Enhanced Long term Creep Strength of SUS 347 Stainless Steel through the Self-Healing Effect of Creep Cavity

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The failure in metals and alloys used in high temperature services proceeds with the nucleation, growth and interlinkage of grain boundary creep cavities. Suppressing the creep cavitation by self-healing process it is expected to improve the rupture life of heat resisting alloys. By preventing the segregation of S on cavity surface through the addition of Ce, it may be possible to precipitate out BN on cavity surface to suppress the cavity growth in alloy containing B and N during creep exposure. Alloy chemistry of SUS 347 stainless steel has been modified through the addition of minor alloy elements B, Ce and N to improve its long term creep strength. Initial creep results indicate an improvement of long term creep strength of the alloy over SUS 347. Possible reasons for the improvement have been discussed.

Key words: 347 stainless steel, creep cavitation, self-healing effect and B, N and Ce addition

INTRODUCTION

Austenitic 18Cr-8Ni stainless steels have better strength and oxidation resistance at high temperatures than low-alloy and carbon steels, and are less expensive than Ni-base alloys. For this reason they have been used for high-temperature components, such as superheater and reheater tubings of conventional fossil fuel fired boilers, reformer tubings of chemical and petrochemical plants, and high-temperature parts of nuclear reactors. They have a service life of several years. Creep fracture determines the life of such components. There is an ever ending need to improve the higher-temperature creep strength of such steels so as to increase the thermal efficiency of the plants thereby reducing the environmental pollution. Creep fracture proceeds with the nucleation, growth and linkage of cavities and cracks on grain boundary. By suppressing the nucleation and growth of grain boundary creep cavities it may be possible to increase the creep strength of such alloys. Grain boundary segregation of impurity elements particularly O and S even at low ppm level causes high temperature embrittlement because of the lowering of grain boundary surface energy thereby increasing the creep cavitation [1]. These impurities must be controlled either by removal during melting or by alloying to increase the creep strength. Minor addition of REM like Ce is found highly effective in removing O and S from the steel through the formation of cerium-oxy-sulphide [2]. B has a beneficial effect on the creep resistance of austenitic stainless steels [3], but the reason is not yet completely understood. In most instances it is assumed that the B is concentrated on the grain boundaries where it enters the precipitates and alters the character of the grain boundary / precipitate interface or matrix / precipitates interface in such a way to suppress the microcavity formation. More recently Shinya et al [4] have put forward a novel idea of suppression of creep

cavity growth through the addition of B, N and Ce in the steel. In the absence of S segregation, B segregates on the tiny creep cavity surface and forms BN compounds. BN compounds on the cavity surface reduces the surface diffusion thereby the cavity growth rate. Conceptually the idea of the enhancement of creep resistance of steel through the addition of B, N and Ce is shown in fig.1.

This study is concerned with the creep strength of SUS 347 stainless steel modified with the addition of N, B and Ce. This is a preliminary report of the investigation. Enhanced creep strength of the steels over the conventional SUS 347 steel has been discussed in light of suppression of creep cavitation by the addition of N, B and Ce.
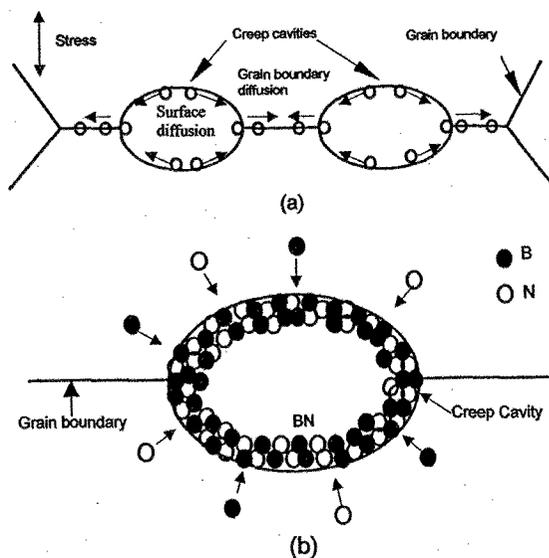
Fig.1 (a) Controlling process for creep cavity growth;
(b) Self-healing mechanism of creep cavity growth

Table 1 Chemical composition of the steel (wt%)

Alloy	C	Si	Mn	P	S	Cr	Ni	Nb	N	B	Ti	Ce
A1	0.080	0.59	1.68	0.001	0.002	17.96	12.04	0.41	0.077	-	-	-
A2	0.078	0.68	1.67	0.001	0.002	18.15	11.90	0.38	0.072	0.069	-	0.016
A3	0.060	0.61	1.66	0.001	0.002	17.66	12.01	0.37	0.073	0.062	0.096	0.013
NRIM Max*	0.053	0.63	1.81	0.027	0.011	17.56	12.24	0.87	0.022	0.003	0.019	-

* + Cu – 0.14, V – 0.041, Co – 0.3

EXPERIMENTAL DETAILS

Three steels of chemical compositions shown in Table-1 were melted in vacuum arc furnace. Table 1 also shows the chemical composition of the best SUS 347 stainless steel of NRIM data sheet [5], for comparison purpose. The chemical composition of the SUS 347 stainless steel has been modified with the addition of (wt %) 0.07 % B, 0.08 % of N and 0.01 % of Ce. The Nb content has been reduced from 0.8 % in SUS 347 stainless steel to 0.4 % to enhance the long-term creep strength through a new concept called "under-stabilizing" effect [6,7]. Also a minor amount of Ti (0.1 %) has been added with the intension of increase in rupture ductility. As received steels were solution heated at 1160, 1180 and 1200 °C for 20 minutes after 36 % cold swaging. Creep rupture tests at 750 °C over a stress range of 69 – 118 MPa have been carried out on the steels both in the as-received as well as heat treated conditions. Creep tests at lower applied stresses are in progress. Optical and SEM metallography was carried out on the steels both before and after the creep tests. SIMS (Secondary Ion Mass Spectrography) analysis was carried out to observe the B distribution in the steels.

RESULTS AND DISCUSSION

Optical photograph of the steels in solution treated at 1160 °C is shown in Fig.2. Uniform austenitic grain size of around 40 μm was observed in all the steels. As-received steel were found to have nonuniform grain size. Second phase segregation was observed in the B treated steels. SIMS analysis indicated that B is associated with Cr, C and N. Excess B in the steel than its solubility limit might have precipitated out as BN particles during cooling after solution treatment or dissolved in $M_{23}(C,N)$ precipitates. S, C, N and Ti were found to be associated with, probably they form tanium carbo-nitro-sulphide $Ti_4(C,N)_2S_2$ [8] to remove the S from the matrix.

The variation of the creep rupture life of the steels with applied stress is shown in Fig.3. Addition of small amount of B and Ce (steels A2 and A3) has remarkable effect on the creep strength of the steel. Creep strength of the steel has increased with the addition of B and Ce, effect of which is more at longer creep exposure. The variation of creep strength with rupture life follows the equation $\sigma = A\, t_r^{-n}$, with n = 0.18 for the steel A1, 0.12 – 0.15 for the steel A2 and 0.12 – 0.13 for the steel A3. The value of 'n' decreased with B addition, indicating less accumulation of creep damage with creep exposure in steel with B leading to higher creep strength.
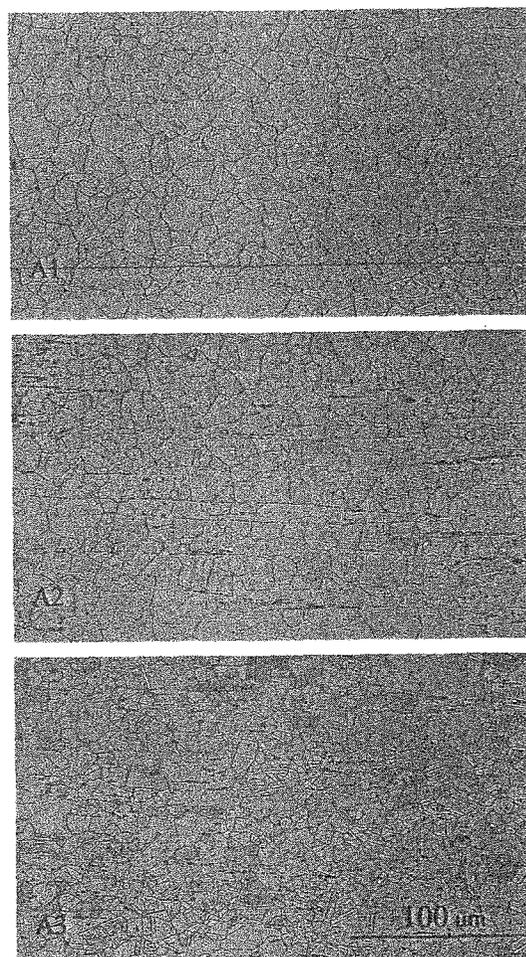
Fig.2 Optical micrograph of the steels

Creep ductility of the steels is shown in Fig.4. Addition of B and Ce increased the creep ductility of the steels along with creep strength. B-containing steel with Ti addition appears to possess higher creep ductility, may be because of more efficient removal of S by the formation of titanium carbosulphide $Ti_4C_2S_2$.

Metallographic investigation of the failed creep specimens indicated both the intergranular creep cavitation as well as surface cavitation in the steels (Figs.5 and 6). Extensive creep damage in terms of intergranular cavities and cracks was observed in the steel A1 without B. Addition of B in steel A2 and A3 has increased the resistance to creep cavitation and hence the creep strength. At lower applied stresses,

Grain size 1 — 1160 °C for 20 minutes / WQ
Grain size 2 — 1180 °C for 20 minutes / WQ
Grain size 3 — 1200 °C for 8 minutes / WQ   As on 31.1.2003
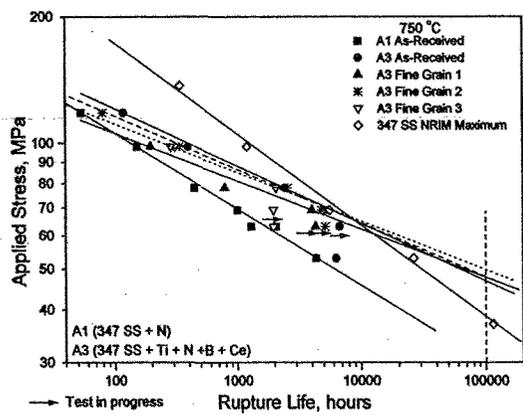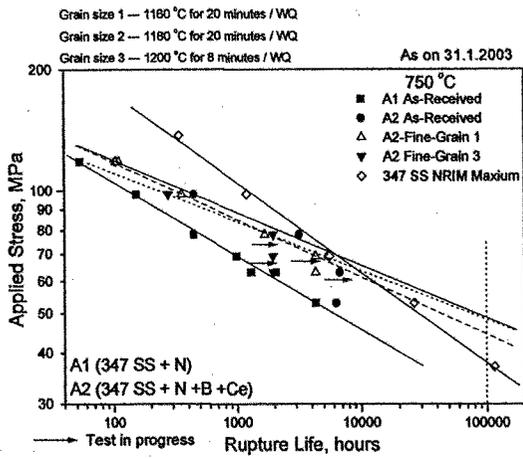
Fig.3 Creep rupture strength of the steels A2 and A3 as compared with those of steel A1 and SUS 347 SS
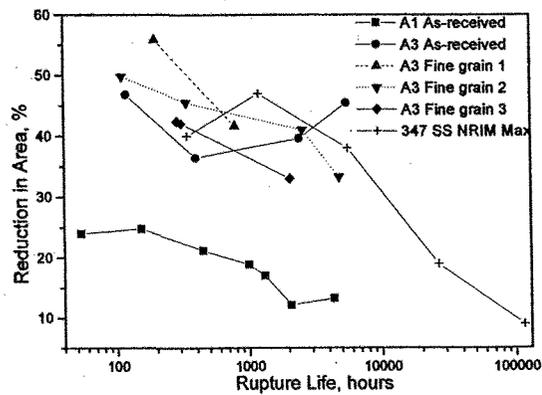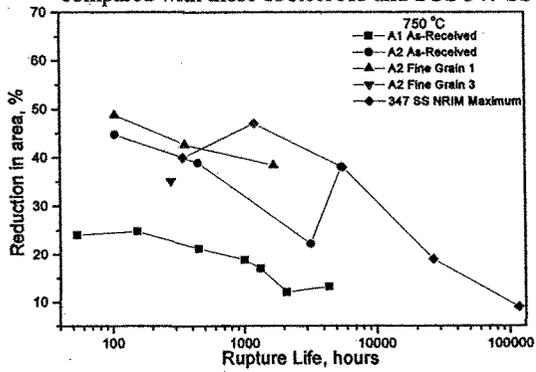
Fig.4 Variation of reduction in area % of the steels with rupture life
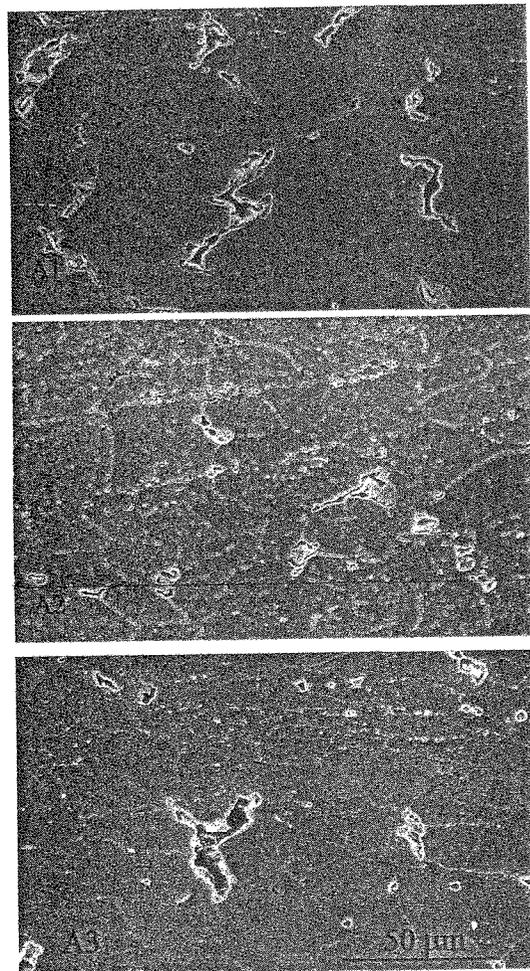
Fig.5 SEM micrograph showing creep cavitation in the steels, creep tested at 69 MPa, 750 °C
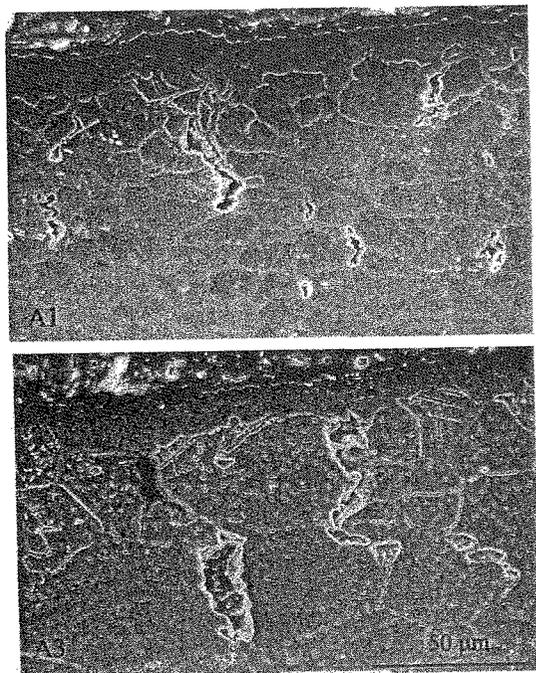
Fig.6 SEM micrograph showing surface cracks in the steels, creep tested at 69 MPa, 750 °C

surface cracking was observed in all the steels (Fig. 6). Surface cracking was found to be relatively more abundant in the B-containing than the creep cavitation. Redissolution of grain boundary $M_{23}C_6$ carbides accompanying the precipitation of σ-phase at grain boundary accelerate grain boundary sliding and initiated the surface cracking [9]. σ-phase formation was found to be relatively less abundant in the B-containing steels than in B-free steel and many cracks are found to be associated with the σ-phase (Fig.7). In B-containing steel, the partial substitution of carbon in $M_{23}C_6$ by B increases it's lattice parameter [8], thereby reduces the mismatch with the austenite and increases its stability against transformation to σ-phase. Surface cracking in the B-containing steel may be partly due the loss of B near the surface by evaporation which in turn increases the grain boundary sliding and cracking.
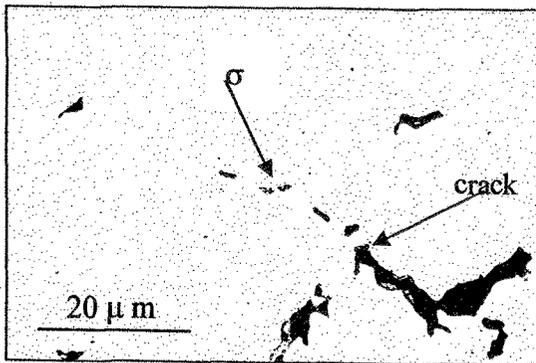
Fig.7　Optical micrograph showing σ-phase (as revealed by KOH etching) associated with the creep cavities of steel A1 tested at 69 MPa

The developed B-containing steels even though possessed lower creep rupture life at higher applied stresses, are expected to have superior creep strength at longer creep exposure than the SUS 347 stainless steel in NRIM creep data sheet (Fig.3). Lower Nb contain of the developed steel than that of SUS 347 stainless steel may be the reason of its lower creep strength at shorter creep exposure. However at long creep exposure when the creep cavitation is the main reason of creep fracture,

suppression of creep damage with addition of the B, N and Ce increases the creep strength of the steel. Observation of the formation of BN as revealed by SIMS study indicates the possible formation of BN particles on the cavity surface to suppress its growth thereby increases the long term creep strength of the steels. However more study is needed to confirm this. An increase of 10 MPa in the 10^5 hours creep strength at 750 °C is expected for the developed steels over that of SUS 347 stainless steel in NRIM creep data sheet [5].

CONCLUSIONS

B, N and Ce addition in SUS 347 stainless steel increased the creep of the steel coupled with the increase in creep ductility. Long term creep strengths of the steels are expected to superior than that of SUS 347 stainless steel.

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