New heat resistant alloys more over 700°C

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Abstract

The carbon and nitrogen free new alloys which were composed of the supersaturated martensitic microstructure with high dislocation density before the creep test have been investigated systematically. These alloys were produced from the new approach which raised creep strength by the utilization of the reverse transformed austenite phase as a matrix and intermetallic compounds such as Laves phase and μ-phase as precipitates during creep test. It is important that these alloys are independent of any carbide as strengthening factors. The high temperature creep test over 700℃ exceeds 30000 hours, and the test is continuous. Creep behavior of the alloys is found to be different from that of the conventional high-Cr ferritic steels. The addition of the boron to the alloy pulled the recrystallization temperature up in high temperature, and it became a creep test in the un- recrystallization condition, and the creep property of high temperature over 700℃ was drastically improved. The minimum creep rates of the Fe-Ni alloys at 700ºC are found to be much lower than that of the conventional steel, which is due to fine dispersion strengthening useful even at 700°C in these alloys. As a result carbon and nitrogen free alloys exhibited superior creep properties at temperatures more over 700°C.

1. Introduction

In the large-diameter tube like main steam pipe and header for the USC power plant boiler, the increase of using steam temperature and pressure requires creep strength in high temperature over 600ºC or improved heat resisting material. The goal steam condition rises to 30MPa at 630ºC at present(1), and it is necessary to develop the new heat resistant steel which is more excellent in creep strength and waterproof steam oxidation characteristic than existing P91 high Cr ferritic heat resistant steels.

In Europe development of boilers and steam turbines for plant operating at temperatures in excess of 700ºC is being carried out within the EU supported AD700 project[2]. The collaborative involves all of the major European power plant manufacturers supported by utilities and research institutes. The first phase of the project began in 1998 and runs until the end of 2003. A second phase began in 2002 and runs until the end of 2005. The objective is the development of all technology necessary for the construction and operation of such plant.

Various carbon-free martensitic alloys were produced based on the new approach that the improvement been applicable for the application which required long time creep properties at high temperatures was attempted[3-8]. These alloys have made the maraging steels which have originally combined high strength and excellent toughness at room temperature as the starting material. This alloy the A_{c1} transformation temperature becomes 700ºC or less, since Ni is abundantly contained, and the reverted transformation to austenite occurs after a few hours during the creep test.

By increasing Ni quantity in the 12%Cr steel, it has been developed of the austenite strengthening type alloy. The four low carbon 12%Cr steels tested all have better rupture properties than the typical carbide hardened steel or Type 304 austenitic stainless steel[9].

Muneki et al.[3] have also noted that the creep behavior of the Fe-Ni-Co alloys exhibited gradual change in the creep rate with strain both in the transition and acceleration creep regions, and gave large strain for the minimum creep rate. Furthermore, the addition of Pd and Cr to the carbon-free Fe-Ni-Co alloy greatly enhanced much the creep resistance at elevated temperatures over 650ºC. As the result, it became clear that the Fe-Ni-Co martensite mainly strengthened by the Laves phase was very effective for the improvement on the creep resistance at high temperatures over 700ºC.

In this study, the effect of 5%Cr addition to the Fe-12Ni-9Co-10W-0.005B alloy on the creep properties at high temperatures over 700ºC and high temperature stability of thermal cycle test has been investigated.

2. Experimental procedure

The chemical composition of alloys used in this study is shown in Table 1. They were melted as 10kg-ingots in a vacuum induction furnace. The ingots were pressed and rolled to 16mm square bars after heating for 1 hour at 1200ºC. Creep rupture tests were conducted in the range of temperatures from 700 to 900ºC and in the range of stresses from 60 to 300MPa using a 6mm diameter and 30mm gauge length tensile specimens in the as solution treated condition.

Fluctuation in the daytime and nighttime and weekend fluctuation of electric power demand increase, and the request of the DSS (Daily Start Stop) operation heightens as a correspondence of these fluctuations in the thermal power plant, and the improvement in the operability is required in addition to the thermal efficiency improvement. That is to say, it is present state that the material which can deal with the thermal cycling load is required.

Table 1 Chemical composition of alloys used (mass%).

Alloy	C	Ni	Co	W	Cr	Ti	Al	B	Fe
Cr-free	0.0014	12.18	9.04	10.06		0.20	0.088	0.005	Bal.
5%Cr	0.0021	11.80	8.62	9.96	4.95	0.19	0.03	0.005	Bal.

The thermal cycle test was carried out by the direct sending of electricity thermal process using the hydraulic universal testing machine. After heating at 700 to 1000ºC for 5 min the specimen was cooled down to 200ºC, and then kept for 5min at 200ºC. Tension stroke between 0.1 and 1mm was given to the specimen during holding time at the given high temperature. For 10mm at gage length of the specimen, these stroke values are correspondent to 1.0 strain from about 0.1. These loading by tension stroke after heating and then cooling processes required the repetition frequency until the specimen broke. The test was stopped, when the specimen did not failure by exceeding 100 times at test number of cycles.

3. Results and discussion

3.1 Transformation behavior

Fig.1 shows the effect of 5% Cr addition on the transformation temperatures of A_s and M_s measured by the dilatometry with heating and cooling with the rates of 5ºC/min. A_s and M_s temperatures of the Cr-free alloy was about 680ºC and 200ºC, respectively. On the other hand, those of 5% Cr added alloy were identified remarkably lower than those of Cr-free alloy.

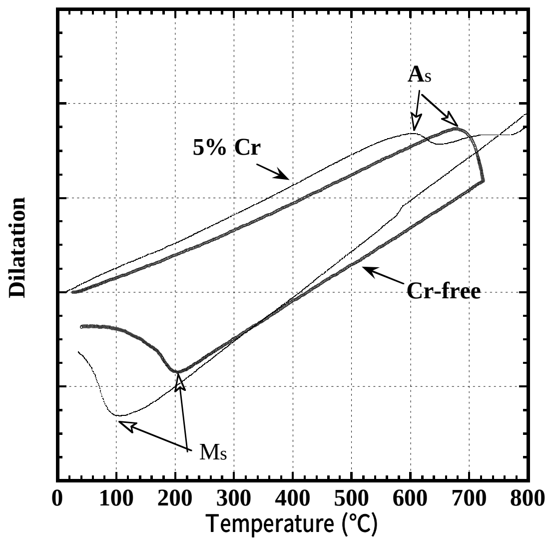

Fig.1 Effect of 5% Cr addition on the thermal expancy of the Fe-12Ni-9Co-10W-0.005B alloys.

As the A_s temperature was lower than that of the cor the microstructure of the matrix of the two alloys are reverted austenite during creep tests at more

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over 700ºC in this study.

3.2 Creep properties at 700ºC

In 200 and 150MPa of the high stress, by the Cr free alloy, it was ruptured under 10 hours, as clearly shown in Fig. 2. The creep resistance increased when the stress lowered at 100MPa, and time to rupture remarkably increased more over 1,000hours. On the other hand, it was broken by the 5%Cr alloy in equivalent about 10 hours, when the stress condition was raised at 300MPa. The about 1000 times rupture life was improved, when the stress was lowered to 150MPa. As the result time to rupture reached at 10,000h. When the applied stress lowered at 100MPa, the minimum creep rate decreased about 1/10, and the testing time exceeded 32,000h. The creep test is continuous for this test piece without yet breaking (, as be shown into the figure in the arrow). It became clear that the creep resistance rapidly improved it by the addition of 5%Cr and that the rupture life drastically increases.

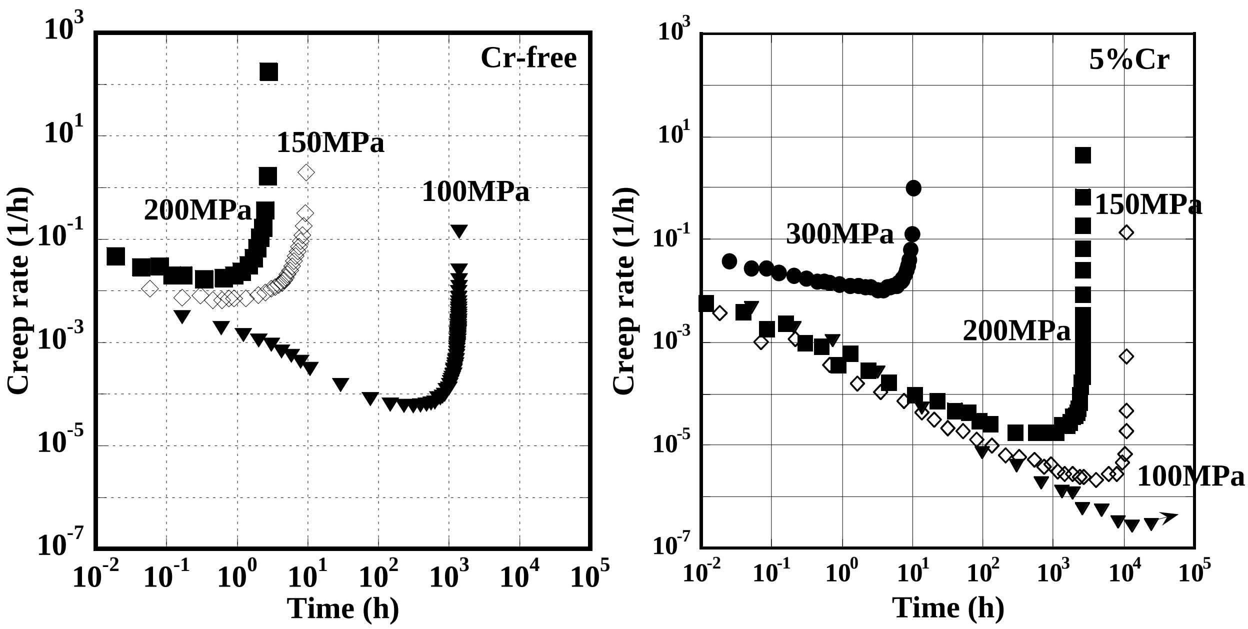

Fig.2 Effect of 5% Cr addition on the relationship between creep rate and time curves of the specimen crept at 700℃ in the Fe-12Ni-9Co-10W-0.005B alloys.

3.3 Creep properties at 750ºC

Fig. 3 shows creep rate vs. time curves of the Fe-12Ni-9Co-10W-0.005B alloys crept at 750ºC and 300-100MPa. Initial and minimum creep rates of 150MPa in the Cr free alloy indicated at about 1.3 x 10^{-1}, and the rate kept for nearly constant values with time. Initial creep rates of 120

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and 100MPa exhibited similar values at 4.5 x 10^{-2}, and the rate gradually decreased with time until 1h, then the rates remarkably decreased and reached at the minimum creep rate and finally ruptured. There is a plateau of the creep rate, and the characteristic curve which decreases afterwards is shown in the transition creep region. While in case of the 5%Cr alloy, creep curve of 300MPa was similar value to that of 120MPa in the Cr free alloy. With decreasing stress to 150MPa from 300MPa in the 5%Cr alloy the minimum creep rate drastically decreased at two orders, and that time to rupture increased at about 1,000times. As compared with applied stress at 150MPa in both alloys creep properties improved about 1,000times by the addition of 5%Cr. Time to rupture of the 5%Cr alloy crept at 750ºC and 100MPa exhibited about 6,900h. Furthermore, time to rupture reached at 17,061h in the 5%Cr alloy crept at 750℃ and 60MPa.

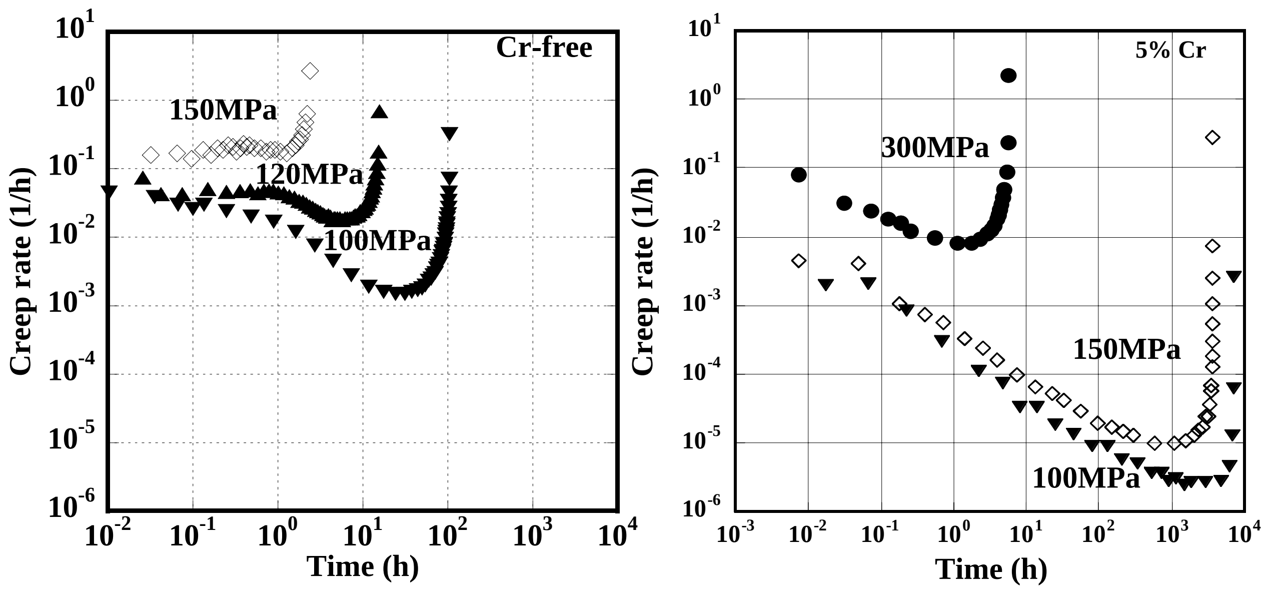

Fig.3 Creep rate vs. time curves of the Fe-12Ni-9Co-10W-0.005B alloys crept at 750℃ and 300 and 100MPa.

3.4 Effect of Cr addition and distribution of aged precipitates on the creep properties

Fig.4 shows the relationship between applied stress and time to rupture of the Fe-12Ni-9Co-10W-0.005B alloys. Time to rupture gradually increased with decreasing the applied stress in Cr-free and 5%Cr alloys. In the condition of 700ºC and 200MPa, specimen of the Cr free alloy ruptured at 2.8h. Time to rupture increased with stress decrease, and it reached at 3117h in 80MPa. With increasing the test temperature, stress and time to rupture relation curve shifted to low stress and short time side as similar tendency as that of 700ºC.

By the addition of 5%Cr, applied stress and time to rupture relation was drastically improved in the temperature range between 700ºC and 900ºC, as clearly shown in this figure. As compared to the time to rupture of both alloys at 100MPa in the applied stress, the time remarkably increased for about 30 to 65 times in the temperature range between 750ºC and 850ºC.

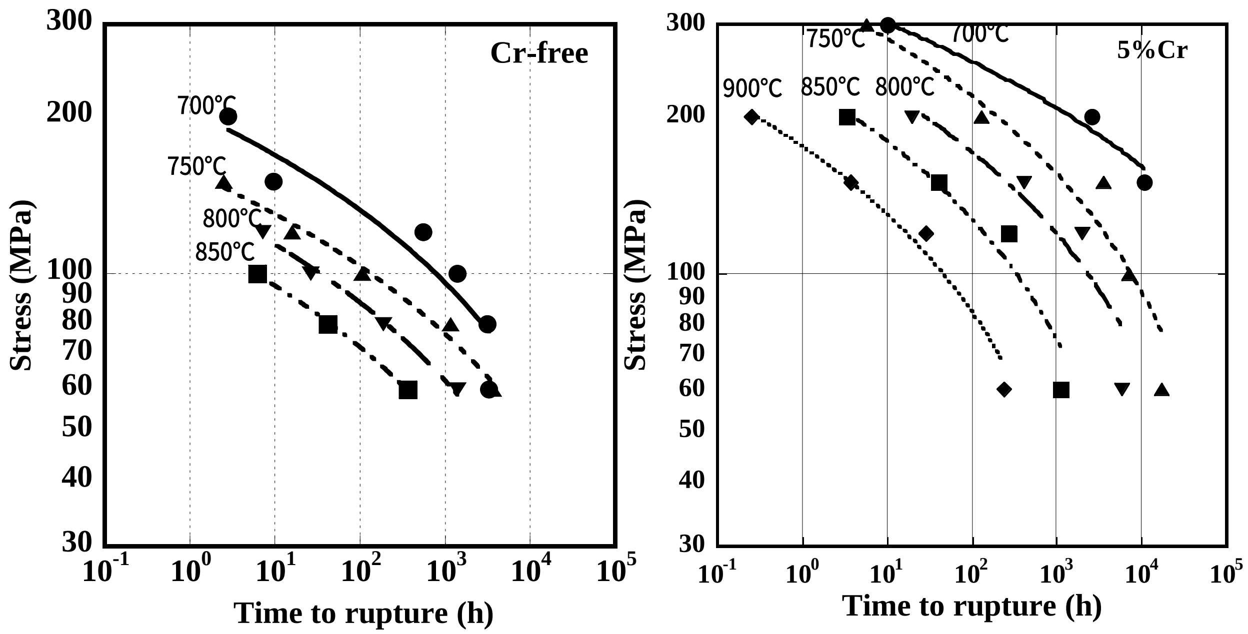

Fig. 4 Relationship between stress and time to rupture of the Fe-12Ni-9Co-10W-0.005B alloys.

Fig.5 shows secondary electron images of the initial microstructure of the specimen interrupted for very short time at 700ºC, 800ºC, 850ºC and 900ºC in the Fe-12Ni-9Co-10W-5Cr-0.005B alloy. Large amounts of white shining particles were distributed finely and uniformly at the grain boundaries and inside the grain even at 850ºC. It has already been identified these particles as a Laves phase like as Fe_2W in the previous report[4)]. In 900℃, the precipitate which exceeds the 200nm diameter is observed in the part.

Fig. 6 shows backscattered electron images of the 5%Cr alloy crept at 700ºC and 800ºC passed over 2,000h. During creep test these precipitates remarkably coarsened at about 2 to 4 times in diameter as compared with the initial stage of the creep test. However, area ratio increased for about twice in the specimen crept at 700ºC, but the ratio did not changed in the specimen crept at 800ºC as clearly shown the investigation of image analysis.

Fig.7 shows the average diameter and area ratio of the precipitates at the gauge portion of the crept specimen of the 5%Cr alloy. The average diameter of the precipitates drastically changed from about 50nm to more over 300nm in the temperature range between 700 and 900ºC with increasing the time to rupture. The average diameter completely did not change at the beginning

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of the test, and it rapidly increased after the fixed time progress. According to increase the test temperature, it is shifting to the short time side in which the rapid coarsening of the average diameter starts.

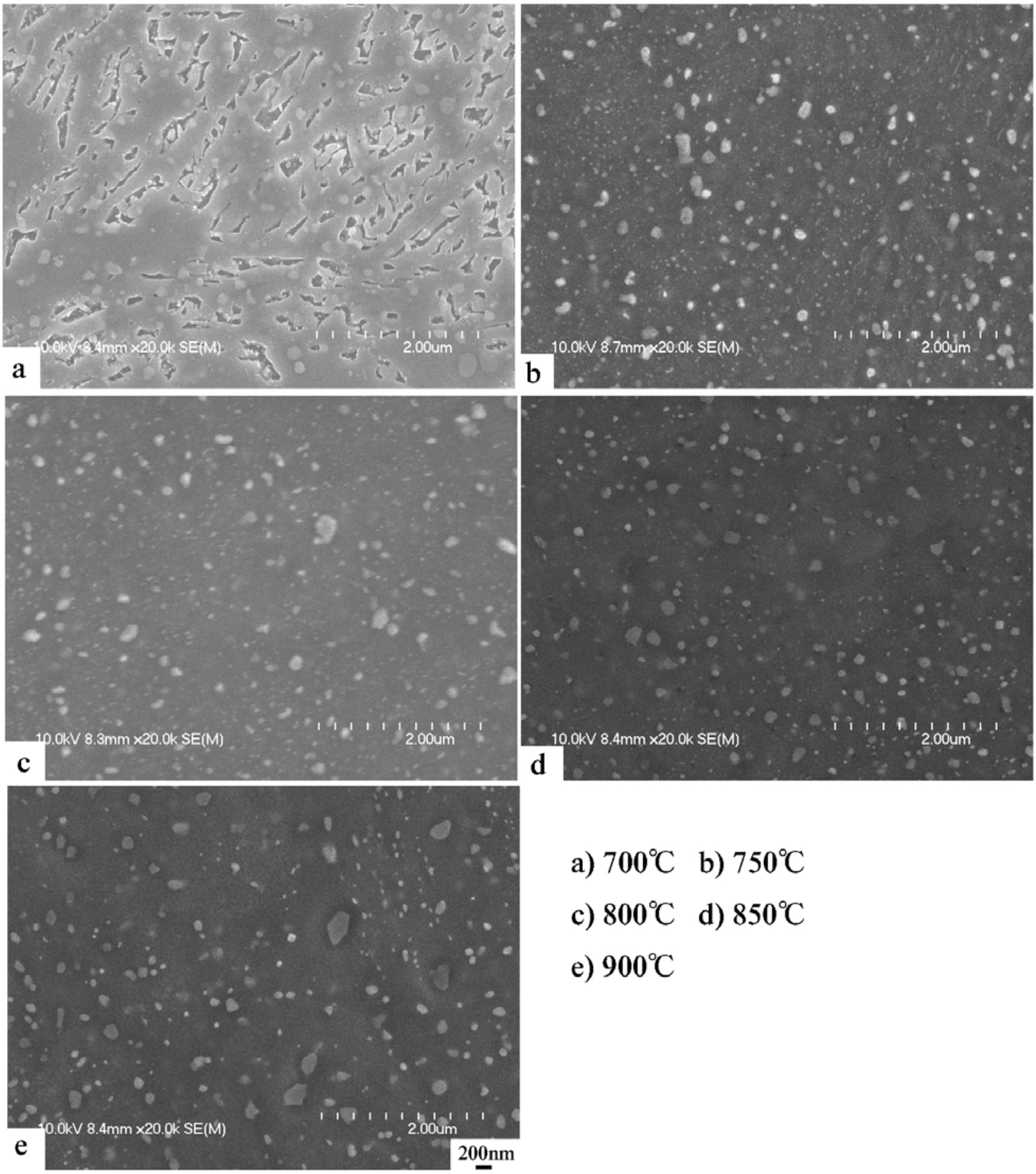

Fig.5 Secondary electron images of the initial microstructure of the specimen crept at 700, 750, 800, 850and 900℃ in the Fe-12Ni-9Co-10W-5Cr-0.005B alloy.

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While area ratio of these precipitates in all test temperatures measured about 10% in maximum. Then, this value did not change, even if the time to rupture exceeded 1,000 hours.

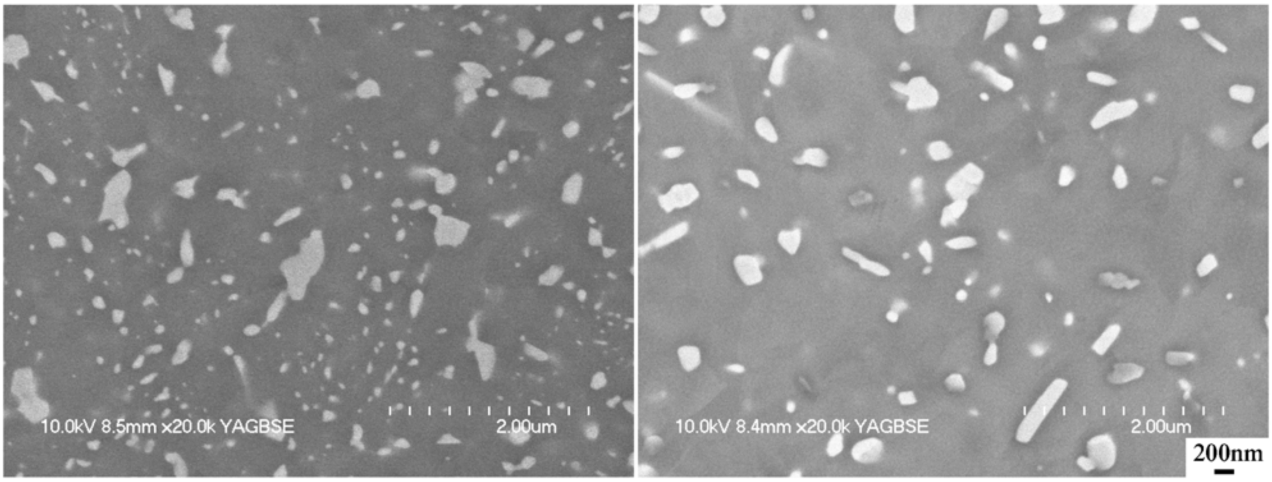

Fig.6 Backscattered electron images of the Fe-12Ni-9Co-10W-5Cr-0.005B alloy crept at a) 700℃ and 2,554h and b) 800℃ and 2,007h.

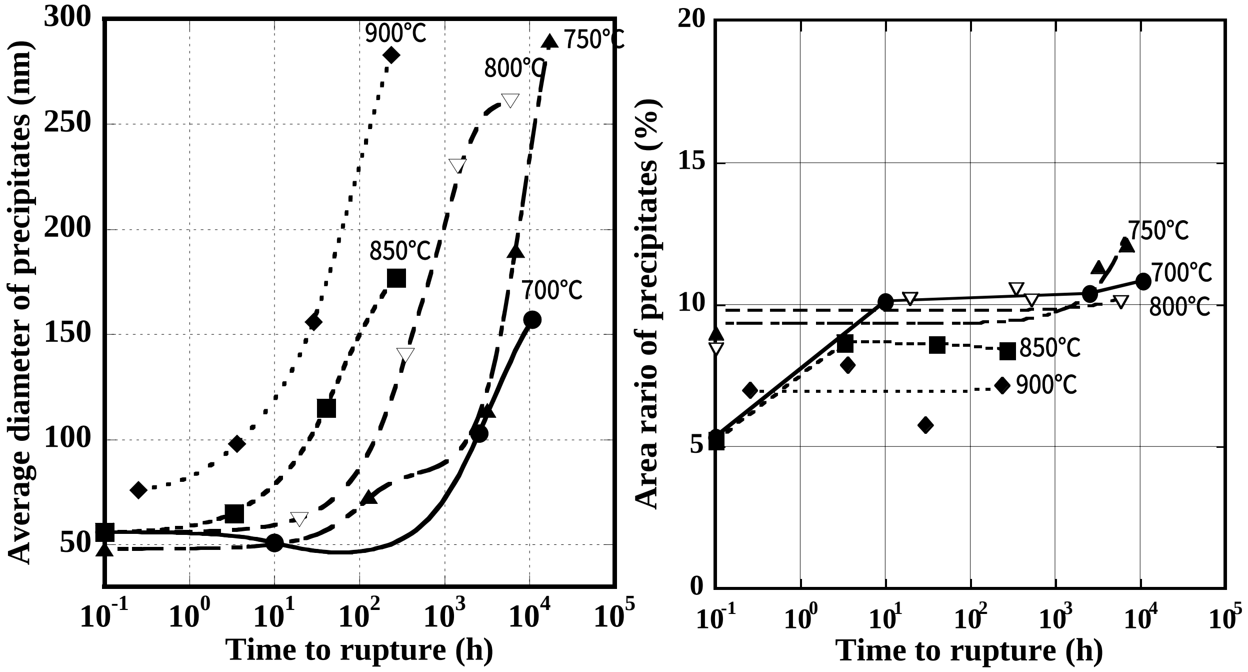

Fig.7 Changes of average diameter and area ratio of precipitates at the gage portion of the crept specimen of Fe-12Ni-9Co-10W-5Cr-0.005B alloy.

3.5 High temperature stability in thermal cycle test

Table 2 shows the result of thermal cycle test of austenitic stainless steel (Type 316) and the 5%Cr (C-free) alloy. Type 316 did not rupture at 800ºC and 0.1mm in tension stroke. When the tension stroke increased, type 316 ruptured after 34 times at 750ºC, and ruptured after only 14 times at 800ºC. While the 5%Cr alloy did not rupture after 100 times at 800ºC and 0.5mm in tension stroke. The 5%Cr alloy ruptured after 5 times at 800ºC and 1mm in tension stroke. This alloy ruptured after 49 times at 900ºC and 0.5mm in tension stroke. It was clearly that the 5%Cr alloy had superior stability at high temperature in thermal cycle test than that of type 316.

Table 2 Result of thermal cycle test of Type 316 and the C-free alloy.

	Type 316				C-free alloy			
Stroke / Temp.	0mm	0.1mm	0.5mm	1mm	0mm	0.1mm	0.5mm	1mm
700°C	NF	NF		1	NF	NF	NF	NF
750°C	NF	NF	34		NF	NF	NF	NF
800°C	NF	NF	14		NF	NF	NF	5
900°C							49	
1000°C							2	

NF means not failure after 100 times

Figure into the table means failure number of cycle.

4 Conclusion

Effect of 5%Cr addition to the Fe-12Ni-9Co-10W-0.005B alloy on the creep properties at high temperatures over 700ºC and high temperature stability of thermal cycle test have been discussed.

a) By the addition of 5%Cr minimum creep rate at 700ºC and 150MPa decreased about three orders in magnitude from 6.7 x 10^{-3} to 2.27 x 10^{-6}, and that time to rupture increased about 1,000 times from about 10h to about 10,700h. Furthermore the testing time are remarkably increasing more over 35,000h at 700℃ and 100MPa.

b) By the addition of 5%Cr, stress-time to rupture relationship at 900ºC from 700ºC was drastically improved. As compared to the time to rupture of both alloys at 100MPa in applied stress, the time remarkably increased for about 30 to 65 times in the temperature range between 750ºC and 850ºC.

c) The average diameter of precipitates into the crept specimens of the

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Fe-12Ni-9Co-10W-5Cr-0.005B alloy changed from about 50nm to more over 200nm in the temperature range between 700ºC and 900ºC. Area ratio of precipitates measured about 5% to 10% in every test temperature until 900ºC.

d) Type 316 ruptured after 34 times and 0.5mm in tension stroke. While the Fe-12Ni-9Co-10W-5Cr-0.005B alloy did not rupture after 100 times at 800ºC and 0.5mm in tension stroke.

It was clearly that the Fe-12Ni-9Co-10W-5Cr-0.005B alloy had superior stability at high temperatures in thermal cycle test than that of type 316.

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