# **Relationship between Creep Strength and Magnetic Properties of Cobalt-bearing High Chromium Ferritic Steel**

# Shigeto YAMASAKI,\* Masatoshi MITSUHARA and Hideharu NAKASHIMA

Department of Engineering Sciences for Electronics and Materials, Kyushu University, 6-1 Kasuga-kouen, Kasuga, Fukuoka, 816-8580 Japan.

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In this study, the relationship between changes in the magnetic properties and creep strength with the addition of 3 or 6 mass% Co was investigated for ferritic steel containing 15 mass% Cr. Co addition up to 6 mass% hardly contributed to solid solution strengthening or precipitation strengthening at room temperature. However, in the range of 650 to 750°C, the steel with the larger amount of Co exhibited higher creep strength, which is explained by a reduction in the diffusion rate associated with a change in magnetic properties by Co addition. An increase of the volume magnetization of the steel with increasing Co content in the range from room temperature to about 800°C was confirmed. Comparing the difference in volume magnetization and the ratio of the creep strain rate for steels with different amounts of Co, a clear correlation was found. That is, at the temperature at which the difference in volume magnetization reached a maximum, the peak of the creep strain rate ratio was also observed. This result is explained as follows. In a low temperature region where the magnetization is large or in a high temperature region above the Curie point of both steels, the steels exhibit no significant difference in the creep strength. However, at a temperature where one steel loses its ferromagnetism but the other steel retains it, a significant difference in the creep strength is observed.

KEY WORDS: ferritic steel; creep; cobalt; magnetic properties; Curie temperature; diffusion.

# 1. Introduction

Pure iron exhibits ferromagnetism below the magnetic transformation temperature of ~770°C and paramagnetism above that temperature. The magnetic transformation of iron and its alloys has a large effect on diffusion, and the diffusion constant and its temperature dependence change in the ferromagnetic and paramagnetic regions.<sup>1-4)</sup> Creep resistance is also known to decrease in the paramagnetic region and in the temperature range just below the magnetic transformation temperature in response to changes in magnetic properties.<sup>5)</sup> In the ferromagnetic state, excess binding energy is generated between atoms due to the interaction between spins, and in this state, local demagnetization is required to form and move vacancies. Therefore, it is understood that the anomaly of diffusion in the ferromagnetic region is due to the extra activation enthalpy of diffusion required compared to the paramagnetic region.<sup>6-9)</sup> The magnetic transformation temperature is the temperature at which ferromagnetism disappears completely due to thermal disturbance. In reality, the magnetization gradually decreases from lower temperatures

toward the magnetic transformation temperature. Therefore, there is a transition region for the diffusion rate referred to as the Curie zone in the ferromagnetic temperature range, and anomalous diffusion rates are observed over a certain temperature range.<sup>9)</sup> Kucera *et al.*<sup>10)</sup> described the correlation between the excessive activation enthalpy of diffusion and the spontaneous magnetization in the ferromagnetic region. Therefore, it is appropriate to understand the effect of magnetic properties on diffusion based on changes in the magnitude of magnetization, rather than discussing whether the material is in the ferromagnetic or paramagnetic state.

The fact that the diffusion rate changes in relation to the magnetic properties seems to be an important aspect of creep deformation when the diffusion rate dominates the strength. The effect of magnetic transformation on the diffusion rate has been described in a textbook on heat-resistant steel<sup>11</sup>) and review papers.<sup>12,13</sup> Gustafson *et al.*<sup>14</sup> reported a study focusing on the effect of magnetic properties on the creep strength of a practical ferritic heat-resistant steel, but to our best knowledge, there are very few studies from such a perspective. This may be related to the fact that conventional ferritic heat-resistant steel is typically used in the ferromagnetic range. For example, at present, the



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<sup>\*</sup> Corresponding author: E-mail: yamasaki.shigeto.259@m.kyushu-u.ac.jp

maximum operating temperature for a steam pipe in a thermal power generation boiler, in which conventional ferritic heat-resistant steel containing 9–12 mass% Cr is applied, is approximately  $620^{\circ}$ C.<sup>15,16</sup>

One of the features of the chemical composition of next-generation ferritic heat-resistant steels that have been developed in recent years for applications at temperatures above 650°C is the addition of Co in ~3 mass%.17-21) All these ferritic heat-resistant steels have a tempered lath martensite structure; to form this microstructure, it is necessary to transform the material to austenite at the normalizing temperature and then transform it to martensite during cooling. However, in these new steels, the amount of W added is increased with the intention of improving the creep strength, so the ferrite-stabilizing effect of W suppresses austenite transformation at high temperatures. As a result, the residual  $\delta$ -ferrite diminishes the toughness of the steel. In these new steels, Co addition is expected to suppress the formation of residual  $\delta$ -ferrite due to its high austenite stabilizing effect.<sup>18)</sup> Thus, the main purpose of adding Co to these new steels is not necessarily creep strengthening.

Although Co addition has been reported as effective for creep strengthening in ferritic heat-resistant steels,<sup>14,22–28)</sup> its effectiveness depends on the composition of the steel or the temperature and time of the creep test.<sup>29–34)</sup> With respect to chemical composition, Co addition was effective for creep strengthening in heat-resistant steels with Cr contents of 9 or 15 mass%,<sup>14,22–28)</sup> but in these cases, the samples had a single-phase martensite or ferrite structure. In contrast, several other studies concluded that the addition of Co was not effective for creep strengthening, but these investigations were conducted on heat-resistant steels with 10.5–12 mass% Cr contents that contained residual  $\delta$  ferrite in part of the martensitic microstructure.<sup>29,30,33</sup>

It is well known that Co raises the magnetic transformation temperature of iron, and it has been reported that Co-bearing steel exhibits a significantly reduced diffusion rate just below the magnetic transformation temperature.<sup>8)</sup> Considering this fact, then, one of the factors for creep strengthening by the addition of Co to ferritic heat-resistant steel is the reduction of the diffusion rate. However, few studies<sup>14,28)</sup> have referred to this phenomenon, and the understanding of creep strength from the perspective of the change in magnetic properties due to the addition of Co to ferritic heat-resistant steel has not advanced. Currently, next-generation ferritic heat-resistant steels that can be used at 700°C are being developed,<sup>35,36)</sup> wherein the Cr content is increased to 15 mass% to improve their oxidation resistance. Figure 1 shows the changes in magnetic transformation temperature  $T_{\rm C}$  when Cr or Co is added to pure iron, as obtained by thermal equilibrium calculations. These results show that Cr, which is added in a large amount to the ferritic heat-resistant steel and has a large solid solution limit, significantly reduces the  $T_{\rm C}$  of iron. In other words, in the next-generation steels of this type, as the operating temperature rises to 700°C and  $T_{\rm C}$  decreases due to the increasing Cr content, the operating environment approaches the paramagnetic region. As also shown in Fig. 1, Co significantly increases the  $T_{\rm C}$  of iron. This suggests that the addition of Co may shift the ferromagnetic region (having a low diffusion rate) to a higher temperature, and as a result, may increase the creep strength in that temperature range. Thus, if the change in magnetic properties due to the addition of Co affects the creep strength of the steel, the effect will become more apparent in a next-generation ferritic heat-resistant steel that is expected to be applied at 700°C or higher.

The purpose of this study was to clarify the relationship between the change in magnetic properties and the creep strength with the addition of Co in ferritic steels containing 15 mass% Cr, which is equivalent to a next-generation ferritic heat-resistant steel. In addition, the temperature at which creep strengthening by the Co addition is most effective in the present steels was clarified.

# 2. Experimental

Samples containing 15 mass% Cr (hereinafter, 15Cr steel) and steels containing 3 or 6 mass% Co (hereinafter, 15Cr-3Co steel and 15Cr-6Co steel) were prepared. Each material was melted in a high frequency induction melting furnace and cast into an ingot of about 5 kg. Chemical composition analysis was performed on the cut surface of each ingot; the results are presented in Table 1. The data confirm that the target amounts of Cr and Co were achieved, and other impurity elements including C were suppressed to low levels. Each ingot was heated at 1 200°C for 1 h and then hot rolled. The hot-rolled material was further cold rolled. After cold rolling, the 15Cr and 15Cr-3Co steels were heat-treated at 800°C for 2 h. The 15Cr-6Co steel was heat-treated at 1 200°C for 10 h, cooled in a furnace at 90°C/h to 750°C, and further heat-treated at 750°C for 24 h. Scanning electron microscope (SEM, Carl Zeiss ULTRA55)



**Fig. 1.** Curie temperature  $(T_{\rm C})$  change by addition of Cr or Co to Fe calculated using Thermo-Calc software.

Table 1. Chemical composition (mass%)

	Fe	Cr	Со	С	Mn	Si	S	Р
15Cr	bal.	14.89	< 0.01	0.0014	< 0.01	0.01	< 0.001	< 0.002
15Cr-3Co	bal.	14.90	3.00	0.0010	< 0.01	0.02	< 0.001	< 0.002
15Cr-6Co	bal.	14.88	6.04	0.0018	< 0.01	0.02	< 0.001	< 0.002

was used to observe the microstructures of the samples. For SEM observation, samples of the heat-treated materials were cut into small pieces and polished to a mirror finish. Then, mechano-chemical polishing using colloidal silica was carried out for ~90 min to remove surface strain. In the SEM observations, a backscattered electron (BSE) image was adopted. In addition, crystal orientation mapping by the electron backscattered diffraction (EBSD) method and elemental composition analysis by energy dispersive X-ray spectroscopy (EDS) were also performed. These observations and measurements were carried out at an accelerating voltage of 15 kV and a working distance of 8.5 to 15 mm. To estimate the contributions of Cr and Co addition to solid solution strengthening, lattice constants were measured on the samples polished for SEM observation by X-ray diffraction (XRD, Rigaku SmartLab SE diffractometer). Co K $\alpha$ radiation operating at 40 kV and 25 mA was used for the measurement and Co K $\beta$  radiation was removed by an Fe filter. The diffraction profiles were obtained by varying  $2\theta$ from 50° to 130° with a scan speed of  $1^{\circ}$ /min and a scan step of 0.01° using a high-speed one-dimensional X-ray detector.

The hardness of the samples was measured by the Vickers hardness test. An indenter was pressed into 16 points on the polished surface of the SEM observation sample with a load of 0.2 kgf. The size of the indentation was approximately 50  $\mu$ m. Since the minimum grain size of the Co-added high chromium steel used in this study is about 100  $\mu$ m, the hardness evaluated in this experiment is the value of that within the ferrite grains. The average of the measured values was calculated, and the standard deviation was described as the error.

Differential scanning calorimetry (DSC) was performed to measure the austenite transformation ( $A_{c1}$ ) temperature and magnetic transformation temperature  $T_C$ . Pieces (~100 mg) cut from the cold-rolled material were used as samples for DSC measurement. The surface of the DSC sample that contacted the sample pan was smoothed by polishing. A pan made of a composite material of platinum-rhodium alloy and alumina was used as a reference sample. The measurement was performed in the range of 600 to 900°C at a heating/cooling rate of 10°C/min. During the measurement, Ar gas was swept at a flow rate of 20 mL/min to prevent sample oxidation.

The magnetization of the sample steel was measured using a vibrating sample magnetometer (VSM, model BHV-5, Riken Denshi Co., Ltd.). A sample of about  $5 \times 5 \times 1$  mm<sup>3</sup> was acquired from the cold-rolled material for each steel. Magnetization-field (M-H) curves were measured by applying a maximum magnetic field of 398 kA/m (5 kÖe) at room temperature. In addition, the magnetization of the sample in an applied magnetic field of 398 kA/m was measured in vacuum from room temperature to 800°C at a heating rate of 5°C/min.

A uniaxial tensile creep test was performed on each sample. A cylindrical creep test piece with a gauge length of 30 mm was prepared from the heat-treated material. The creep test was started after holding at the test temperature for 2–12 h in order to stabilize the temperature of the entire testing system. The displacement was measured using a linear gauge with a displacement resolution of 1  $\mu$ m via an extensometer attached to the test piece. The creep tests were conducted at 650, 675, 700, 715, 725, and 750°C with a load

stress of 20 MPa. In addition, the 15Cr and 15Cr-6Co steels were tested at 775 and 800°C. The creep test was performed until the test piece broke or the accelerated creep region was reached.

### 3. Results and Discussion

#### 3.1. Microstructure

**Figure 2** shows the DSC curves for the 15Cr, 15Cr-3Co, and 15Cr-6Co steels with increasing temperature from 600 to 850°C. The magnetic transformation appears as an endothermic peak during the heating phase of the DSC measurement.<sup>37,38)</sup> Endothermic peaks observed at 708°C for 15Cr steel, 723°C for 15Cr-3Co steel, and 733°C for 15Cr-6Co steel correspond to their respective magnetic transformations. The second endothermic peak observed at 770°C in 15Cr-6Co steel is due to austenite transformation; the heat treatment conditions for 15Cr-6Co steel were determined based on this temperature (the A<sub>c1</sub> point). Since no peaks corresponding to A<sub>c1</sub> are observed in the 15Cr and 15Cr-3Co steels, both likely maintain the ferrite single phase, even at temperatures as high as 900°C, which is the upper temperature limit for the DSC measurement.

SEM observations were performed to inspect the microstructure. Figure 3 shows the crystal orientation map for each steel obtained by SEM-EBSD measurement. The 15Cr and 15Cr-3Co steels have structures composed of coarse ferrite grains, with grain sizes of  $\sim 300$  to 800  $\mu$ m. In comparison, the 15Cr-6Co steel has slightly finer crystal grains, and martensite grains are also observed. Figure 4 shows the SEM-BSE image of 15Cr-6Co steel, which confirms that the ferrite and martensite grains are mixed. The area ratio of the martensite grains in this image was evaluated as 39.7%. Each sample contains inclusions, as indicated by the white arrows in Fig. 4; these were identified as Cr oxides by EDS elemental analysis. The amounts and sizes of these Cr oxides are similar in the three steel types, and since they are coarse and sparsely dispersed, they are considered to have little effect on strength. The absence of second phase par-







Fig. 3. Crystal orientation maps of (a) 15Cr, (b) 15Cr-3Co, and (c) 15Cr-6Co after annealing. (Online version in color.)



Fig. 4. SEM-BSE image of 15Cr-6Co. The rectangles represent the areas where EDS analysis was performed. (Online version in color.)

ticles other than the Cr oxide in the sample steels confirms that no precipitation phase was formed by the addition of Cr or Co. **Table 2** summarizes the results of the EDS quantita-

 
 Table 2.
 Chemical composition of ferrite and martensite in 15Cr-6Co measured by SEM-EDS (mass%).

		area 2	area 4	area 6	area 8	avg.
<b>F</b>	Fe	76.9	77.0	77.1	78.1	77.3
Ferrite	Cr	17.2	16.5	16.6	14.7	16.2
	Со	5.9	6.5	6.3	7.2	6.5
		area 1	area 3	area 5	area 7	avg.
Mantanaita	Fe	78.5	79.1	78.9	78.6	78.8
Martensite	Cr	13.4	13.3	13.4	13.7	13.4
	Со	8.1	7.7	7.7	7.7	7.8

tive analyses performed on the ferrite grains (red frames) and martensite grains (blue frames) in the regions indicated by the rectangles in Fig. 4. The ferrite grains contain  $\sim 16$ mass% Cr and ~6.5 mass% Co, while the martensite grains contain ~13 mass% Cr and ~7.8 mass% Co. It is understood that this difference in concentration occurs because Co is concentrated in the austenite grains and Cr is discharged to the ferrite grains at 1 200°C, at which the matrix consists of a ferrite-austenite dual phase. It is understood that the austenite grains remain after the heat treatment at 750°C for 24 h due to this difference in concentration, and the martensite transformation occurs when air-cooled to room temperature. In creep deformation, coarse-grained materials with few grain boundaries that act as short circuit diffusion paths have higher creep resistance.<sup>39,40)</sup> Therefore, the microstructure of 15Cr-6Co steel, with a matrix composed of fine ferrite and martensite grains, is inferior in creep strength to the other two steels in terms of the matrix microstructure.

# 3.2. Effect of Cr and Co Addition on Solid Solution Strengthening

Figure 5 shows a comparison of XRD line profiles near the 211 peak. Since the peak positions are almost the same among the steels, the change in lattice constant due to the addition of Co is extremely small. Table 3 shows the lattice constants calculated from the 211 peak positions. The lattice constants of the sample steels are ~0.28725 nm, which is  $\sim 6.0 \times 10^{-4}$  nm larger than the lattice constant of pure iron (0.28664 nm).<sup>41)</sup> Calculating the rate of change in the lattice constant of iron due to the solid solution of Cr as +5.5  $\times$  $10^{-5}$  nm per mol%<sup>42)</sup> affords a value of +8.9 × 10<sup>-4</sup> nm at 15 mass% (16.1 mol%), which nearly agrees with the measurement result. The rate of change in the lattice constant of iron due to the solid solution of Co is reported to be  $+0.8 \times 10^{-5}$ nm<sup>42)</sup> per mol%, and the change in the lattice constant when 6 mass% (5.7 mol%) is added is  $+0.5 \times 10^{-4}$  nm. Since this value is very small, that the measured lattice constants are quite similar regardless of the Co content is not unexpected. Table 3 also presents the results of the Vickers hardness tests conducted to compare the magnitude of solid solution strengthening. As described in the experimental section, the Vickers indentation size (~50  $\mu$ m) is smaller than the average crystal grain sizes in the samples, and thus, the Vickers hardness can be regarded as the value within the ferrite grains. The Vickers hardness of each steel is about 130 HV0.2, and the hardness difference between samples with different Co contents falls within the error range. Therefore,



Fig. 5. XRD line profiles around the 211 diffraction peak. (Online version in color.)

Table 3.Summary of lattice constant, Vickers hardness and Curie<br/>temperature.

	lattice constant	Vickers	Curie temperature, $T_{\rm C}$ [°C]		
	(XRD) [nm]	hardness HV0.2	DSC	VSM	
15Cr	0.28725	129 ± 3	708	720	
15Cr-3Co	0.28725	$130 \pm 3$	723	734	
15Cr-6Co	0.28724	132 ± 3	733	752	

Co addition does not substantially contribute to solid solution strengthening at room temperature, as expected from the lattice constant measurements by XRD. The diffusion rate of the solute atoms is also an important factor for solid solution strengthening by the solute drag mechanism at high temperatures. In this mechanism, elements with slower diffusion rates have greater strengthening abilities. However, since the diffusion rate of Co in iron is almost the same as that of the self-diffusion of iron,<sup>4)</sup> this effect can be ignored. From these results, the effect of Co solid solution strengthening on creep strength is negligible in these three steels with different Co contents.

### 3.3. Magnetic Properties

**Figure 6** shows the relationship between the volume magnetization and magnetic field for each steel. By applying an external magnetic field of 398 kA/m at maximum at room temperature, the magnetizations of all three steels become nearly saturated. Figure 6(b) presents an enlarged view of the red broken rectangle in Fig. 6(a). The maximum magnetization of the sample increases with increasing Co content at room temperature. **Figure 7**(a) shows the relationship between the volume magnetization and temperature from room temperature to 800°C. The magnetization of all three steels decreases as the temperature rises; indeed, magnetism is nearly absent at 800°C. From the enlarged view of the magnetization-temperature curves from 640 to 760°C shown in Fig. 7(b), it is clear that the higher the Co content, the

higher the magnetization of the sample, even at high temperatures. As indicated by the arrows in Fig. 7(b),  $T_{\rm C}$  can be evaluated from the intersection of the horizontal axis by the tangent line drawn from the section of the magnetizationtemperature curve with the largest gradient. The evaluated  $T_{\rm C}$  are listed in Table 3 along with the values measured by DSC. The  $T_{\rm C}$  values measured by VSM are 11–19°C higher than those by DSC. However, the  $T_{\rm C}$  values evaluated by either measurement method are higher in the sample with the larger amount of Co, and this tendency corresponds to the magnitude of the magnetization.

# 3.4. Creep Deformation Behavior

Figure 8 shows the creep strain over time curves for each steel from 650 to 750°C. The triangular symbol represents the interruption point of the creep test. A reverse-transition-type creep curve shape, in which transition creep hardly appears, is observed under many test conditions. Figure 9 shows the strain rate-time curves at each test temperature. Due to the reverse-transition-type creep behavior described above, the decreases in strain rate in the transition creep region are small. Since the minimum strain rate at the same temperature is lower as the Co content rises, creep strengthening is caused by the addition of Co. Reverse-transition-type creep is a characteristic feature of alloys<sup>43)</sup> in which solid solution strengthening occurs due to the solute drag mechanism. Since this behavior is observed even in the 15Cr steel to which Co was not added, it is likely that solute drag is caused by the solid solution Cr. Although it is difficult to estimate the contribution of Co to high temperature solid solution strengthening from the creep behavior alone, by considering the lattice strain and diffusion rate mentioned above, the effect of Co on solute drag should be small compared to the effect of 15 mass% Cr. On the other hand, since the minimum strain rate is lowered by the addition of Co, Co contributes to creep strengthening by some mechanism other than solute drag.

## 3.5. Discussion

Figure 10 shows the Arrhenius plots of the minimum strain rates for the three steels. In addition to the results from 650 to 750°C, the minimum strain rates at 775°C for 15Cr steel and 775 and 800°C for 15Cr-6Co steel are also plotted in the figure. At all temperatures, steels with higher Co addition display lower minimum strain rates. In the 15Cr-6Co steel, the minimum strain rate at 775°C is smaller than that at 750°C. From the DSC measurement results for the 15Cr-6Co steel, which exhibits a partial austenite transformation at ~770°C, it can be understood that the sharp decrease in the minimum strain rate in this temperature range is due to the appearance of austenite with a lower diffusion rate than that of ferrite. The slope of the Arrhenius plot corresponding to the apparent activation energy of creep deformation is not uniform from 650 to 775°C. In 15Cr steel, the apparent activation energy of creep deformation evaluated from 750 to 775°C is 247 kJ/mol, which is close to the activation energy of the self-diffusion of iron in the paramagnetic region (251 kJ/mol).<sup>4)</sup> However, the apparent activation energy of 15Cr steel changes drastically in the temperature range below 750°C and reaches a large value of 624 kJ/mol from 650 to 725°C. The apparent acti-



Fig. 6. M-H curves at room temperature. (a) Whole curves and (b) enlarged view of the rectangle shown in (a).



Fig. 7. Magnetization-Temperature curves (a) from room temperature to 800°C and (b) an enlarged view from 640 to 760°C.

vation energies of 15Cr-3Co and 15Cr-6Co steels are also larger than those of iron self-diffusion. The values change at ~690°C for 15Cr-3Co steel and ~715°C for 15Cr-6Co steel, and are evaluated to be ~1 000 kJ/mol in the higher temperature range and ~500 kJ/mol in the lower temperature range. The activation energy  $Q_f$  for lattice diffusion in the ferromagnetic region is expressed by the formula,<sup>44)</sup>

# $Q_f = Q_p (1 + \alpha s^2),$

where  $Q_p$  is the activation energy in the paramagnetic region (self-diffusion of iron: 251 kJ/mol, Cr diffusion in iron: 267 kJ/mol, Co diffusion in iron: 251 kJ/mol), *s* is the ratio of saturation magnetization at 0 K and *T* K, and  $\alpha$  is a constant (self-diffusion of iron: 0.156, Cr diffusion in iron: 0.133, Co diffusion in iron: 0.23). From this relationship, a larger activation energy can be estimated in the ferromagnetic region than in the paramagnetic region. However, even when *s* = 1, the activation energies of iron self-diffusion, Cr diffusion in iron, and Co diffusion in iron are 290, 303, and 309 kJ/ mol, respectively. Therefore, the values estimated from the above equation cannot explain the large activation energies measured in this study. It has been reported that the apparent activation energy has an abnormally large value in the transition temperature range from the paramagnetic to the ferromagnetic region.<sup>9)</sup> Therefore, the large activation energies measured in this study are considered to correspond to this transition.

Comparing the minimum strain rates of the three steels in the 650–750°C range, the difference in creep strength depends on the temperature. The difference in the minimum strain rate between the 15Cr and 15Cr-6Co steels is the smallest at 750°C. The largest value is observed at 715°C, and then, the difference tends to decline again at lower temperatures. In addition, the minimum strain rate of the 15Cr-3Co steel is always located between those of the 15Cr and 15Cr-6Co steels, but it is closer to that of 15Cr steel in the high temperature region and that of 15Cr-6Co steel in the low temperature region. To examine the factors underlying the difference in the minimum strain rate among the sample steels in correspondence with the magnitude of



**Fig. 8.** Creep strain-Time curves. (a)–(c) Whole curves and (d)–(f) enlarged views at small strain and a short time range. The triangles in the figure represent the creep interruption points.





Fig. 10. Arrhenius plot of minimum strain rates.

the magnetization, the changes in the ratio of the minimum strain rate and the difference in the volume magnetization with respect to temperature were compared. The results are shown in Fig. 11. The ratio of the minimum strain rate of high-creep-strength steel to that of low-creep-strength steel at the same temperature is indicated by an open symbol, and the difference in volume magnetization between the two is indicated by a blue line. From the comparison of the 15Cr-6Co and 15Cr steels shown in Fig. 11(a), the temperature at which the minimum strain rate ratio is the largest among the temperatures at which the creep test was performed is 715°C. This temperature is almost the same as that where the difference in volume magnetization is the largest (713°C). Since both the ratio of the minimum strain rate and the difference in the volume magnetization becomes smaller at temperatures higher or lower than this peak temperature, very good correlation is confirmed with the changes in these values. A similar tendency is observed for the comparison of



Fig. 11. Comparison of the ratio of the minimum strain rate and the difference in the volume magnetization of each sample steel: (a) 15Cr-6Co versus 15Cr, and (b) 15Cr-6Co versus 15Cr-3Co. (Online version in color.)

the 15Cr-6Co and 15Cr-3Co steels (Fig. 11(b)). That is, the peak temperature of the difference in volume magnetization (724°C) coincides with the peak temperature for the ratio of the minimum strain rates (725°C). In addition, the fact that these peak temperatures are immediately below the  $T_{\rm C}$ of steels with low creep strength is also a common feature in both the 15Cr-6Co/15Cr and 15Cr-6Co/15Cr-3Co comparisons. In other words, this peak temperature corresponds to the temperature at which magnetism is almost lost for low-strength steel (low  $T_{\rm C}$  steel), while it is maintained for high-strength steel (high  $T_{\rm C}$  steel). The findings that the magnitude of creep strengthening due to Co addition differs depending on the test temperature and that a peak strength difference occurs in the intermediate temperature range cannot be explained by high temperature solid solution strengthening via the solute drag mechanism.<sup>45)</sup> Therefore, it is likely that this tendency is due to the difference in the diffusion rate between the compared steels became maximum at the peak temperature, as a result of the reduction in the diffusion rate by the increase in the magnetization due to Co addition. These results mean that a chemical composition design that increases the magnetization of the steel at the service temperature would be useful as a new creep strengthening method for ferritic heat-resistant steel. In Fig. 11, the value of the difference in volume magnetization is used for convenience in order to compare the magnetic properties of the sample steels. However, it is not clear what the physical meaning of this value is or whether this value is the best parameter for comparing magnetic properties related to creep strength. Further investigation is required to determine a suitable parameter for associating magnetic properties with creep strength, such as the absolute value of magnetization or the spatial distribution of magnetic domains that may affect the diffusion in steel.

#### 4. Conclusions

The effect of Co addition on the creep strength of ferritic heat-resistant steel was investigated by focusing on the changes in the magnetic properties of iron due to Co. The conclusions of this study are summarized below.

(1) Co addition up to 6 mass% hardly changed the lattice constant and did not contribute to the solid solution strengthening. The addition of Co does not increase the Vickers hardness at room temperature. On the other hand, the creep strength in the temperature range from 650 to 750°C improved with the amount of Co added.

(2) The addition of Co increased the volume magnetization of the steel in the temperature range from room temperature to about 800°C. The effect was greater as the amount of Co added increased.

(3) The ratio of the minimum strain rate and the difference of volume magnetization between steels with different Co contents underwent similar changes with temperature. These results indicate that the magnitude of the magnetization of steel is closely related to the creep strength, and the creep strength increases as the magnetization increases by Co addition.

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