in such nitrides is high.

Table III. Qualitative Compositional Results (identified elements) for X-ray EDS analysis of all alloys (including microconstitiuents and matrix) after creep testing at 850ºC and 75MPa

Alloy	Matrix	Interdendritic & Intergranular		Inclusions	
		$M_{23}C_6$	NbC	MnS	AlN
Base	Fe, Ni, Cr, Mn	Cr, Fe, Mn	Nb	Mn, S	none
Base+B	Fe, Ni, Cr, Mn	Cr, Fe, Mn	Nb	Mn, S, Si	none
Base+W	Fe, Ni, Cr, Mn	Cr, Fe, Mn, W	Nb	Mn, S	none
Base+Cu	Fe, Ni, Cr, Mn, Cu	Cr, Fe, Mn	Nb	Mn, S	none
Base+Al	Fe, Ni, Cr, Mn	Cr, Fe, Mn	Nb	Mn, S	Al, N

Discussion

Base+B

The addition of 0.005 wt% B caused a reduction in tensile strength and creep strength in the CF8C-Plus steel. Electron microscopy did not show any large microstructural differences between the base and base+B. B cannot be detected by X-ray EDS unless large quantities of B (50wt% or higher) are present, so there was no way to observe subtle B effects in this work. It is possible that the B removed some N from the matrix by forming BN precipitates, but with only 0.005wt% B this would only affect a small amount of the N. A second possible B effect is the size of the nano-structured NbC in the matrix. TEM analysis comparing the nano-sized NbCs present in the base+B matrix with the NbCs in the base matrix would be needed to study this effect.

Base+W

The addition of approximately 0.5 wt% W had no noticeable effect on the tensile and creep properties of the base alloy. The EDS results, Table III, identified the W with the $M_{23}C_6$ carbides. W is typically observed to enrich $M_{23}C_6$ particles and stabilize them when added to 9-12Cr ferritic steels [10]. Although no short-term mechanical properties were improved with the addition of W, the result is promising because $M_{23}C_6$ carbides containing some W have been shown to be more stable (resist coarsening) compared to $M_{23}C_6$ without W [5,6]. W would also be expected to provide the similar solid solution strengthening to Mo in the CF8C-Plus steel.

Base+Cu

The addition of 2.5 wt% Cu improved the creep resistance of the CF8C-Plus at 750 and 850ºC. A modest improvement in rupture life was observed at 750ºC, but no change was observed in tensile behavior. Substantial research has shown that the addition of 3% Cu improves the high temperature tensile strength and creep properties of MC forming stainless steels, but has little effect on the room temperature tensile strength [8]. It is generally thought that Cu does not provide solid solution strengthening in stainless steels because the lattice parameter mismatch between Cu and austenite is small [13], so room temperature properties do not improve with Cu additions. Sawargi and Hirano [14] have observed nano-scale Cu precipitates in a lean austenitic stainless steel when more than 2.5% Cu was added. Wu et al [13] confirmed the presence of nano-scale Cu-rich precipitates ranging from 15 to 50 nm in diameter after aging Super 304H, a copper-bearing austenitic stainless steel, at 700ºC for various times. It does appear that the addition of Cu to the cast CF8C-Plus steel has the same effect as shown in various wrought alloys. The creep test and high-temperature tensile test at 850ºC did not show a strength advantage for the base+Cu compared to base, while the creep test at 750ºC did show a significant improvement in creep strength. Most of the creep and tensile data available on the Cu effect in stainless steels are available below 800ºC. Based on the limited data, it appears that the Cu strengthening effect in CF8C-Plus steel is limited to temperatures below 850ºC.

Base+Al

The addition of 1.3% Al had a detrimental effect on tensile and creep properties of the CF8C-Plus steel. Figure 6 shows the presence of large AlN inclusions. These AlN particles also reduce the level of N in the matrix, and hence decrease the overall strength of the CF8C-Plus steel. Comparing the creep strength of the base+Al to the base composition, figure 2, is roughly equivalent to the creep-rupture strength difference between the standard CF8C and CF8C-Plus shown in figure 1, indicating the reduction in N due to AlN particles reduces the strength of the CF8C-Plus steel to the level of CF8C steel which does not contain N.

Conclusions

The effects of four alloying additions, B, W, Cu, and Al, on CF8C-Plus steel were investigated. The addition of B reduced the tensile strength and creep strength of the CF8C-Plus steel. No clear evidence for this loss of strength was observed by microstructural analysis using SEM and EDS. The addition of W did not affect the mechanical properties of the CF8C-Plus steel, but W enrichment was identified with the $M_{23}C_6$ carbides. This may have a beneficial effect on the long-term stability these carbides. The addition of Cu improved the creep strength of the alloy at 750ºC, which is consistent with Cu additions to wrought stainless steel alloys. The limited data in this study did not show a strengthening effect of Cu at 850ºC. The addition of Al was particularly detrimental to the room temperature and elevated temperature properties of CF8C-Plus. Large AlN inclusions were identified throughout the casting. These AlN particles reduced the N in the austenite matrix of the base metal and caused a loss in tensile and creep strength. The results of this study show that additions of Cu and W both have the potential to improve the high-temperature tensile and long-term creep strength of CF8C-Plus.

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