Analysis on Degradation in Creep Strength of 9Cr-W Martensitic Steel

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Abstract

In order to clarify the creep mechanism of high Cr martensitic steel, creep curves of 9Cr-1W and 9Cr-4W steels were analyzed applying an exponential law to the temperature, stress, and time parameters. The activation energy, Q, the activation volume, V, and the Larson-Miller constant, C, are obtained as functions of creep strain. At the beginning of creep, sub-grain boundary strengthening by swept dislocations out of sub-grains occurs followed by strengthening due to the rearrangement of $M_{23}C_6$ and the precipitation of Laves phase. After Q reaches a peak, heterogeneous recovery and subsequent heterogeneous deformation begin at an early stage of transient creep in the vicinity of some weakest boundaries due to coarsening of precipitates, which triggers the unexpected degradation in strength due to the accelerating coarsening of precipitates. Stabilizing not only $M_{23}C_6$ but also Laves phase is important to mitigate the degradation of rupture strength of martensitic steel. The above creep mechanism for martensitic steel can be applicable to the explanation for the degradation in long term rupture strength of high Cr martensitic steel, Grades 91 and 92.

Keywords: creep, exponential law, martensitic steel, Grade 91, Grade 92, degradation mechanism, Laves phase

1. Introduction

It has been discussed that the rupture strength of the martensitic steel is lowered unexpectedly in creep testing longer than several tens of thousands of hours (Kushima, Kimura, & Abe, 1999; Sawada, Kushima, Kimura, & Tabuchi, 2007). The formation of both coarse Z-phase particles consuming finely dispersed MX particles and recovery zones in the vicinity of the primary austenite grain boundaries (PAGBs) is pointed out as major causes of the unexpected drop in strength (Kushima, Kimura, & Abe, 1999; Suzuki, Kumai, Kushima, Kimura, & Abe, 2003; Sawada, Kushima, & Kimura, 2006; Danielsen, 2007; Hald, 2008; Kimura, Sawada, Kushima, & Toda, 2013), where MX denotes carbonitride with cubic structure and M denotes metallic elements mainly Nb, V, and Cr and X denotes carbon and/or N. On the otherhand, Hu et al. (2009) and Di-Gianfransesco, Vipraio, & Venditti (2013) proposed a question that the direct cause of the unexpected drop in rupture strength may possibly depend on the stability of Laves phase. Though the proposed question is not accepted in general, it is important to investigate the actual cause of the unexpected drop in rupture strength for the purpose of improving rupture strength of high Cr martensitic heat resistant steel.

In this study, in order to solve this problem creep behavior of high Cr martensitic steel was investigated in another point of view. Abe (2005) indicated from both the creep curves and the observation of the microstructures of 9Cr-W steels (the W contents are 0, 1, 2, and 4%) that when the creep rate in a transient range of 9Cr-4W steel decreases sharply at low stresses due to finely precipitated Laves phase on the boundaries, the coarsening of Laves phase occurred rapidly resulting in the reduction of rupture lives as compared to the rupture lives as expected from the minimum creep rates (*MCR*, hereinafter) at higher stresses. Though the rupture lives deeply depend on the creep behaviors themselves as seen from this example, creep curves of heat resistant steel have not been studied intensively with respect of rupture strength.

The aim of this study is to deepen the knowledge on the unexpected drop in rupture strength of high strength martensitic steel. Since the microstructural changes of these high strength steels during long-term creep are very complex, creep behavior of simple alloy systems, 9Cr-1W and 9Cr-4W steels, is investigated. Three important

parameters, the activation energy, Q, the activation volume, V, and the Larson and Miller (L-M) constant, C, (Larson & Miller, 1952) for long-term rupture data of typical heat resistant steels for practical uses can be deduced by analyzing the creep data using an exponential law (Tamura, Esaka, & Shinozuka, 1999). The metallurgical meanings of these parameters, Q, V, and C, obtained using an exponential law are easily explainable as compared to a typical parameter of the stress exponent, n, obtained using a power law, which is commonly used. Following fruitful research findings are presented by analyzing creep data using an exponential law; namely, changes in microstructures during long-term creep of typical heat resistant steels (Tamura, Esaka, & Shinozuka, 2000), applicability of an exponential law in creep of metals including nickel base alloys and solders (Tamura, Esaka, & Shinozuka, 2003), precipitates analysis of Grade 91 steel during creep (Kabadwal, Tamura, Shinozuka, & Esaka, 2010). Larson-Miller constant of heat resistant steel and the physical meaning of the constant (Tamura, Abe, Shiba, Sakasegawa, & Tanigawa, 2013), changes in dislocation density during creep of 9Cr-1W steel (Tamura & Abe, 2015), and physical meaning of dislocation density in steady state creep by analyzing creep data of 21 types of ferritic/martensitic and austenitic steels including pure metals using an exponential law (Tamura, 2017). Sherby, Orr, & Dorn (1953) empirically found the well-known relationship that creep rates of pure metals are controlled by the self-diffusion of each metal and this relationship has been believed also to be a major principle for interpreting the creep phenomena of complex alloy systems. Tamura's report (2017) clearly showed theoretically from steady state creep rate using an exponential law that the Sherby's principle is true even for complex alloy systems. In this way, it is clear that an exponential law is useful to understand the creep phenomena of metals, and therefore, an exponential law is used for analyzing creep data of high Cr martensitic steels in this study.

2. Analysis method and the meanings of the parameters, Q, V, and C

2.1 Formulation of time to rupture

Time to rupture of heat resistant steel, t_r , can be expressed as

$$t_r = t_{r0} \exp\{(Q - \sigma V)/RT\},\tag{1}$$

where R, T, and σ are gas constant, absolute temperature (K), and the applied normal tensile stress, respectively (Tamura et al., 1999). When the pre-exponential factor, t_{r0} , of Equation 1 is related with C, the well-known L-M constant.

$$t_{r0} = 10^{-C}.$$
 (2)

From Equations 1 and 2, we obtain

$$\log t_r = Q/2.3RT - V/2.3R \cdot \sigma/T - C = [Q] - [V] - C.$$
(3)

When regression analysis for $\log t_r$ is made as a function of 1/T and σ/T according to Equation 3, we obtain three parameters, Q, V, and C (hereinafter, QVC for all parameters). In Equation 3, [Q] = Q/2.3RT and $[V] = \sigma V/2.3RT$ are absolute numbers, respectively, and we use these parameters in later sections. Q and V in Equation 1 are the apparent activation energy and the apparent activation volume for rupture, respectively, but for simplicity, we call them the activation energy and the activation volume, respectively. Usually, the stress vs. time to rupture data are plotted in a double log figure according to the Norton' law (Norton, 1929). However, we assume Equation 1 and so, a linear relationship for the stress vs. time to rupture is obtained in a semi-logarithmic diagram (the vertical axis is linear stress and the horizontal axis is logarithm of time to rupture, same as in the later sections). Tamura et al. (1999) confirmed for several heat resistant steels that when long-term rupture data are classified into 2 or 3 groups according to test conditions, the rupture data for each data group satisfies Equation 1. One of the technical merits of applying an exponential law to the rupture data is that it is easy to extrapolate the linear relationship obtained from a specific data group using Equation 1 in a semi-logarithmic diagram to a given test condition beyond the test conditions of the data group.

When we introduce Equation 1, we assume the average velocity of dislocations that glide through a crystal in a thermal activated process (Tamura et al., 1999):

$$v = v_0 \exp\{-(Q - \sigma V)/RT\},\tag{4}$$

and use the Orowan equation (Orowan, 1940)

$$\dot{\varepsilon} = M\rho bv \tag{5}$$

with the Monkman-Grant relationship (Monkman & Grant, 1956)

$$MCR = C_{MG}/t_r.$$
 (6)

Here, $\dot{\varepsilon}$ is the creep rate and v, v_0 , M, ρ , b, MCR, and C_{MG} are the average dislocation velocity, the pre-exponential factor of Equation 4, the factor conversion from shear strain to tensile strain, the dislocation

density, the length of the Burgers vector, the Monkman-Grant constant, respectively. We obtain from Equations 1, 4-6 assuming $\dot{\varepsilon} = MCR$

$$t_{r0} = C_{MG} / M \rho b v. \tag{7}$$

Namely, it is comprehensible from Equations 1, 2, and 7 that though the dislocation density is inversely proportional to the time to rupture, it is generally accepted that the dislocation density together with the velocity are not treated as independent variables, but they are encompassed in the Monkman-Grant relationship in considering the time to rupture of heat resistant steel. Here, we must also remind that the dislocation density for glide motions of dislocations corresponding to an observable creep strain, i.e., plastically deformed strain, is defined as the swept out number of dislocations from a crystal divided by the cross section of a crystal (Cottrell, 1964) and the dislocation density is not equal to the dislocation density in a crystal, though the dislocation density in the Orowan equation indicates all dislocation glided in a crystal including dislocations in a crystal, because the Orowan equation is applicable to a general work-hardening theory.

2.2 Broad Interpretation of Equation 1 to time to a specific strain

When we apply Equation 1 to time to a specific strain, the linear relationship between the σ and logarithm of time to a specific strain for a given data group should be confirmed for a wide range of test conditions and also the linear relationship between *MCR* and time to a specific strain in a double logarithmic diagram should be confirmed according to the Monkman-Grant relationship. We checked for all data studied, and among these typical examples will be shown in Appendix A, for simplicity.

In the Data Sheets of several heat resistant steels, for example Grade 92, No. 48B (the National Institute for Materials Science (NIMS), 2018), an instantaneous strain, ε_0 , time to 0.5, 1, 2, 5% strain and t_r together with *MCR* are listed and so, strain rate, $\dot{\varepsilon}(\varepsilon_i)$ at a strain of ε_i , where *i* is the order number from the minimum strain reported, can be calculated as

$$\dot{\varepsilon}(\varepsilon_i) = (\varepsilon_i - \varepsilon_{i-1})/(t_i - t_{i-1}),\tag{8}$$

where t_i is time to an i^{th} strain. The accuracy of the strain rate calculated using Equation 8 is not so high, because strain intervals are rather large. Special attentions should be paid for creep rates near the MCR because the strain rate near *MCR* is rather small and the sign of an increase rate of strain rate changes from minus to plus with increasing creep time. Moreover, the creep rates just before rupture are also calculated in order to utilize the data of t_r and rupture elongation (*EL*), though the strain rates are largely affected by necking for $t_i/t_r > 0.9$ (Lim et al., 2011). Concerning 9Cr-1W and 9Cr-4W steels studied, more data with small strain intervals are prepared, but only discrete data are adopted following the data structure of Grade 92 for comparison in future.

2.3 Metallurgical meanings of Q, V, and C

2.3.1 Activation energy

The activation energy is the magnitude of a barrier to be overcome for a dislocation in an activation process, when we consider a model based on crystallography. On the other hand, the activation energy calculated from Equation 3 is the apparent activation energy calculated from measurable and macroscopic variables, T, σ , and t_r or t_i and so, the value of Q is obtained assuming C does not depend on T. Therefore, Q contains not only the magnitude of the average creep resistance to mobile dislocations but the effect of temperature dependence of C namely t_{r0} in Equation 7 (Schoeck, 1980; Tamura et al., 2000). Moreover, Q contains the effect of back stress against a moving dislocation caused by grain boundaries, sub-boundaries, and the stress field arising from nearby dislocations and precipitates (Tamura, 2000). Therefore, when the sub-grains grow, the dislocation density decreases, and the precipitates are coarsened during long-term creep at high temperatures, the Q decreases due to the reduction of the back stress. However, the value of Q does not decrease without limit. It is well-known that the Q in a steady state creep at high temperature of pure metals are almost equivalent to the activation energies for self-diffusion (Sherby et al., 1953; Tamura, 2017). Therefore, the lower limit of Q approximately approaches to the activation energy for self-diffusion of alpha-iron, 267 kJmol⁻¹ (Oikawa, 1982).

2.3.2 Larson-Miller constant

The *C* can be calculated as a third term of Equation 3 and it is well-known that the value of *C* is approximately 20 for many heat resistant steels when test temperature and time to rupture are given in units of Kelvin and hours, respectively (in this study the value of *C* is treated as an absolute value, and so hereinafter the explanation for the units of *C* is omitted). The L-M constant is formulated as

$$C = \log(\rho \lambda v_{eff} b / 2C_{MG}) + \Delta S / 2.3R$$
(9)

where λ is the maximum distance that a dislocation can move from a start point to the next stable position through the activation process, v_{eff} is the effective attempt frequency per unit time to overcome the obstacles, and ΔS is the entropy change in the activation process (Tamura et al., 2013). The ρ in Equation 9 is not the observable dislocation density in sub-grains, ρ_{ob} , but the dislocation density that contributes to the detectable creep strain as already explained concerning Equation 5. But, we can assume $\rho \sim \rho_{ob}$ at sufficiently high temperatures (Tamura et al., 2013; Tamura, 2017; Tamura, 2018). For many cases, the assumption of $C \sim 20$ is common in arranging data when the sufficient data for optimizing the value of C is not obtained. However, the value of C affects largely the time to rupture according to Equations 1 and 2, because the time to rupture decreases by one order of magnitude when C increases only by 1. Substituting $\rho = 1E12 \text{ m}^{-2}$, $\lambda = 8E - 6 \text{ m}$, $v_{eff} = 3600E13 \text{ h}^{-1}$, $C_{MG} =$ 10 (%), and b = 2.5E - 10 m into the first term in the right side of Equation 9, we obtain $\log(\rho \lambda v_{eff} b/2C_{MG}) = 12.7 (h, \%)$. In this calculation, the logarithmic term increases only by 1 for the increase in ρ by one order of magnitude. This change is not so large as compared to the commonly accepted value, $C \sim 20$. In other words, the entropy term, $\Delta S/2.3R = 20 - 12.7 = 7.3$, the second term of Equation 9 is considerably large. Therefore, the main component of $C \sim 20$ is considered to be come from the entropy change for the formation and migration of vacancies during creep controlled by self-diffusion.

Moving dislocations receive not only the applied stress but also the back stress arising from surroundings. At the same time, the surroundings are received the effect of stress and strain field of moving dislocations. However, these influences and kinetic energy of moving dislocations are irrelevant to the observed creep strain. Therefore, these energies are treated as heat loss in a system at a constant temperature when we analyze creep rate and time to rupture assuming a thermally activated process. This heat loss is counted in the formulation of the Gibbs free energy as the entropy change, i.e. a part of C. The influence of the back stress is also counted in Q as a barrier to be overcome. Therefore, both Q and C increase with increases in dislocation density and the formation of finer sub-structures, and consequently, the values of Q and C for martesitic steels are generally large, typically, $Q = 800 \text{ k}\text{Imol}^{-1}$ and C = 35. On the contrary, both Q and C are small when dislocation density is low and the sub-grain size increases after long-term creep. In extreme cases, the value of Q and C for creep of a single crystal of pure iron are calculated as 294.0 kJmol⁻¹ and 12.06, respectively, analyzing creep data reported by Karashima, likubo, Watanabe, & Oikawa, (1971) and the value of Q and C for creep of polyctrystals of pure iron are calculated as 259.2 kJmol⁻¹ and 10.94, respectively, analyzing creep data reported by Karashima, likubo, & Oikawa, (1972). Moreover, the values that $Q = 259.2 \text{ kJmol}^{-1}$ and C = 18.56 for 0.2% carbon steel (Tamura et al., 2013) and $Q = 418 \text{ kJmol}^{-1}$ and C = 20.99 in the average for 3 heats of 0.5Cr-0.5Mo steel (Tamura et al., 1999) are obtained. Like these facts, $C \sim 20$ are confirmed for many heat resistant steels for practical uses. On the contrary, the values of C for creep of martensitic heat resistant steels studied are considerably large, C > 30. This is because martensitic steel contains a lot of dislocations and has very fine sub-structures, and therefore, energy loss, i.e. an increase in entropy, becomes so large for the migration of dislocations. Namely, in roughly saying, the changes in the L-M constant, C, can be substantially regarded as the changes in the entropy term of $\Delta S/2.3R$ in Equation 9, when martensitic sub-structures are maintained even after the long-term creep of high Cr martensitic steel with high strength.

2.3.3 Activation volume

From Equation 3, V is formulated as

$$V = -2.3RT(\partial \log t_r / \partial \sigma)_T.$$
(10)

This indicates that the magnitude of V is visually judged in a semi-logarithmic diagram of a $\sigma - \log t_r$ relationship, because V is inversely proportional to the magnitude of the slope of the $\sigma - \log t_r$ relationship at a constant temperature. The term, σV , in Equation 1 is equal to the work done by a specimen on a loading system in an activated state or the potential drop of the loading system (Esherby, 1956; Mura & Mori, 1976). Also, the potential drop is equal to the force on a dislocation, τb , times the area swept out of the dislocation in an activated state, where τ is a shear stress on a slip plane and is proportional to σ . Therefore, the V generally increases after long-term creep, because the swept out area by a dislocation motion increases in a sub-grain when the size of sub-grains is enlarged or the densities of obstacles for a dislocation decrease due to recovery (Tamura et al., 2000).

2.3.4 Inter-relationships between Q, V, and C

Q is an important parameter for creep strength, but it is not true that the creep strength is high when Q is large. This is because it is found from Equations 1 and 2 that the t_r is a product of a very large value, $\exp\{(Q - \sigma V)/RT\}$ and a very small value of 10^{-C} . Since Q is large as compared with σV , Q and C should have strong positive correlationship. Figure A1 in Appendix A typically shows relationship between Q and C of 9Cr-4W. As seen in Figure A1, the two parameters have a very strong positive correlation. However, it is reminded that Q and C have the different meanings with each other. Q denotes the magnitude of a barrier to be overcome for a moving dislocation, which is caused by nearby precipitates, dislocations, boundaries, and whole of a specimen. On the other hand, V is also an important parameter in creep, but V is a factor reflecting the movable area for a dislocation. Namely, V is a parameter relating to the microstructures only inside sub-grains and this point is essentially different from Q.

2.4 Heterogeneous deformation

In the previous sections we assumed uniform deformation, but Kushima et al. (1999) reported that the extremely recovered zone in the vicinity of the PAGBs with the width of approximately 1 µm was formed in a ruptured specimen of Grade T91 tested at 600 °C under 100 MPa ($t_r = 34\,141\,h$), where the unexpected drop in rupture strength was clearly confirmed. Strain concentration should occur in these heterogeneously recovered zones (HRZ). The strain rate in the HRZ should become higher than the observed creep rate, and consequently, the stress concentration should occur around in the HRZ. The "time to rupture" corresponding to the higher strain rate in the HRZ decreases referring to the Monkman-Grant relationship (Monkman & Grant, 1956). In this case, if we assume Q and V do not change, the value of C increases according to Equations 1 and 2, and it is clear that V decreases for stress concentration in the HRZ from Equation 1 assuming other variables are constant. These changes are more easily understood in case studies using Equation 1. Table 1 shows the calculated results for six cases of heterogeneous deformation using a data set of rupture: case A; standard condition with temperature interval $\Delta T = 50$ K, case B; strain concentration ($t_r = 0.1$ A), case C; stress concentration ($\sigma = 1.5$ A), case D; stress and strain concentration ($t_r = 0.1A, \sigma = 1.5A$), case E; the occurrence of remarkable and heterogeneous recovery simulated by increasing temperature interval ($\Delta T = A + 10$ K), which decreases Q, and case F; stress and strain concentration with remarkable and heterogeneous recovery ($t_r = 0.1A, \sigma = 1.5A, \Delta T = A + 10$ K), where A means the corresponding test conditions of the standard case, A, to each case. It is found from Table 1 that Vdecreases in cases C and D, and C increases in cases B and D as compared with case A and when the temperature interval increases in case E, both Q and C decrease. Finally when we suppose the occurrence of the stress and strain concentration in HRZ, i.e., case F, all of QVC clearly decrease as compared to the uniform deformation of case A. The case F is set up supposing the formation of the extremely recovered zone along the PAGBs observed by Kushima et al. (1999) in a ruptured specimen the time to rupture of which becomes unexpectedly short. As a matter of course, time to rupture for the case F is shorter than that of the case A.

Conditions	А	В	С	D	E	F
	Standard $(\Delta T=50 \text{ K})$	$t_r = 0.1 \text{A}$	σ =1.5A	B*C	Increase in ΔT , (ΔT =60 K)	E*B*C
Q / kJmol ⁻¹	485.5	485.5	485.5	485.5	408.8	408.8
$V/ \text{ cm}^3 \text{mol}^{-1}$	365.8	365.8	243.9	243.9	365.8	243.9
C	22.48	23.48	22.48	23.48	18.13	19.13

Table 1. Results of *QVC* calculation for six test conditions. Test conditions are explained in the text. Bold italics indicate the changes from the standard test condition, A

2.5 Rupture strength of welded joints

Typical creep rupture behavior of a heterogeneously recovered and deformed zone can be observed in the creep tests of the welded joints. Figure 1 shows the results of rupture tests of the welded joints made of Grade 91 plate with 25 mm thickness fabricated by tungsten inert gas (TIG) welding and post weld heat treatment (PWHT) at 745 °C for 60 min (Hongo, Tabuchi, Li, & Takahashi, 2009). In the figure, the results of the base metal and the simulated heat affected zone (HAZ) with the same PWHT as the TIG welded joint are also shown. The TIG welded joint specimens are ruptured at HAZ except for two specimens tested at 550 °C under higher two stresses. Simulated HAZ specimens are rapidly heated to an approximate temperature of the A_{C3} transformation (~900 °C) followed by rapid cooling, where the whole specimen is heat-treated simulating the microstructure of HAZ of TIG welding, which results in minimizing rupture lives of the simulated HAZ. Therefore, it is naturally accepted that rupture lives of the welded joint is between those of base metal and the simulated HAZ. Moreover, the reliability of the tests is also confirmed from that the rupture lives of the welded joint which ruptured at HAZ, the

base metal, and the simulated HAZ are calculated according to Equation 3 and the results are listed in Table 2. It is found from Table 2 that the value of Q for the simulated HAZ is higher than that of the base metal, but at the same time C of the simulated HAZ increases much more than that of the base metal, as a result, rupture lives of the simulated HAZ become shorter than the base metal. The most important point obtained from Table 2 is that the QVC of the welded joint are smaller than all of those of the base metal and this fact is similar to the results for the case F in Table 1, where the microstructure is supposing the formation of the extremely recovered zone along the PAGBs reported by Kushima et al. (1999).



Figure 1. Stress-rupture life relationship for TIG welded joint, the simulated HAZ, and the base metal of Grade 91

Table 2. The results of *QVC* analyses on the rupture data shown in Figure 1 of the base metal of Grade 91, the simulated HAZ, and the TIG welded joint

Grade 91	Base metal	Simulated. HAZ	Welded joint ruptured at HAZ
Q / kJmol ⁻¹	798.3	974.2	561.4
$V/ \text{ cm}^3 \text{mol}^{-1}$	549.7	598.8	274.6
С	39.82	51.67	28.32

Hongo et al. (2009) also performed the rupture tests of the TIG welded joint also at 650 °C, and the similar conclusion is obtained using the data at 600 and 650 °C with the results mention above. It is confirmed by using the data of Ogata, Sakaki, & Yaguchi (2009) that the QVC of the gas tungsten arc welded (GTAW) joint ruptured at HAZ of Grade P91 are smaller than those of the simulated HAZ and the base metal and it is also confirmed by using the data of Tabuchi et al. (2001) that the V of the GTAW joint and the electron beam welding (EBW) joint of Grade P122 at 650 °C are smaller than the base metal and the simulated HAZ, though the Q and C cannot be calculated. Morimoto, Ohkita, and Sakurai (1997) also reported the rupture lives of the welded joints of Grade 92 and the QVC calculated from the rupture data were smaller than the base metal. These rupture phenomena of the welded joints are the typical cases of heterogeneous deformation. Therefore, it is phenomenologically understood from the above that the all parameters of QVC for the heterogeneous deformation become smaller than those for the cases of the base metal, i.e., uniform deformation.

3. Materials analyzed and their microstructure

3.1 Materials analyzed

9Cr-1W steel (Abe, Araki, & Noda, 1991; Abe, 2003) and 9Cr-4W steel (Abe et al., 1991; Abe, Nakazawa, Araki, & Noda, 1992; Abe, 2005), are prepared in a laboratory scale. The names of 9Cr-1W, 9Cr-4W are used for each steel in this study, and moreover, the abbreviated names, 1W and 4W are also used in some cases.

3.2 9Cr-W steel

Microstructure of quenched and tempered 9Cr-1W is tempered martensite and the precipitates before the rupture test and during the creep test are only $M_{23}C_6$ and Laves phase is not confirmed, where M denotes metallic element such as Cr, Fe, Mo, and W (Abe et al., 1991; Abe, 2005). Microstructure of quenched and tempered 9Cr-4W is mainly tempered martensite but containing 10 volume % of delta ferrite (Abe et al., 1991). Vickors hardness numbers for 9Cr-1W and 9Cr-4W are 203 and 211, respectively. 9Cr-4W steel contains $M_{23}C_6$ and small amount of M_6C where M denotes Fe and W before the creep tests and Laves phase was not confirmed. During transient creep at 600 and 650 °C, fine laves phase precipitates were observed on Lath martensite boundaries, which contributes to strengthen the grain- and sub-boundaries together with $M_{23}C_6$ precipitates, but Laves phase precipitates are coarsened soon and consequently accelerate the creep rate (Abe, 2005). The nose point of a time-temperature-precipitation (TTP) curve for Laves phase in the delta ferrite of aged specimens is 650 °C and 15 h (Abe et al., 1991; Abe et al., 1992).

4. Results of Analysis and Discussion

4.1 9Cr-1W steel

4.1.1 Time to rupture and analysis of creep curves

The relationship between stress and time to rupture of 9Cr-1W steel was obtained at 550 - 650 °C (Abe et al., 1992). The data were classified into three groups, Grs. I - III, and the regression lines were obtained using Equation 3 for each temperature in each group. The results are shown in Figure 2. In the classification, stress vs. time to a specific strain, t_{ε} , diagrams were obtained using the original creep curves and were referred, where $\varepsilon = 0.25 - 10^{-10}$ 10%. The typical diagrams are shown in Figure A2. In Figure A2a, $t_{0.25}$ denotes time to 0.25% strain and the similar symbols are used in this paper. Linear relationships between linear stress and logarithmic time are confirmed in Figure A2 in the same way as Figure 2, which indicates that time to a specific strain can be applied to Equation 1 if we replace t_r with t_s . Figure 2 shows that the lower the stress is, the longer the t_r is at a constant temperature or the $\sigma - t_r$ relationship changes in inverse J-shape along Gr.I to Gr.III at 600 °C. This trend is the same in the $\sigma - t_{\varepsilon}$ relationships for $\varepsilon = 1 - 10\%$. But, concerning the $\sigma - t_1$ relationship, there is little difference between Gr.I and Gr.II, and on the contrary, $t_{0.25}$ for Gr.II is shorter than that estimated from the data for Gr.I, then we call it Z-shape (Figure A2a). The inverse J-shape relationship in a $\sigma - t_{\varepsilon}$ diagram is frequently observed in high temperature creep of metal, and the inverse J-shape relationship is of course confirmed in a double logarithmic plot of σ and t_r , usually used. In such cases, the creep data are used to be plotted in a double logarithmic diagram of sinh($\alpha\sigma$) and t_r , where α is a parameter to obtain a linear relationship at a temperature in the diagram (Garofalo, 1963). However, there is no physical meaning in an adjustable parameter, α and thus we cannot infer what happens in a wide range of time to rupture. On the other hand, Equation 1 is originally introduced as an approximate equation for high stresses of a theoretical equation, $\dot{\varepsilon} \propto \sinh\sigma$, proposed for a thermally activated process applied to a dislocation motion (Schoeck, 1980). Equation 1 holds when $X = \sigma V/RT > 1$, and we obtain the relationship $X \sim n$ based on an extremely rough approximation, where n is the well-known stress exponent in a power law (Tamura et al., 2003). But, as a matter of course, the physical meaning of $X \sim n$ cannot be solved. We obtain $\sigma > 9.8$ MPa for X > 1 substituting the average temperature and the value of V for Gr.III. The minimum stress for Gr.III is 29.4 MPa and is much larger than the critical value of 9.8 MPa, and thus, there is no problem applying Equation 1 to Gr.III for 9Cr-1W steel. Therefore, the phenomenon that the time to rupture for 9Cr-1W steel under lower stresses are prolonged as compared to those estimated from data under higher stresses and lower temperatures should be able to be explained metallurgically.



Figure 2. Relationship between stress and time to rupture for 9Cr-1W steel. Regression lines for each data group are explained in Section 4.1.1 and the data were analyzed employing the exponential method explained in Section 2 (Similar explanation is omitted, hereinafter).

Figure 3 shows the relationship between strain and the average normalized strain rate plotted in a double logarithmic diagram, where a strain rate at a specific strain is divided by each *MCR* (named by *NSR*) and then the normalized *NSR*s are averaged for each group. In the figure, the strain in the far right for each group is the average of the *EL* (the same, hereinafter). In Figure 3, characteristics of each group are clearly shown, namely, the average *NSR*s for *Gr.II* at an early stage of transition creep are rather high as compared to those for *Gr.II* followed by rapid hardening (the slope, $\Delta \log(average NSR)/\Delta \log \varepsilon$, is steep), and this trend becomes clearer for *Gr.III*. Strains for the *MCR*s for each group in Figure 3 are ranging between 2 - 5%. In accelerating creep the average *NSR*s for *Gr.II* are rather small, but the slope are the same for all in accelerating creep. It is thought from Figure 3 that the rupture behavior of 1W steel shown in Figure 2.



Figure 3. Average NSR vs. strain relationship for 9Cr-1W steel

Figure 4 shows the variations of QVC as functions of strain for each group. Strains to the *MCR* and the maximum value in the vertical axis are marked by a solid and a large mark, respectively, for each group (the same for all similar figures, but the explanation is omitted hereinafter). The values of Q at rupture for all groups in Figure 4 are approximately 400 kJmol⁻¹ and are little larger than the activation energy of self-diffusion of alpha iron (Oikawa, 1982), and moreover, the values of C are approximately 20, which are the same values confirmed in many heat resistant steel (Tamura et al, 2013). Therefore, although the microstructure before testing of 1W steel is tempered martensite, the steel are judged to be ruptured in a fully recovered state.



Figure 4. The results of the *QVC* analysis are shown as functions of creep strain for each group of 9Cr-1W steel; a) the activation energy, b) the activation volume, and c) the Larson-Miller constant. The values for MCR and the maximum values are marked for each group by solid and large marks, respectively. On the right side of each figure, the guide lines for the metallurgical reactions corresponding to the increase and decrease of each variable, *QVC*, are indicated (the same for the similar diagrams, hereinafter).

4.1.2 Gr.I

Q and C shown in Figure 4 increase up to a strain of 1% in a transient creep range, and then tend to slightly decrease with increasing strain. The increase in Q denotes strain hardening and the increase in C denotes the increase in entropy associated with the movement of dislocations. V tends to increase slightly in an approximately whole duration of creep, which indicates certainly that recovery inside the sub-grains continuously occurs. The observations of microstructure of this steel (Abe et al., 1991, 2003, and 2005) indicated that the dislocation density inside the sub-grains decreases during creep and any precipitates except for M₂₃C₆ do not form under the average conditions of Gr.I, i.e., 563 °C, 167 MPa, and t_r =155 h. In this study, a term of sub-grain denotes, hereinafter, a general term as a minimum unit of creep deformation including the martensite lath, block, packet, and also the sub-grains themselves.

In a strain range of up to 1% strain, hardening, i.e., the increase in Q, and recovery, i.e., the simultaneous increase in V, are certainly confirmed. However, these are not contradictory statements each other. This takes place, because the increase in V denotes recovery only inside the sub-grains, and consequently the swept out dislocations during creep from the sub-grains to the PAGBs and boundaries of packet, block, and lath martensite are accumulated, however, these accumulated dislocations cannot move or annihilate at a time, because many sub-grains nearby jostle and do not deform freely each other. We call this phenomenon *Sub-grain Boundary Strengthening by Dislocations* (SBSD). In other words, SBSD is explained as follows; boundaries are strengthened due to the dislocations caused by the recovery inside the sub-grains, which results in the increase in Q, as a consequence the back stress to a dislocation increases, the effective stress decreases, the dislocation velocity decreases, and therefore, the creep rate at an early stage of creep decreases with increasing strain, as shown in Figure 3. Martensitic steel contains a lot of dislocations, and therefore SBSD may easily happen like a traffic jam as compared with other soft materials. SBSD is always observed in an early stage of transient creep and is an essential hardening mechanism for martensitic steel. The term of SBSD is used hereinafter without any explanation. After *MCR* at 2% strain, Q and C tend to decrease and V increases with an increase in strain, and so, accelerating creep is in progress recovering microstructure. Though transient creep is still continued in a strain range of 1 - 2% strains, both Q and C decrease, which reminds us that recovery may begin from 1% strain. However, V also slightly decreases, and therefore, another mechanism than that in an accelerating creep range should occur in a strain range of 1 - 2% strains. A phenomenon of a decrease in V in a transition creep range is more clearly observed in *Gr.III* and therefore this phenomenon will be explained in detail in Section 4.1.6.

4.1.3 Gr.II

Both Q and V increase largely up to 5% strain, near the *MCR* strain, and at higher strains both Q and V are roughly constant. On the other hand, C increases rapidly up to 1% strain and then remains flat. Therefore, SBSD occurs rightly in *Gr.II* up to 1% strain like in *Gr.I*, but both Q and V still continue to increase until higher strains than $\varepsilon = 1\%$, where the Q for *Gr.I* begins to decrease. Coarsening of M₂₃C₆ occurs in *Gr.II* (Abe et al., 2003), because the average test conditions of *Gr.II* are 583 °C, 114 MPa, and $t_r=1198$ h and the average temperature is higher than that in *Gr.I.* It is generally accepted that the dislocation density inside sub-grains decreases and the sub-grain size increases with increasing creep strain (Abe et al., 1992; Sawada et al., 2011). In these cases, some of the M₂₃C₆ particles precipitated on the sub-grain boundaries temporarily dissolve into the matrix accompanying the migration of the sub-boundaries (Abe et al., 1991). We call this phenomenon *Dissolving and Finely Re-Precipitation* (DFRP), hereinafter. If this mechanism did not operate for *Gr.II*, Q should decrease continuously after SBSD like *Gr.I* or the strong SBSD could continue through an accelerating creep range, but that is not actually true. As a consequence, the increases in both Q due to fine precipitates and V due to the growth of sub-grains continue up to higher creep strains than those in *Gr.I* lead to elongate t_{ε} and t_r of *Gr.II* as estimated from that of *Gr.II* (see Figures 2 and A2).

4.1.4 Gr.III

Q increases largely up to 2% strain and then decreases slightly from 5% strain. *C* changes same as *Q*. On the other hand, *V* increases largely up to 1% strain and then clearly decreases up to 10% strain, followed by a slight decrease up to rupture. SBSD occurs up 1% strain like *Grs.I* and *II*. The DFRP mechanism for M₂₃C₆ caused by the growth of sub-grains is considered to operate remarkably in $\varepsilon = 1 - 5\%$ as compared to *Gr.II*. The reason for this is as follows: Since the average test conditions of *Gr.III* (630 °C, 62.8 MPa, and t_r =3857 h) are positioned in a higher temperature and longer time range than those for *Gr.III* are smaller than those of *Gr.III*, which indicates that microstructure of *Gr.III* is recovered more progressively than that of *Gr.II*.

The values of V are considerably high in a whole range of creep strain, and therefore recovery inside sub-grains should occur remarkably. On the other hand, V decreases clearly after the peak at 1% strain and so an inverse phenomenon against recovery must occur. However, precipitation hardening that can explain the decrease in V should never occur inside the sub-grains of 9Cr-1W steel. Therefore, the decrease in V at higher strains than 1% must be caused by heterogeneous creep deformation like the creep phenomena for welded joints, explained in Section 2.5. Namely, when SBSD reaches a peak at 1% strain, the recovered zones or sub-grains are newly created near the weakest boundaries including PAGBs accidentally formed by an SBSD phenomenon, followed by strain-and stress concentration and the consequent stress relaxation due to heterogeneous deformation. These sequential phenomena usually should take place just after the final stage of SBSD, an initial creep deformation mechanism for martensitic steel explained in Section 4.1.2. We call this series process *Heterogeneous Recovery and Heterogeneous Deformation* (HRHD), hereinafter.

If we imagine a simple local deformation occurs continuously after 1% strain, accelerating creep may take place. However, as seen in Figure 4a, Q clearly increases up to $\varepsilon = 5\%$ and consequently strain rate decreases as seen in Figure 3. Therefore, during the occurrence of HRHD at strains higher than 1%, the DFRP mechanism for M₂₃C₆ takes place continuously and actively, and so, Q for *Gr.III* become higher than that for *Gr.II* as seen in Figure 4a. This mechanism is lowering the strain rate and as a result, the t_{ε} and t_r are elongated as compared to those of *Gr.II*. By the way, V continues to decrease after 5% strain, but the decreasing rate becomes slow down. There are two choices of interpretations for this phenomenon; first one is that the degree of HRHD is essentially slow down and the second, the increase in V due to the growth of sub-grains usually occurred during creep. Metallurgical observations are needed to explain the decrease in V due to HRHD.

4.1.5 SBSD and HRHD

In the previous sections, 4.1.2 - 4.1.4, it was explained that the decrease in creep rate in an early stage of transient creep of 9Cr-1W martensitic steel is caused by SBSD and that the decrease in creep rate in a later stage of transient creep for *Gr.III* after the peak of *V* is caused by HRHD accompanying the DFRP for M₂₃C₆. Both SBSD and subsequently occurred HRHD are new concepts, respectively and therefore, the validities of these concepts must be verified further.

In the above analyses, QVC are obtained using t_r and t_{ε} and not the strain rates at a specific strain. The reasons for this are that the rupture data are most popular and the number of t_r accumulated is very large and that the creep rates near rupture calculated using Equation 8 are remarkably affected by necking of a specimen, though the strain rate is an important parameter reflecting adequately a state of microstructure at a given strain. Therefore, for the purpose to analyze both SBSD and HRHD in detail which are observed in transient creep of Gr.III of 9Cr-1W steel, the activation energy, Q_s , the activation volume, V_s , and Larson-Miller constant, C_s , are evaluated anew using the strain rates at a specific strain calculated using Equation 8, instead of t_r and t_{ε} . Following equation similar to Equation 3 is obtained from Equations 1, 2, and 6 and the regression analyses were made.

$$\log \dot{\varepsilon} = -[Q_s] + [V_s] + C_s, \tag{11}$$

where the square blankets denote the same as Equation 3. The results of Q_s , V_s , and C_s for Gr.III of 9Cr-1W steel are shown as functions of creep strain in Figure 5. The variations in Q_s , V_s , and C_s are very similar with those shown in Figure 4 for Gr.III. The values of Q_s , V_s , and C_s in Figure 5 are 0.81 - 1.26 times of those of QVC in Figure 4. Analyses were made for all data including a creep rate at rupture, but the values of Q_s , V_s , and C_s at rupture are not discussed deeply hereinafter in the similar figures shown in later, because the creep rate at rupture are affected by necking of a specimen. The Q_s , V_s , and C_s shown in Figure 5 all increase up to 1% strain and therefore, the occurrence of SBSD is reconfirmed. In the strain range of 1 - 5% of transient creep, though the increasing rates of both Q_s and C_s slow down and the V_s decreases, both the Q_s and C_s still increase and the V_s keeps high level, therefore, the SBSD phenomena are considered to continue to an MCR point. However, since the $V_{\rm s}$ decreases between a strain range of 1 – 5%, an additive reaction other than the SBSD must be took place. To solve this problem, the relationship between the changes in Q_s , V_s , and C_s with increasing strain and the changes in the corresponding strain rate was analyzed. Table 3 shows the differences in the $[Q_s]$, $[V_s]$, C_s , and $\log \dot{\varepsilon}$ in Equation 11 between two adjacent strains, $\Delta[Q_s]$, $\Delta[V_s]$, ΔC_s , and $\Delta \log \dot{e}$ at an average temperature and under an average stress for Gr.III of 9Cr-1W steel. Take care that negative values for $\Delta[Q_s]$ are listed in Table 3 to set the summation of above three in each column equal to $\Delta \log \dot{e}$ and the determinant terms for the strain rate are indicated in bold italics. Table 3 seems to show that the changes in $\Delta \log \dot{\epsilon}$ can be explained by the changes in

 $\Delta[Q_s]$, when we look only at the changes in Q_s , i.e., the magnitude of resistance to the mobile dislocations. As seen in Table 3, $-\Delta[Q_s] < 0$ is really a determinant term in $\varepsilon = 1 - 5\%$, but with just that the change in strain rate does not become negative or transient creep does not hold. The fact of $\Delta[V_s] < 0$ is an absolutely necessary condition to keep transient creep in a strain range of 1 - 5%. In other words, if we remind that $-\Delta[Q_s] < 0$ is also

a determinant term and Q for *Gr.III* is larger than that for *Gr.I* as shown in Figure 3, it can be understood that the sequential processes of heterogeneous recovery and heterogeneous deformation, i.e., HRHD, followed by both the creation of new sub-grains and the DFRP mechanism operating on M₂₃C₆, as mentioned in Section 4.1.3, are an absolutely necessary packaged-process for transient creep in the strain range of 1 - 5% for *Gr.III* of 9Cr-1W steel.

Table 3. The differences in Q_s , V_s , C_s , and $\log(\dot{\varepsilon})$ between two adjacent strains at an average temperature and under an average stress for *Gr.III* of 9Cr-1W steel. Bold italics indicate determinant terms.

Strain range	[0.25 - 0.5%]	[0.5 - 1%]	[1 - 2%]	[2 - 5%]	[5 - 10%]	$[10\% - t_r]$
$-\Delta[Q_s]$	-4.59	-3.18	-0.80	-0.08	0.63	0.90
$\Delta[V_s]$	1.07	0.35	-0.32	-0.40	-0.28	-0.26
ΔC_s	3.07	2.53	0.82	0.42	-0.06	0.39
$\Delta \log(\dot{\epsilon}, \%/h)$	-0.45	-0.30	-0.30	-0.06	0.30	1.03

When new and small sub-grains are created by heterogeneous recovery, the average migration distance or movable area for dislocations may decrease locally, which causes a decrease in V. But, recovery essentially continues during creep, and so, the newly born sub-grains easily grow, i.e., V increases soon, if there is no pinning obstacles against grain growth. However, Figure 5 shows not only the decrease in V_s , but Q_s also increases within $\varepsilon = 1 - 5\%$. This suggests that when the DFRP mechanism should operate on M₂₃C₆ particles, the prevention of the excess growth of the newly created sub-grains occurs. This means that even though the HRHD occurs within this strain range, clear hardening that resists the softening effect due to HRHD surely occurs by the DFRP mechanism. This is the origin of the increase in Q_s within $\varepsilon = 1 - 5\%$ for Gr.III of 1W steel in spite of the occurrence of the HRHD.

In the above story, the V for the welded joint is smaller than that of the base metal and so, we can assume that heterogeneous deformation should occur in martensitic steel when V decreases. However, we do not image the occurrence of macroscopic local deformation like welded joints, but we image the size of heterogeneous recovery is at most 10 μ m, the size of the primary austenite grains. Such recovered areas are randomly arising near the weak boundaries with less SBSD through a specimen. Therefore, macroscopically the specimen deforms uniformly.

By the way, an early stage of transient creep of martensitic steel is frequently explained by another story, not by SBSD: there are a lot of excess dislocations inside a sub-grain, the dislocation density inside the sub-grain decreases with the progress of creep strain, and so, the strain rate decreases according to the Orowan equation, Equation 5. This explanation is qualitatively correct, but the quantitative examination is necessary. It is hardly occur that the dislocation density inside a sub-grain decreases by one order of magnitude within a short range of strain, but assuming the dislocation density decreases by one order of magnitude up to 1% strain, dislocation density increases by one order of magnitude due to the swept out dislocations, and in this case, the value of C in Equation 9 increases only by one. However, Figure 4 shows that the evaluated values of C increase at least by 3.9 for Gr.III through the increase in creep strain from 0.25% to 1% and therefore, the explanation that the decrease in the strain rate of martensitic steel is caused by the decrease in the excess dislocations inside sub-grains is considered to be insufficient. The decrease in strain rate in an early stage of creep should be explained preferably based on the fact that both the second term of Equation 9, i.e., the entropy term, and Q_s increase during this strain range. Certainly, as seen in Table 3, both ΔQ_s and ΔC_s increase largely up to 1% strain. The increase in Q_s denotes the increase in the back stress against the motion of dislocations caused by the accumulated dislocations swept out of sub-grains on the sub-boundaries. The increase in C_s is caused mainly by the increase in entropy associated with the dislocation movement. Table 3 also shows that V_s increases largely up to 1% strain, which denotes that a lot of dislocation are swept out of the sub-grains and so the movable area of dislocations increases. These facts support the concept of SBSD explained in Section 4.1.2.

In Section 4.1.2, we mentioned that both Q and C also decrease in $\varepsilon = 1 - 2\%$ for Gr.I where V decreases. This situation is just differ from the case for Gr.III, though V decreases in both groups. Therefore, we tried the $Q_sV_sC_s$ analyses similar with those shown in Table 4 were made on the data of $\varepsilon = 1 - 2\%$ of Gr.I. It was confirmed from the analyses that the determinant terms to reduce the strain rate are the decreases in both $\Delta[V_s]$ and ΔC_s , though the table is omitted for simplicity. Namely, HRHD is also necessary to reducing creep rate in $\varepsilon = 1 - 2\%$ for Gr.I of 1W steel. Table 4 summarizes for convenience in what conditions SBSD, DFRP, and HRHD occur based on the above discussion and the $Q_sV_sC_s$ analyses for 9Cr-1W steel. It is found from the above that SBSD is an essential creep process at the beginning of creep of martensitic steel. In a later stage of transient creep, from 1% strain to an *MCR* point, though recovery is the basic process for martensitic steel, the decrease in creep rate is maintained through the combination process of a decrease in the entropy term, C_s , hardening due to DFRP of M₂₃C₆, or HRHD. In accelerating creep, decrease in Q_s due to recovery is the determinant term, but when Q_s does not decrease with an increase in strain for example due to DFRP for M₂₃C₆, an increase in C_s is the determinant term (*Grs. I* and *II*). Both SBSD and HRHD are also frequently observed in transient creep of the strengthened martensitic steels, Grades 91 and 92, which will be presented in near furture.

Table 4. Summary for the operation of SBSD, DFRP, and HRMD as functions of creep stages for each data group of 9Cr-1W steel. Q_{s+} etc. and Q_{s-} etc. denote an increase and a decrease, respectively, for indicated creep stages. Determinant terms in each creep range are shown in bold italics. Parentheses denote phenomena are weak

Grs. and	Tr	ansient creep	Accelerating creep	
temperature	emperature $\mathcal{E} < 1\%$ $1\% - MCR$		<i>MCR</i> – 10%	
<i>Gr.I</i>	$\boldsymbol{Q}_{s+}, \ \boldsymbol{V}_{s+}, \ \boldsymbol{C}_{s+}$	Q _{s-} , <i>V_{s-}, C_{s-}</i>	$\boldsymbol{Q}_{s-}, \ \boldsymbol{V}_{s+}, \ \boldsymbol{C}_{s-}$ and then $\boldsymbol{Q}_{s-}, \ \boldsymbol{V}_{s+}, \ \boldsymbol{C}_{s+}$	
563 °C	SBSD	HRHD, (recovery)	Recovery	
<i>Gr.II</i>	$\boldsymbol{Q}_{s+}, \ \boldsymbol{V}_{s+}, \ \boldsymbol{C}_{s+}$	$\boldsymbol{Q}_{s+}, \ \boldsymbol{V}_{s+}, \ \boldsymbol{C}_{s+}$	$(Q_{s+}, V_{s-}), C_{s+}$	
583 °C	SBSD	Recovery, DFRP for $M_{23}C_6$	(Recovery), DFRP for $M_{23}C_6$	
<i>Gr.III</i>	$\boldsymbol{Q}_{s+}, \ \boldsymbol{V}_{s+}, \ \boldsymbol{C}_{s+}$	Q_{s+}, V_{s-}, C_{s+}	$\boldsymbol{Q}_{s-}, \ \mathrm{V}_{s-}, \ \mathrm{C}_{s-}$ (HRHD), DFRP for $\mathrm{M}_{23}\mathrm{C}_{6}$	
630 °C	SBSD	HRHD, DFRP for $M_{23}C_6$		

4.1.6 Factors for the increase in strength of Gr. III as compared to those of Gr. II

HRHD denotes a series of plural number of processes approaching to creep rupture without any hardening process. However, we confirmed from the above that t_{ε} and t_{τ} in Gr.III are longer than those estimated from Gr.II for all strains and that HRHD surely occurs in Gr.III and does not occur apparently in Gr.II. Therefore, to investigate the relationship between this fact and metallurgical reactions, t_{ε} and t_r for Grs.II and III under the conditions of the average temperature and stress of Gr.III were calculated (these variables are symbolized as t_{II} and t_{III} , respectively, hereinafter), [Q], [V], and C were calculated according to Equation 3, and the differences between the obtained values of [Q], [V], and C, $(\Delta[Q], \Delta[V])$, and ΔC , hereinafter) were also calculated. The results for each strain are shown in Table 5. In the table, the differences between logarithmic t_{III} and t_{II} , i.e., $\log(t_{III}/t_{II})$, and key factors for the differences are also shown. In Table 5, the values of $-\Delta[V]$ and $-\Delta C$ are listed so that the summation of each term becomes $\log(t_{III}/t_{II})$ and moreover, the determinant terms for $\log t_{III} > \log t_{II}$ are indicated in **bold** italics. It is found from Table 5 that the increase in strength for Gr.III as compared to the strength estimated from Gr.II is caused mainly by the recovery due to the decrease in ΔC except for 2% strain. However, that is not all. Table 5 shows clearly that the increases in $\Delta[Q]$ are also an important key factor under an almost whole duration of creep from 0.25% to 10% strain excepting 0.5% strain for the increase in strength of Gr.III, $logt_{III} > logt_{II}$, where the DFRP mechanism for $M_{23}C_6$ is operating. Therefore, this suggests that retaining the refinement and stabilization of $M_{23}C_6$ during creep is judged to be very important for development of heat resistant steel.

Table 5. Key factors determining increase in strength for *Gr.III* of 1W steel, $\log(t_{III}/t_{II})$, for each creep strain. Bold italics indicate determinant terms.

Strain (%)	0.25	0.5	1	2	5	10	45.2
$\Delta[Q]$	1.59	0.10	1.32	2.01	1.19	0.51	-0.01
$-\Delta[V]$	-1.74	-2.14	-2.26	-1.89	-1.40	-1.24	-1.13
$-\Delta C$	0.69	2.64	1.51	0.39	0.59	1.08	1.46
$\log(t_{III}/t_{II})$	0.53	0.60	0.57	0.51	0.38	0.35	0.32
	Grain boundary hardening	Recovery due to $\Delta C < 0$	DFRP for M ₂₃ C ₆		Recover ΔC	ry due to < 0	

4.1.7 Schematic illustration for changes in microstructure during creep of 9C-1W steel

The changes in microstructure during creep for Grs.I - III of 9Cr-1W steel are illustrated in Figure 6 based on the discussion on the changes of the QVCs of 1W steel during creep. Two matters are pointed out that the grain boundary-hardening caused by the SBSD mechanism occurs at a beginning of creep and that HRHD occurs immediately after SBSD during transient creep. Further, in Grs.II and III the DFRP mechanism is operating on $M_{23}C_6$ and the growth of the pre-existing sub-grains or newly created sub-grains associated with HRHD are prevented. In the figure, pre-existing $M_{23}C_6$ particles are omitted for simplicity.



Figure 6. Schematic illustration of changes in microstructure during creep of 9Cr-1W steel. *Gr.1*: SBSD (bold line) for $\varepsilon < 1\%$ followed by weak HRHD in transient creep and then, general recovery in accelerating creep. *Gr.II*: SBSD followed by the growth of sub-grains and the DFRP mechanism for M₂₃C₆ on the newly migrated boundaries. *Gr.III*: Compaction of deformation processes of *Gr.II* within a short strain followed by HRHD and DFRP, which results in the elongated time to rupture as compared to those of *Gr.II*.

4.2 9Cr-4W steel

4.2.1 Time to rupture and analysis of creep curves

Figure 7 shows the stress vs. time to rupture relationship for 9Cr-4W steel (Abe et al., 1992). The data were classified into three groups, Grs.I - III, and the regression lines were obtained using the same method as 9Cr-1W steel (Section 4.1.1). In the classification, $\sigma - t_{\varepsilon}$ diagrams were referred and the $\sigma - t_{0.5}$, t_2 , and t_5 diagrams are shown in Figure A3, as typical examples. Linear relationships between stress and logarithmic time are confirmed in Figure A3 in the same way as shown in Figure 7, which indicates that t_{ε} can be applied to Equation 1 if we replace t_r with t_{ε} . The t_rs of Gr.II are longer than the extrapolated t_rs of Gr.I for the stresses in Gr.II, i.e., $t_{II} > t_I$, but $t_{III} < t_{II}$ at higher temperatures and lower stresses. The $\sigma - t_r$ relationship at 600 °C of Figure 7 looks like to change in S-shape, or the degradation in rupture strength seems to occur after several thousands of hours, corresponding to Gr.III. The degradation in strength is obviously confirmed at 650 °C for longer than 1000 h, i.e., Gr.III. As shown in Figure A3, these trends are similar with the $\sigma - t_5$ and t_{10} diagrams, but the $\sigma - t_2$ diagrams the sum of $\sigma - t_2$.



Figure 7. Stress vs. time to rupture relationship for 9Cr-4W steel

Figure 8 shows the relationship between strain and the average NSR. MCR were observed between 2 - 5% strain, but the average NSR for Gr. III at 5% strain is slightly higher than 2 due to the characteristics of data for Gr.III. Though the average NSRs for Gr.II at an early stage of transient creep are larger than those for Gr.I, but the average NSR of Gr.II decreases rapidly and the slope for Gr.II, $\Delta \log(average NSR)/\Delta \log \varepsilon$, is larger than that for Gr.I. That is, rapid strain hardening occurs in transient creep of Gr.II. This trend becomes clearer for Gr.III. The slopes in accelerating creep for all groups are similar with each other. The higher strain hardening in transient creep of Gr.III may be responsible for the shortening of t_r , i.e., the degradation in strength for Gr.III observed in Figure 7. This degradation tendency is also confirmed for t_{ε} larger than $\varepsilon > 5\%$ as shown in Figure A3, the details of which is discussed in Section 4.2.4.



Figure 8. The average NSR vs strain relationship for 9Cr-4W steel

As shown in Figure A3 the linear relationships between σ and $\log t_{\varepsilon}$ for $\varepsilon = 0.5 - 5\%$ were already confirmed for each group. Therefore, it is reasonable that t_{ε} is applied to Equation 1 when we replace t_r with t_{ε} . However, since Equation 1 is introduced using the Mankman-Grant relation, Equation 6, it is desirable to confirm the relation between *MCR* and t_{ε} . Figure A4 shows the relationships between *MCR* vs. t_r and t_{ε} for 9Cr-4W. Though the scattering for $t_{0.5}$ is rather large, the validity of applying Equation 1 to t_{ε} is reconfirmed from Figures A3 and A4. Figure 9 shows variations of *QVC* as functions of strain for each group. The values of *Q* at rupture for *Grs.1* and

III in Figure 9 are approximately 450 kJmol⁻¹ and are a little larger than the activation energy of alpha iron of self-diffusion, and moreover, the values of C are approximately 20, which are the similar values confirmed in

many heat resistant steel (Tamura et al, 2013). On the other hand, $Q \sim 600 \text{ kJmol}^{-1}$ and $C \sim 30$ are obtained for *Gr.II* at rupture, which means that the hard microstructure is maintained until rupture.

4.2.2 Gr.I

Variations of QVC for Gr.I shown in Figure 9 is not so large, though the data at 0.25% strain are not obtained with sufficient accuracy. SBSD may happen as similar with the early stage of transient creep for Gr.I of 1W steel, because Q and V increase slightly up to 10% strain. The average test conditions are 567 °C, 235 MPa, and $t_r = 116$ h. In such conditions precipitation of Laves phase hardly occurs (Abe et al., 1991). The recovery inside sub-grains and the growth of the sub-grains with DFRP for M₂₃C₆ may happen keeping lath martensite structure, MCR is observed near at 5% strain. Accelerating creep at $\varepsilon > 10\%$ is caused by recovery due to decreases in Q and C. There is no evidence of obvious precipitation hardening except for M₂₃C₆ through a whole duration of creep, though a few numbers of Laves phase with 500 nm in length were observed on lath boundaries (Abe, 2003).



Figure 9. The results of the *QVC* analysis are shown as functions of creep strain for each group of 9Cr-4W steel; a) the activation energy, b) the activation volume, and c) the Larson-Miller constant.

4.2.3 Gr.II

The average test conditions for Gr.II are 600 °C, 163 MPa, and $t_r = 1546$ h. Laves phase is confirmed in such conditions (Abe, 2005). Remarkable increases in QVC up to 5% strain indicate strengthening of sub-boundaries due to precipitation of fine Laves phase and M₂₃C₆ together with SBSD at an early stage of transient creep. Accelerating creep at higher strains of 5% is caused mainly by the growth of sub-grains keeping grain-boundary strengthening due to Laves phase and M₂₃C₆, because high levels of QVC are maintained up to rupture. To investigate the metallurgical reactions during creep in more detail, the Q_s , V_s , and C_s analysis were made also on this group in the same way shown in Table 3. Though the table is omitted, it was found that all of Q_s , V_s , and C_s increase up to 5% strain and then decrease in accelerating creep and that the determinant term is Q_s during the metallurgical reactions in transient creep which is inferred based on the QVC analysis. Moreover, the results show that after the grain-boundary strengthening due to Laves phase and M₂₃C₆ starts to be in progress together with the sub-grain growth in

accelerating creep. However, it is found based on both the QVC and Q_s , V_s , and C_s analyses that hardening due to Laves phase and M₂₃C₆ with fine martenensitic structure is almost maintained up to rupture.

4.2.4 Gr.III

The average test conditions for Gr.III are 638 °C, 93 MPa, and $t_r = 3507$ h. Laves phase forms under these conditions (Abe, 2005). Rapid increases in QVC up to 1% strain are caused by the accelerating reactions of fine Laves phase observed in Gr.II together with SBSD at an early stage of transient creep. Therefore, in this strain range, t_{ε} is longer than those expected from Gr.II (Figure A3). On the other hand, after 1% strain QVC turn over decreasing largely and this situation continues up to 5% strain of the MCR point. In more detail, both Q and Cdecrease between 1-2% strain more largely than those for 2-5%, on the other hand V decreases linearly against $\log \varepsilon$ through 1-5% strain. These decreases in QVC should be essentially explained by the HRHD processes, because Laves phase precipitates only on boundaries, but has not been confirmed inside sub-grains in 9Cr-4W steel (Abe, 2005). It is also noticed that the values of Q and C at the MRC point are both still smaller than those of Gr.I, where Laves phase hardly precipitates. Therefore, coarsening of Laves phase and $M_{23}C_6$ should take place rapidly during the later stage of transient creep together with the progress of HRHD. The above mentioned interpretation on the variations of QVC in the transient creep for Gr.III must correspond to the trend for the changes in $\sigma - t_{\varepsilon}$ diagrams shown in Figure A3. Namely, in a 1 - 2% strain range, the $\sigma - t_{\varepsilon}$ relationships change in inverse J-shape as shown in Figure A3b or $t_{III} > t_{II}$, and Q for Gr.III is higher than that for Gr.II as shown in Figure 9. Therefore, the strengthening effect due to Laves phase is maintained, but in 2-5% strain range the strengthening effect due to Laves phase is scarce and only HRHD is in progress. Finally, at 5% strain the $\sigma - t_{\varepsilon}$ relationship changes in S-shape as shown in Figure A3c, or $t_{III} < t_{II}$. In accelerating creep, the values of QVC approximately hold low values as those at MCR, and therefore, strain rate increases recovering microstructure, accompanying the growth of sub-grains, and coarsening precipitates together with the HRHD processes.

4.2.5 Strain rate analysis for Gr.III of 4W



Figure 10. Q_s , V_s , and C_s for Gr.III of 9Cr-4W steel are shown as functions of creep strain.

Table 6. Changes in Q_s , V_s , C_s , and $\log(\dot{\varepsilon})$ between two adjacent strains for *Gr.III* of 9Cr-4W steel. *MCR* is near 5% strain. Bold italics indicate determinant terms.

Strain range	[0.25 - 0.5%]	[0.5 - 1%]	[1 - 2%]	[2-5%]	[5 - 10%]	$[10\% - t_r]$
$-\Delta[Q_s]$	-18.60	-3.52	20.55	4.08	-7.29	-1.49
$\Delta[V_s]$	1.85	0.52	-1.51	-1.54	0.33	0.49
ΔC_s	16.32	2.47	-19.61	-2.62	7.47	2.30
$\log(\dot{\epsilon}, \%/h)$	-0.43	-0.52	-0.58	-0.08	0.51	1.29

That all of QVC decrease between 1-5% strain for Gr.III is a similar phenomenon with that observed for Gr.II of 4W in accelerating creep, however the phenomenon in Gr.III occurs in transient creep and therefore, the creep mechanism for this phenomenon is differ from that of Gr.II. In the sense that V decreases in transient creep, creep behavior between 1-5% strain for Gr.III of 1W steel is the same as that for 4W steel, but in contrast with that O and C decrease for 4W steel, in 9Cr-1W steel both Q and C increase. Excepting for the degrees of the changes in QVC, the most similar case to the case for Gr.III of 9Cr-4W steel is the creep behavior for Gr.I of 9Cr-1W steel between 1-2% strain. To clarify the creep behavior for Gr.III of 4W steel between 1-5% strain, the Q_s , V_s , and C_s analyses were made as same method shown in Figure 5 and Table 3. The results are shown in Figure 10 and Table 6. The changes in the obtained Q_s , V_s , and C_s shown in Figure 10 is similar with those of QVC in Figure 9. However, that all of Q_s , V_s , and C_s increase clearly in accelerating creep in Figure 10 is differ from that for QVC in Figure 9, excepting for the data at rupture. It is found from Table 6 that the determinant term for $\dot{\varepsilon}$ up to 1% strain is the increase in $[Q_s]$, which is caused by the grain boundary strengthening due to the swept out dislocations, $M_{23}C_6$, and Laves phase, and the determinant term for $\dot{\epsilon}$ in accelerating creep is the increase in C_s . Between 1-5%strain, the decreases in not only C_s but also $[V_s]$ are the determinant terms to decrease $\dot{\varepsilon}$ in transient creep. If we are watching only the changes in large values of $[Q_s]$ and C_s , it is easily to consider that accelerating creep begins from 1% strain, because $[Q_s]$ decreases largely, but it is misleading. Between 1-5% strain, the decrease in $\dot{\varepsilon}$ cannot be explained only by the decrease in C_s , and therefore, an decrease in $[V_s]$ or HRHD is absolutely necessary to keep transient creep. In other words, Laves phase particles grow rapidly in an HRHD zone formed, which causes the large decreases in $[Q_s]$ and C_s and consequently transient creep is maintained when C_s + $[V_s] < [Q_s]$. This process propagates repeatedly whole over the specimen and thus t_{ε} for $\varepsilon < 2\%$ for Gr.III is longer than that estimated from Gr.II as shown in Figure A3. On the other hand, an increase in C_s is the determinant term in accelerating creep, where t_{ε} for Gr.III is shorter than that estimated from Gr.II as shown in Figure 7 and Figure A3c. Although during this strain range, recovery inside sub-grains and/or the growth of sub-grains occur, because V_s increases, HRHD also should take place, because the value of V_s is rather small. Therefore, Table 6 shows that accelerating creep is caused by that the increase in entropy term associated with the local movement of dislocations is larger than the increase in $[Q_s]$. The rather large increase in $[Q_s]$ in accelerating creep seems to be strange. However, this phenomenon is not a special case, because similar phenomena, in many cases accompanying HRHD, are seen in the cases not only for Grs. I and II of 1W and Gr. I of 4W, but also for T92/MJT and T91/MGC, respectively, which will be presented in near future.

4.2.6 Degradation in creep strength for Gr.III

Creep strength for Gr.III of 4W steel decreases as compared with those expected from Gr.II when $\varepsilon > 5\%$ (Figure 7, Figure A3c). Figure 11 shows the comparison among the $Q_{\rm s}$ s for 1W and 4W as functions of strain. Among the $Q_s - \varepsilon$ relationships, those for Gr.I of 1W and Gr.III of 4W are drawn using real lines, because they are phenomenologically very similar with each other. They show a peak at 1% strain, a minimum at near the MCR point, and an increase in accelerating creep. Moreover, The Vs for both data groups also decrease between 1% strain to each MCR point, which clearly indicate the occurrence of HRHD (Figures 4 and 7). However, it is understand that the occurrence of HRHD may not be a direct cause for the degradation of strength, because in the $\sigma - t_2$ diagram for 4W shown in Figure A3b the degradation in strength does not occur yet, but HRHD surely takes place at $\varepsilon = 2\%$ for Gr.III of 4W (Figures 9 and 10), because V decreases clearly in this strain range. More than that, it is a problem that at $\varepsilon = 5\%$, near the MCR point of 4W the minimum Q_s (382.0 kJmol⁻¹) for Gr.III of 4W is smaller than that for Gr.I of 1W (402.7 kJmol⁻¹). The fact that $Q_s(4W) < Q_s(1W)$ indicates that Laves phase particles in 4W grow extremely large and lose even the meaning of the existence, though they should contribute strengthening up to 1% strain. If we correlate this fact with the observations that massive Laves phase is formed nearby or adjacent to M₂₃C₆ particles in Grade 92 (Dimmler et al., 2003; Dudko et al., 2013; Nie et al., 2014; Xu et al., 2015; Maddi et al., 2016), following hypothesis is possible; the vicious circle of the coarsening of both $M_{23}C_6$ and Laves phase begins with HRHD as momentum, namely Laves phase decomposes some of $M_{23}C_6$ particles and absorbs the decomposed soluble W atoms and therefore, not only Laves phase grow further but also $M_{23}C_6$ with less W content easily grows fast, which results in loss of strengthening factors of both $M_{23}C_6$ and Laves phase. When we think this way, the main reason for the degradation observed in Gr.III of 9Cr-4W steel for $\varepsilon > 5\%$ is considered to be the extreme coarsening of M₂₃C₆ and Laves phase caused by the HRHD as an underlying trigger. The above hypothesis suggests that material design based on the grain-boundary strengthening using precipitates such as Laves phase is effective according to the test conditions, but at high temperatures and for long-terms tests HRHD triggers extreme coarsening of precipitates in accelerating creep, and consequently the

degradation in strength. To prevent the degradation of this type it is necessary to moderate the excess Laves phase hardening during transient creep or before test.



Figure 11. Activation energy, Q_s , as functions of strain for 9Cr-1W and 9Cr-4W steels. The average temperature and time to rupture are shown in the figure for each data group.

Table 7. The differences in *QVC* for *Grs.II* and *III* at an indicated strain of 9Cr-4W steel and the calculated t_{II} and t_{III} at the average temperature and stress for *Gr.III*. Determining term(s) for $\log(t_{III}/t_{II})$ is (are) shown in bold italics. Key factors determining $\log(t_{III}/t_{II})$ are shown in the bottom.

Strain (%)	0.5	1	2	5	10	39.8
$\Delta[Q]$	17.44	19.00	-0.57	-12.78	-10.96	-7.57
$-\Delta[V]$	-2.48	-2.74	-1.13	1.23	1.20	0.80
-ΔC	-14.39	-15.59	2.39	11.51	9.58	6.66
$\log(t_{III}/t_{II})$	0.58	0.67	0.69	-0.04	-0.18	-0.11
	SBSD, $M_{23}C_6$ and Laves phase hardening ($\varepsilon < 1\%$)		Recovery due to $\Delta C < 0 (\epsilon \sim 2\%)$	Recovery	due to coarseni $M_{23}C_6$, ($\varepsilon \ge 5$	ng of Laves, %)

Rupture strength of Gr.III shown in Figure 7 decreases clearly as compared with the expected values from Gr.II. However, it is found from Figures 7 and A3 that the strength degradation occurs only when $\varepsilon > 5\%$ and on the contrary rupture strength of Gr.III is higher than that expected from Gr.II for time to smaller strains. To investigate this phenomenon metallurgically, the similar QVC analysis as shown in Table 5 for Gr.III of 9Cr-1W steel was made under the average test condition of Gr.III. The results are shown in Table 7. It is found from Table 7 that at $\varepsilon \ge 5\%$ degradation in strength is determined by decrease in [Q] which is caused by the growth of sub-grains and coarsening of Laves phase and $M_{23}C_6$ and that for $\varepsilon \le 1\%$ an increase in strength is determined by an increase in [Q] which is caused SBSD and grain boundary strengthening due to $M_{23}C_6$ and Laves phase. It is also noticed that for $\varepsilon \ge 2\%$ the change in ΔC of the entropy term due to HRHD begins to decrease and for $\varepsilon = 2\%$ of transient creep, t_2 in Gr.III becomes larger than that in Gr.II, because the decrease in ΔC becomes larger than the decrease in [0]As shown in Figures 2 and 7, though the remarkable degradation in rupture strength is observed in Gr.III of 4W steel, on the contrary the prolonged time to rupture is observed in Gr.III of 1W steel. In both cases, recovery of martensite structure caused by HRHD takes place, however the estimated rupture strength of 4W at 600 °C for 10 000 h, 50MPa, is clearly higher than the estimated strength of 31 MPa for 1W steel for the same condition. Namely, it is also reminded that though the microstructure of 4W is decomposed destructively at rupture due to HRHD, the rupture strength at high temperatures is still stronger than that of 1W steel without Laves phase. The values of Q and C for 1W and 4W steel are approximately the same with each other as shown in Figures 4

and 9, but the value V for 4W, $366 \text{ cm}^3 \text{mol}^{-1}$, is about half of that for 1W steel 766 cm $^3 \text{mol}^{-1}$. This indicates that the movable area for the dislocations for 4W is narrower than that for 1W steel, which corresponds to the difference in sub-grain size, because there are few obstacles inside sub-grains in both cases of *Gr.III*. By the way, the widths of lath martensite for 1W and 4W aged at 600 °C for 3000 h are 0.75 m and 0.53 m, respectively (Abe et al., 1991), and the sub-grain size of 4W at rupture may be judged to be smaller than that of 1W steel. The reason for this is considered to be caused by that $M_{23}C_6$ in 4W is finer than that in 1W because of the higher content of W in 4W steel (Yoshizawa et al., 2005; Abe, 2006; Danielsen, 2007). This also suggests that stabilizing the sub-grain size utilizing particles like $M_{23}C_6$ is very important to prevent the degradation in long-term rupture strength of martensitic steel.

5. Heterogeneous Deformation and Degradation in Strength of Grades 91 and 92

A concept of HRHD is evoked from the following two points of views: The first one is the three parameters of QVC decrease after QVC_{max} simultaneously in a later section of transient creep as seen in Figures 4 and 9, which indicates that recovery should take place within a small nominal strain range after remarkable strain hardening by DFRP of M₂₃C₆ and precipitation of fine Laves phase at the beginning of creep. The second one is that the QVC for the welded joints are also small as compared to those of the base metal as shown in Figure 1, Tables 1 and 2. Hence, it follows that we have explained the creep phenomena of the martensitic steel on the assumption that HRHD takes place by analogy when V decreases with increase in strain as explained in Sections 4.1 and 4.2. Namely, if we can assume the existence of a locally recovered zone, we can easily suppose the strain concentration in this area and therefore, we can judge that the coarsening of M₂₃C₆ and Laves phase precipitates is promoted in the HRHD zone based on the following experimental results: the sizes of M₂₃C₆ in a gauge portion in crept specimens of Grade P92 are larger than those for a grip (Ennis, Zielinska-Lipiec, & Czyrska-Filemonowicz, 2000; Ennis & Czyrska-Filemonowicz, 2003) and the sizes of Laves phase in a gauge portion in ruptured specimens are larger than those for a grip in ruptured specimens of a low carbon 9Cr-3Co-2W-0.4MoVNbMB steel (Fedorova, Kipelova, Belyakov, & Kaibyshev, 2013),

The occurrence of HRHD, i.e. the decrease in V with increase in strain in transient creep, does not always mean that accelerating creep begins immediately as shown in Figures 9 and 10. In this strain range, the decreases in both $[V]_s$ and C_s with increase in strain are determinant terms for decreasing strain rate as shown in Table 6, even though $[Q]_s$ decreases due to the coarsening of the M₂₃C₆ and Laves phase particles. When the particles continue to be coarsened, creep rate begins to increase with increase in strain and finally rupture lives are shorten under the conditions where HRHD occurs. Namely, HRHD triggers extreme coarsening of precipitates especially in accelerating creep, and consequently the degradation in strength. Therefore, stabilizing M₂₃C₆ and Laves phase is very important to mitigate the degradation of rupture lives in *Gr.III* of 9Cr-4W steel.

Similar creep phenomena should happen also in high Cr martensitic steel of Grades 91 and 92. In these alloy systems it is well known that Z-phase is formed during creep and the long term rupture strengths of these steels drop unexpectedly. The formation of Z-phase should be promoted in the HRHD zone based on the experimental results that creep strain promotes the formation of Z-phase (Sawada et al., 2006; 2011). Therefore, the formation of Z-phase which is promoted in an HRHD zone should occur even within a small nominal strain before reaching an MCR point. The formation of Z-phase in an HRHD zone is caused by the dissolution or disappearance of a strengthening factor of MX. However, since Laves phase is coarsened faster at 600 °C than Z-phase in Grade 91 (Suzuki, Kumai, Kushima, Kimura, & Abe, 2000), it is more feasible that coarsening of Laves phase rather than Z-phase causes the formation of an HRHD zone which triggers the degradation in long term rupture strength. Anyway, which precipitate between $M_{23}C_6$, Laves phase, and Z-phase causes the formation of an HRHD zone should be investigated deeply in future. The above explanation to the creep phenomena of martensitic steel is self-consistent and therefore, we come to believe the existence of HRHD for Grades 91 and 92...

Experimentally, a locally recovered zone is observed in a ruptured specimen for Grade T91 (Kushima et al.,1999) and Grade T92 (Sawada & Kimura (2019) and also in the crept specimens for accelerating creep of Grade T91 (Kimura, Suzuki, Toda, Kushima, & Abe, 2002). However, unfortunately a locally recovered area in a crept specimen to a small strain in transient creep is not yet confirmed. Moreover, not only the size, shape, and distribution, but also the degree of straining of a locally recovered zone, i.e., the characteristics of an HRHD zone, are not yet investigated systematically. These factors may influence the formability of Z-phase, and thus the degradation in strength of high Cr martensitic steel. When such information on an HRHD zone is clarified, the degradation behavior of high Cr martensitic steel can be explained more deeply. Morooka, Tomoda, Adachi, Morito, & Kamiyama (2008) observed heterogeneous deformation inside a sub-block of martensitic structure employing both an electron back-scattered diffraction method and a neutron diffraction method, and therefore, the characterization of an HRHD zone during creep will be clarified more deeply in future.

6. Conclusions

Laboratory-prepared steel of 9Cr-1W and 9Cr-4W steel were analyzed applying an exponential law to the test temperature, T, stress, σ , and time to rupture or time to a specific strain, t_r or t_{ε} . The observed creep variables of T, σ , and t_r or t_{ε} are converted to the activation energy, Q, the activation volume, V, and the Larson-Miller constant, C, without using any adjustable parameters. The variations of Q, V, and C as functions of creep strain are discussed metallurgically and following conclusions are obtained.

1) Sub-grain boundary strengthening by the swept out dislocations (SBSD) is an essential process at an initial stage of creep of martensitic steel.

2) Hardening by dissolving and finely re-precipitation of $M_{23}C_6$ and precipitation of Laves phase are added to SBSD for high Cr martensitic steel, which increase in Q.

3) After the peak of Q, V, and C, heterogeneous recovery and simultaneously occuring heterogeneous deformation (HRHD) should begin at an early stage of transient creep in the vicinity of some weakest boundaries due to coarsening of the precipitates, which triggers the unexpected degradation in strength due to coarsening of Laves phase. The microstructural investigation in an HRHD zone which is inferred to occur in the later stage of transient creep is an issue for future.

4) Stabilizing not only $M_{23}C_6$ but also Laves phase is important to mitigate the degradation in rupture strength of martensitic steel.

List of Symbols and Abbreviations

- ε Strain
- ε_i Strain of i^{th} in Equation 8
- $\dot{\varepsilon}$ Creep rate
- λ Maximum distance that a dislocation can move from a start point to the next stable position
- ρ Dislocation density
- ρ_{ob} Observable dislocation density in sub-grains
- σ Applied stress
- σ_b Back stress
- ΔS Entropy change in the activation process
- v_{eff} Effective attempt frequency per unit time to overcome the obstacles
- *b* Length of the Burgers vector
- C Larson and Miller (L-M) constant
- C_s L-M constant calculated based on strain rate
- C_{MG} Monkman-Grant constant
- DFRP Dissolving and finely re-precipitation
- *EL* Rupture elongation
- EBW Electron beam welding
- GTAW Gas tungsten arc welding
- HAZHeat affected zone
- HDZHeterogeneous deformed zone
- HRZ Heterogeneously recovered zone
- HRHD Heterogeneous recovery and heterogeneous deformation
- *M* Factor conversion from shear strain to tensile strain
- *MCR* Minimum creep rate
- NIMS National Institutes for Materials Science in Tsukuba, Japan
- *NSR* Strain rate at a specific strain is divided by each MCR

- PAGB Prior austenitic grain boundary
- PWHT Post weld heat treatment
- *Q* Activation energy
- Q_s Activation energy calculated based on strain rate
- [Q] Q/2.3RT
- $[Q]_s Q_s/2.3RT$
- QVC Q, V, and C
- R Gas constant
- SBSD Sub-grain boundary strengthening by dislocations
- T Temperature in K
- t_{ε} Time to specific strain, $\varepsilon\%$
- t_i Time to a specific strain for a i^{th} strain, ε_i
- t_I Time to a specific strain for Gr.I
- t_r Time to rupture
- t_{r0} Pre-exponential factor of Equation 2
- TIG Tungsten inert gas (welding)
- TTP Time-temperature-precipitation
- v Average dislocation velocity
- v_0 Pre-exponential factor of Equation 4
- V Activation volume
- V_s Activation volume calculated based on strain rate
- [V] $\sigma V/2.3RT$

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Appendix: Figures relating on creep curves



Figure A1. Relationship between Q and C for time to rupture of 9Cr-4W. Definition of *Gr.I* etc. are explained in Section 4.1.



Figure A2. Stress vs. time to specific strains relationships for 9Cr-1W steel; a) 0.25% strain, Z-type, b) 1% strain, inverse J-type, and c) 5% strain, inverse J-type. Definitions of each data group are the same as Figure 2.



Figure A3. Stress vs. time to specific strains for9C-4W steel analyzed employing the exponential method shown in Section 2 and regression lines for each data group explained in Section 4.2. a) 0.5% strain, Z-type, b) 2% strain, inverse-J-type, and 5% strain, S-type. Definitions of each data group are the same as Figure 7.



Figure A4. Monkman-Grant relationship and minimum creep rate vs. time to a specific strain relationship as indicated for 9Cr-4W steel.

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