Transactions of the Materials Research Society of Japan 29 [8] 3485-3488 (2004)

Improvement in Creep Strength and Impact Toughness of Advanced Creep Resistant Steel Based on Ferrite Matrix

Yoshiaki Toda, Hideaki Kushima, Kazuhiro Kimura* and Fujio Abe
National Institute for Materials Science: 1-2-1, Sengen, Tsukuba, 305-0047 Japan
Fax: 81-29-859-2101, e-mail: TODA.Yoshiaki@nims.go.jp
* National Institute for Materials Science: 2-2-54, Nakameguro, Meguro-ku, Tokyo, 153-0061 Japan
Fax: 81-3-3719-2177, e-mail: KIMURA.Kazuhiro@nims.go.jp

Fully annealed and precipitation strengthened high Cr ferritic creep resistant steel with ferrite matrix has been investigated as candidate materials for high temperature structural components in fossil fired power plants. In this study, effects of chemical composition and heat treatment on mechanical properties and microstructures of 15Cr-1Mo-0.2V-0.05Nb-3W-0.003B ferritic steels have been investigated in order to discuss a possibility of improvement in long-term creep strength and impact toughness. Increase in W and Co contents and optimization of C and N contents extended creep rupture lives of the steels at 923K up to about ten times longer than that of ASME T92 steel, which possesses the highest creep strength among the conventional ferritic creep resistant steels. Charpy impact values of the steels were lower than 15J/cm^2 at room temperature. However, drastic improvement in impact toughness has been attained by controlling of C and N contents, addition of Ni and increase in cooling rate after annealing, and ductile-brittle transition temperature has been lowered. It has been considered that oxidation resistance of the 15Cr steel is higher than that of the conventional one because of its higher Cr content. It has been concluded, consequently, that a fully annealed and precipitation strengthened high Cr ferritic steel should be a candidate high strength creep resistant materials in the next generation.
Key words: ferritic heat resistant steel, precipitation strengthen, alloy element, cooling rate

1. INTRODUCTION

Recently, improvement of energy efficiency in fossil fired power generation has been requested from a global environmental viewpoint in order to reduce CO_2 emissions and conserve energy resources such as oil, coal and natural gas. In order to improve the energy efficiency, creep strength of high temperature structural components such as header and main steam pipe in power plants should be advanced, and steam temperature and pressure must be increased. Consequently, many efforts have been conducted on research and development of new high strength materials, such as ferritic creep resistant steels that is available for large components of fossil fired power plants [1].

Generally, the microstructure of conventional high strength ferritic creep resistant steels is tempered martensite. However, the creep strength of these materials decreases remarkably by microstructural degradation during long-term service at the elevated temperatures, since the tempered martensitic microstructure is unstable at the elevated temperatures. For example, recovery preferentially takes place at the vicinity of prior austenite grain boundaries and expansion of such area has been pointed out as a degradation mechanism of a 9Cr-1Mo-V-Nb (ASME T91) steel [2]. Suppression of the degradation through the improvement in microstructural stability is a key concept to maintain high creep strength during long-term service [3].

Under the above backgrounds, a new possibility to obtain higher long-term creep strength through annealed microstructure instead of tempered martensitic microstructure has been pointed out by Kimura et al. [4]. They have investigated effects of initial microstructure on the long-term creep strength of a 0.5Cr-0.5Mo steel. As a result, long-term creep strength of the fully annealed steel with ferrite and pearlite microstructures was found to be higher than those with martensitic, tempered martensitic and bainitic microstructures. This result suggests that higher long-term creep strength may be obtained by fully annealed ferritic microstructure.

The chromium content of the conventional ferritic creep resistant steel is restricted to be less than about 12mass% in order to avoid a formation of δ-ferrite and to obtain a full martensitic microstructure. However, from the above results on 0.5Cr-0.5Mo steel, higher chromium content than that of the conventional ferritic creep resistant steel is suitable for not only fully annealed ferritic microstructure but also better oxidation resistance. In this study, consequently, the effects of alloying elements on the creep strength of fully annealed ferritic steel with higher chromium content than that of the conventional ferritic steels have been investigated, and a possibility of improvement in creep strength of the steel with ferrite matrix instead of tempered martensitic microstructure have been discussed.

2. EXPERIMENTAL PROCEDURE

Chemical compositions of the steels investigated in this study are shown in Table 1. Base steel with a composition of Fe-0.1C-15Cr-1Mo-3W-0.2V-0.05Nb-0.07N-0.003B (mass%) and seven steels with various compositions of W, Co, C and N were used to investi-

Table 1 Chemical compositions (mass%) of the present studied steels.

	C	Cr	Mo	W	V	Nb	Co	N	B
Base	0.110	15.21	0.98	2.95	0.20	0.051	–	0.072	0.0028
6W-0Co	0.095	15.10	0.98	**5.96**	0.19	0.06	–	0.083	0.0030
3W-3Co	0.096	15.11	0.99	3.01	0.19	0.06	**3.01**	0.083	0.0030
6W-3Co	0.096	15.10	0.99	**5.94**	0.18	0.06	**3.00**	0.082	0.0027
0C-0N	**0.001**	14.91	1.01	6.03	0.19	0.045	2.96	**0.0018**	0.0031
0C-7N	**0.003**	14.91	1.01	6.00	0.19	0.045	2.96	0.066	0.0028
10C-0N	0.10	14.88	1.01	6.01	0.19	0.045	2.96	**0.0019**	0.0028
5C-3N	**0.046**	15.00	1.00	6.07	0.19	0.043	2.97	**0.033**	0.0030

gate the influence of alloy elements on the creep strength. In addition to those steels, 0C-7N and 5C-3N steels containing 0.4, 0.8, 1.2, 1.6 and 2.0 mass% of Ni were used to investigate the effect of Ni contents on the impact toughness of the steels. These steels were prepared in a vacuum induction furnace. The ingots with a weight of 10kg were hot forged into bars with a diameter of about 15mm and annealed for 30min at 1473K, followed by furnace cooling. Also water quenching was employed for cooling condition for the Ni added steels.

Dimension of creep test specimen was 6mm in gauge diameter and 30mm in gauge length according to Type 14A in Japanese Industrial Standard (JIS) Z 2201 (1998). Creep tests were conducted at 923K and a range of stresses from 60 to 200MPa up to about 23,000h in the air. Charpy impact test was carried out at room temperature (RT) and 370K using V-notch type specimen in JIS Z 2202 (1998). Microstructure of the steels as annealed condition and creep ruptured specimen was examined under an optical microscope (OM) and a scanning electron microscope (SEM). X-ray diffraction analysis was conducted on the electrolytically extracted residue taken from the specimens isothermally aged for 1,000h at 923K in order to identify the precipitates in the steels.

3. RESULTS

3.1 Creep strength properties

Figure 1 shows stress vs. time to rupture curves of the steels at 923K. The curves of 9Cr-1Mo-V-Nb (ASME T91) steel [5] and 9Cr-0.5Mo-1.8W-V-Nb (ASME T92) steel [6], which are the conventional ferritic creep resistant steels with tempered martensitic microstructure, are also shown by the dotted and dashed lines in the same figure. Increase in W content (6W-0Co) and addition of Co (3W-3Co) extended the creep rupture lives of the steels about 3 times and 10 times longer than that of the base steel, respectively. Moreover, the creep rupture life of the steel was extended about 100 times longer than that of the base steel by a combination of increase in W content and addition of Co (6W-3Co), and the creep rupture strength of that was almost the same as that of ASME T92. However, slope of the stress vs. time to rupture curve of 6W-3Co steel was relatively large, and resulted in abrupt decrease in creep strength in the long-term. Then, as a result of optimizing of C and N contents, creep rupture lives of 0C-7N and 5C-3N steels were extended also in the long-term condition and those were longer than that of the ASME T92 steel at stresses higher than 120MPa.

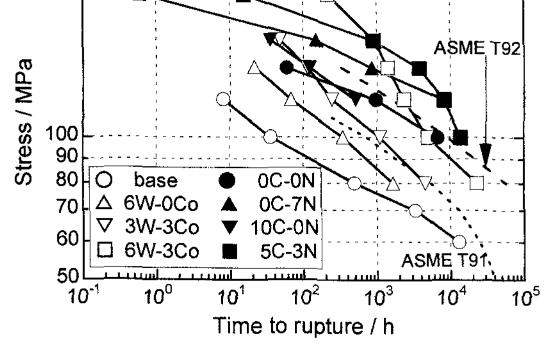

Fig. 1 Stress vs. time to rupture curves of the present studied steels and two conventional ferritic heat resistant steels using tempered martensitic microstructure.

3.2 Microstructure

Although martensite phase was observed in some steels, almost of the matrix was ferrite phase for all the steels in the as-annealed condition. Coarse block type precipitates with several micrometers in size were also observed on grain boundaries in some steels. These precipitates were formed during furnace cooling from the annealing temperature of 1473K.

Figure 2 shows SEM micrographs of (a) base; (b) 6W-3Co; (c) 5C-3N and (d) 0C-7N steels creep ruptured at 923K and 120MPa. The t_r values indicated in each micrograph are time to rupture, and the latter three steels possess superior creep strength. The combination of increase in W content and addition of Co increased in coarse blocky precipitates at grain boundaries and fine distribution of plate type small particles within the grain interiors. In 5C-3N and 0C-7N steels, whose C and N contents were optimized for creep strength, a lot of plate type particles within grains with several hundreds nanometers in length were still fine even after long-term creep exposure for about 8,000h at 923K. It seems that these precipitates are very stable and growth rates of those are very small. Moreover, there were only a few coarse block type precipitate and a little precipitate free zone around them in 0C-7N steel. The fine particles of this steel were distributed more uniformly than any other steels.

Figure 3 shows X-ray diffraction profiles of the isothermal aged (a) base; (b) 6W-3Co; (c) 5C-3N and (d) 0C-7N steels. By comparing these profiles with the JCPDS cards, the peaks in the profiles have been identified as those from Laves phase (Fe_2W), μ-phase (Fe_7W_6)

Fig. 2 SEM micrographs of the (a) base; (b) 6W-3Co; (c) 5C-3N and (d) 0C-7N steels creep ruptured at 923K and 120MPa. The t_r values indicated in each micrograph are times to rupture.

and χ-phase ($Fe_{36}Cr_{12}W_{10}$), which are intermetallic compounds classified into topologically close packed (TCP) phase [7], and $M_{23}C_6$. Therefore, it has been concluded that the excellent long-term creep strength of 0C-7N steel may be obtained by uniform distribution of many fine particles of TCP phases and by the small growth rate of those precipitates during long-term creep exposure at the elevated temperatures.

3.3 Impact toughness

Figure 4 shows Charpy impact values of the furnace cooled and water quenched 0C-7N; 5C-3N and 6W-3Co steels at room temperature (RT) and 370K. Charpy impact values of all the furnace cooled steels are lower than 15J/cm^2 independent of the C and N contents at both RT and 370K. On the other hand, the impact values of the water quenched steels are higher than those of the furnace cooled one. For 5C-3N steel, impact value of water quenched steel was two or three times higher than that of furnace cooled one at both temperatures. For 6W-3Co steel, drastic increase in impact value from 5J/cm^2 in the furnace cooled condition to 99J/cm^2 was attained by water quenching. From the above results, it has been found that Charpy impact value increases with increase in cooling rate from the annealing temperature of 1473K, and such improving effect of cooling rate strongly depend on the C and N contents.

It is well known that toughness is increased by an addition of Ni, therefore, the influence of Ni addition on Charpy impact value of 0C-7N and 5C-3N steels has been investigated. Since the long term creep strength of 0C-7N and 5C-3N steels was higher than the others,

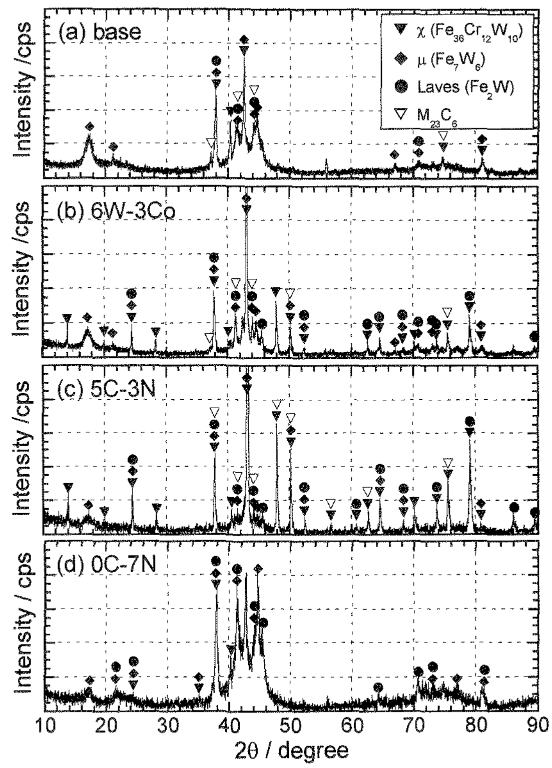

Fig. 3 X-ray diffraction profiles of the electrolytically extracted residue of (a) base; (b) 6W-3Co; (c) 0C-7N and (d) 5C-3N steels isothermally aged for 1000h at 923K.

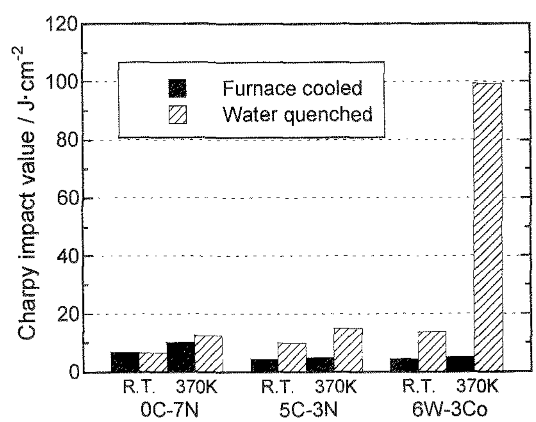

Fig. 4 Charpy impact values of the furnace cooled and water quenched 0C-7N; 5C-3N and 6W-3Co steels at room temperature (RT) and 370K.

these two steels were used as base compositions. Moreover, water quenching has been employed for cooling condition from annealing temperature. Charpy impact values of the water quenched 0C-7N and 5C-3N steels were plotted against Ni content and shown in Fig. 5. For 0C-7N steel, influence of Ni addition on Charpy impact value was very small at room temperature, and it slightly increased to about 65J/cm^2 at 370K with the addition of 2mass% Ni. On the other hand, significant increase in impact value with increase in Ni concentration was observed in 5C-3N steel. Charpy impact value at room

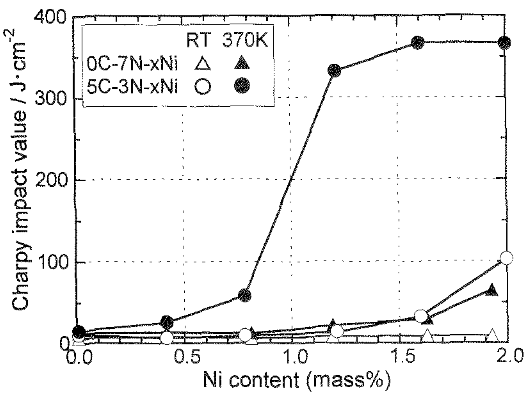

Fig. 5 Influence of Ni content on the Charpy impact values of the water quenched 0C-7N and 5C-3N steels at room temperature (RT) and 370K.

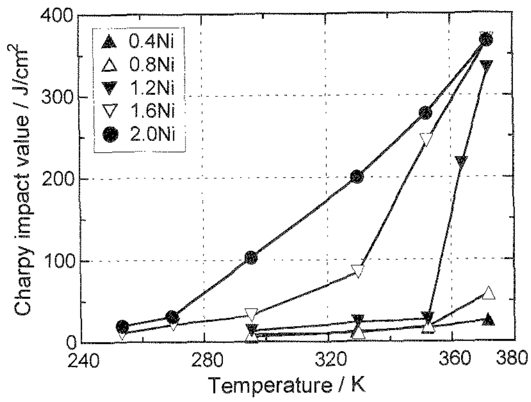

Fig. 6 Change in the Charpy impact values of the water quenched 5C-3N steels containing various contents of Ni with temperature.

temperature was increased to about 100J/cm^2 with addition of 2mass% Ni, and it was increased to be higher than 300J/cm^2 at 370K with addition of 1.2mass% of Ni and more.

Figure 6 shows change in the Charpy impact value of the water quenched 5C-3N steels containing various contents of Ni with temperature. It is obvious that the impact toughness is improved with increase in Ni contents. And the ductile-brittle transition temperature (DBTT) decreases with increase in Ni contents. The DBTT is about 320K in the water quenched 5C-3N steels containing 2mass% Ni. Therefore, it has been found that the drastic improvement of the impact toughness and DBTT has been attained by the optimizing of C and N contents, addition of Ni and increase in cooling rate after annealing for the precipitation strengthened high Cr ferritic steels with ferrite matrix.

As a result of OM and SEM observation, microstructural features of the furnace cooled and water quenched Ni added steels are summarized as follows; 1) Although only a small amount of very fine precipitates are observed on grain boundaries in the water quenched condition, precipitation of many particles takes place along grain boundaries during furnace cooling from the annealing temperature. 2) Grain size decreases with increase in Ni content in the both furnace cooled and water quenched conditions. 3) Volume fraction of martensitic phase increases with increase in Ni content in the both cooling condition, it is more prominence in the furnace cooled condition. However, increase in impact toughness can not be explained by these individual microstructural factors of volume fraction of martensitic phase, grain size and precipitates. It has been supposed, consequently, that improvement in impact toughness of the high Cr steel with addition of Ni and water quenching should be attained by increase in toughness of ferrite matrix itself.

4. CONCLUSION

The main contribution of this paper is the finding on possibility of improvement in long-term creep strength of a high Cr ferritic steel with ferrite matrix by controlling the alloy composition through the uniformly distributed a lot of nanometer level fine and stable precipitates. And the design principles for improvement in impact toughness, which is an obstacle to develop the materials, are also obtained by the optimizing alloying elements, the addition of Ni and increase in cooling rate from annealing temperature. In addition, because of its higher Cr content, these steels are expected to possess better oxidation resistance than those of the conventional ferritic heat resistant steels. Thus, it can be reasonable to conclude that the fully annealed and precipitation strengthened high Cr ferritic steel with ferrite matrix is a promising creep resistant material for fossil power plants in the future.

References

[1] F. Masuyama, *ISIJ Int.*, **41**, 612-25 (2001).

[2] K. Kimura, H. Kushima, F. Abe, K. Suzuki, S. Kumai and A. Satoh, "Proc. of the 5th Int. Charles Parsons Turbine Conf.", Ed. by A. Strang et al., IOM Communications Ltd., London, (2000) pp. 590-602.

[3] K. Maruyama, K. Sawada and J. Koike, *ISIJ Int.*, **41**, 641-53 (2001).

[4] K. Kimura, H. Kushima, E. Baba, T. Shimizu, Y. Asai, and F. Abe, "Proc. of the 5th Int. Charles Parsons Turbine Conf.", Ed. by A. Strang et al., IOM Communications Ltd., London, (2000) pp. 558-71.

[5] NRIM Creep Data Sheet, No.43, National Research Institute for Metals, Tsukuba, (1996).

[6] Data Package for NF616 Ferritic Steel (9Cr-0.5Mo-1.8W-Nb-V), 2nd Edition, Nippon Steel Corporation, (1994).

[7] F. C. Frank and J. S. Kasper, *Acta Cryst.*, **11**, 184-190 (1958).

(Received December 1, 2003; Accepted April 19, 2004)