Effects of Alloying Additions and Material Microstructure on the Accuracy of the Predictive Law of Creep Crack Growth for W-Strengthened 9–12%Cr Ferritic Heat-Resistant Steel*

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*This Paper was Originally Published in Japanese in J. Japan Inst. Metals Vol. 48, No. 11 (2007) pp. 2928 to 2936

The life of creep crack growth for W-strengthened 9–12%Cr steel is sensitive to the alloying additions and to differences in material microstructure, such as lath martensitic structure and grain size caused by differences in cooling rates in the steel ingots during the manufacturing process, which results in the large scatter of experimental data from the law of creep crack growth life. In the present study, creep crack growth tests were conducted using W-strengthened 9–12%Cr steels with various contents of alloying additions and the dimensions of micro-nano structures. The effects of the composition of alloying additions and material microstructures on the life of creep crack growth for W-strengthened 9–12%Cr steel were clarified.

(Received May 15, 2007; Accepted August 28, 2007; Published October 25, 2007)

Keywords: tungsten strengthened 9–12%chromium ferritic heat-resistant steel, molybdenum equivalence (molybdenum% + 1/2tungsten%), lath martensitic structure, grain size, creep, crack growth

1. Introduction

The research on heat-resistant steels for the application of fuel-fired power plants has progressed remarkably for the past 50 years, resulting in the improvement of electrical efficiency for coal-fired fossil fuel power plants.1,2 At the present time, there are programs to develop ultra-supercritical plants aimed at operations under steam temperature and pressure conditions of 600/650°C and 32 MPa. The W-strengthened 9–12%Cr ferritic heat-resistant steel has been developed as boiler and turbine rotor materials for this ultra-supercritical plant.1–7

Until now, the fundamental mechanical properties of the W-strengthened 9–12%Cr ferritic heat-resistant steels have been investigated by conducting Charpy impact tests, creep tests and tensile tests using smooth specimens.6,7

However, when these materials are applied for practical component structures, there will be some possibilities of crack initiation and damage progression due to various applied loading factors. Therefore, on the basis of the previously proposed predictive method of crack growth life,8,9 some of the present authors have derived laws of creep crack growth and its life for these materials by conducting creep crack growth tests.10–12

However, the life of creep crack growth for W-strengthened 9–12%Cr ferritic heat-resistant steel is sensitive to the alloying additions and to differences in material microstructure, such as lath martensitic structure and grain size caused by differences in cooling rates in the steel ingots during the manufacturing process.13 This resulted in an increase in the sensitivity of creep crack growth resistance to material microstructure. This naturally causes an increase in data scatter from mechanical laws for the life of creep crack growth under high-temperature creep conditions.

Therefore, clarification of the effects of the composition of alloying additions and material microstructure on the law of creep crack growth life is considered to contribute to the improvement of the high-accuracy prediction of the life of creep crack growth.

In the present study, creep crack growth tests were conducted using W-strengthened 9–12%Cr ferritic heat-resistant steel with various contents of alloying additions and microstructural dimensions. The effects of the composition of alloying additions and material structures on the life of creep crack growth for W-strengthened 9–12%Cr ferritic heat-resistant steel were clarified. Furthermore, the degree of improvement on the predictive accuracy of creep crack growth life was discussed.

2. Experimental Procedure

2.1 Materials and specimens

The material used is W-strengthened 9–12%Cr ferritic heat-resistant steel with the Mo equivalent ([Mo] + 1/2[W]) (mass%) value kept at 1.5%.4 Six kinds of materials with variation in W and Mo contents under the condition of 1.5% Mo equivalence were prepared for creep crack growth tests. W-strengthened 9–12%Cr ferritic heat-resistant steel, developed by substituting part of the Mo content with W, has been reported to have excellent characteristics of creep strength and ductility when the value of the Mo equivalent ([Mo] + 1/2[W]) (mass%) takes the value of 1.5%.4

Depending on the operating temperature, under the
constant Mo equivalence of 1.5%, ((W)/([Mo] + 1/2[W])) (mass%) and (([Mo] + 1/2[W])) (mass%) are designed to take higher values in the regions of higher and lower temperatures, respectively.\(^4\)

9 and 12%Cr ferritic heat-resistant steels have been developed for the application to the components of boiler and turbine rotors at the temperatures of 593 and 650 °C, respectively.

The chemical composition, mechanical properties and manufacturing processes of the materials are shown in Tables 1, 2 and 3, respectively.

On the basis of ASTM E1457-00, the specimen used is manufactured into a standardized CT specimen for creep crack growth tests as shown in Fig. 1.\(^14\)

2.2 Test method and conditions

Creep crack growth tests were performed using a lever arm creep testing machine (RT-30) manufactured by TOSHIN KOGYO.

The crack length was measured by an electrical potential method.\(^15,16\) An electrical current is applied to the specimen and the value of the electric potential drop is measured. The crack length is usually calculated using Johnson’s equation given by eq. (1).\(^15,16\)

\[
a = \frac{2W}{\pi} \cos^{-1} \left[ \frac{\cosh(\pi y/2W) \cos(\pi y/2W)/\cos(\pi a_0/2W)}{\cosh(\pi y/2W)/\cos(\pi y/2W)} \right] \tag{1}
\]

The observations of material structures were carried out on tested specimens. Specimens of suitable size for AFM observation were cut from an area away from the damaged surface. They were mechanically polished and buff-finished to a mirror surface with 0.06 μm Al₂O₃ particles. Finally, the specimens were etched in a mixture of FeCl₂ (10 g), HCl (30 ml), and H₂O (100 ml) to observe the material microstructures.

3. Experimental Results

3.1 Scatter of experimental results caused by the differences in the alloying additions and material structures

Values of the creep crack growth life of W-strengthened 12%Cr ferritic heat-resistant steels with the Mo equivalence being constant at 1.5% were considered to have the same
characteristic under the same experimental conditions in terms of parameters such as applied loads, temperatures and specimen geometries.

However, in many cases, there are differences in the grain size and variation of W and Mo contents despite the similar conditions of heat treatments and Mo equivalence.

In the present study, scatter of the values of creep crack growth life caused by differences in the alloying additions and material microstructures for W-strengthened 12%Cr steels and also 9%Cr steels were investigated.

Creep crack growth tests of W-strengthened 9–12%Cr steels were conducted for six samples of materials with various W and Mo contents under the conditions of 1.5% Mo equivalence under the constant load of 311.8 MPa at a temperature of 650°C, as shown in Table 1.

The experimental results of creep crack growth life show scatter in the range from 11.2 to 426 h and the standard deviation from the average value was more than 100%.

The reasons for scatter in the experimental data are considered to be the differences in the composition of alloy additions and material microstructures due to the differences in cooling rates induced by the effect of different masses of steel ingots.

In this section, the effects of the alloy additions and the variations of material microstructures on the law of creep crack growth life are investigated.

These results will promote the development of the control technique for material structure that will enable us to accurately predict crack growth life and will contribute to the realization of high accuracy in the law for predicting the creep crack growth life.

3.2 Effect of alloy composition on the law of creep crack growth life

In this section, the effect of alloy composition on the law of creep crack growth life is investigated.

In order to determine the dominant effect of the alloy addition on creep crack growth life, the correlation between the life of creep crack growth obtained from experimental results and the amount of alloy addition was investigated. The results showed that the alloy addition that causes the greatest change in the law of creep crack growth is the absolute amount of Mo under the condition of 1.5% Mo equivalence. The effect of the absolute amount of Mo is to give a linear change in the life of creep crack growth, as shown in Fig. 2.

Figure 2 shows that the data of the creep crack growth life are clearly classified into two groups denoted A and B. One is the group of data for specimens sampled from the large-scale ingot of 20 or 80 tons (Group A). The other is the group of data for specimens that are sampled from the small-scale ingot of 50 kg (Group B).

For the experimental results of each group, the characteristic of the creep crack growth life shows a linear relationship against the absolute amount of Mo. In order to clarify the effect of Mo content on the life of creep crack growth, the relationship between the inverse value of the creep crack growth life, $1/t$, and the inverse value of the absolute temperature, $1/T$, are shown in Figs. 3 and 4 for groups A and B, respectively.
Within a group (A or B), the gradient of the linear relationships between 1/t\(_f\) and 1/T was found to be constant, as shown in Figs. 3 and 4 for groups A and B, respectively. Therefore, the effect of Mo content on the life of creep crack growth is to cause a parallel shift in the linear relationship between 1/t\(_f\) and 1/T. These characteristics show that since the activation energy of the crack growth life corresponds to the gradient of the linear relationship between ln 1/t\(_f\) and 1/T, the numerical values of the activation energy of creep crack growth life is found not to be influenced by the Mo content, and the effect of Mo content on the law of creep crack growth life causes the proportional change of the creep crack growth life. The numerical values of the activation energy for groups A and B are 225 and 434 kJ/mol, respectively.

The relationships between the inverse value of the creep crack growth life, 1/t\(_f\), and the initial stress intensity factor, K\(_{in}\), are shown in Figs. 5 and 6 for groups A and B, respectively.

Linear relationships between 1/t\(_f\) versus K\(_{in}\) appear and they were found to shift in a parallel manner for different amounts of Mo. These characteristics show that the values of the exponent of the initial stress intensity factor are not influenced by Mo content for groups A and B. The values of the exponent of K\(_{in}\) are 10 and 6.0 for groups A and B, respectively.

From the results mentioned above, the laws of creep crack growth life have unique characteristic values of the activation energy and power coefficient of initial stress intensity factor for groups A and B. That is, the effect of Mo content on the law for predicting the life of creep crack growth shows the proportional effect on the law.

Therefore, for each group of A and B, the law for predicting the life of creep crack growth, which incorporates the effect of Mo content, is derived and the degree of improvement in the predictive accuracy of creep crack growth life is discussed.

For creep-brittle materials, the equation of creep crack growth rate is defined by eq. (2) on the basis of the Q\(^*\) concept:8,9)

\[
\frac{da}{dt} = A \exp(Q^*) = AK_{in}^n \exp\left(-\frac{\Delta H_g}{RT}\right) \quad (2)
\]

where A is a constant, Q\(^*\) is the Q\(^*\) parameter, K\(_{in}\) is the initial stress intensity factor (MPa m\(^{1/2}\)), n is the exponent of K\(_{in}\), \(\Delta H_g\) is the activation energy (kJ/mol), R is the gas constant (= 8.3145 J/K mol) and T is the absolute temperature (K).

The life of creep crack growth t\(_f\) is obtained by integrating eq. (2) from \(a_i\) to \(a_f\), as given by eq. (3):

\[
t_f = \int_{a_i}^{a_f} \frac{dt}{\Lambda \exp(Q^*)} = \frac{1}{\Lambda} \exp(-Q^*) (a_f - a_i) = \frac{1}{\Lambda^*} \exp(-Q^*)
\]

where t\(_f\) is the life of creep crack growth (h), \(a_i\) is the initial crack length (mm), \(a_f\) is the final crack length (mm) and \(\Lambda^*\) is a constant \([\Lambda = A/(\alpha_f - \alpha_i)]\).

From eq. (3), the following equation is obtained:

\[
\frac{1}{t_f} = \Lambda^* K_{in}^n \exp\left(-\frac{\Delta H_g}{RT}\right)
\]

(4)

On the basis of eq. (4), the law of creep crack growth life that incorporates the effect of Mo content is derived as shown in eqs. (5) and (6) for groups A and B, respectively.

**Group A**

\[
\frac{1}{t_f} = f_1(Mo%)K_{in}^{10.0} \exp\left(-\frac{225}{RT}\right)
\]

(5)

where \(f_1(Mo%) = 1.87 \times 10^{-20} \exp(32 \times Mo\%)\) and Mo\% is the absolute amount of Mo.

**Group B**

\[
\frac{1}{t_f} = f_2(Mo%)K_{in}^{6.0} \exp\left(-\frac{434}{RT}\right)
\]

(6)

where \(f_2(Mo%) = 3.12 \times 10^{-13} \exp(9.55 \times Mo\%).\)
In order to investigate the degree of improvement in the predictive accuracy of creep crack growth life given by eqs. (5) and (6), the $Q^*$ parameter is derived for each group of A and B to estimate the life of creep crack growth. This is defined in eq. (2).8,9)

For the large-scale ingot (Group A), the $Q^*$ parameter is derived on the basis of eq. (5). This is given by

$$Q^* = 32Mo\% + 10\log K_{in} \frac{225}{RT}$$

(7)

The characteristics of the creep crack growth life for the large-scale ingot (Group A) are evaluated using this $Q^*$ parameter as shown in Fig. 8; they are compared with the scattering feature of crack growth life plotted against the absolute amount of Mo, as shown in Fig. 7.

This result shows that the accuracy of the prediction of creep crack growth life was improved and the data scatter decreased from 100% to 11% as shown in Figs. 7 and 8.

For the small-scale ingot (Group B), the estimation of creep crack growth life is also conducted using the $Q^*$ parameter. The $Q^*$ parameter is derived on the basis of eq. (6). This is given in eq. (8).

$$Q^* = 9.55Mo\% + 6.0\log K_{in} \frac{434}{RT}$$

(8)

The creep crack growth life for the small-scale ingot (Group B) is plotted against the $Q^*$ parameter as shown in Fig. 9.

This result shows that the accuracy of the prediction of creep crack growth life was improved and the data scatter decreased from 100% to 17% as shown in Figs. 7 and 9.

The reason why the experimental data were divided into two groups, as shown in Fig. 2, is discussed in section 3.3.

### 3.3 Investigation of the relationship between creep fracture mechanism and material microstructure by microscopic observation

#### 3.3.1 Observation of creep fracture surface by laser scanning microscopy

In the relationship between the absolute value of Mo content and the creep crack growth life shown in Fig. 2, the experimental data were found to be divided into groups A and B. Furthermore, the activation energy and power coefficient value of initial stress intensity factor in the law of the life of creep crack growth were found to be different between these two groups. Therefore, in this section, on the basis of metallographical investigation, the characterizations of the creep fracture surface are presented and the reason why the experimental characteristics were divided into groups A and B are clarified.

Three-dimensional representations of the creep fracture surface obtained by laser scanning microscopy for groups A (large-scale ingot: 20, 80 tons) and B (small-scale ingot: 50 kg) are shown in Figs. 10 and 11, respectively.

The experimental results in Figs. 10 and 11 show that...
creep cracks of both groups A and B grew in a periodic convexo-concave manner. The length of periodic convexo-concave segments of the creep fracture surface was measured and quantitative characterization of the creep fracture surface was conducted. The measurement method of a segment is as follows. The base line was drawn at the level of the mean value of the maximum and minimum heights of the convexo-concave segment. The distance between the points of intersection of the base line and creep fracture surface was defined as the length of a segment. The length of this periodic convexo-concave segment unit was denoted as the fracture area (FA).

On the basis of the results in Fig. 10, the average length of the FA of the specimen of group A (No. 1) is found to be 210 μm. Since the grain size of this material is 200 μm, the FA is found to be almost equal to the grain size. Therefore, the mechanism of creep crack growth of the specimen of group A (No. 1) is considered to be intergranular cracking, which is also found for the other specimens of group A.

On the other hand, on the basis of the results in Fig. 11, the average length of the FA of the specimen of group B (No. 6) is found to be 945 μm. Since the grain size of this material is 30 μm, the average length of the FA is found to be larger than the grain size. Therefore, the mechanism of creep crack growth of the specimen of group B (No. 6) is considered to be composed of a characteristic FA beyond the scale of the grain size. These Fracture Areas are considered to be caused by the growth of branched creep cracks that are larger than the grain size induced by the constraint of intergranular cracking due to the strengthened mechanism such as a martensitic lath. Similar results are also found for the other specimens of group B.

From the experimental results mentioned above, it is considered that the scale of the FA on the creep crack growth fracture surface is the origin of the difference in the law of the creep crack growth between groups A and B. Not only a difference in grain size but also a difference in fracture mechanism, such as intergranular cracking and the mechanism of FA beyond the grain size, exists between groups A and B. Correspondingly as is shown in section 3.2, the difference in activation energy $\Delta H_g$ was found between groups A and B ($\Delta H_g$ for group A is 225 kJ/mol and that for group B is 434 kJ/mol). This may come from the effects of the grain size and the coarsening of the martensitic lath due to the difference in cooling rate during the manufacturing process of steel ingots that have different weight volumes. Therefore, in the next section, the effect of the scale of the lath martensitic structure on the life of creep crack growth is investigated.

### 3.3.2 Observation of microstructure of material by AFM

In the previous section, the difference in the laws for predicting the creep crack growth life between groups A and B caused by the differences in cooling rates during the manufacturing process of steel ingots that have different weight volumes is considered to appear not only in the grain size but also in the microstructure of materials such as martensitic lath. Therefore, on the basis of the method described in section 2.2, the tested specimens were polished and etched. The observations of microstructures were carried out using atomic force microscopy (AFM). The results were then related to the grain size.

Three-dimensional representations of material surfaces obtained by AFM for groups A (large-scale ingot: 20, 80 tons) and B (small-scale ingot: 50 kg) are shown in Figs. 12 and 13, respectively.

The experimental results in Figs. 12 and 13 show that...
material surfaces of both groups A and B also had a periodic convexo-concave manner. The length of the periodic convexo-concave segment of the material surface was found to be different between groups A and B.

On the basis of the result in Fig. 12, the length of a segment for the specimen of group A (No. 1) was found to be 0.5~0.8 μm. On the other hand, on the basis of the result in Fig. 13, the length of a segment for the specimen of group B (No. 6) was found to be 0.25~0.42 μm. The length of a segment in Fig. 12 is found to be equal to the average width of a coarsened martensitic lath. The length of a segment in Fig. 13 is found to be equal to the width of noncoarsened martensitic lath. Therefore, the difference in the experimental results mentioned above is considered to be related to the difference in the width of martensitic lath induced by the differences in the cooling rates during the manufacturing process of steel ingots that have different weight volumes. The relationship between the grain size and the width of martensitic lath is shown in Fig. 14. From the result in Fig. 14, the grain size and the width of martensitic lath are found to be well correlated (correlation coefficient value: 0.98).

The experimental results presented above show that the difference in the laws for predicting the creep crack growth life between groups A and B due to the differences in the cooling rates during the manufacturing process of steel ingots that have different weight volumes appears not only in the grain size but also in the martensitic-lath-strengthened structure.

These results suggest that measurement of the grain size or the width of martensitic lath enables us to clarify whether the fracture mechanism is dominated by the intergranular cracking (group A) or the mechanism of the FA (group B) where the scale is larger than the grain size.

On the basis of eqs. (5) and (6) in section 3.2, the law of creep crack growth life that incorporates the effect of Mo content and microstructure is given by

\[
\frac{1}{t_f} = f_3(Mo\%, d^*) \left( \frac{K_m}{K_{00}} \right)^{n(d^*)} \exp \left( -\frac{\Delta H_d(d^*)}{RT} \right).
\]

where \(d^* = d / d_0\) (d: grain size (μm), \(d_0\): 1 μm), \(K_{00} = 1\) MPa m \(^{1/2}\), and \(f_3(Mo\%, d^*)\), \(n(d^*)\) and \(\Delta H_d(d^*)\) are given by eqs. (10), (11) and (12), respectively.

\[
f_3(Mo\%, d^*) = (-1.83 \times 10^{-9} d^* + 3.67 \times 10^{-13}) \times \exp(1.32 \times 10^3 d^* + 5.59)Mo\%\]

\[
n(d^*) = 2.35 \times 10^3 d^* + 5.29
\]

\[
\Delta H_d(d^*) = 471 - 1.23 \times 10^6 d^*
\]

On the basis of eq. (9), the \(Q^*\) parameter is derived as
where \( f_4(Mo\%, d^*) = (1.32 \times 10^5 d^* + 5.59)Mo\% - 9.88d^* \)

The creep crack growth life both for the large-scale ingot (Group A) and the small-scale ingot (Group B) are plotted against the \( Q^* \) parameter as shown in Fig. 16, and they are compared with the scattering feature of crack growth life plotted against the absolute amount of Mo, as shown in Fig. 15.

This result shows that the accuracy of the prediction of creep crack growth life is improved and the data scatter decreases from 100% to 30% as shown in Figs. 15 and 16. These results are considered to generally improve the accuracy of the predicted life of creep crack growth.

### 3.3.3 Relationship between the life of creep crack growth, the absolute content of Mo and the fracture area (FA)

The experimental results in the previous section showed that there are good correlations between the life of creep crack growth, the absolute content of Mo and the FA. In this section, these relationships are investigated in detail.

The relationship between the logarithmic value of \( 1/t_f \) and the FA is shown in Fig. 17 and the relationship between the FA and the absolute content of Mo is shown in Fig. 18. From the results in Figs. 17 and 18, the experimental relationships are found to be clearly classified into two groups of A and B, and there are good correlations in both groups, respectively.

The experimental results presented above indicate a good correlation between the life of creep crack growth, the absolute content of Mo and the FA. Furthermore, in order to conduct a detailed investigation of the correlation between them, the equation that is derived experimentally from Figs. 2 and 17 is compared with the equation that is derived from Fig. 18.
From the results of Figs. 2 and 17, the expression for the relationship between the absolute content of Mo and the FA on the life of creep crack growth is given by

\[
\frac{1}{t_f} = 1.71 \times 10^4 \exp(-31.9Mo\%) \\
= 1.24 \exp(2.11 \times 10^{-2}FA)
\]

(14)

where \( t_f \) is the life of creep crack growth (h), Mo\% is the absolute content of Mo (%) and FA is the fracture area (\( \mu m \)).

On the basis of eq. (14), the expression for the relationship between the absolute content of Mo and the FA is obtained as follows.

\[
FA = 453 - 1514Mo\%
\]

(15)

On the other hand, from the result in Fig. 18, the direct expression for the relationship between the FA and the absolute content of Mo is given by eq. (16).

\[
FA = 414 - 1300Mo\%
\]

(16)

Equation (15) is in quantitatively good agreement with eq. (16). These results indicate that the life of creep crack growth, the absolute content of Mo and the FA are well correlated.

4. Conclusions

Creep crack growth tests were conducted using W-strengthened 9–12%Cr steels with various contents of alloy additions and different microstructure dimensions. The effects of the composition of alloy additions and material microstructures on the life of creep crack growth for W-strengthened 9–12%Cr steel were clarified. Furthermore, the degree of improvement on the predictive accuracy of creep crack growth life was investigated. The following results were obtained.

1) The life of creep crack growth for W-strengthened 9–12%Cr steels was found to be sensitive to the absolute content of Mo under the condition of 1.5% Mo equivalence. The effect of Mo content on the law for predicting the life of creep crack growth showed the proportional effect in the law.

2) The differences in the cooling rates during the manufacturing process of steel ingots were found to affect not only the grain size but also the martensitic-lath-strengthened structure, which dominates quantitatively the activation energy and the values of the exponent of initial stress intensity factor in the law of creep crack growth life.

3) The law for predicting the life of creep crack growth that incorporates the effect of the Mo content and the microstructure of the material was derived. Using this law for predicting the life of creep crack growth, the accuracy of the prediction of creep crack growth life was improved and the data scatter was reduced from 100% to 30%. These results are considered to generally improve the accuracy of predicting the life of creep crack growth.

Acknowledgement

The authors acknowledge the 129 committee of the Japan Society for the Promotion of Science for supporting this research (Chairman: Prof. T. Yokobori). The authors thank the support of the 21st COE Program, “The Exploration of the Frontiers of Mechanical Science Based on Nanotechnology” from the Ministry of Education, Culture, Sports, Science and Technology. The authors also thank Dr. V. A. Yardley in Tohoku University for fruitful discussion.

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