Transactions of the Materials Research Society of Japan. Vol. 20

Effect of alloy elements on creep rupture strength of conventional heat resistant steels

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In order to achieve ecomaterials for conventional heat resistant steels, effect of constituent and/or trace elements on creep rupture strength has been investigated for STBA24, STBA26 and SUS304HTB. Mo can be reduced from 1.0% to 0.8% without decreasing creep rupture strength of STBA24. The addition of 0.05%V as the impurity element increases creep rupture strength of STBA26. The addition of 0.0015%B as the impurity element raises creep rupture strength of SUS304HTB. These results suggest that it is possible to achieve ecomaterials for STBA24, STBA26 and SUS304HTB by reducing constituent elements or addition of minor alloy elements.

1. INTRODUCTION

Big environmental loads are given to the society in the high energy consumption industries and it is hoped to apply ecomaterials harmonized with the environment in the future.

In general, ecomaterials are considered the materials which is suitable for recycling. However, performance and making to long life using contribute to reduction of environmental loads rather than recycling for heat resistant steels. That is, the construction of plants, where the operating life is long and the energy efficiency is high, will be possible by developing the material which can maintain excellent high temperature strength for a long time. That reduces environmental loads from the point of view of energy conservation and saving resources. Moreover, if high temperature strength which is comparable with that of conventional steels is able to achieve by addition of a minimum of alloy elements, it is possible to conserve alloy elements and environmental loads can be reduced.

In order to achieve ecomaterials for conventional heat resistant steels by making them high performance or conserving alloy elements, it is necessary to clarify the controlling factors which affect creep strength depending on time, because these heat resistant steels are used for over 100,000 hours (about 11 years).

It is often reported that the long term creep rupture strength is changed by impurity or minor alloy elements. However, few systematic researches or creep databases about these phenomenon have been reported. Then, the effect of alloy elements on creep rupture strength of conventional heat resistant steels has been studied. STBA24(2.25Cr-1Mo), STBA26(9Cr-1Mo) and SUS304HTB(18Cr-8Ni), which are popular steels for thermal power boilers, were chosen for investigation. The creep database of these steels[1)] was analyzed, so the followings became clear; The long term creep rupture strength of STBA24 was affected by Mo. That of STBA26 was influenced by V. That of SUS304HTB was changed by B. V and B were contained as impurities.

Therefore, in the present work, the effect of Mo on STBA24, that of V on STBA26 and that of B on SUS304HTB have been investigated.

2. EXPERIMENTAL PROCEDURE

The chemical compositions and heat treatments of the steels tested are shown in Table 1. Mo content for STBA24, V content for

Table 1 Chemical compositions of the steels tested.

steel	mark	C	Si	Mn	P	S	Ni	Cr	Mo	V	B	N
STBA24	CM1	0. 100	0. 40	0. 46	0. 015	0. 001	–	2. 30	0. 51	–	–	0. 012
	CM2	0. 110	0. 40	0. 46	0. 015	0. 001	–	2. 29	0. 79	–	–	0. 013
	CM3	0. 093	0. 40	0. 46	0. 015	0. 001	–	2. 36	1. 03	–	–	0. 012
STBA26	CR1	0. 110	0. 62	0. 46	0. 017	0. 001	–	9. 01	0. 99	–	–	0. 015
	CR2	0. 100	0. 60	0. 45	0. 017	0. 001	–	9. 20	1. 02	0. 050	–	0. 016
	CR3	0. 100	0. 58	0. 44	0. 019	0. 001	–	9. 15	0. 97	0. 080	–	0. 014
SUS304 HTB	ST1	0. 064	0. 50	1. 39	0. 015	0. 002	9. 37	17. 66	–	–		0. 031
	ST2	0. 066	0. 50	1. 45	0. 017	0. 002	9. 72	18. 21	–	–	0. 0015	0. 032
	ST3	0. 068	0. 49	1. 48	0. 019	0. 002	9. 75	18. 19	–	–	0. 0033	0. 033

STBA24 : 920℃×0. 5h A. C. → 730℃×1h A. C.
STBA26 : 920℃×0. 5h A. C. → 760℃×1h A. C.
SUS304HTB : 1100℃×15min. W. Q.

STBA26 and B content for SUS304HTB were changed systematically. These steels were prepared by vacuum induction melting. All ingots were forged and processed to the plates before heat treatment.

Creep rupture specimens with 6mm in diameter and 30mm in gauge length were machined from these plates. Creep rupture tests were carried out in air. Charpy impact values after aging were also investigated. STBA24 and STBA26 were aged at 500-650℃ for 3000 hours. SUS304HTB was aged at 600-750℃ for 3000 hours.

3. RESULTS

3.1 Creep rupture strength

Fig. 1 shows the creep rupture strength of the STBA24 steels. The creep rupture strength at 500-600℃ of them decreases clearly when the amount of Mo is decreased to 0.5% (CM1). However, there is little difference in the creep rupture strength between 0.79Mo steel (CM2) and 1.0Mo steel (CM3). This suggests that the creep rupture strength which is comparable with 1.0Mo steel (CM3) can be obtained even if the amount of Mo is decreased to about 0.8%. The creep rupture elongation of the STBA24 steels increases with decreasing Mo content.

Fig. 2 shows the creep rupture strength of the STBA26 steels. It is noted that the creep rupture strength of short time side at 550-600 ℃ rises as the amount of V increases. Though

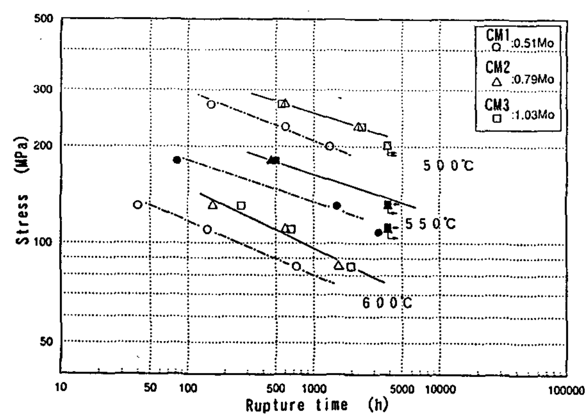


Fig. 1 Creep rupture strength of STBA24.

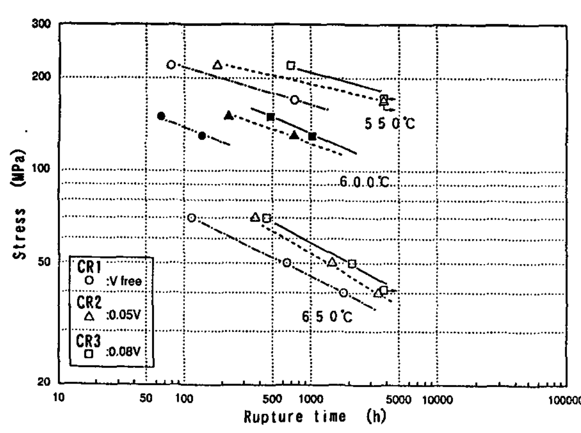


Fig. 2 Creep rupture strength of STBA26.

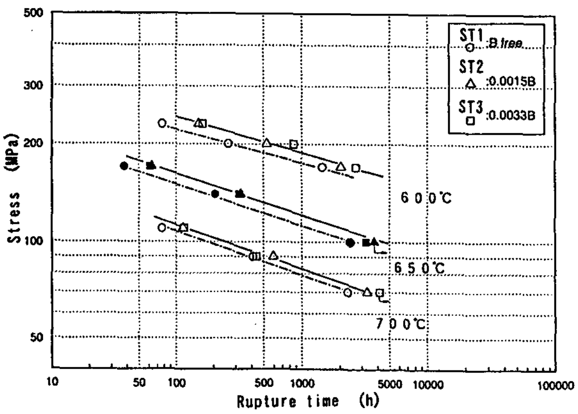


Fig. 3 Creep rupture strength of SUS304HTB.

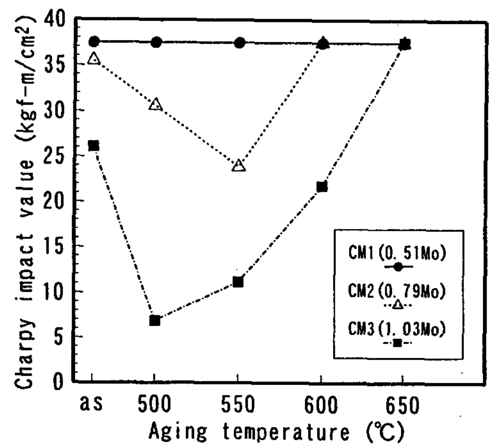


Fig. 4 Charpy impact properties at 0 ℃ of STBA24 after 3000h aging.

the V addition to the STBA26 is also effective for increasing creep rupture strength in longer time side at 600-650℃, the strength change between 0.05V steel (CR2) and 0.08V steel (CR3) is small. The creep rupture elongation of the STBA26 steels at 550℃ decreases with the addition of V, but there is no differences in that at 650℃ between V addition steel and V-less steel.

Fig. 3 shows the creep rupture strength of the SUS304HTB steels. It is found that the creep rupture strength at 600℃ rises as the amount of B increases. The effect of B on strength improvement is small at 650℃ or more.

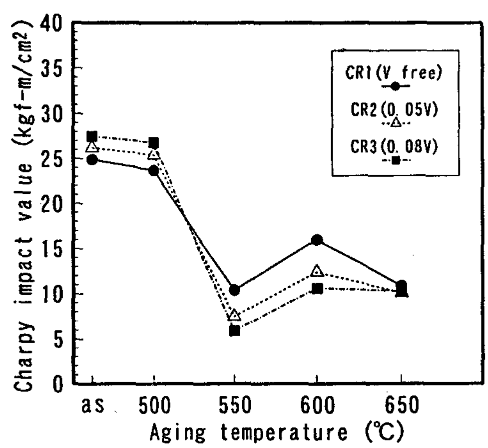


Fig. 5 Charpy impact properties at 0℃ of STBA26 after 3000h aging.

3.2 Toughness after aging

Fig. 4 shows the Charpy impact property of the STBA24 steels aged for 3000 hours. It is found that the Charpy impact values at 0℃ increase remarkably with decreasing Mo content. The Charpy impact values haven't decreased by aging at 550-650℃ in 0.5Mo steel (CM1) at all. The impact values of 0.79Mo steel (CM2) decrease most at 550℃. However, it shows enough toughness compared with 1.0Mo steel (CM3).

Fig. 5 shows the Charpy impact property of the STBA26 steels aged for 3000 hours. It is noted that the Charpy impact values at 0℃ decrease largely by the aging at 550℃ or more. Those decrease as the V content increases. However, the impact values of 0.08V steel (CR3) are values without the problem on

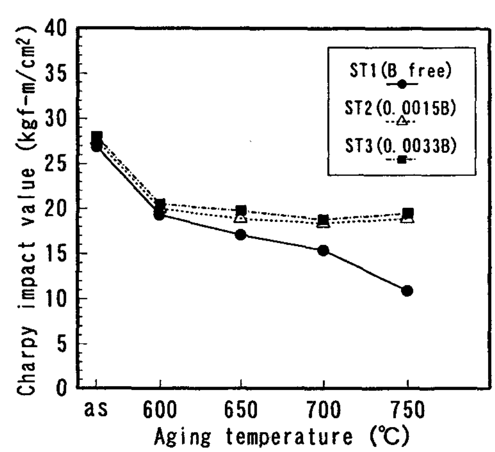


Fig. 6 Charpy impact properties at 0℃ of SUS304HTB after 3000h aging.

practical use.

Fig. 6 shows the Charpy impact property of the SUS304HTB steels aged for 3000 hours. It is found that the Charpy impact values at 0℃ have been improved significantly by the addition of 0.0015% or more B. This effect is remarkable as the aging temperature rises.

4. DISCUSSION

4.1 Effect of Mo on creep rupture strength of STBA24

The extracted residues of aged and unaged materials were investigated in order to clarify the effect of Mo on creep rupture strength. It has been identified that there was a big difference in the amount of Mo in extracted residues depending on the Mo content, though there was little difference in the amount of Cr, Fe and Mn. Then, the amount of solute Mo in aged and unaged materials obtained from extracted residues analysis is shown in Fig. 7.

It is found that the amount of solute Mo in unaged materials decreases with decreasing Mo content. However, there is little difference in the amount of solute Mo depending on the difference of Mo content after the aging at 650 ℃ for 3000 hours. Fig. 8 shows the amount of Mo precipitated in the aging. It is noted that the difference in the amount of precipitated Mo between the 0.79Mo steel (CM2) and the 1.0Mo steel (CM3) is relatively small, though the amount of precipitated Mo decreases as the Mo content reduces. These results indicate the low creep rupture strength of 0.5Mo steel (CM1) originates from the fact that the amount of precipitation of carbide, which contains Mo, is little. It is also suggested that the creep rupture strength difference between 0.79Mo steel (CM2) and 1.0Mo steel (CM3) is small because the difference of the amount of the carbide precipitation in those steels is small.

TEM observation of extracted replica for the aged materials was performed in order to clarify the precipitation behavior. It has been revealed that fine feather like M_2C and relatively coarse plate like $M_{23}C_6$ or M_7C_3 precipitated in the tempered bainite region and M_2C and M_6C also precipitated in the ferrite region. M_2C, which mainly consists of Mo and

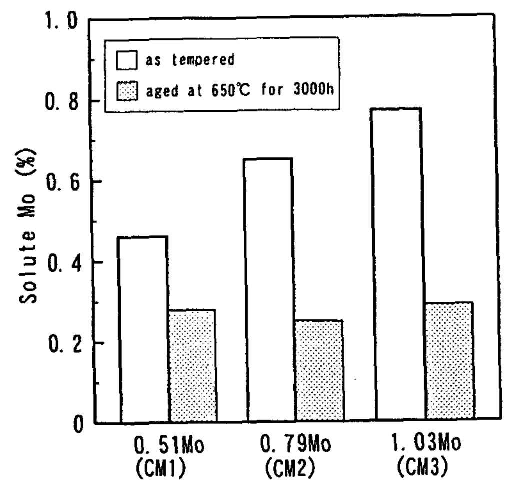


Fig. 7 The amount of solute Mo.

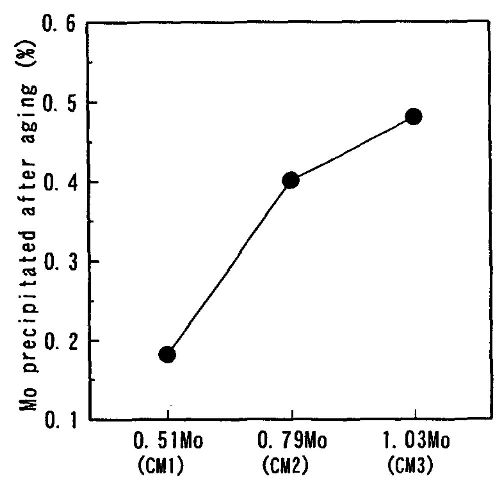
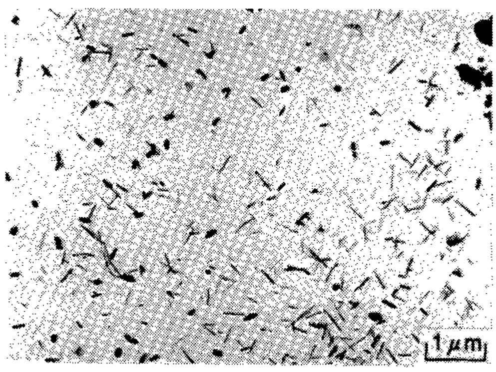
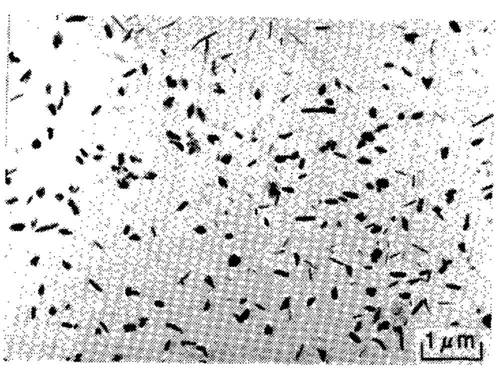


Fig. 8 The amount of Mo precipitated after 3000h aging at 650℃.

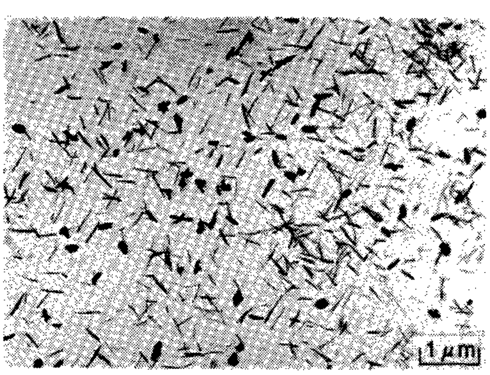
Cr, precipitates during creep and contributes to creep strength by interaction with dislocations[2]. Fig. 9 shows the TEM micrographs of extracted replica for the aged materials. It is noted that the amount of precipitation of M_2C and M_6C in the 0.5Mo steel (CM1) is less than the others. Moreover, the difference in the amount of precipitation between 0.79Mo (CM2) steel and 1.0Mo (CM3) steel is small. These results correspond to the results of extracted residues analysis. Then, it is considered that the difference in the creep rupture strength is caused by the difference in the amount of carbides which mainly consist of Mo.



0.5Mo (CM1)



0.79Mo (CM2)



1.0Mo (CM3)

Fig. 9 TEM micrographs of extracted replica for STBA24 aged at 500℃ for 3000h.

4.2 Effect of V on creep rupture strength of STBA26

Fig. 10 shows the result of extracted residues analysis of aged and unaged materials.

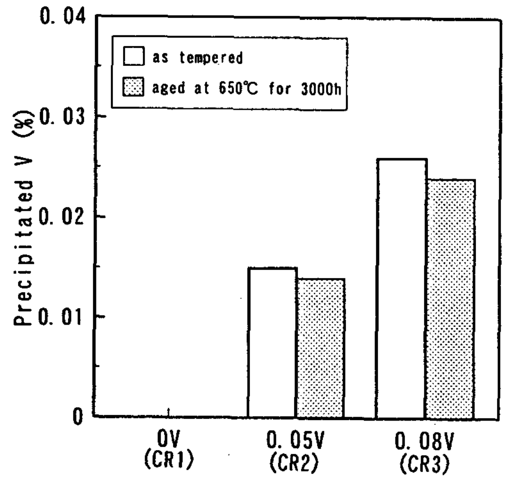


Fig. 10 The amount of V precipitated as carbides or nitrides.

No difference has been identified in the amount of residues except V. It is found that the vanadium carbides or nitrides precipitate in the unaged materials containing V (CR5, CR6). The amounts of precipitates increase with increasing V content. The same tendency has been identified in the aged materials.

$M_{23}C_6$, M_7C_3 and M_6C have been observed in the aged materials by extracted replica. A fine V(C, N) observed in the mod. 9Cr-1Mo steel[3], which contains V and Nb, has not been identified in this observation. Though further detail observation is necessary to clarify the presence of V(C, N), it is clear that the carbides or nitrides which contain V precipitate in the V addition steels during the temper.

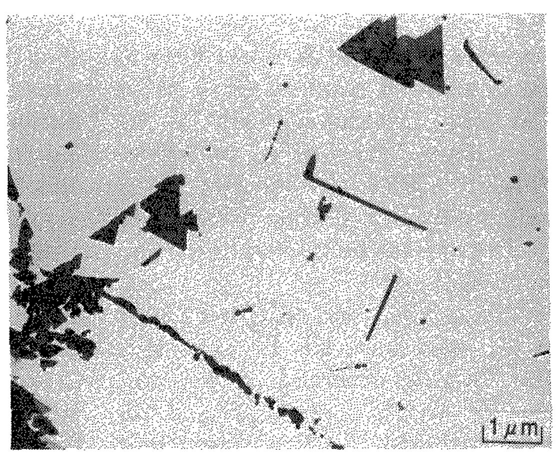
These results suggest that the carbides and/or nitrides containing V, which precipitate in the tempering, improve the creep rupture strength of V addition steels.

The creep rupture strength of the 0.05V steel (CR2) and the 0.08V steel (CR3) in the high temperature and the long time side becomes close as shown in Fig. 2. It is supposed that the carbides and/or nitrides coarsening contributes to this behavior, because little difference has been identified in the amount of V residues of aged and unaged materials as shown in Fig. 10.

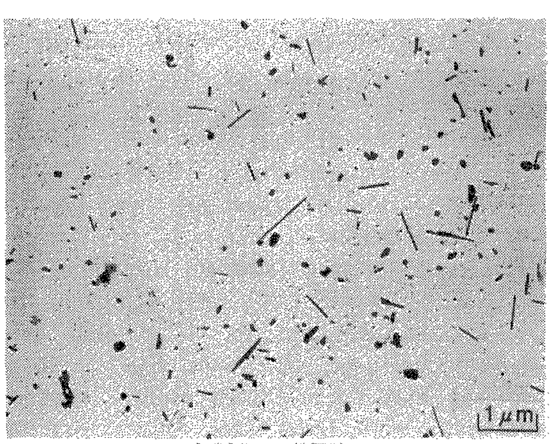
4.3 Effect of B on creep rupture strength of SUS304HTB

Extracted residues analysis has been performed for aged and unaged materials. However, no difference has been identified in the amount of residues whether B is added or not added to the steels.

Fig. 11 shows the TEM micrographs of extracted replica for the aged materials. It has been observed that $M_{23}C_6$ precipitates in grains and grain boundaries of both B addition and B-less steel. It is noted that $M_{23}C_6$ which precipitates in the B addition steel is very fine. Therefore, it is considered that the improvement of creep rupture strength by B addition is effect of fine $M_{23}C_6$ precipitates[4].



B-less (ST1)



0.0033B (ST3)

Fig. 11 TEM micrographs of extracted replica for SUS304HTB aged at 750℃ for 3000h.

5. CONCLUSIONS

In order to achieve ecomaterials for conventional heat resistant steels, effect of alloy elements on creep rupture strength of STBA24, STBA26 and SUS304HTB has been investigated.

The effect of Mo on creep rupture strength of STBA24 has been studied. No difference has been identified between 1.0%Mo and 0.79%Mo steels. However, reducing the amount of Mo from 0.79% to 0.5% decreases creep rupture strength. This is caused by the difference in the amount of the carbides which mainly consist of Mo.

The effect of V, as the impurity elements, on creep rupture strength of STBA26 has been examined. The addition of 0.05%V increases the creep rupture strength. It is found that precipitation of carbides or nitrides containing V improves that.

The effect of B, as the impurity elements, on creep rupture strength of SUS304HTB has been investigated. The addition of 0.0015%B raises the creep rupture strength. It is revealed that $M_{23}C_6$ carbides in the B addition steel precipitate more finely than those in the B-less steel. The addition of B also improves the Charpy impact values after aging.

These results suggest that it is possible to achieve ecomaterials for STBA24, STBA26 and SUS304HTB by reducing constituent elements or addition of minor alloy elements.

Acknowledgement

This research was sponsored by the Science and Technology Agency of Japan

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