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**Study on Microstructure Control of Reduced
Activation F82H-ODS Ferritic steels**

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2014

**Study on Microstructure Control of Reduced
Activation F82H-ODS Ferritic steels**

**A Dissertation Submitted to Hokkaido University
for Doctoral Degree in Engineering**

by

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Chapter 1 Introduction

1.1 Nuclear power plants

Along with the development of the world, human beings need much more resources to produce the energy that used in industry and daily life. But the traditional fossil and mineral fuels such as petroleum, coal and natural gas will be totally used up in several decades with the present utilizing rate. [1] In addition, the burning of the fossil fuels also leads to many environmental problems, such as the global warming and air pollution.

As a new energy source which has great potential and wide applications, the nuclear power plants are developed rapidly in the past decades of years because of its high efficiency.

1.1.1 Fission reactor and power plants

Thermal reactors (the most common type of nuclear reactor) use slowed or thermal neutrons to keep up the fission of their fuel. Almost all current reactors are of this type. These contain neutron moderator materials that slow neutrons until their neutron temperature is thermalized, that is, until their kinetic energy approaches the average kinetic energy of the surrounding particles. Thermal neutrons have a far higher cross-section (probability) of fissioning the fissile nuclei uranium-235, plutonium-239, and plutonium-241, and a relatively lower probability of neutron capture by uranium-238 (U-238) compared to the faster neutrons that originally result from fission, allowing use of low-enriched uranium or even natural uranium fuel. The moderator is often also the coolant, usually water under high pressure to increase the boiling point. These are surrounded by a reactor vessel, instrumentation to monitor and control the

reactor, radiation shielding, and a containment building. [2]

Fast neutron reactors use fast neutrons to cause fission in their fuel. They do not have a neutron moderator, and use less-moderating coolants. Maintaining a chain reaction requires the fuel to be more highly enriched in fissile material (about 20% or more) due to the relatively lower probability of fission versus capture by U-238. Fast reactors have the potential to produce less transuranic waste because all actinides are fissionable with fast neutrons, but they are more difficult to build and more expensive to operate. Overall, fast reactors are less common than thermal reactors in most applications. Some early power stations were fast reactors, as are some Russian naval propulsion units. Construction of prototypes is continuing. [2]

1.1.2 Fusion reactor and fusion power plants

Fusion power is the power generated by nuclear fusion processes. In fusion reactions two light atomic nuclei fuse together to form a heavier nucleus and release tremendous amounts of energy. Among all candidate energy sources for the future, fusion power is considered to be one of the best energy source. Firstly, fusion power would provide much more energy for a given weight of fuel than any technology currently in use [3] and the fuel itself (primarily deuterium) exists abundantly in the Earth's ocean: about 1 in 6500 hydrogen atoms in seawater is deuterium. [4] Although this may seem a low proportion (about 0.015%), because nuclear fusion reactions are so much more energetic than chemical combustion and seawater is easier to access and more plentiful than fossil fuels, fusion could potentially supply the world's energy needs for millions of years. [5] The nuclear fusion requires precisely controlled temperature, pressure, and magnetic field parameters to generate net energy. If the reactor were damaged, these parameters would be disrupted and the heat generation in the reactor would rapidly

cease. [6]

Fig 1-1 shows a device of fusion reactor under construction called International Thermonuclear Experimental Reactor (ITER). It is an international nuclear fusion research and engineering project, which is currently building the world's largest experimental tokamak nuclear fusion reactor at the Cadarache facility in the south of France. The project is funded and run by seven member entities — the European Union (EU), America, Russia, Japan, China, India and South Korea.[7]

1.2 Application of ODS ferritic steels in nuclear plants

Materials selection for application in nuclear reactors is dependent on a variety of factors including economics, safety, and reactor environment. It must be able to maintain reliable performance in a severe environment which subjects materials to high temperatures, massive thermal and mechanical stresses, and intense radiation damage.

Because of the high creep rupture strength and excellent radiation resistance, oxide dispersion strengthened (ODS) ferritic steels are most promising candidates to be used in different types of advanced nuclear reactors as cladding and core structural materials. [8, 9, 10]

1.2.1 9CrODS ferritic steels

9CrODS ferritic steel, which has high temperature strength and excellent radiation resistance, is promising candidate material for the advanced fission blanket system [11]. In former research [12-14], it was confirmed that 9CrODS steel consists of a dual phase; that is a martensite phase and a residual ferrite phase. The formation and strengthening mechanism of the residual ferrite phase were studied in details [15]. We also found that a transform ferrite phase induced by hot-rolling can improve the tensile

strength of 9CrODS steels [16].

1.2.2 Reduced activation F82H-ODS ferritic steels

Reduced-activation ferritic/martensitic (RAFM) steels have been considered to be the prime candidate for the fusion blanket structural material. The irradiation data obtained up to now indicates rather high feasibility of the steels for application to fusion reactors because of their high resistance to degradation of material performance caused by both the irradiation-induced displacement damage and transmutation helium atoms. The martensitic structure of RAFM steels consists of a large number of lattice defects before the irradiation, which strongly retards the formation of displacement damage through absorption and annihilation of the point defects generated by irradiation. Transmutation helium can be also trapped at those defects in the martensitic structure so that the growth of helium bubbles at grain boundaries is suppressed. The major properties of the steels are well within our knowledge, and processing technologies are mostly developed for fusion application [17, 18].

A reduced activation ferritic steel, 8Cr-2W-V-Ta designated as F82H, has been developed in Japan for the blanket structural material of the advanced fusion reactor [19]. The oxide dispersion strengthened (ODS) ferritic steels are also being developed for future application to the fusion blanket system in order to increase the coolant outlet temperature.

1.3 Objective of the research

Above all, the purpose of this thesis is to improve the microstructure and high temperature properties and investigate the strengthening mechanism and phase transformation mechanism of 9CrODS ferritic steels and F82H-ODS ferritic steels.

In this study, F82H-ODS ferritic steels with the same chemical composition as J1-lot are manufactured. The parallel specimen without Y_2O_3 is also prepared, and designated as 8CrFMS, which is different from F82H; it contains 0.2% Ti and higher carbon content of 0.16 mass% than F82H of 0.1 mass%. The microstructure of the manufactured J1-lot, which is designated as 8CrODS, is analyzed, and formation process of the ferrite is investigated by conducting an annealing experiment. The effect of hot-rolling on microstructure and tensile strength in 8CrODS ferritic steel was investigated, where 8CrODS ferritic steel has the same chemical composition with J1-lot. Three kinds of heat treatment processing were conducted for air-cooling just after hot-rolling, subsequent tempering and normalizing-tempering, and the tensile properties and microstructure were evaluated.

For 9Cr-ODS ferritic steels, we investigate effects of hot-rolling at the γ -austenite region and subsequent cooling at different cooling rate that could modify the microstructure and mechanical properties. For those specimens, hardness and high-temperature tensile properties are measured. Inverse pole figure (IPF) and kernel average misorientation (KAM) are analyzed to evaluate the microstructural change and strengthening mechanism.

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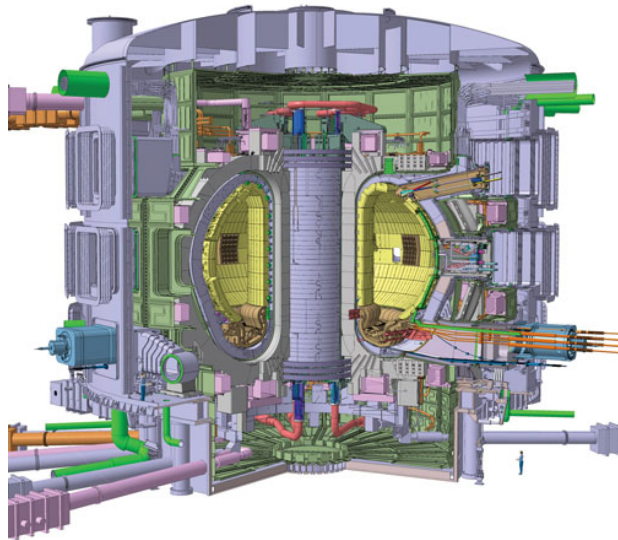


Fig.1-1 the device of fusion reactor

Chapter 2 Experimental and Analytical Methodology

2.1 Materials and specimen preparation

This section shows a typical procedure to make a specimen which is used in this thesis. A description of the material and its condition as well as the experimental details is also given.

2.1.1 Material

9CrODS ferritic steel and reduced activation F82H-ODS ferritic steel were employed for the research. The chemical composition of them are 9Cr-0.13C-2W- 0.2Ti-0.35Y₂O₃ (mass%) and Fe-0.16C-8Cr-1.95W-0.09Ta-0.21V-0.17Ti-0.33Y₂O₃-0.08Ex.O (mass%), respectively.

2.1.2 Mechanical alloying

Mechanical Alloying (MA) is an alloying process to the powders by giving them severely plastic deformation repeatedly in a high-energy ball mill [1]. The mechanical alloying was conducted by planetary mills according to the following parameters:

- Type of mill: Fritsch P5 and P6 ;
- Milling speed: 400 rpm for P6 and 300 rpm for P5;
- Milling time: 48-hour milling with 24-hour pause;
- Ball-to-powder ratio: 10:1;
- Milling atmosphere: Argon;

2.1.3 Spark plasma sintering

Spark plasma sintering (SPS) was applied to consolidate the mechanical-alloyed powders, and the parameters for the sintering are shown below:

- Load: 800kg;
- Temperature: 1150 °C;

- Sintering time: 2 hours;
- Temperature measurement: Infrared radiation thermometer;
- Atmosphere: Vacuum (start heating from 0.1 Pa);

2.1.4 Hot-rolling

A size of the consolidated specimen is 12 mm in diameter and 40 mm in height, and these cylindrical specimens were embedded into plates made of stainless steel (SS) in the thickness of 25 mm. Such kind of specimens were kept at temperature of 1100 °C in the electric furnace, and subsequently processed by hot-rolling. Within a limited period that the temperature is maintained above A_{r3} point after taking out the electric furnace, the SS plate was hot-rolled (HRed) three times in a reduction of thickness from 25 mm to 12 mm, then plate was returned back to the electric furnace to keep again 1100 °C. Subsequently, three times hot-rolling was repeated to reduce a thickness from 12 mm to 4 mm, corresponding to total reduction rate of 84 %. During this period, temperature fell to 862 °C, and HRed specimens were cooled by different cooling rate according to different experiments.

2.1.5 Normalizing

Some specimens were normalized at 1050 °C for 1 hours.

2.1.6 Tempering

Some specimens were tempered at 750 °C for 1 hours.

2.1.7 Annealing

Some specimens were annealed at 1250 °C for different durations

2.2 Analysis methods

2.2.1 Tensile test

Tensile test was conducted by using miniaturized size specimens at 700 °C by a strain

rate of 1.0×10^{-3} /s under an argon gas atmosphere.

2.2.2 High temperature XRD analysis

The XRD analysis was conducted by using a specimen which is kept at high temperature (600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C)

2.2.3 Thermal expansion measurement

A thermo-mechanical analysis (TMA) for measuring specimen length change was also conducted by using specimen in the dimension of $2 \times 2 \times 10$ mm to characterize the transformation temperature from austenite to ferrite. The temperature range for TMA analysis is from room temperature to 1150°C. These data were analysed by THERMOFLEX-TAS 300 thermal analysis system.

2.2.4 FE-SEM and EBSD

Microstructures of the specimens were analyzed by means of JEOL JSM-6500F field-emission scanning electron microscope (FE-SEM). The electron back scattering diffraction patterns (EBSD) analyses were also conducted; OIM-Analysis 4 (TexSEM Laboratories) provided information on grain texture and crystal orientation.

Electron backscattered diffraction (EBSD) is a good way to examine the texture of crystalline materials. When electron beam hit the surface of specimens in the scanning electron microscope, electron backscattered diffraction patterns are produced. In polycrystalline materials, EBSD patterns from grains with different orientations are different. Therefore, by acquiring these patterns using CCD camera and index them using data analysis software, we can know the texture of material.

2.2.5 Nano indentation

In nanoindentation, small loadings are used, so the indentation area may only be a few square micrometres or even nanometres. This presents problems in determining the

hardness, as the contact area is not easily found. While indenting, various parameters such as load and depth of penetration can be measured. A record of these values can be plotted on a graph to create a load-displacement curve. These curves can be used to extract mechanical properties of the material.

2.2.6 TEM

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEM was used to observe the microstructure of the target material through bright field image, dark field image and get the reflection direction from the diffraction pattern.

The TEM specimen was prepared as a 3mm-diameter disk which was mechanically thinned to 0.15 μm with silicon paper. And then, it was electrically polished with a TENUPO device. Perchloric acid (HClO_4): acetic acid (CH_3COOH) = 1:19 was used as electrolytic solution for twin jet polishing. The parameters for the polishing is shown below:

- Electrolytic voltage: 20~40V (depend on the specimens);
- Electrolytic current: 10~50 mA;
- Electrolytic flow: 9~20
- Temperature: room temperature.

Oxide particles were imaged with TEM (JEOL JET-2010F) with the acceleration voltage 200kV, and the oxide particle size was measured with image processing

software MacView.

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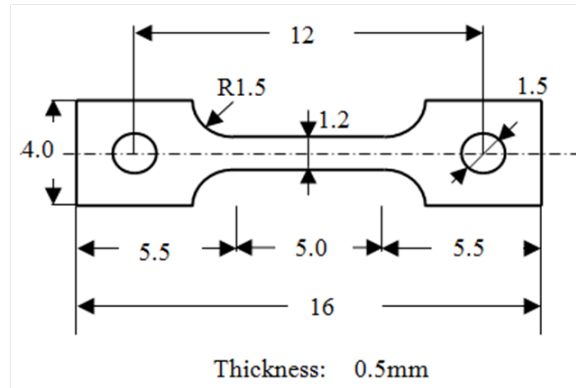


Fig 2-1 Dimensions of specimens used in tensile test

Chapter 3 Microstructure Characterization of Reduced Activation F82H-ODS Ferritic Steel

3.1 Introduction

As the introduction in chapter 1, two types of the reduced activation F82H-ODS ferritic steels, J1 and J2, have been fabricated so far for the fusion application [1]. The J1-lot is composed of Fe-0.16C-8Cr-2W-0.2V-0.1Ta-0.2Ti-0.37Y₂O₃-0.09Ex.O (mass %), and the J2-lot is simple composition of Fe-0.16C-8Cr-1W-0.2Ti-0.38Y₂O₃-0.09Ex.O. Normalizing and tempering conditions of both lots are 1050 °C for 1 h and 750 °C for 1 h, respectively. It was reported by Shinozuka et al. that a ferrite is involved 15 % in J1-lot and 10 % in J2-lot [1], that leads to superior creep strength in J1-lot as compared with J2-lot. A higher content of ferrite leads to a higher strength, which is opposite to conventional steels. In Dr. Shinozuka's paper, the ferrite phase was designated as δ -ferrite, but how it was formed and why it lead to a strengthening, there is no related studies in the world till now.

So, the objective of this study is to clarify the ferrite phase formation in F82H-ODS ferritic steels. In our experiment, F82H-ODS ferritic steels with the same chemical composition as J1-lot are manufactured. The parallel specimen without Y₂O₃ is also prepared, and designated as 8CrFMS, which is different from F82H; it contains 0.2% Ti and higher carbon content of 0.16 mass% than F82H of 0.1 mass%. The microstructure of the manufactured J1-lot, which is designated as 8CrODS, is analyzed, and formation process of the ferrite is investigated by conducting an annealing experiment.

3.2 Experimental procedure

The mechanical alloying for producing the 8CrODS and 8CrFMS specimens was conducted by using attrition-type ball mill for 48 hours under argon gas atmosphere.

Both the mechanically alloyed 8CrODS and 8CrFMS powders were consolidated by spark plasma sintering at 1150 °C for 2 h and a stress of 44 MPa under a vacuum of 0.1 Pa. The dimension of the consolidated specimens is 12 mm in diameter and 25 mm in height, and these cylindrical type of specimens were embedded into a mold made of stainless steel (SS) in a dimension of 15×15×25 mm. Then, the molds containing 8CrODS and 8CrFMS specimens were kept at temperature of 1100 °C in the electric furnace. Subsequently, hot-rolling was conducted with a reduction rate of 80 %. The final heat treatment was carried out by normalizing at 1050 °C for 1 h and tempering at 750 °C for 1 h.

Table 3-1 lists the chemical composition of the 8CrODS and 8CrFMS powders, which were produced by the mechanical alloying. The basic composition of 8CrODS is Fe-0.16C-8Cr-2W-0.1Ta-0.2V-0.2Ti-0.35Y₂O₃ (mass%), which is the same as J1-lot. The composition of the parallel specimen, 8CrFMS, is the same as 8CrODS without Y₂O₃. High-temperature XRD analyses of the mechanically alloyed powders was conducted by using Philips X'pert PRO with a TCU 2000 temperature control unit to search α and γ phases at the room temperatures, 900 °C and 1100 °C. The microstructure of 8CrODS and 8CrFMS specimens was observed by JEOL JSM-6500F field-emission scanning electron microscope (FE-SEM). The dilatometric measurements were performed using a Rigaku TMA-8140C during the temperature rising and cooling between room temperature and 1150°C. The rate of temperature rising was set at 5 °C/min, and a size of the dilatometric specimens is 2×2×10 mm.

Some of the 8CrODS specimens were annealed at 1250 °C for various durations of 20 h, 40 h, 60 h, 80 h and 100 h to make the oxide particles coarser, subsequently these annealed specimens were quenched by water, and the microstructures of the

annealed-quenched specimens were checked by FE-SEM. Some of these annealed-quenched specimens were also normalized at 1050 °C for 1 h in order to analyze the α - γ phase transformation. Microstructures and area fraction of these annealed-quenched-normalized specimens were analyzed by Macro-view system. The size of the oxide particles and their distribution were also analyzed by TEM (JEOL JEM 2000). The computed phase diagram and a free energy for α and γ phases at various carbon contents were analyzed by using Pandat code 8.2 version.

3.3 Results

3.3.1 Microstructure characterization

Fig. 3-1 shows a computed phase diagram of 8CrFMS without Y_2O_3 calculated by Pandat 8.2 version as a function of carbon content. The γ phase alone is stable at the normalized temperature of 1050 °C, when the carbon content is 0.16 mass%, suggesting that a matrix of 8CrODS could be full martensite structure after cooling.

To reveal the phase transformation process of 8CrODS, the dilatometric measurement was carried out from room temperature to 1150°C with a heating and cooling rate at 5°C/min. **Fig.3-2** compares the dilatometric curve during temperature rising for 8CrFMS and 8CrODS. The length of 8CrFMS shrinks at temperatures between A_{C1} (830°C) and A_{C3} (855°C), which corresponds to the ferrite to austenite phase transformation, however for 8CrODS, this shrinkage is limited and A_{C1} and A_{C3} temperatures increase to 870°C and 920°C, respectively. Considering that the 8CrODS has a same composition with parallel 8CrFMS except for containing Y_2O_3 , retardation of ferrite to austenite phase transformation in 8CrODS is ascribed to a pinning of interfacial boundaries by Y_2O_3 oxide particles.

This behavior can be confirmed by the high-temperature XRD analyses of the

mechanically alloyed 8CrODS powders. As shown in **Fig.3-3(a)**, at 25°C, only α phase peaks can be found at the diffraction angle 2θ selected between 18° and 30°. When the temperature rises to 900°C between A_{C1} and A_{C3} , the γ phase peaks appear and the intensity of α phase peaks becomes weak. Then, the XRD analysis was conducted at 1100°C, after keeping at 1100°C for long period enough to make sure that the α phase can be transformed into γ phase. However, the α phase peaks still remain as shown in **Fig. 3-3**. While in **Fig.3-3(b)**, which shows the high-temperature XRD analyses of the 8CrFMS powders, when the specimens were kept at 1100°C for long enough time, all of the α phase transformed into γ phase, and only γ peak can be found at last. Based on above results of experiments including the computed phase diagram, this α phase is not equilibrium δ phase, but it should be a meta-stable phase. Therefore, this α phase is designated as a residual-ferrite that has been reported in the previous studies of the 9CrODS for the fast reactor fuel cladding [2-6].

The typical microstructures of 8CrODS and 8CrFMS after normalizing heat treatment are shown in **Fig. 3-4**. The 8CrODS is composed of a dual phase; dark color flat-surface area corresponds to the residual-ferrite and rough-surface white color area belongs to martensite, whereas the parallel 8CrFMS consists of single full martensite.

3.3.2 Change of residual-ferrite fraction and oxide particle size by annealing

An annealing experiment was designed to reveal how the oxide particles affect the α - γ phase transformation in 8CrODS. The specimens were annealed at 1250°C for different durations to make the oxide particles coarsening, some of them just quenched by water directly, and then the change of the microstructure was observed by FE-SEM, which is shown in **Fig. 3-5**. While others were normalized and quenched, then the structures were observed, which were shown in **Fig. 3-6**. For the annealed and quenched

(A-Q) specimens, the microstructures of all these 5 kinds of specimens (20hours-A-Q, 40hours-A-Q, 60hours-A-Q, 80hours-A-Q, 100hours-A-Q) contain a dual phase of ferrite and martensite, which are same as the non-annealed specimens. And the area fraction of ferrite in these A-Q specimens looks changed slightly along with annealing time rising. Such kind of data was quantitatively measured by Mav-View 3.5, which is shown as a dash line in **Fig. 3-7**. But compare with the microstructure before annealing, even in 100hours-A-Q specimens, the change of the microstructure is not so much. In order to get much clear microstructures, the A-Q specimens were normalized and then quenched again. The microstructures of these A-N-Q specimens are shown in **Fig. 3-6**. Compared with the microstructure before annealing shown in **Fig. 3-4 (a)**, the area of martensite region in 20hours-A-N-Q (annealed-normalized-quenched) specimen spreads, and the martensite and residual-ferrite phase are clearly separated each other as shown in **Fig. 3-6(a)**. In 60hours-A-N-Q specimen, shown in **Fig. 3-6(b)**, the area of martensite grows to much larger, and only a few residual-ferrite is left. **Fig. 3-6(c)** shows that only martensite can be found in 100hours-A-N-Q specimen. **Fig. 3-7** shows the area fraction of the residual-ferrite in the annealed specimens, which was quantitatively measured by Mav-View 3.5. Along with increasing annealing time, the area fraction of residual-ferrite becomes smaller, and there is almost no residual-ferrite phase left, when the annealing time is over 100 hours. The reasons for the difference of A-Q and A-N-Q are discussed later.

The distribution and morphology of the oxide particles in the annealed 8CrODS specimens were analyzed by TEM, and those results are shown in **Fig. 3-8**. The sizes distribution measured quantitatively by Mac-view is also shown in **Fig. 3-9**. In the 20 hours annealed specimen, the oxide particles are homogeneously distributed in the size

between 1.5 nm and 10 nm with the average size of 6 nm. In the 40 hours and 60 hours annealed specimens, some oxide particles become slightly coarser while some of them also keep a small size. Their average size increases to 7 nm and 9 nm. In 80 hours and 100 hours annealed specimens, quite larger size of oxide particles can be found, and the number density of the oxide particles decrease significantly. Their average size of the oxide particles is 11 nm and 12 nm, respectively. These results are plotted in **Fig. 3-10**, in the average size of oxide particles vs. annealing time at 1250°C.

3.4 Discussion

Through above results of annealing experiment represented in **Fig. 3-7** and **Fig. 3-10**, it was obviously demonstrated that the amount of the residual-ferrite decreases with coarsening of the oxide particles in 8CrODS specimens. This result suggests that the α to γ transformation easily proceeds and the residual-ferrite cannot be retained as a meta-stable state, when the oxide particles are coarsened. Considering that the α to γ transformation takes place by the movement of α - γ interfacial boundaries across the oxide particles, an extent of this transformation could be dominated by pinning force of the dispersed oxide particles against movement of the α - γ interfacial boundaries. Therefore, the ferrite remains as the meta-stable state, if the oxide particle pinning force is beyond the driving force for the α to γ transformation.

The pinning force by the dispersed oxide particles at the α - γ interface is able to be predicted, according to the following Zener equation [7],

$$F = \frac{3}{4} \frac{\sigma \cdot f_p^{2/3}}{r} \quad \text{--- (1)}$$

where σ (J/m²) is the α - γ interfacial energy, r (m) is the radius of the oxide particles in α -phase, f_p is the volume fraction of dispersed oxide particles. Substituting 0.56 J/m² as σ [8] and TEM data into equation (1), the pinning force (F) calculated for the annealed 8CrODS specimens for various duration is shown in **Fig.3-11**. The pinning force by the oxide particles decreases with increasing annealing time, namely with coarsening of the oxide particles. Here, we should point out that these results were derived using average radius of the oxide particles. However, particle size has some distribution as shown in **Fig. 3-9**. The oxide particles in the size smaller than average value yield higher pinning force, thus giving a large amount of residual-ferrite, and in contrast larger oxide particles give a small amount of residual-ferrite, even at the same average size of the oxide particles. This situation leads to heterogeneous distribution of the residual-ferrite.

The chemical driving force for the γ phase formation from α phase at normalizing temperature of 1050 °C was estimated by using Pandat 8.2. In order to investigate the reasons for the difference between A-Q specimens and A-N-Q specimens, the chemical driving force of α - γ phase transformation at 1250 °C was also calculated. **Fig. 3-12** (a) and (b) shows the Gibbs free energy for α and γ phase at 1050 °C and 1250 °C as a function of carbon content separately. It shows that, for the nominal carbon content of 0.16%, the driving force of α - γ phase transformation at 1250 °C is about 15 MJ/m³, which is much lower than the value of 25 MJ/m³ at 1050 °C. From **Fig. 3-12(b)**, only γ phase is stable at 0.16% carbon content at 1250°C. Since the driving force for the α - γ phase transformation at 1250 °C is less than at 1050 °C, reduction of the residual ferrite fraction is limited as shown in **Fig. 3-7**. So, in order to explain the ferrite formation mechanism clearly, we mainly use A-N-Q specimens to the discussion.

The Gibbs free energy of α phase can be estimated at a carbon content of 0.02 mass % as a solubility limit, whereas that of γ phase corresponds to 0.16 mass % carbon as a nominal composition. Difference of Gibbs free energy of γ phase at 0.16 mass % carbon from tangent line at 0.02 mass % carbon in α phase corresponds to the driving force of α - γ transformation at 1050 °C. This process is represented in **Fig. 3-12**, where the chemical driving force of α - γ transformation is designated as $\Delta G_{\alpha-\gamma}$. This value is estimated to be 5.0 MJ/m³, and plotted by line in **Fig. 3-11**. The 20 hours hours annealed specimen, where the the pinning force is higher than driving force for α - γ transformation, gives some extent of residual-ferrite, and the opposite case of 100 hours annealed specimen contains no residual-ferrite. These results show a good agreement with SEM observation represented in **Fig. 3-6**. These results support that the residual-ferrite is meta-stable, and its formation is ascribed to pinning of α - γ interfacial boundaries by the dispersed nano-size oxide particles.

3.5 Summary

The results of the study are summarized as follow;

- (1) The 8CrODS specimen, which is the same chemical composition as J1-lot of F82H-ODS ferritic steel, was manufactured by means of mechanical alloying, spark plasma sintering and hot-rolling. This 8CrODS is composed of the dual phase of ferrite and martensite. This ferrite phase turned out to be meta-stable phase that doesn't exist in the computed phase diagram, thus designated as residual-ferrite.
- (2) Through the annealing experiment for the various durations at 1250 °C, the residual-ferrite disappeared with increasing annealing time and coarsening of the oxide particles. Formation of the residual-ferrite is attributed to pinning of α - γ interfacial boundaries by the oxide particles.

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Table 3-1 Chemical composition of mechanically alloyed powders

Elements (mass%) Specimens	C	Cr	W	V	Ti	Ta	Y ₂ O ₃	Fe
8CrODS	0.16	8.02	1.95	0.21	0.17	0.09	0.33	Bal.
8CrFMS	0.16	8.0	2.0	0.2	0.2	0.1	0	Bal.

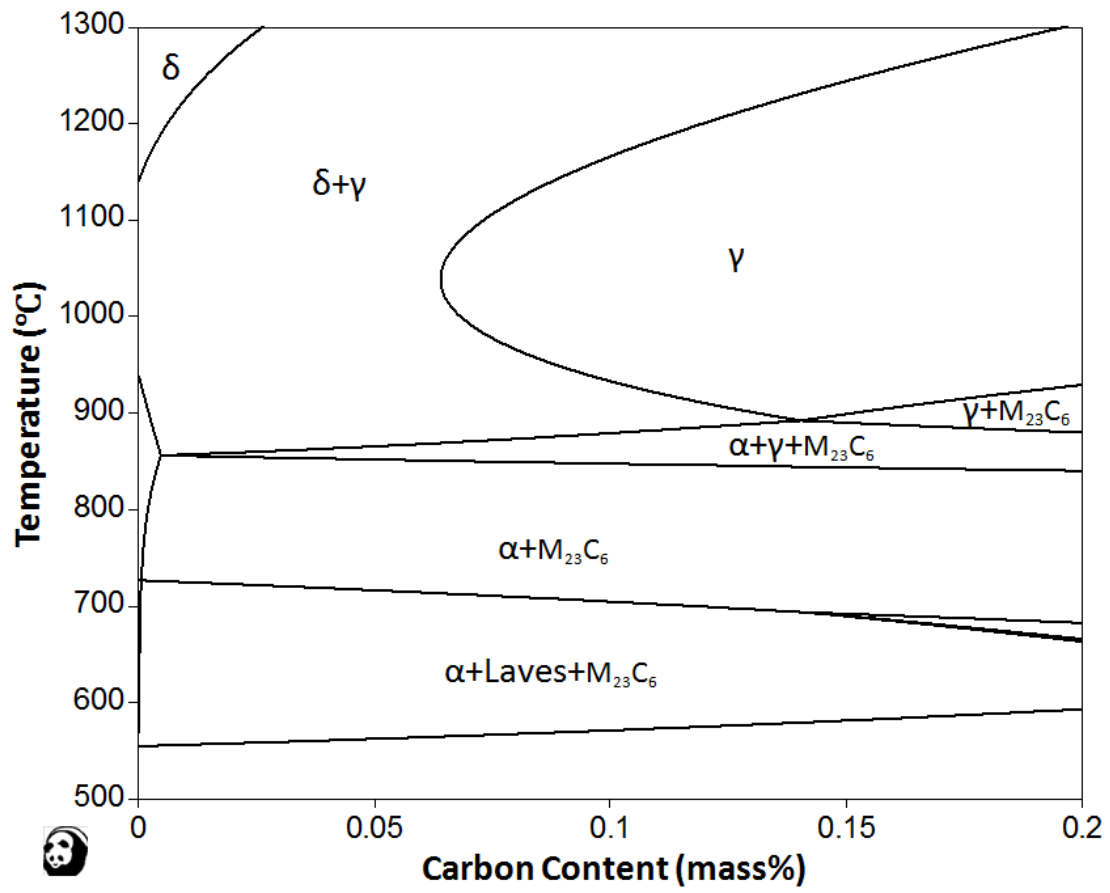
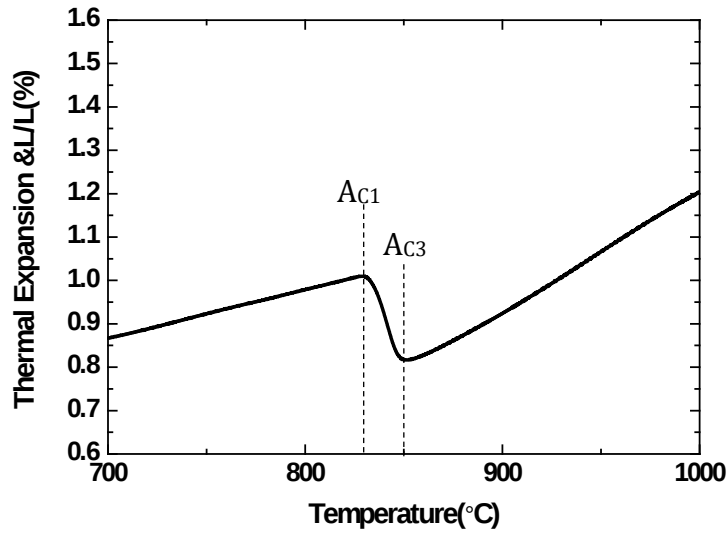
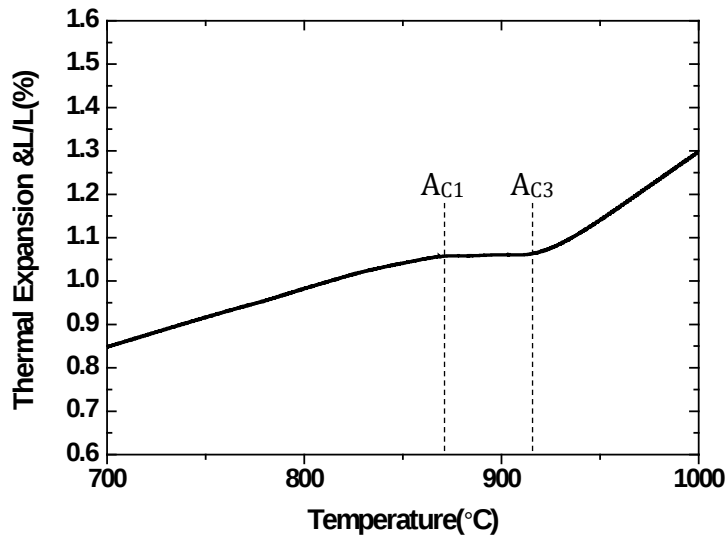


Fig. 3-1 Phase diagram of 8CrFMS without yttria calculated by Pandat 8.2 version.

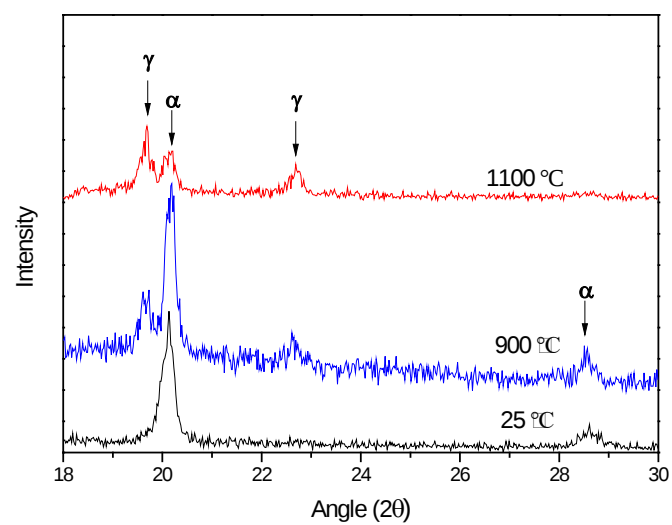


(a) 8CrFMS

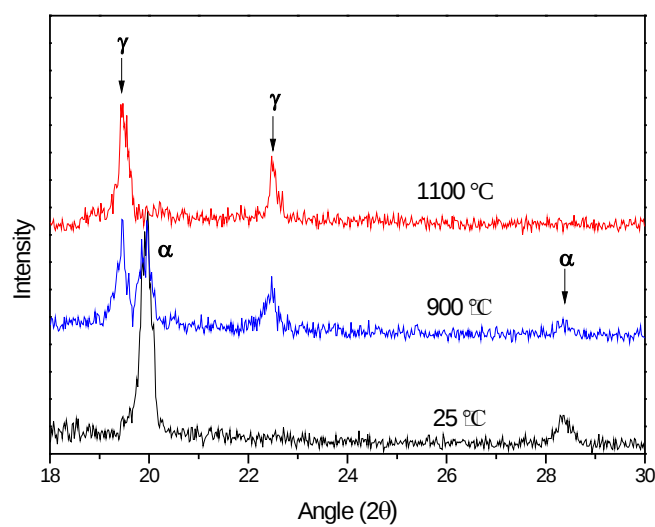


(b) 8CrODS

Fig. 3-2 Dilatometric curves of 8CrFMS and 8CrODS specimens during temperature rising at 5 °C/min.

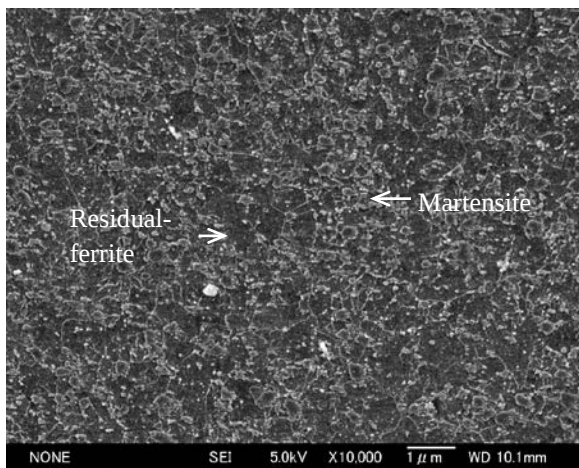


(a) 8CrODS

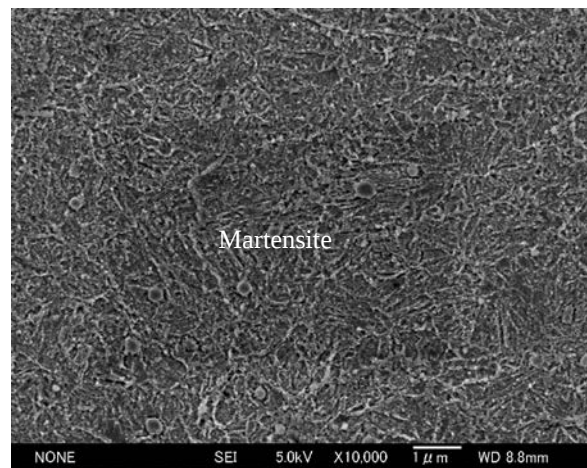


(b) 8CrFMS

Fig.3-3 High-temperature XRD Analyses of 8CrODS and 8CrFM powders at 25 °C , 900 °C and 1100 °C.

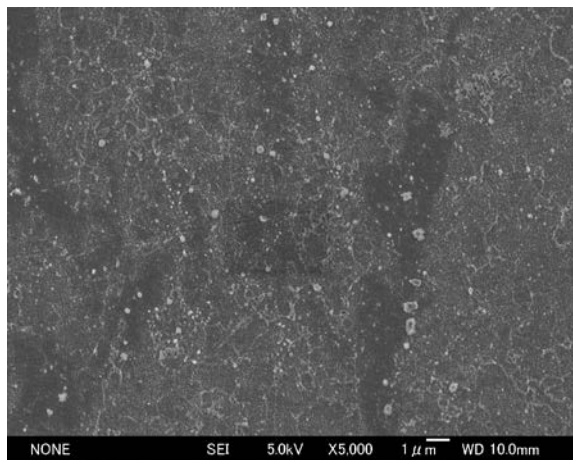


(a) 8CrODS

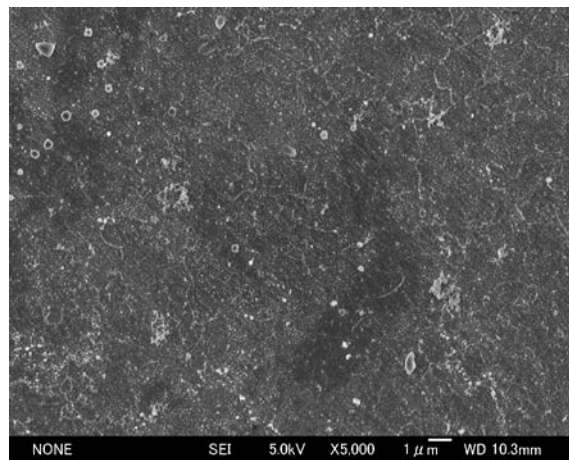


(b) 8CrFMS

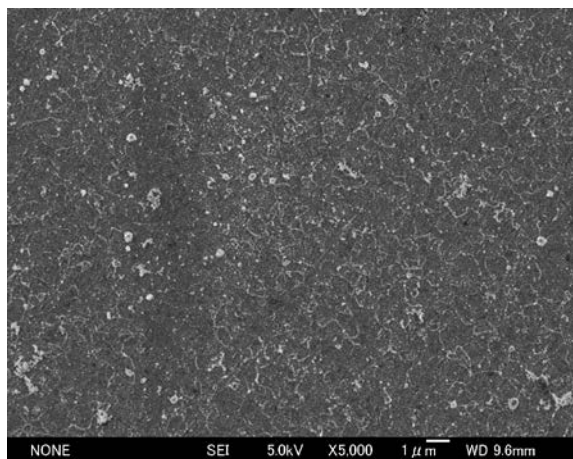
Fig. 3-4 SEM micrographs of 8CrODS and 8CrFMS specimens after normalizing heat treatment.



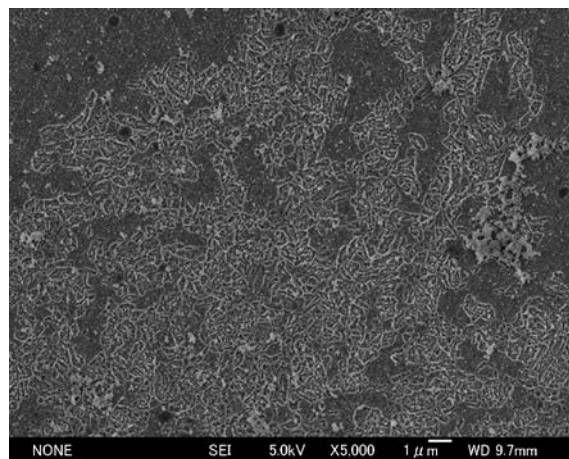
(a) 20hours-A-Q



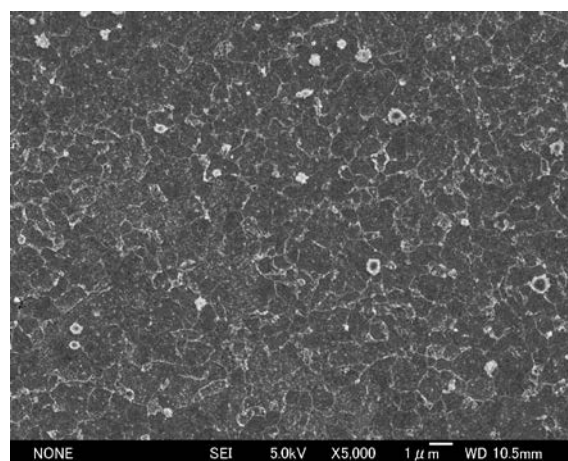
(b) 40hours-A-Q



(c) 60hours-A-Q

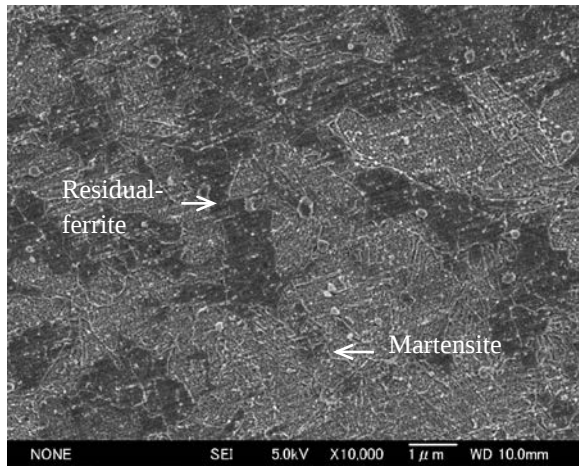


(d) 80hours-A-Q

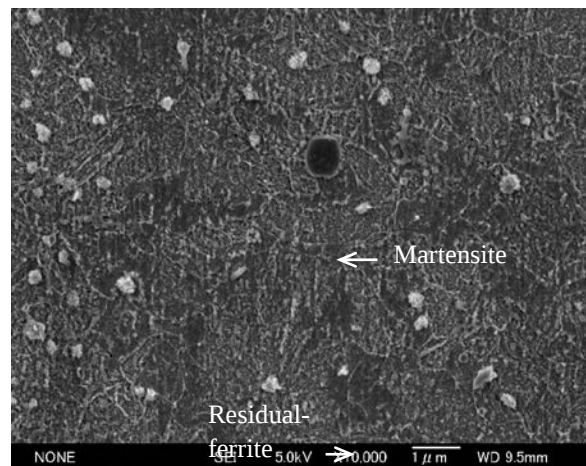


(e) 100hours-A-Q

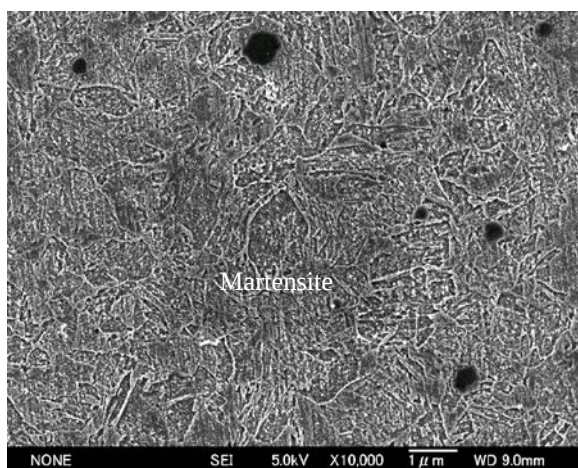
Fig.3-5 FE-SEM micrographs of 8CrODS specimens annealed at 1250 °C and then quenched (A-Q)



(a) 20 hours annealing



(b) 60hours annealing



(c) 100 hours annealing

Fig.3-6 FE-SEM micrographs of 8CrODS specimens for different annealing duration at 1250 °C

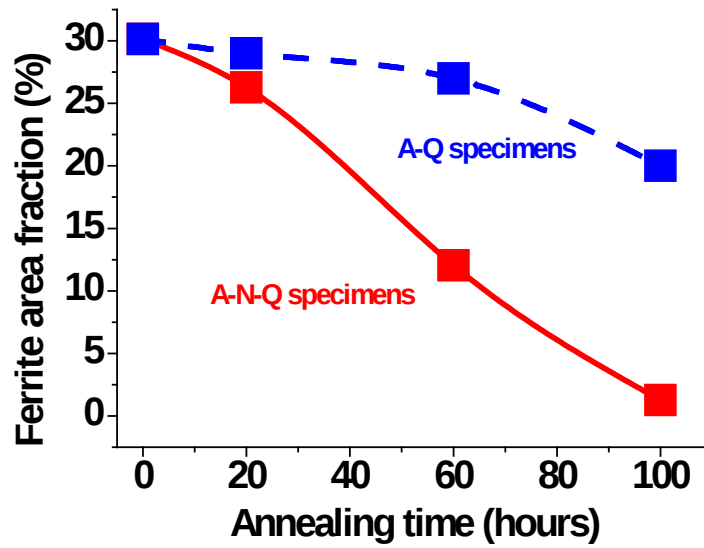
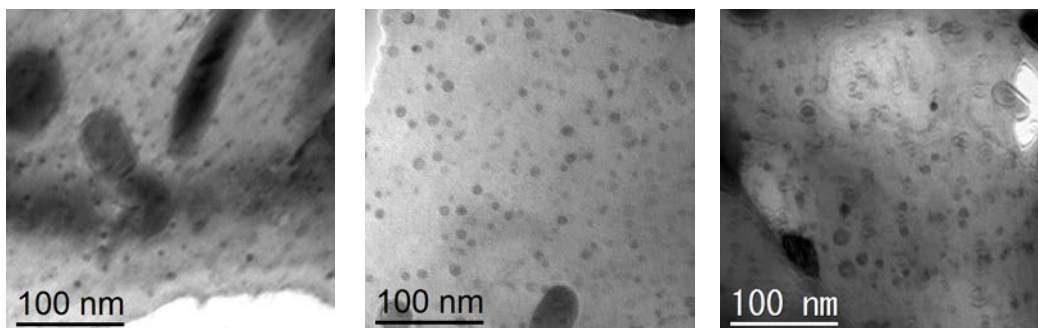


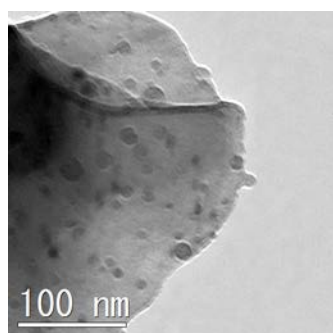
Fig.3-7 Area fraction of the residual-ferrite after annealing and normalizing. These data were estimated by SEM observation and Macro-view.



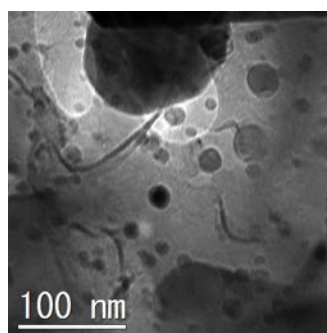
(a) 20 hours

(b) 40 hours

(c) 60 hours



(d) 80 hours



(e) 100 hours

Fig.3-8 TEM micrographs of the oxide particles for the 8CrODS specimens annealed for different duration at 1250 °C.

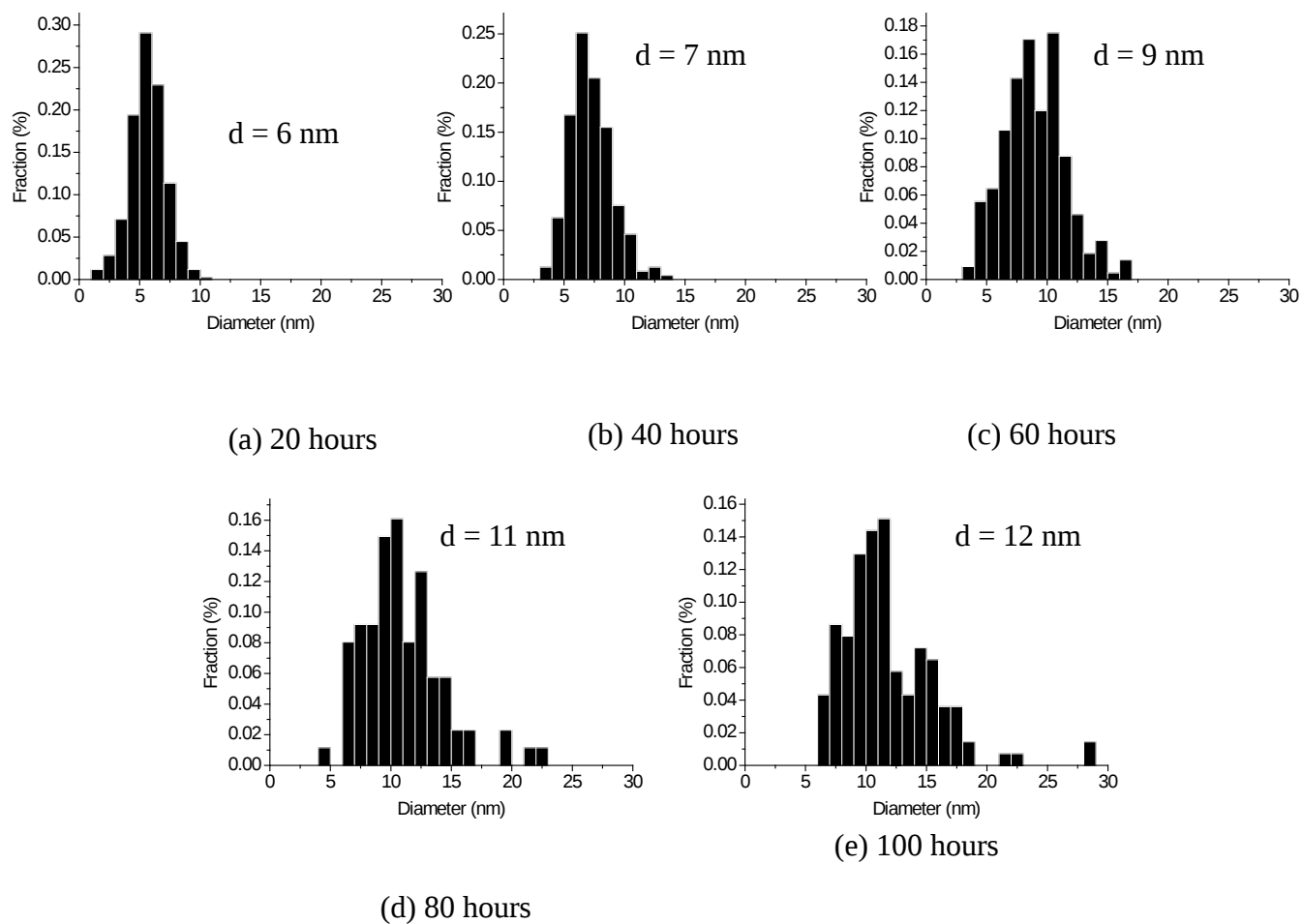


Fig.3-9 The size distribution of the oxide particles in annealed 8CrODS specimens.

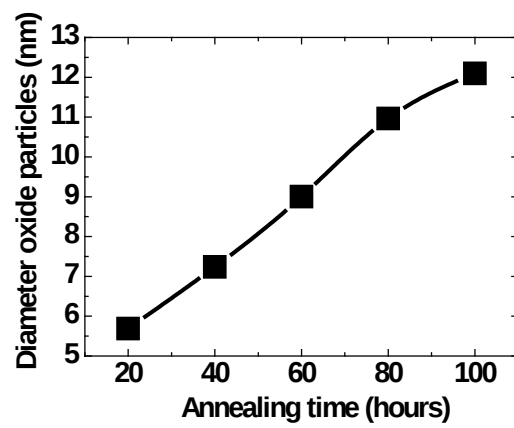


Fig.3-10 Diameter of the oxide particles with annealing time at 1250 °C.

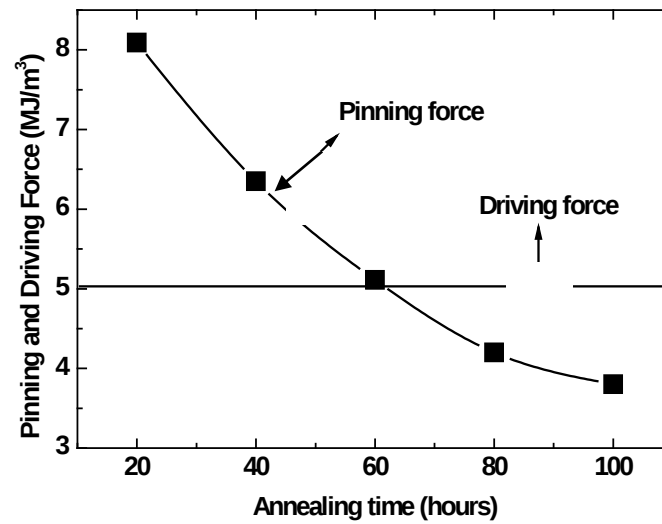
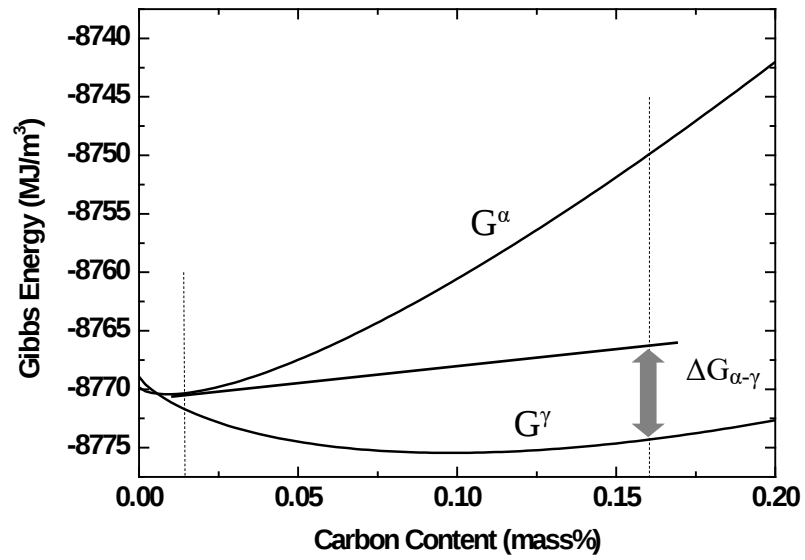
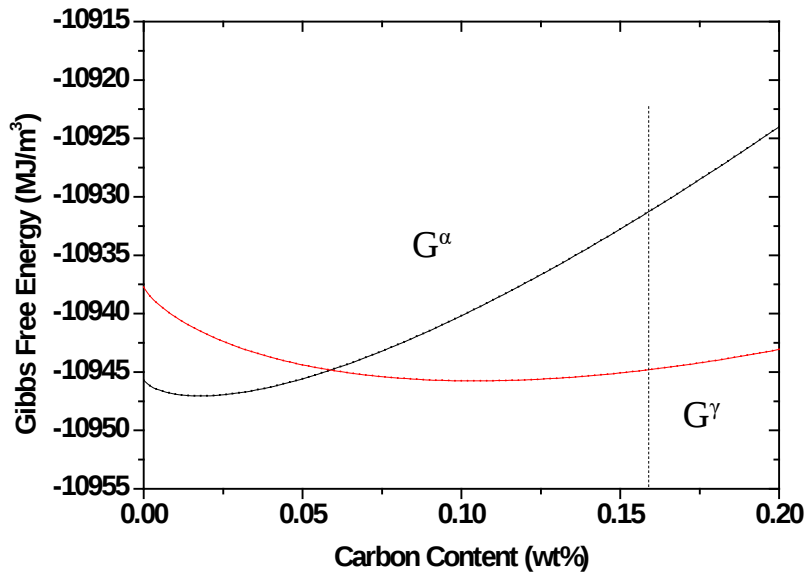


Fig.3-11 Results of calculation of pinning force of the oxide particles and driving force for α - γ transformation at the different annealing time at 1250 °C.



(a) 1050 °C



(b) 1250 °C

Fig.3-12 Gibbs free energy vs. carbon content for α and γ phases at 1050 °C and 1250°C. Driving force for α to γ transformation is shown by $\Delta G_{\alpha-\gamma}$.

Chapter 4 Hot-rolling of Reduced Activation F82H-ODS Ferritic Steel

4.1 Introduction

F82H-ODS (oxide dispersion strengthened) ferritic steels are being developed for future application to the fusion blanket system in order to increase the coolant outlet temperature. Two types of the reduced activation F82H-ODS ferritic steels, J1 and J2, have been fabricated so far for the fusion application [1]. The J1-lot is composed of Fe-0.16C-8Cr-2W-0.2V-0.1Ta-0.2Ti-0.37Y₂O₃-0.09Ex.O (mass %), which is identical to the F82H except for titanium and Y₂O₃. J1-lot exhibited a higher strength than J2-lot.

In this study, the effect of hot-rolling on microstructure and tensile strength in F82H-ODS ferritic steel was investigated, where F82H-ODS ferritic steel has the same chemical composition with J1-lot. Three kinds of heat treatment processing were conducted for air-cooling just after hot-rolling, subsequent tempering and normalizing-tempering, and the tensile properties and microstructure were evaluated.

The objective of this research is try to improve the high temperature properties of F82H-ODS ferritic steel by using hot-rolling. The mechanisms of structure change and strengthening caused by hot-rolling were also investigated.

4.2 Experimental procedure

The alloyed powder and Y₂O₃ powder were mechanically alloyed in Ar gas atmosphere by using attrition-type ball mill for 48 hours. **Table 4-1** lists the chemical composition of the mechanically alloyed powder, which is Fe-0.16C-8Cr-1.95W-0.09Ta-0.21V-0.17Ti-0.33Y₂O₃-0.08Ex.O. This composition is based on J1-lot. Then, spark plasma sintering was conducted at 1150 °C for 2 hours and the stress of 44 MPa under a vacuum of 0.1 Pa to consolidate the powders.

A size of the consolidated specimen is 12 mm in diameter and 40 mm in height, and

these cylindrical specimens were embedded into plates made of stainless steel (SS) in the thickness of 25 mm. The SS plates containing 8CrODS steel cylinders were kept at temperature of 1100 °C in the electric furnace; subsequent process for the hot-rolling is schematically represented in **Fig.4-1**. Within a limited period that the temperature is maintained above A_{r3} point after taking out the electric furnace, the SS plate was hot-rolled (HRed) three times in a reduction of thickness from 25 mm to 12 mm, then plate was returned back to the electric furnace to keep again 1100 °C. Subsequently, three times hot-rolling was repeated to reduce a thickness from 12 mm to 4 mm, corresponding to total reduction rate of 84 %. During this period, temperature fell to 862 °C, and HRed specimens were followed by air-cooling (AC) to room temperature at a cooling rate of about 6,000 °C/h, as shown in **Fig. 4-1**. The hot-rolled specimen is designated as HR specimen, and some of the HR specimens were subsequently tempered at 750 °C for 1h (HR-T), or normalized at 1050 °C for 1 h and tempered at 750 °C for 1h (HR-NT).

Thermo-mechanical analysis (TMA) for measuring specimen length change was also conducted by using HR specimen in the dimension of 2×2×10 mm to characterize the transformation temperature from austenite to ferrite. In order to make sure that the hot-rolling was conducted above A_{r3} temperature of 8CrODS steel, a TMA analysis was carried out from room temperature to 1150°C, and the temperature rising/cooling rate was 5 °C/min. For a further study, we try to draw the CCT diagram which can help us to analyze the phase transformation processing in 8CrODS steel. Many other TMA analysis were also conducted with a temperature range from room temperature to 1050°C, and the temperature cooling rates were 1 K/min, 3 K/min, 6 K/min, 10 K/min, 12 K/min, 30 K/min, 60 K/min, 300 K/min, 600 K/min separately. Due to some

restrictions of test conditions, the 1 K/min, 3 K/min, 6 K/min and 10 K/min cooled specimens were analyzed in Hokkaido University, and 12 K/min, 30 K/min, 60 K/min, 300 K/min, 600 K/min cooled specimens were conducted in the company. All of the TMA data were analysed by THERMOFLEX-TAS 300 thermal analysis system.

Miniaturized size specimens for the tensile test were prepared by using an electro-discharge processing machine. The tensile test was conducted at the elevated temperature of 700 °C by a strain rate of 1.0×10^{-3} /s under an argon gas atmosphere. The metallographic specimens were polishing with 400-4000 emery paper, 1 μ m diamond paste and alumina colloidal silica, and microstructure was analyzed by means of JEOL JSM-6500F field-emission scanning electron microscope (FE-SEM). The electron back scattering diffraction patterns (EBSD) analyses were also conducted; OIM-Analysis 4 (TexSEM Laboratories) provided information on grain texture and crystal orientation.

4.3 Results

4.3.1 Austenite to ferrite transformation temperature

The transformation temperature from austenite to ferrite in F82H-ODS ferritic steel was measured by TMA, and the results of dilatometric curve are shown in **Fig.4-2**. The A_{r1} and A_{r3} point during cooling were separately identified as 678 °C and 716 °C. As mentioned in Section 2, the temperature at the final of the hot-rolling fell to 862 °C, which is still higher than A_{r3} point. Therefore, it was confirmed that the temperature is maintained above A_{r3} point during the entire period of the hot-rolling processing.

4.3.2 Microstructure

Fig. 4-3 shows SEM micrographs of HR, HR-T and HR-NT specimens. The structure of HR-NT specimen seems to be similar to that of the conventional J1-lot

reported in ref. [1], and thus it consists of the tempered martensite and residual α -ferrite as shown in **Fig. 4-3(c)**. This means that normalizing heat treatment almost destroyed the HR structure. The white color dots distributed in the tempered martensite belong to the carbides precipitated during tempering. On the other hand, HR specimen has coarser structure, and we can barely distinguish dark color ferrite and slightly light color martensite in **Fig. 4-3(a)**. By tempering heat treatment after HR, martensite grains are more clearly identified by carbide precipitates shown in **Fig. 4-3(b)**. Comparing with HR-NT specimen, HR and HR-T specimen involves larger amount of ferrite. Above all, it is considered that hot-rolling can induce slightly coarser ferrite structure in F82H-ODS ferritic steel.

4.3.3 Phase Transformation

In order to investigate the phase transformation in 8CrODS specimen and the effect of hot-rolling on the phase transformation, the dilatometric curves were plotted out which could show the Ar1 and Ar3 temperature at various cooling rate. **Fig. 4-4** shows the results of these TMA analyses. The curve of 1K/min cooled specimen is shown in **Fig. 4-4(a)**, the Ar1 and Ar3 points are selected as the inflection points of this curve, which are confirmed by data analysis of Origin 8.0. And according to the results, the Ar1 and Ar3 points of 1K/min cooled specimen are 696 °C and 739 °C separately. There is no martensite transformation in 1K/min cooled specimen. According to **Fig. 4-4(b)**, the Ar1 and Ar3 temperatures of 3K/min cooled specimen are 693 °C and 756 °C separately. There is almost no martensite transformation in 3K/min cooled specimen. **Fig. 4-4(c)** shows the Ar1 and Ar3 points of 8CrODS specimen at a cooling rate of 6K/min are 668 °C and 733 °C separately, and there is a martensite transformation. The M_s temperature is 382 °C, while the M_f temperature is 310 °C. **Fig. 4-4(d)** reveals the

Ar1 and Ar3 points of 10K/min cooled specimen are 707 °C and 788 °C separately; the M_s and M_f temperatures are 375 °C and 435 °C separately. **Fig. 4-4(e)** shows the Ar1 and Ar3 points of 12K/min cooled specimen are 629 °C and 737 °C separately, while the M_s and M_f temperatures are 361 °C and 455 °C separately. **Fig. 4-4(f)** shows the Ar1 and Ar3 points of 30K/min cooled specimen are 629 °C and 710 °C separately, while the M_s and M_f temperatures are 318 °C and 435 °C separately. **Fig. 4-4(g)** shows the Ar1 and Ar3 points of 60K/min cooled specimen are 637 °C and 707 °C separately, while the M_s and M_f temperatures are 293 °C and 440 °C separately. There is no ferrite transformation in 300k/min cooled specimen, which is shown as **Fig. 4-4(h)**. The temperatures of M_s and M_f are 230 °C and 414 °C separately. There is also only martensite phase transformation in 600k/min cooled specimen, which is shown as **Fig. 4-4(i)**. And the M_s and M_f temperatures of 8CrODS specimen are 249 °C and 411 °C separately, when the cooling rate is 600k/min.

Based on the thermal expansion curves of **Fig. 4-4**, the CCT diagram of 8CrODS specimen was plotted out as **Fig. 4-5**.

4.3.4 Texture analyses

In order to make clear increasing fraction of ferrite in HR-T, inverse pole figure (IPF) and orientation distribution function (ODF) were derived for HR-T and HR-NT specimens by means of EBSD. The tempering after HR was provided for EBSD analyses, since severe strain induced by HR caused a lot of noise in IPF, but texture and crystalline orientation are considered to be similar before and after tempering for HR specimen.

Fig. 4-6(a) represents the IPF of HR-T specimen. The red color grains have $\{001\}<011>$ orientation from ODF analyses shown in the upper figure of **Fig. 4-6(b)**.

These are typical orientation produced by hot-rolling of the residual α -ferrite [2]. Focusing on slightly larger size of purple color grains, their ODF is represented at the lower part of the **Fig. 4-6(b)**. Recent analyses by Tomita et al. [3] have demonstrated that the hot-rolling of fcc γ -austenite in steel induces a Brass type of orientation of $\{110\}\langle 112\rangle$, and the unique orientation is produced by γ to α phase transformation during cooling, keeping KS relation such as $\{111\}_{\gamma} // \{110\}_{\alpha}$ and $\langle 011\rangle_{\gamma} // \langle 111\rangle_{\alpha}$ [4]. This orientation is shown by circles in **Fig. 4-7**. Comparing ODF shown in the lower of **Fig. 4-6(b)** and **Fig. 4-7**, it is considered that purple color grains belong to the transformed ferrite from the hot-rolled γ -austenite during cooling. It was also shown that ODF plots of the blue color grains in **Fig. 4-6(a)** is included in that of **Fig. 4-7**, suggesting these also correspond to the transformed ferrite from the hot-rolled γ -austenite during cooling.

The IPF of HR-NT specimen is shown in **Fig. 4-6(c)**. Its grain size is very homogeneous, and larger size of the purple color grains are considerably limited. The red color grains seem to be hot-rolled residual α -ferrite as the same as HR-T specimen.

4.3.5 Tensile strength

The stress-strain curves at 700 °C for HR, HR-T and HR-NT specimens are shown in **Fig. 4-8**. The HR-NT specimen exhibits similar strength property as the non HRed common F82H-ODS steels[5], which means that the normalizing can reset the structures induced by hot-rolling. **Fig.4-9** shows the estimated 0.2% proof stress, tensile stress, uniform elongation and total elongation of these three kinds of specimens at 700°C. Comparing with HR-NT specimen, HR and HR-T specimen have much higher 0.2% proof stress and tensile stress, which is ascribed to the effect of hot-rolling. The uniform elongation of HR and HR-T specimens is so limited, but

that of HR-NT specimen is significantly improved. Concerning the total elongation, HR specimen can get a really good ductility by tempering heat treatment. This may be due to the recovery of the dislocation induced by HR. Contrast with HR-NT specimen, we can see that hot-rolling processing can highly improve the strength, keeping ductility for F82H-ODS ferritic steels.

4.4 Discussion

The hot-rolling and normalizing are conducted at the temperature above A_{C3} , thus most of the ferrite transform into austenite. However, because of the existence of the nanosized oxide particles distributed densely in ODS steel, some of the ferrite can not transform into austenite due to pinning of α/γ interface by nanosized oxide particles. We have extensively analyzed this behavior, and designated as residual α -ferrite [6-9]. When the specimens are cooled down, this residual ferrite remains ferrite, but the other austenite will transform into martensite or ferrite. We designate this kind of ferrite as transformed ferrite.

In general, based on continuous cooling transform (CCT) diagram of 9CrODS ferritic steels [6], the transformed ferrite can be easily produced even at the usual cooling rate, because the transformed ferrite will be precipitated during cooling at the austenite grain boundaries that can be considerably fined by hot-rolling processing. Therefore, HR specimen could involve slightly larger amount of transformed ferrite, which is represented by purple and blue color grains in **Fig. 4-6(a)**.

By selecting two areas, we try to explain a mechanism for slightly coarsening of the transformed ferrite represented by purple and blue color grains. As shown in **Fig. 4-10**, area **a** has two relatively small grains, and area **b** has one relatively large grain. According to their IPF, all of these grains are transformed ferrite. We made a

point-to-point and point-to-origin misorientation analyses along the black line. Just as a gradation can be seen in the IPF of area **b**, it is suggested occurrence of the crystalline rotation to make similar orientation. In contrast, for area **a**, it is indicated that two grains grows up, and the misorientation angle of both orientations reaches 14 degrees. This condition creates a sub-boundary, but not a grain boundary, because the misorientation angle is less than 15 degrees. Therefore, it is considered that coarsening of the transformed ferrite is attributed to the crystalline rotation and coalescence of the similarly orientated grains [10, 11].

If compared with 9CrODS steels, the coarsen ferrite grain induced by hot-rolling in F82H-ODS ferritic steel has a smaller size. This could be owing to the CCT diagram difference. CCT diagram of 9CrODS steels is shown in **Fig.5-1** of the next chapter. It is found that ferrite formation during cooling proceeds at higher cooling rate for 9CrODS steels, comparing with CCT diagram of F82H-ODS ferritic steel shown in **Fig.4-5**. Easy formation of ferrite could lead to a larger transformed ferrite grain in 9CrODS steels.

In order to consider the reason of the strength improvement in the HR and HR-T specimens, the IPF and its Kernel Average Misorientation (KAM) maps were taken before and after tensile test, which are shown in **Fig. 4-11**. As shown in KAM distribution before tensile test, a large amount of strains are accumulated in HR specimen even after tempering, compared with HR-NT one at the fabrication condition. These strains were stored in the type of dislocation network produced by HR processing. One of the possible reasons of the improved strength in HR and HR-T specimens could be attributed to higher dislocation density in these specimens. Furthermore, noticing the IPF of the HR specimen after tensile test, strains induced by tensile test are mainly concentrated at around tempered martensite region, because this area is covered by the

dotted noise, while tensile strain seems not to be accumulated and be extremely low strain in the larger size of transformed ferrite. It is considered that many block boundaries inside martensite structure are sites for the localized deformation at the high-temperature. Hence, the another reason for strengthening improvement by HR is ascribed to the replacement of easily deformed martensite with the transformed coarse ferrite.

4.5 Summary

The effect of hot-rolling on the microstructure and tensile strength in F82H-ODS ferritic steel similar composition to J1-lot was evaluated for the different heat treatment (HR, HR-T, HR-NT). The results of this study are summarized as following:

- (3) Hot-rolling processing was conducted at temperature above 862 °C, which is higher than A_{F3} point (716 °C) measured in F82H-ODS ferritic steel.
- (4) HR and HR-T specimens involve slightly larger amount of ferrite, comparing with HR-NT specimen which consists of tempered martensite and residual α -ferrite as the same as the conventional J1-lot. This means that normalizing heat treatment can destroy the hot-rolled structure.
- (5) The increased fraction of ferrite in HR and HR-T specimen was identified as a ferrite transformed from hot-rolled austenite. Hot-rolling tends to lead a ferrite transformation rather than martensite transformation due to making fine grains of austenite. It was considered that the coarsening of the transformed ferrite in HR and HR-T specimen can be attributed to the crystalline orientation rotation and coalescence of the similarly oriented grains.
- (6) Hot-rolling can highly improve the strength of F82H-ODS ferritic steel from two reasons: increase of the dislocation density and replacement of easily deformed

martensite with the transformed coarse ferrite.

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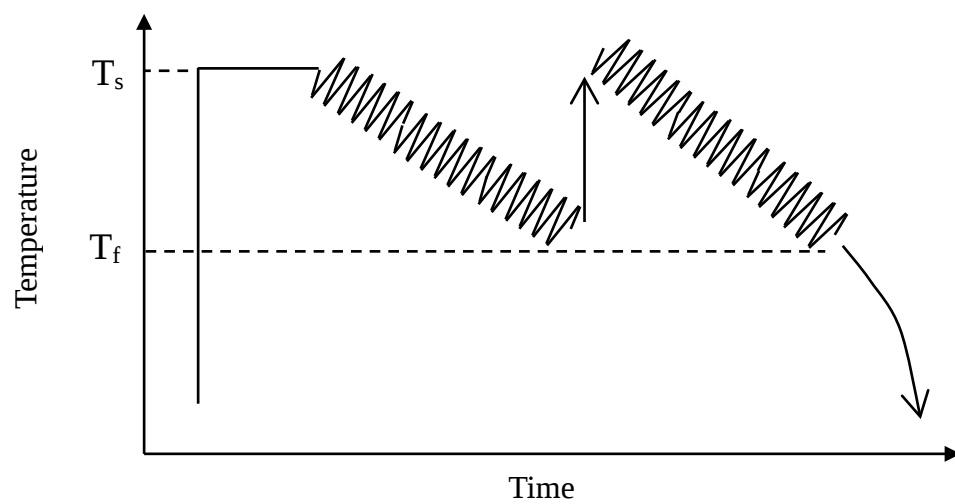
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Table 4-1 Chemical composition of mechanically alloyed powder

element	C	Cr	W	Mn	Si	V	Ti	Ta	N	Al	Y ₂ O ₃	Fe
wt%	0.16	8.02	1.95	0.02	0.02	0.21	0.17	0.09	0.009	0.014	0.33	Bal.



HR number	No.1	No.2	No.3		No.4	No.5	No.6
Thickness (mm)	25 to 20	20 to 16	16 to 12		12 to 9	9 to 6	6 to 4
Temperature (°C)	1100	to	947	947 to 1100	1100	to	862

Fig. 4-1 Hot-rolling process of F82H-ODS ferritic steel

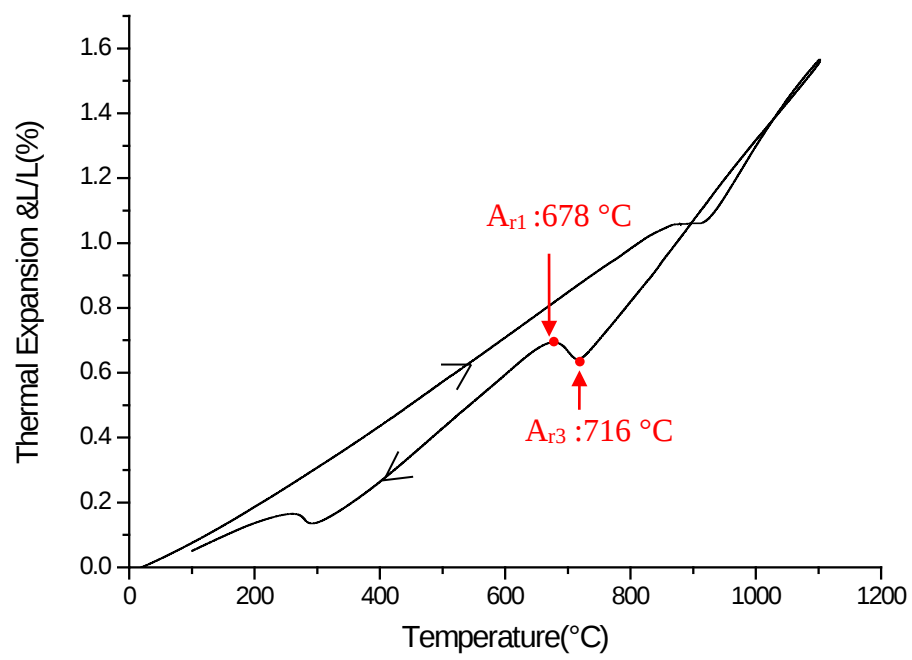
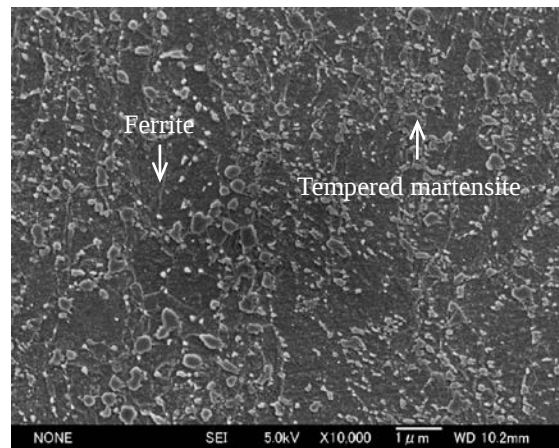


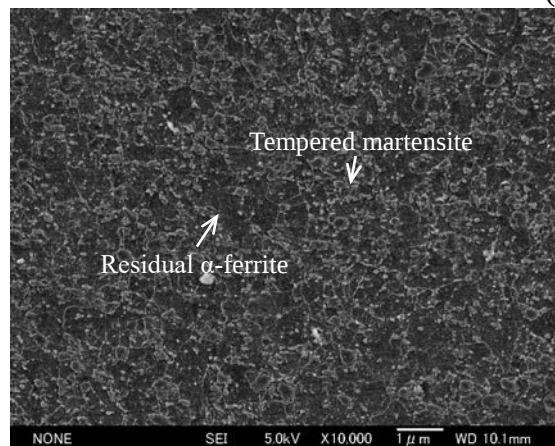
Fig.4-2 Dilatometric curve of F82H-ODS ferritic steel



(a) HR

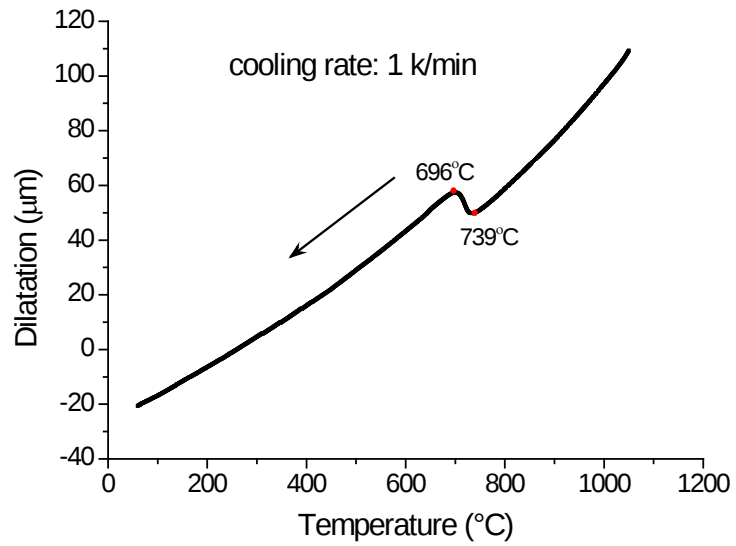


(b)

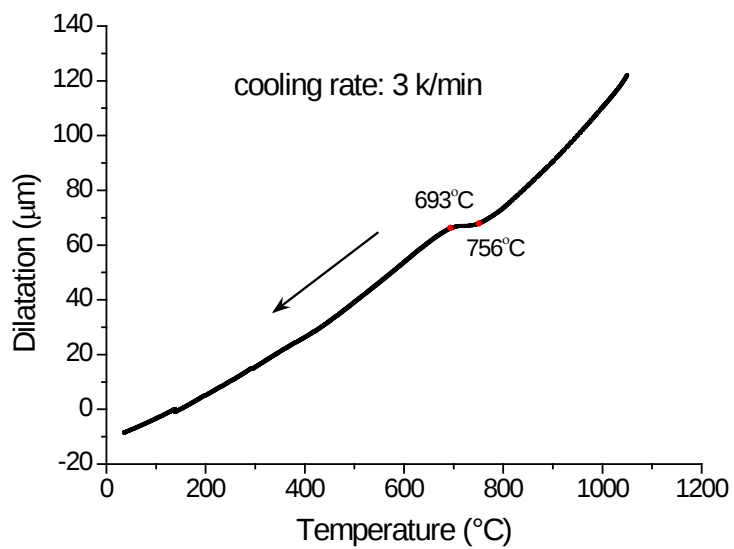


(c) HR-NT

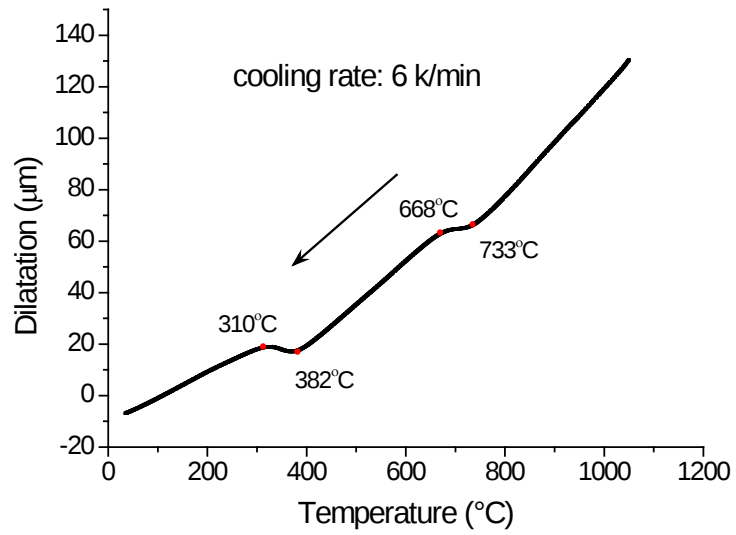
Fig. 4-3 SEM micrographs of specimens: (a) hot-rolled (HR), (b) hot-rolled and tempered (HR-T) and (c) hot-rolled and normalized & tempered (HR-NT).



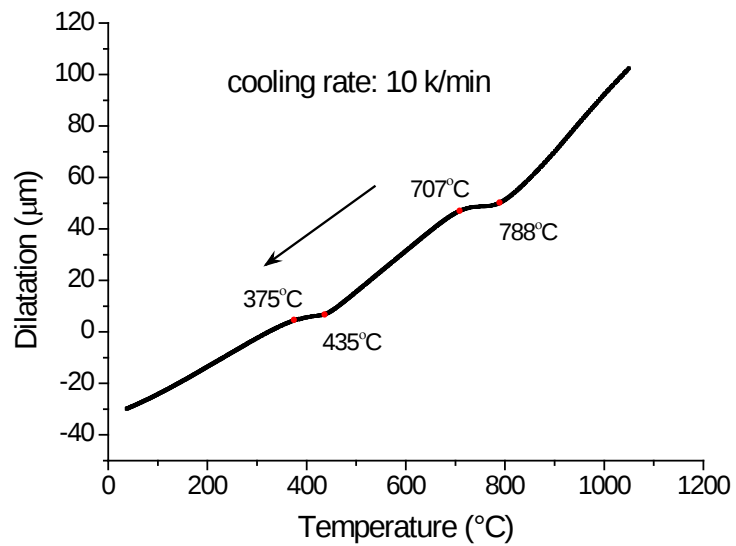
(a) Dilatometric curve of 1K/min cooled specimen



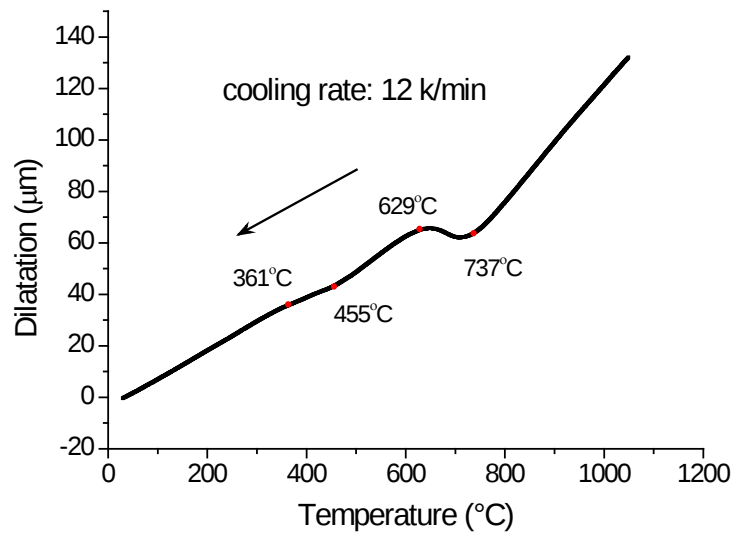
(b) Dilatometric curve of 3K/min cooled specimen



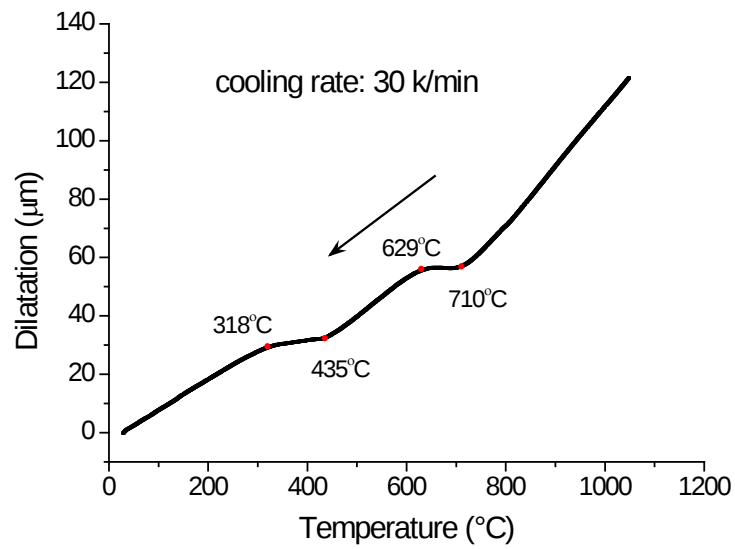
(c) Dilatometric curve of 6K/min cooled specimen



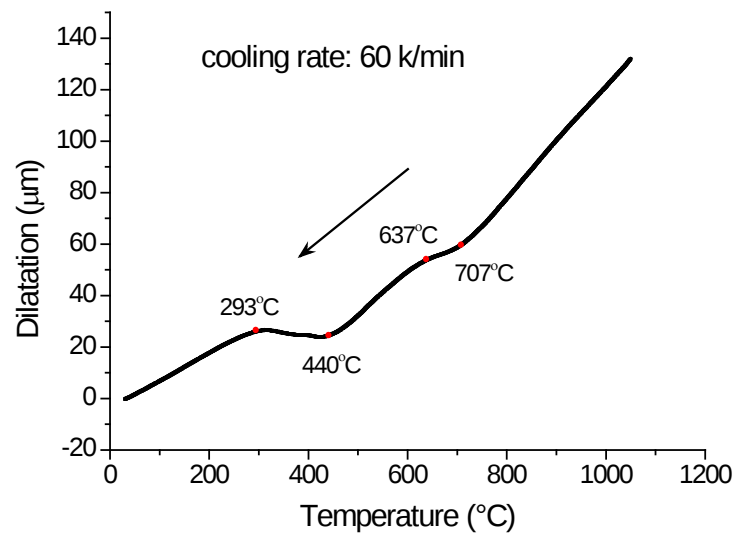
(d) Dilatometric curve of 10 K/min cooled



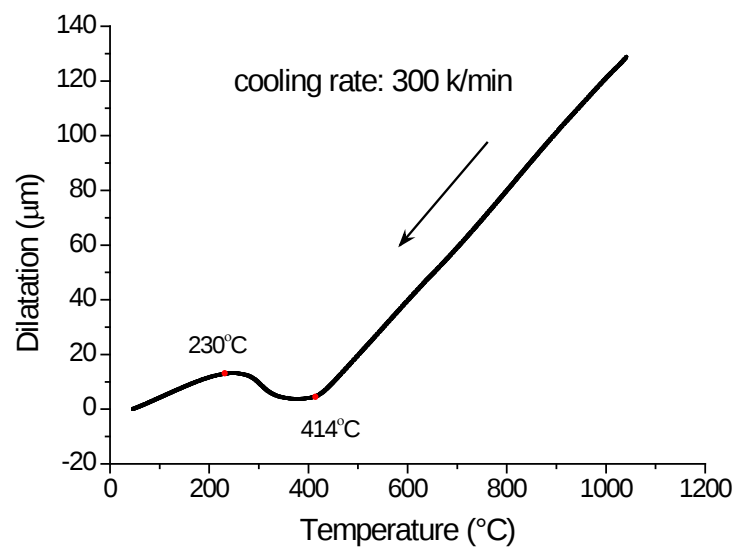
(e) Dilatometric curve of 12K/min cooled



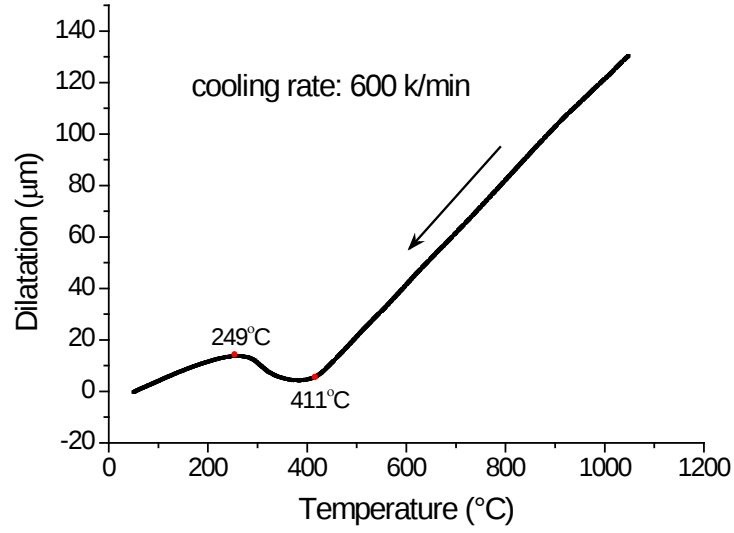
(f) Dilatometric curve of 30K/min cooled



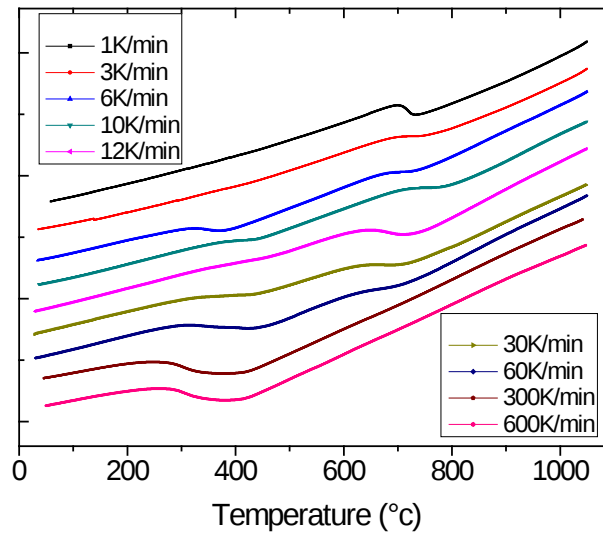
(g) Dilatometric curve of 60K/min cooled



(h) Dilatometric curve of 300K/min cooled



(i) Dilatometric curve of 600K/min cooled



(j) Summary curves

Fig. 4-4 Dilatometric curve of F82H-ODS ferritic steel measured at different cooling rate:

(a) 1K/min, (b) 3K/min, (c) 6K/min, (d) 10K/min, (e) 12K/min, (f) 30K/min, (g) 60K/min, (h) 300K/min, (i) 600 K/min, (j) Summary curves.

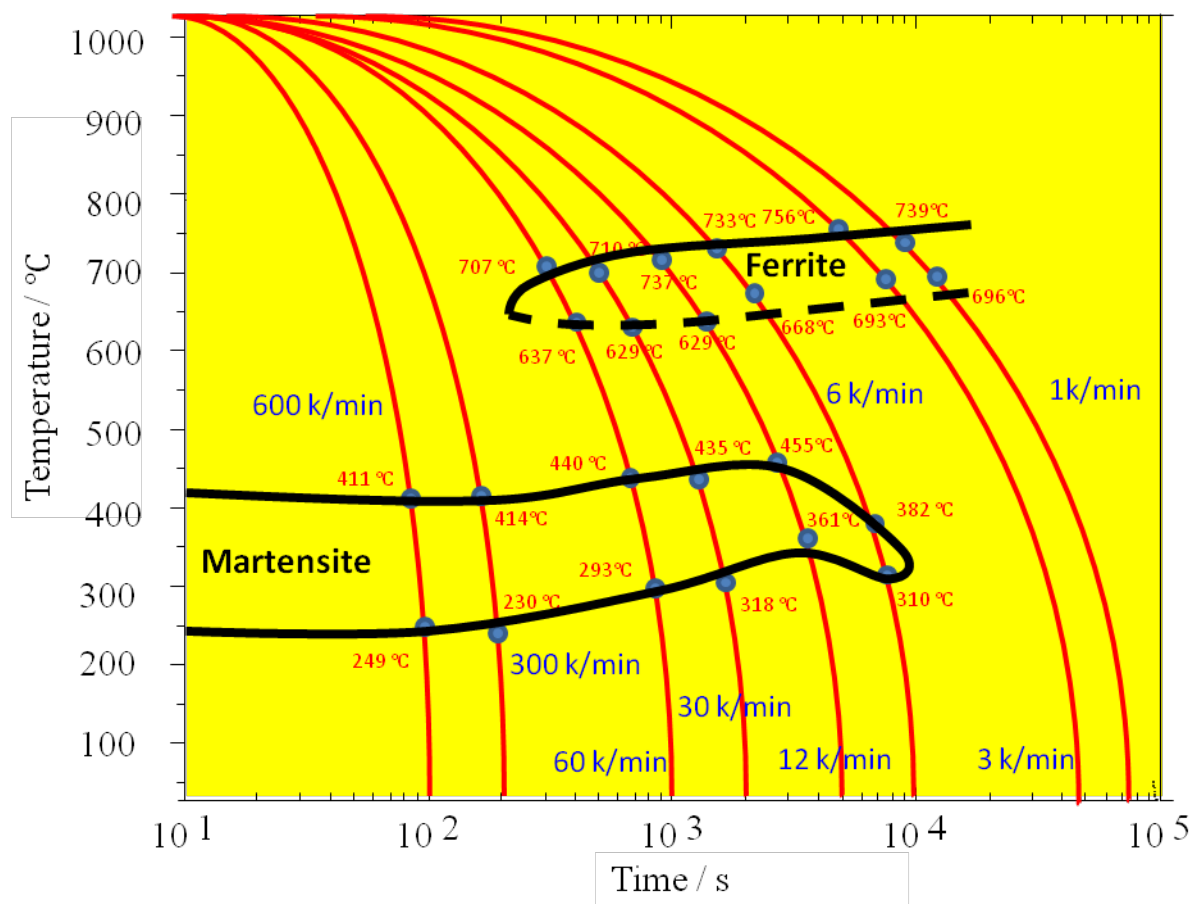


Fig. 4-5 CCT diagram of F82H-ODS ferritic steel

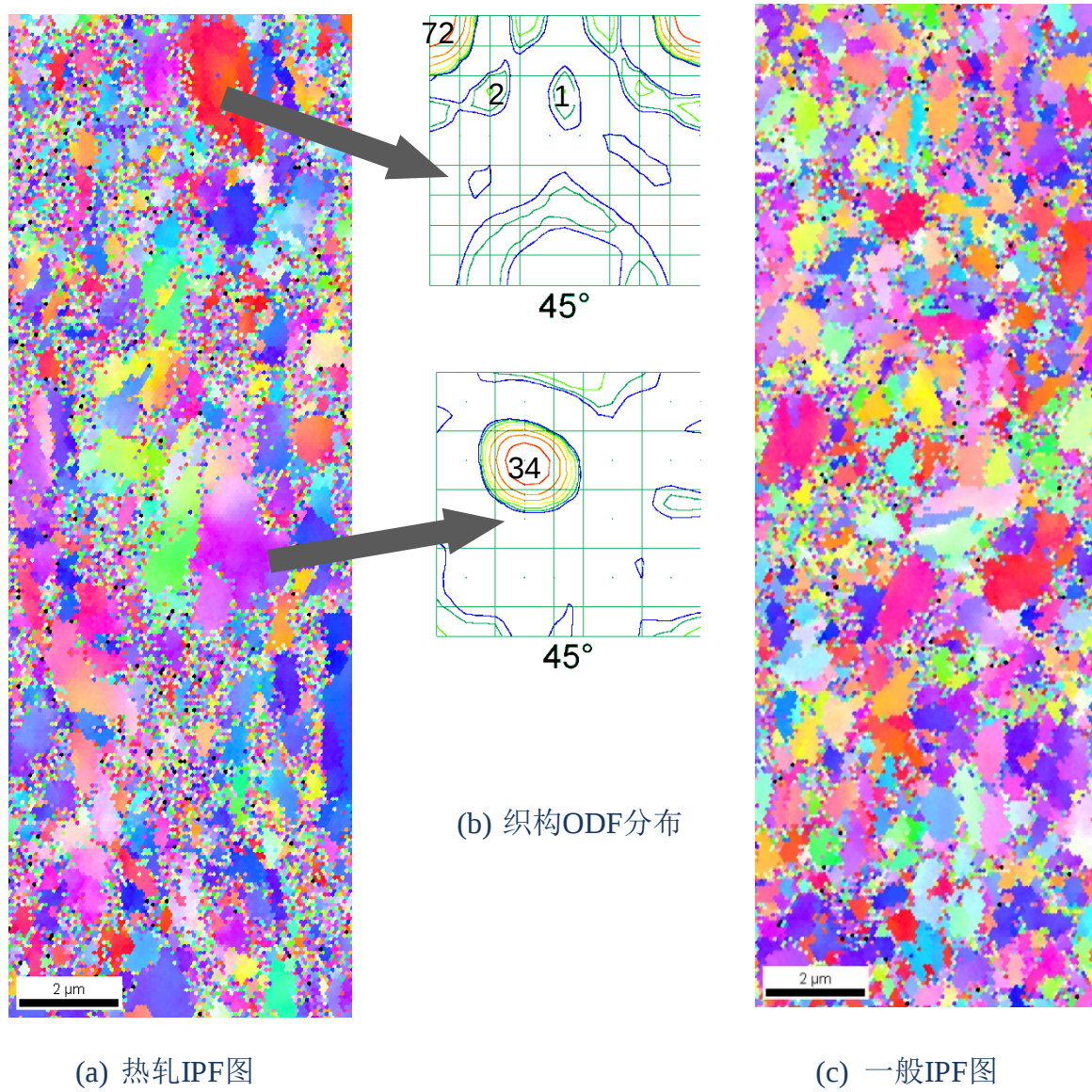


Fig. 4-6 Inverse pole figure (IPF) and orientation distribution function (ODF) for HR-T specimen and IPF of HR-NT specimen.

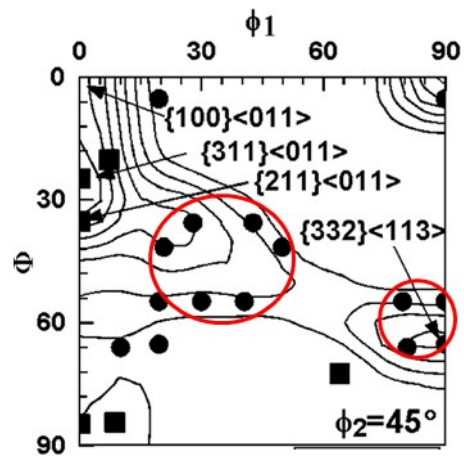


Fig.4-7 ODF of HR and air-cooled steel referred from Tomida et al.[4]

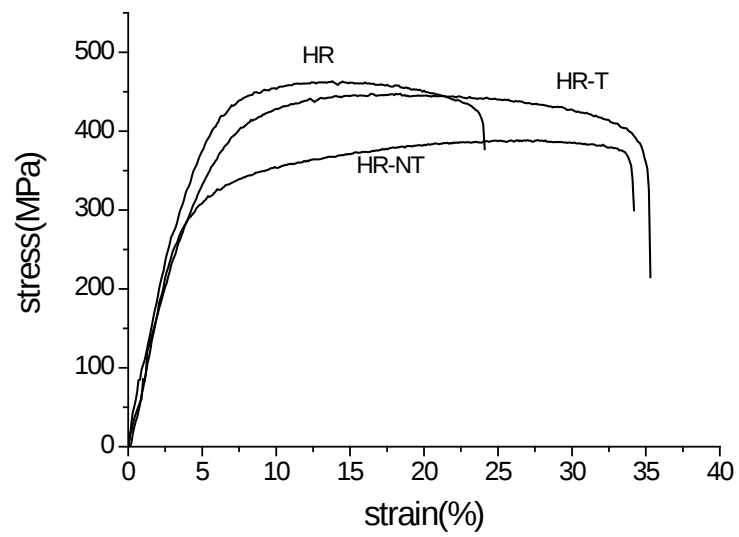


Fig. 4-8 The results of tensile test conducted at 700°C

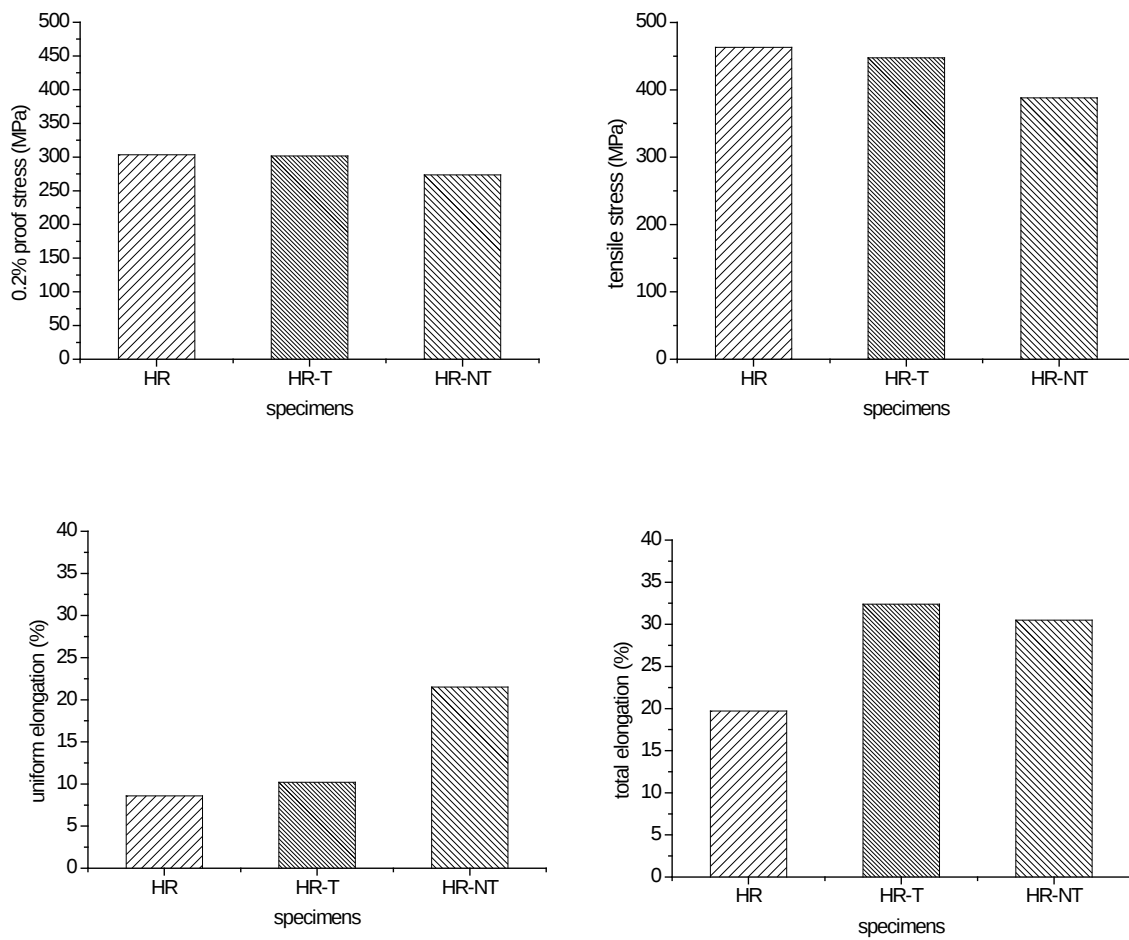


Fig. 4-9 Estimated 0.2 % proof stress and tensile stress, uniform elongation and total elongation of F82H-ODS ferritic steel

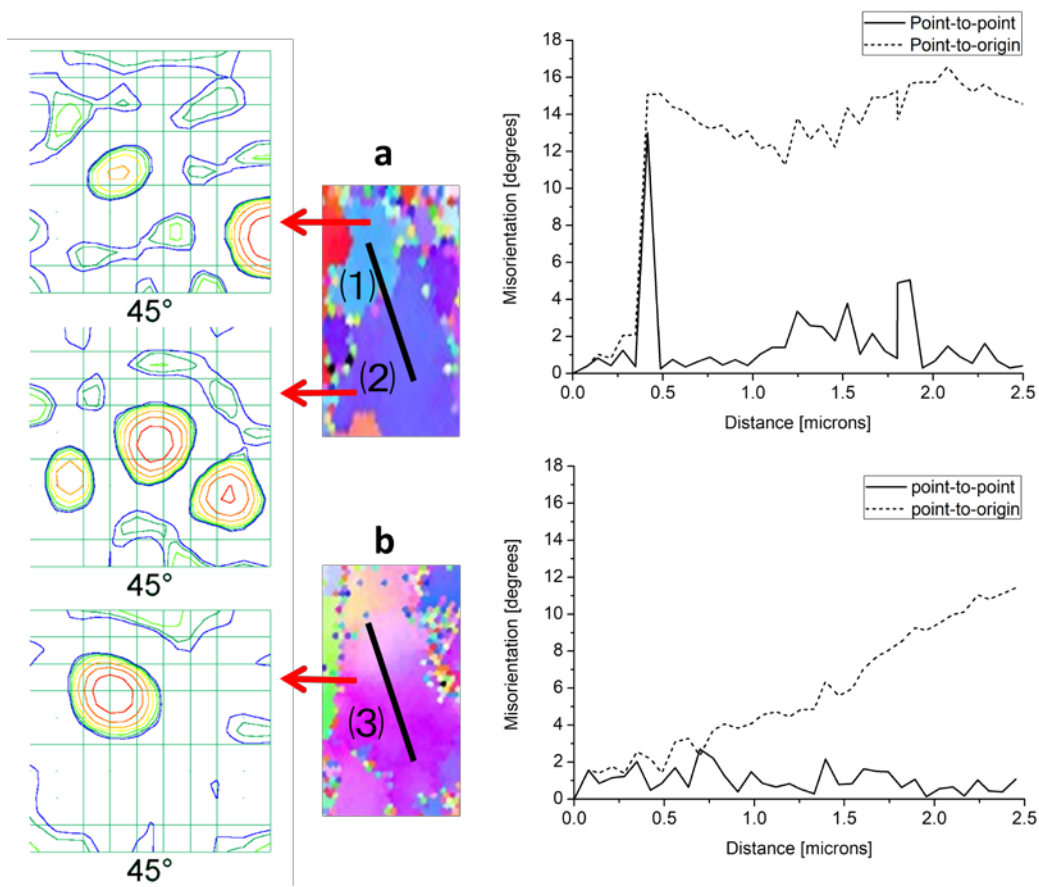


Fig.4-10 ODF, IPF and line analyses of misorientation by means of EBSD: the crystalline orientation rotation and similarly oriented grains coalescence caused by hot-rolling.

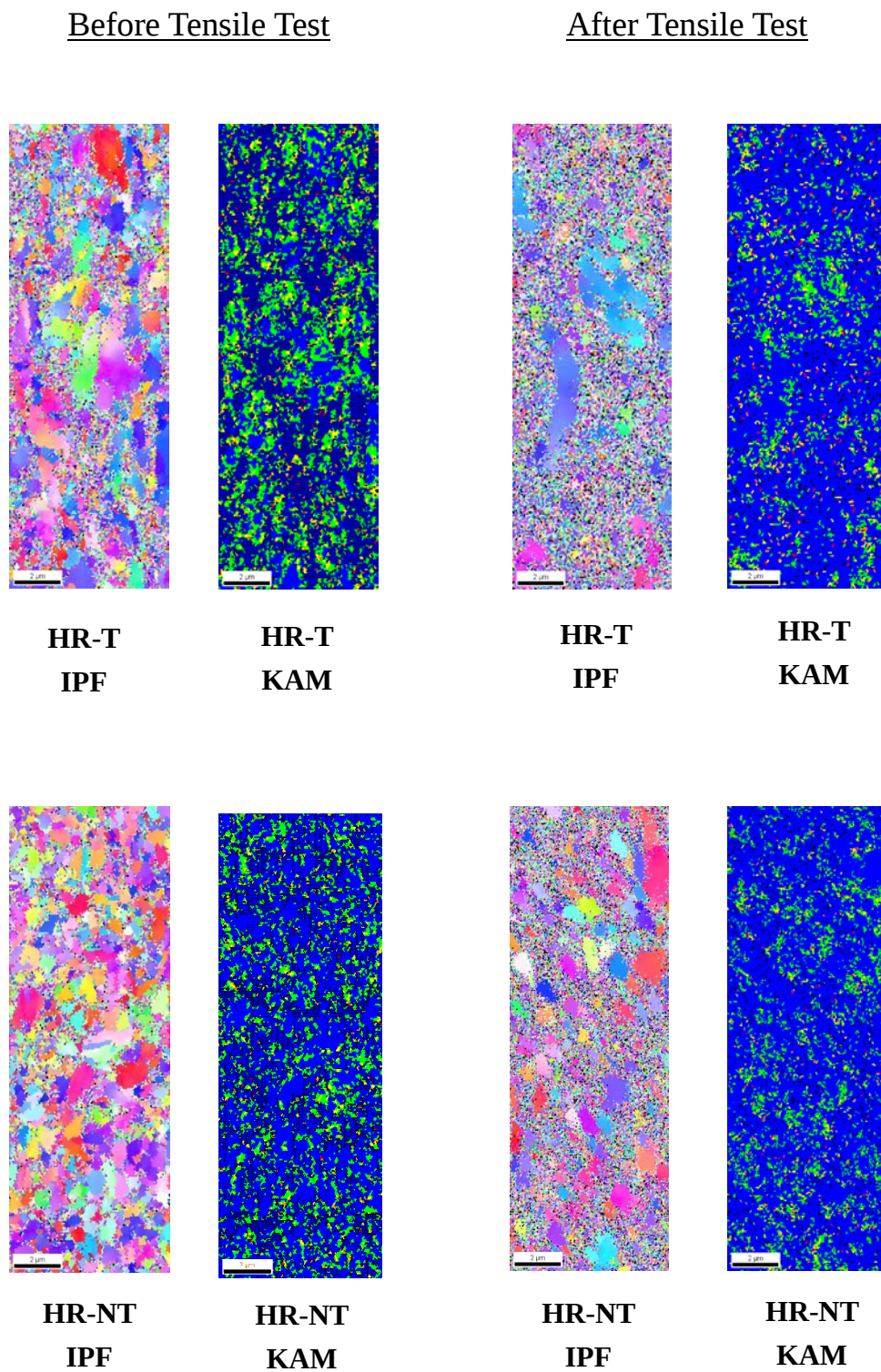


Fig. 4-11 IPF and KAM data analyses of F82H-ODS ferritic steel before and after tensile test

Chapter 5 Effect of Hot-Rolling and Cooling Rate on Microstructure and High-Temperature Strength in 9CrODS Steel

5.1 Introduction

9CrODS (oxide-dispersion-strengthened) ferritic steel, which has high temperature strength and excellent radiation resistance, is promising candidate material for the advanced fission and fusion blanket system [1]. In former research [2-4], it was confirmed that 9CrODS steel consists of a dual phase; that is a martensite phase and a residual ferrite phase. The formation and strengthening mechanism of the residual ferrite phase were studied in details [5]. We also found that a transform ferrite phase induced by hot-rolling can improve the tensile strength of 9CrODS steels [6]. In this paper, for furthermore study, we investigate effects of hot-rolling at the γ -austenite region and subsequent cooling at different cooling rate that could modify the microstructure and mechanical properties. For those specimens, hardness and high-temperature tensile properties are measured. Inverse pole figure (IPF) and kernel average misorientation (KAM) are analyzed to evaluate the microstructural change and strengthening mechanism.

5.2 Experimental produce

The pure metal powders were mixed together in composition of 9Cr-0.13C-2W-0.2Ti-0.35Y₂O₃ (wt%); then they were mechanically alloyed by a planetary-type ball mill (Fritsch P-5) for 48 hours in argon gas atmosphere. A weight ratio of the powder to ball is 1/10. The rotation speed is 300 rpm. The mechanically alloyed powders were consolidated by spark plasma sintering (SPS) at 1100 °C for 2 hours with a loading pressure of 44 MPa. Then, the consolidated specimens were hot-rolled in a reduction of 80% at γ austenite region and followed by two type of cooling. One is furnace cooling (FC) by returning the hot-rolled (HR) specimen into a furnace at

temperature of 850 °C then it was cooled at a cooling rate of 100 °C/h, which is designated as HR-FC. The other is air cooling (AC) at 10,000 °C/h after hot-rolling; it is designated as HR-AC. As a control specimen, normalizing (N) specimens were prepared at 1050 °C for 1 hour, then followed by furnace cooling, designated as N-FC, or air cooling, N-AC.

Micro-hardness of the specimens were measured by Shimadzu HVM-2 micro hardness tester at a loading of 9.8N and duration of 5 seconds. The high-temperature tensile test was conducted by using miniaturized specimens at 700 °C and strain rate of 1.0×10^{-3} /s under argon gas atmosphere. The IPF and KAM figures were analyzed by field-emission (FE) type scanning electron microscope (SEM).

5.3 Results and Discussion

5.3.1 Phase characterization

According to a continuous cooling transformation (CCT) diagram of normalized 9CrODS steels [7], as showed in **Figure 5-1**, the phase compositions of the specimens was analyzed. When the specimens are cooled from the austenite region at the cooling rate of about 10,000 °C/h, the cooling curve almost doesn't cross the ferrite transformation region, but quickly come across the martensite transformation. Thus, the austenite will transform into martensite. The previous study of 9CrODS steels also reported that the normalized specimen has a residual ferrite phase that cannot be transformed into austenite when it was heated up above A_{C3} temperature [5]. Based on above information, the N-AC specimen consists of martensite and residual ferrite. However, the situation of HR specimen is different, because hot-rolling can shift the ferrite transformation region toward the left side of the diagram. That means, when HR specimen is cooled down at the same cooling rate as AC (10,000 °C/h) condition, it

will cross the ferrite transformation region. We designated this ferrite as transform-ferrite[6]. Thus, HR-AC specimen contains three different phases; residual ferrite, transform-ferrite and martensite, where the residual ferrite and transform-ferrite have the same crystalline structure. However, microstructure and hardness in both ferrites could be different.

The cooling rate of FC specimen is 100 °C/h. For both N specimen and HR specimen, cooling curve cannot cross the martensite transformation region when they cooled from austenite phase, suggesting that they are composed of both residual ferrite and transform-ferrite. These phase characterization is summarized in **Table 5-1**.

5.3.2 IPF analyses

The microstructures of specimens analyzed by IPF are shown in **Figure 5-2**. These data are characterized on the basis of CCT diagram mentioned in section 3.1. The HR-AC specimen shown in **Figure 5-2(a)** consists of some irregular shape small grains and a few coarse grains. The formation mechanism of the coarse grains was extensively evaluated in the previous study, and these coarse grains were proven to be transform-ferrite [6]. The process of the ferrite-transformation and resultant coarse grain formation in the conventional steels induced by HR-AC is reviewed by Furuhashi et al.[8]. Some areas of the figure contain full of noise, which correspond to martensite having a lot of strains. Other small red color grains are also identified as the residual ferrite.

The HR-FC specimen was composed of nearly equiaxed grains, and most of them are in a similar size as shown in **Figure 5-2(b)**. Although there are also some small grains, they are quite uniform microstructure in round shape. As previously mentioned, HR-FC specimen is composed of the residual ferrite and transform-ferrite, but it is

difficult to distinguish them from the IPFmap. From **Figure 5-3(a) and (b)** showing the size distribution measured in these two specimens, the grain size of HR-FC specimen ranges from 0.2 μm to 5 μm , and it distributes more uniformly as compared with HR-AC specimen.

As shown in **Figure 5-2(c)**, N-AC specimen consists of many irregular shaped small grains. These grains belong to the martensite phase and residual ferrite phase. Concerning the effect of hot-rolling on microstructures, we compare the grain size distribution of HR-AC specimen with N-AC specimen, which is shown in **Figure 5-3(a) and (c)**. N-AC specimen doesn't have large grains, and the grain size mainly arranges from 0.1 μm to 2 μm , and most of them are smaller than 1 μm .

The N-FC specimen showed in **Figure 5-2(d)** has a similar uniform structure to HR-FC specimen, but the grain size is slightly smaller. Again, it's impossible to identify the each phase in IPF map. Concerning the effect of cooling rate, it can be found that N-FC specimen has a much uniform structure, and the grain size become larger than N-AC specimen. Smaller grain size in N-FC specimen compared with HR-FC one could be ascribed to slightly higher cooling rate even around 100 $^{\circ}\text{C}/\text{h}$.

5.3.3 Hardness measurement

Figure 5-4 shows the results of hardness measurement for four kinds of specimens. Concerning the effect of hot-rolling, by comparing HR-AC specimen with N-AC specimen, we find that at the same air cooling (10,000 $^{\circ}\text{C}/\text{h}$) hot-rolling increases the hardness of specimens. However, when we compare HR-FC specimen with N-FC specimen at similar furnace cooling (100 $^{\circ}\text{C}/\text{h}$), hot-rolling slightly reduces the hardness of specimens. The hardness increase in HR-AC specimen as compared with N-AC one is due to the amount of strains induced by hot-rolling. On the other hand, decrease

of hardness by hot-rolling in furnace cooling specimen could be attributed to larger grain size in HR-AC than N-AC, as seen in **Figure 5-2**. Concerning the effect of cooling rate, it is clear that furnace cooling leads to lower hardness for both hot-rolling and normalizing specimens due to transformation to soft ferrite phase. The air cooling induces formation of martensite phase that is strengthened by large amount of dislocations and strains.

5.3.4 Tensile properties

Results of tensile test conducted at 700 °C are shown in **Figure 5-5**. HR induces higher strength at both cooling rates of AC and FC, compared with N condition. Concerning the effect of cooling rate, AC leads to higher strength in HR specimens, whereas AC gives lowest strength in N specimens, as compared with FC condition. Noted that FC specimen exhibits higher strength than AC specimen in N condition, although hardness of N-FC specimen is considerably lower than that of N-AC specimen. It can be said, therefore, that high-temperature strength at 700 °C can't be predicted from the hardness data at room temperature.

Analyses of KAM maps, which are related to an amount of strain accumulated in specimens, were performed to study the strengthening mechanism. **Figure 5-6** shows KAM maps of the HR-FC specimen before and after tensile test. Before tensile test shown in **Figure 5-6(a)**, KAM value is very low, showing that specimen has less strain due to ferrite formation during furnace cooling. In contrast, the strain is accumulated at grain boundaries after tensile test as illustrated in **Figure 5-6(b)**. This means that the deformation is localized at grain boundaries at 700 °C. Comparing IPF of N-AC with N-FC illustrated in **Figure 5-2(c) and (d)**, N-AC specimen involves the fine martensite structure that could locally accelerate the deformation. That is reason why

the tensile strength in N-AC is lower than that of N-FC. Similarly, the higher tensile strength in HR-FC than that of N-FC could be attributed to larger grain size in HR-FC as compared in **Figure 5-2 (b) and (d)**. Although at room temperature the fine grains lead to the increased tensile strength by blocking of the moving dislocation at the grain boundaries, it is well known that at high-temperature enough to give an atomic diffusion, the fine grains induce the reduced tensile strength due to the localized deformation and the grain boundary sliding [9, 10]. As previously mentioned, this localized deformation at the grain boundaries is indicated by trace of yellow color in **Fig. 5-6(b)**. The HR-AC specimen records the highest tensile strength, which may be resulted from the unique structure involving coarser transform ferrite shown in **Figure 5-2(a)**, however, elucidation of the precise strengthen mechanism in HR-AC specimen needs more information.

5.4 Summary

Concerning the effect of hot-rolling for air-cooled specimen (10,000 °C/h), it was confirmed that hot-rolling can induce a coarser transformed ferrite grains in 9CrODS steel (HR-AC vs. N-AC). The coarser ferrite grains improve the strength at high-temperature. For furnace-cooled specimen (100 °C/h), hot-rolling also gives rise to higher strength due to larger size of grains that might result from slower cooling than N-FC specimen even at around 100 °C/h (HR-FC vs. N-FC). Concerning the effect of cooling rate for normalized specimen, furnace-cooled specimen improves the high-temperature strength by making a uniform larger size of ferrite grains, comparing with air-cooled specimen (N-FC vs. N-AC). The high-temperature strength of 9CrODS steel is significantly improved with increasing grain size that can be induced

by hot-rolling or furnace-slow cooling, where the localized grain boundary deformation can be suppressed.

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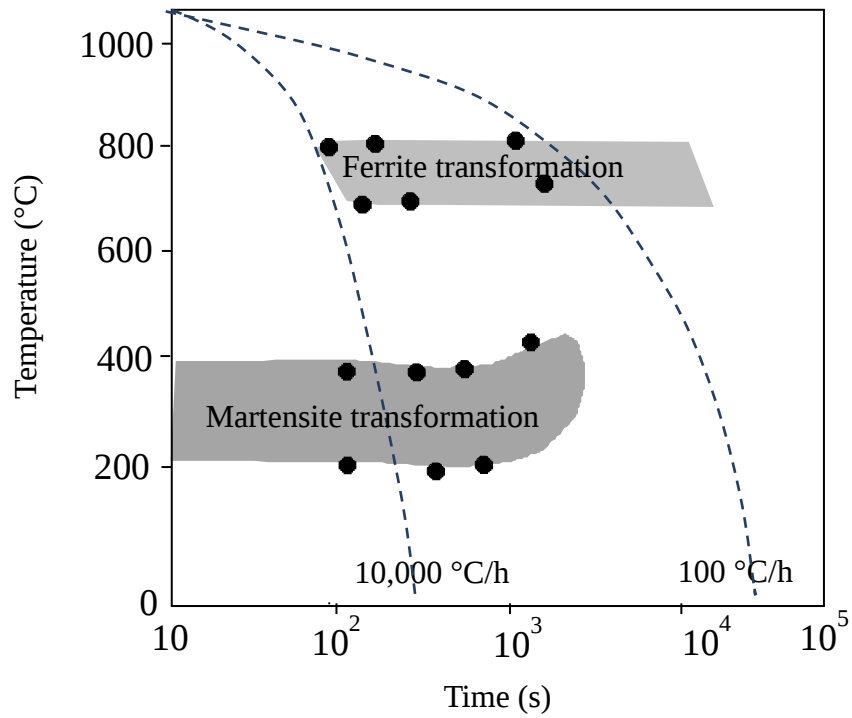


Figure 5-1 Continuous cooling transformation (CCT) diagram of normalized 9CrODS steels; black dots show the boundaries measured by thermal expansion method during the various cooling rate.

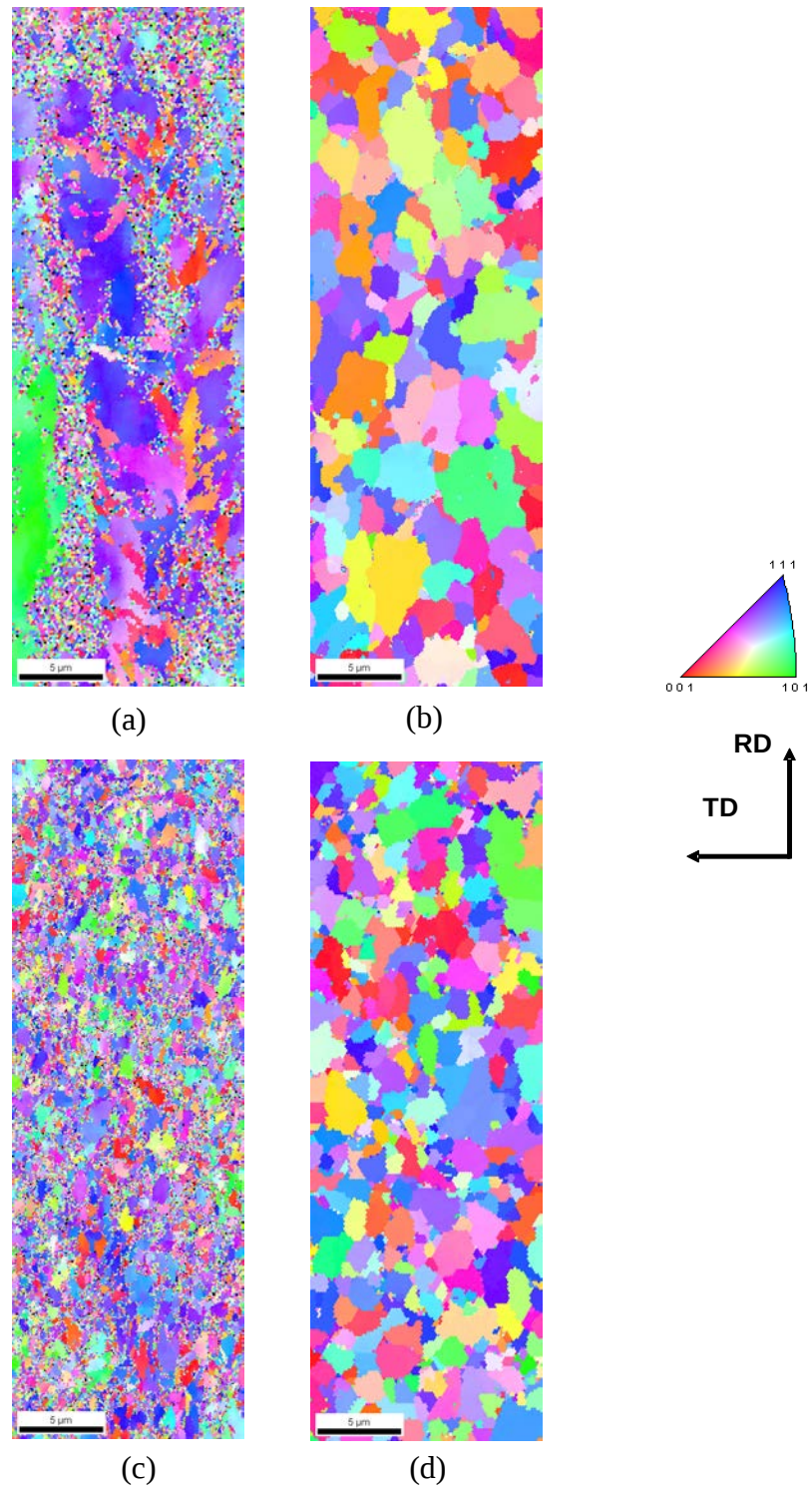


Figure 5-2 The microstructures of specimens analyzed by IPF: (a) hot-rolling and air-cooling (HR-AC), (b) hot-rolling and furnace cooling(HR-FC), (c) normalizing and air-cooling (N-AC), (d) normalizing and furnace-cooling

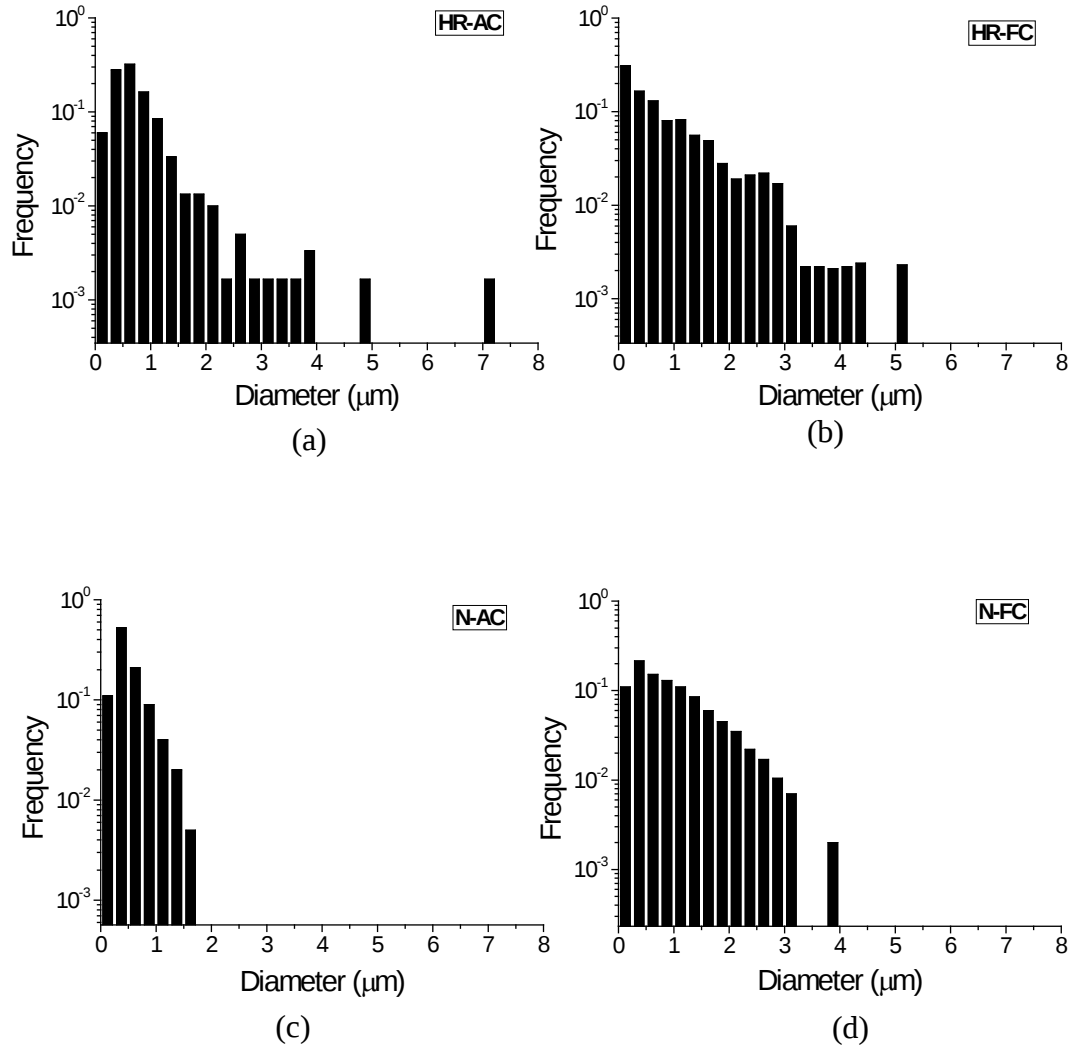


Fig 5-3 The grain size distribution of specimens: (a) HR-AC specimens, (b) HR-FC specimens, (c) N-AC specimens, (d) N-FC specimens

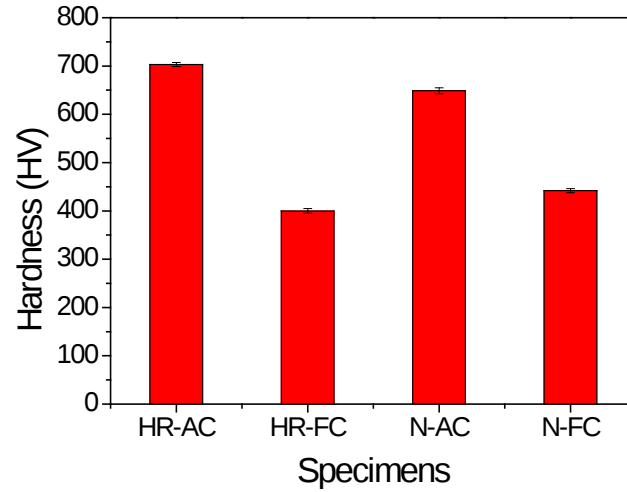


Figure 5-4 Micro-hardness of 9CrODS steels

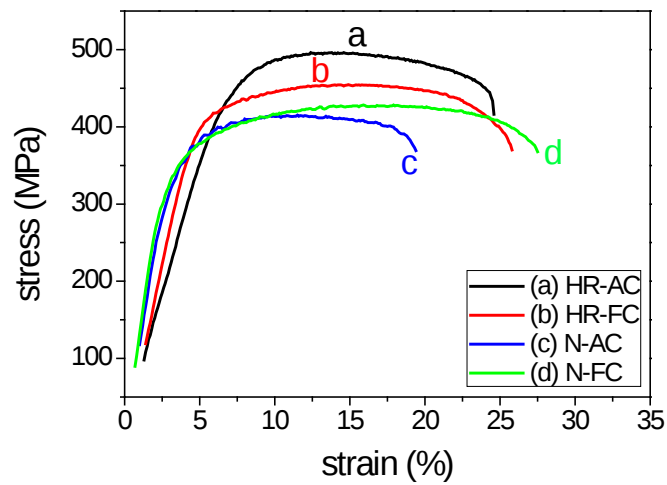


Figure 5-5 Tensile test of 9Cr-ODS steels conducted at 700°C:

(a) hot-rolling and air-cooling (HR-AC), (b) hot-rolling and furnace cooling (HR-FC), (c) normalizing and air cooling (N-AC) (d) normalizing and furnace cooling (N-FC)

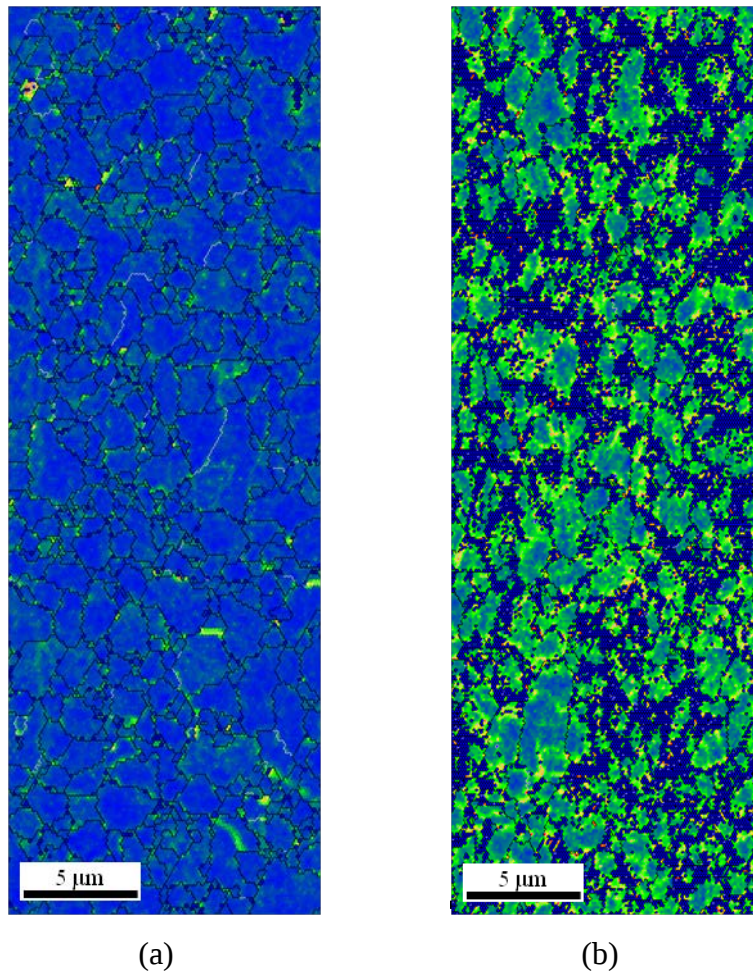


Figure 5-6 KAM figures of the HR-FC specimen before and after tensile test: (a) Before tensile test (b) after tensile test

Table 5-1. Phase composition of the specimens

Specimens	Phase Composition
HR-AC	residual ferrite +transformed ferrite +martensite
HR-FC	residual ferrite +transformed ferrite
N-AC	residual ferrite +martensite
N-FC	residual ferrite +transformed ferrite

Chapter 6 Conclusions

Over all, in this thesis, I studied the structure control of ODS ferritic steels, especially the contents mainly focus on F82H-ODS ferritic steels. There are three aspects in this thesis. First, through changing the ferrite area fraction in F82H-ODS ferritic steel by annealing, I revealed the residual-ferrite formation mechanism in F82H-ODS ferritic steel. Secondly, through changing the microstructure of F82H-ODS ferritic steel by hot-rolling, I improve the properties of F82H-ODS ferritic steel, and also the mechanisms for strengthening and structure changing were revealed. The third one, I modified the structures of 9CrODS steels by changing the cooling rate, and analyze the change of properties.

The main conclusions can be summarized as follow:

- (1) A meta-stable residual phase was confirmed to existing in F82H-ODS ferritic steel. Formation of the residual-ferrite in F82H-ODS ferritic steel is attributed to pinning of α - γ interfacial boundaries by the oxide particles, which is revealed by annealing experiment.
- (2) Hot-rolling can make the transformed ferrite phase in F82H-ODS ferritic steel slight coarser. The increased fraction of ferrite in hot-rolled F82H-ODS ferritic steel was identified as a ferrite transformed from hot-rolled austenite. The coarsening of the transformed ferrite in hot-rolled F82H-ODS ferritic steel is attributed to the crystalline orientation rotation and coalescence of the similarly oriented grains.
- (3) Hot-rolling can highly improve the strength of F82H-ODS ferritic steel from two reasons: increase of the dislocation density and replacement of easily deformed martensite with the transformed coarse ferrite.
- (4) Furnace-cooling can improve the high-temperature strength of 9CrODS ferritic steel by making a uniform larger size of ferrite grains.

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