http://dx.doi.org/10.5516/NET.07.2013.096

INFLUENCE OF MECHANICAL ALLOYING ATMOSPHERES ON THE MICROSTRUCTURES AND MECHANICAL PROPERTIES OF 15Cr ODS STEELS

SANGHOON NOH*, BYOUNG-KWON CHOI, SUK HOON KANG, and TAE KYU KIM
Nuclear Materials Division, Korea Atomic Energy Research Institute, Yuseong-gu, Daejeon, 305-353, Republic of Korea
*Corresponding author. E-mail : shnoh@kaeri.re.kr

Received November 07, 2013
Accepted for Publication July 10, 2014

Mechanical alloying under various gas atmospheres such as Ar, an Ar-H_2 mixture, and He gases were carried out, and its effects on the powder properties, microstructure and mechanical properties of ODS ferritic steels were investigated. Hot isostatic pressing and hot rolling processes were employed to consolidate the ODS steel plates. While the mechanical alloyed powder in He had a high oxygen concentration, a milling in Ar showed fine particle diameters with comparably low oxygen concentration. The microstructural observation revealed that low oxygen concentration contributed to the formation of fine grains and homogeneous oxide particle distribution by the Y-Ti-O complex oxides. A milling in Ar was sufficient to lower the oxygen concentration, and this led a high tensile strength and fracture elongation at a high temperature. It is concluded that the mechanical alloying atmosphere affects oxygen concentration as well as powder particle properties. This leads to a homogeneous grain and oxide particle distribution with excellent creep strength at high temperature.

KEYWORDS : Oxide Dispersion Strengthened Steel, Mechanical Alloying Atmosphere, Oxygen Concentration, Oxide Particle, Creep Strength

1. INTRODUCTION

Oxide dispersion strengthened (ODS) steel is the most promising candidate for use as a core structural material of the next-generation nuclear systems such as a Gen. IV fission and DEMO fusion reactor [1]. This is due to its excellent creep strength at an elevated temperature, irradiation resistance, and compatibility with coolants [2-5]. Finely dispersed nano-oxide particles with a high number density in the homogeneous grain structure are essential to achieve the superior mechanical properties at high temperatures, and these unique microstructures can be obtained through mechanical alloying (MA) and a hot consolidation process. The microstructure and mechanical properties of ODS steels significantly depend on its powder property and purity after the MA process. These contents should be carefully controlled to improve the mechanical property at elevated temperatures. In particular, oxygen plays an important role in forming the fine particles, and thus the appropriate control of its concentration improves the mechanical property of ODS steels at high temperature. S. Ukai et al. reported that oxygen concentration can be controlled by the additions of Fe_2O_3 and FeY intermetallics [6]. An effective method is considered to be one which controls the mechanical alloying atmosphere by high purity inert gas. It was reported that a mechanical alloying atmosphere such as argon and hydrogen can change the oxygen concentration, and the impact properties were significantly changed in the 14Cr and 16Cr reduced activation ferritic ODS steels [7, 8].

In the present study, ODS ferritic steels were fabricated through mechanical alloying in various gas atmospheres and hot isostatic pressing. To investigate the effects of mechanical alloying atmospheres, MA powder particles of particle size distribution and oxygen concentration were analyzed. ODS steels were consolidated by hot isostatic pressing and hot rolling, and their microstructural and mechanical properties were also evaluated.

2. EXPERIMENTAL

The ODS ferritic steels used in this study are Fe-15Cr-1Mo-0.3Ti with 0.35Y_2O_3 in wt%. The ODS steels were fabricated by mechanical alloying, hot isostactic pressing (HIP), and hot rolling. Metallic raw powders and Y_2O_3 powder were pre-mixed and mechanically alloyed using a horizontal ball-mill apparatus (Model: Simoloyer CM20). Mechanical alloying atmospheres are thoroughly controlled in three kinds of atmosphere gas, i.e., high purity argon (99.999%), a mixture gas (Argon-4vol.% Hydrogen, 99.999%), and helium (99.999%). The mechanical alloying was performed at an impeller rotation speed of 240 rpm for 48h with a ball-to-powder weight ratio of 15:1. Detailed conditions for the mechanical alloying process are summarized in Table 1. After the mechanical alloying process, the particle distribution was measured using a laser diffraction scattering method with a particle size analyzer. SEM was utilized to observe the surface morphology of the MA powders. The chemical composition and oxygen concentration of the MA powders were analyzed by ICP-AES and inert gas fusion methods, respectively. The MA powders were then sieved and charged in a stainless steel capsule. All powder processes for the weighing, collection, sieving, and charging were handled in a completely controlled high purity argon atmosphere to prevent oxygen contamination during the fabrication process. Sealed capsules were then degassed at 400 ºC below 5×10^{-4} torr for 3h. The HIP was carried out at 1150 ºC for 3h at a heating rate of 5 ºC/min, and followed by a furnace cooling. Hot rolling at 1150 ºC was conducted in a fixed rolling direction for a plate shape with 65% of the total thickness reduction rate. Final heat treatment after a hot rolling process was done at 1150 ºC for 1h. The fabrication process of ODS steels is schematized in Fig. 1. The grain morphology and oxide particle distribution were observed by FE-SEM and TEM. Samples for FE-SEM observations were electronically polished in a 5% $HClO_4$ + 95% methanol solution in vol. % at a voltage of 18V with a current of 0.5mA at -50 ºC to eliminate the work hardened surface layer induced by the mechanical polishing. Twin-jet polishing and extraction carbon replica methods were employed for the sample fabrication to observe the TEM. Specimens for mechanical property evaluations were taken out by electro-discharge machining in the rolling direction. A sheet type tensile specimen with a gauge length of 25.4mm, width of 3.7mm, and thickness of 1mm was used. The tensile tests were carried out at room temperature and 700 ºC in air at a strain rate of $3.2\times10^{-4}s^{-1}$. Creep rupture tests were carried out under a stress range of 100–120MPa at 700 ºC in air.

3. RESULTS AND DISCUSSION

3.1 Powder Properties after MA Process in Different Atmospheres

The surface morphologies of alloy powder after the MA process in different gas atmospheres are shown in Fig. 2. Powders milled in Ar were irregularly spherical and flake shaped with a somewhat rough surface. A more spherical shape with a smooth surface was observed in an Ar-H_2 mixture gas and He milled MA powders. The

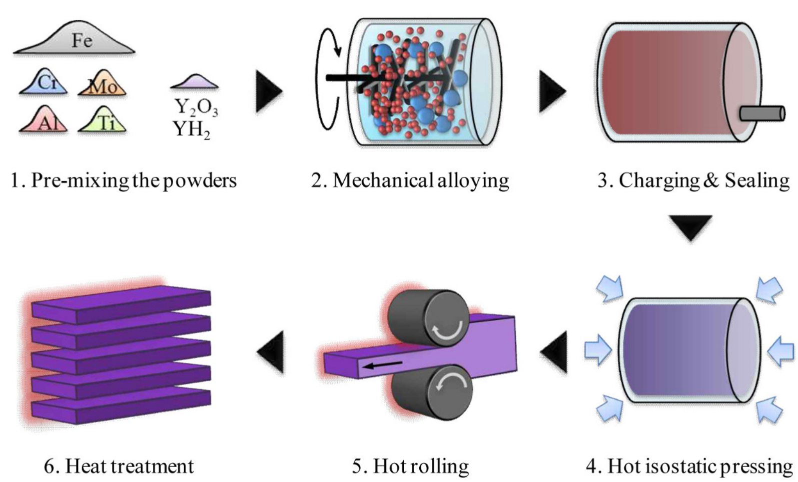

Fig. 1. Fabrication Process of ODS Ferritic Steel Plate.

Table 1. Mechanical Alloying Process Conditions of ODS Ferritic Steels

	Milling time (hrs)	Milling speed (rpm)	BPWR	Atmosphere	Remarks
1	48	240	15:1	Ar (99.999%)	Effect of Ar atm.
2	48	240	15:1	Ar-H_2 (99.999%)	Effect of H_2
3	48	240	15:1	He (99.999%)	Effect of He atm.

spherical shape with the smooth surface means that the pulverization of the raw powders was not sufficient during the MA process and a partial agglomeration occurred. The smooth surface normally contributes to lowering the oxygen contamination owing to less adhesion sites of oxygen on the surface when the powder was exposed in air. However, MA powders milled in Ar had a lower oxygen concentration than that milled in He, as shown in Table 2, which summarizes the results of the chemical composition analysis. It is considered that MA powders were not exposed in air by completely controlling the inert gas atmospheres during the process. The size distributions and mean particle size of MA powders are represented in Fig. 3. MA powder milled in Ar and Ar-H_2 showed a mono-modal distribution with a regular peak, while the powder in He has a bi-modal distribution with two peaks in a wide range of particle sizes. The mean particle size of Ar milled MA powder was a lot smaller than the Ar-H_2 mixture and He gases. MA powder

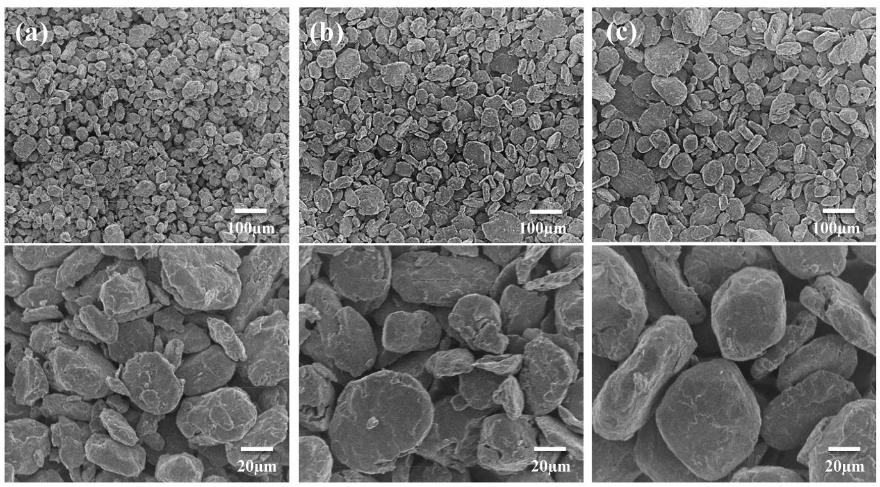

Fig. 2. Surface Morphology of ODS Steel Powders Milled in Various Atmospheres: (a) Ar, (b) Ar-H_2 Mixture Gas, and (c) He.

Table 2. Chemical Compositions of ODS Ferritic Steels

	Specimen	Fe	C	Cr	Mo	Ti	Y	O	Y_2O_3	*Ex.O
1	Ar	bal.	0.014	14.66	0.99	0.33	0.26	0.20	0.33	0.12
2	Ar-H_2		0.007	14.85	0.99	0.31	0.26	0.25	0.33	0.18
3	He		0.006	14.81	0.99	0.31	0.26	0.23	0.33	0.16

*Ex.O = Total oxygen conc. - oxygen conc. in Y_2O_3

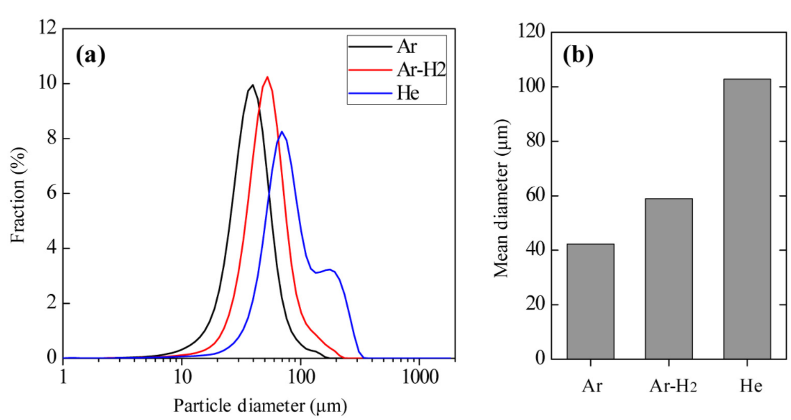

Fig. 3. The Results of MA Powder Analysis showing (a) Particle Size Distributions and (b) Mean Particle Diameters.

in He had the largest mean particle size among the three kinds of MA atmospheres. Smaller MA powder with irregular shapes normally has an advantage in a higher charging density when a capsule fills with MA powders, and thus the milling in Ar is more favorable from this point of view. Meanwhile, the prior particle boundary (PPB) pores, which come from the packing of various sizes of powders, usually affects the creep property of the powder consolidated alloys, because they become an origin of the fracture and develop into large creep cavities when deformed at high temperatures. Despite the particle size difference of MA powder in various atmospheres, PPB pores were rarely observed in all ODS ferritic steels owing to a hot rolling process at 1150 ºC with a final thickness reduction rate to 65%, which is enough to eliminate the PPB pores in the ODS ferritic steels.

3.2 Microstructures of ODS Ferritic Steels Milled in Different Atmospheres

The SEM images of grain morphology on ODS ferritic steels milled in different atmospheres are shown in Fig. 4. The grains were elongated toward the hot rolling direction, which is parallel to a horizontal direction in the images. Secondary recrystallization seemed to occur during the hot rolling process at 1150 ºC because elongated grains were clearly distinguished by an observation of the back-scattered secondary electron image mode. The grain distributions of ODS steels milled in the Ar and Ar-H_2 mixture gas were quite homogeneous, while the He milled ODS alloy showed the co-existence of fine (<1μm) and coarse (>3μm) grains. Bright field TEM images showing the nano-oxide particle distribution of ODS steels milled in different MA atmospheres. Ar and He, are shown in Fig. 5. The images are slightly under-focused because the nano-oxide particles were extremely fine and located at a different depth. Therefore, black dots normally indicate the nano-oxide particles. Very fine oxide particles were homogeneously distributed in the Ar milled ODS steel, while the ODS steel milled in He had comparably coarse oxide particles. This is due to different excess oxygen concentrations, and Ar milled ODS steel was at 0.12wt%, and He milled ODS alloy was at 0.16wt%. An excess oxygen concentration is usually involved in the formation of nano-oxide particles. The oxide particles in Ti-added ODS steels are precipitated as some complex oxides, namely $Y_2Ti_2O_7$ and Y_2TiO_5, which are formed by a combination of Y, Ti, and O during the hot consolidation process [9]. S. Ohtsuka et al. reported that excess oxygen around 0.1wt% makes the oxide particle finer and more uniform in 9Cr ODS martensitic steels [10]. The TEM images taken

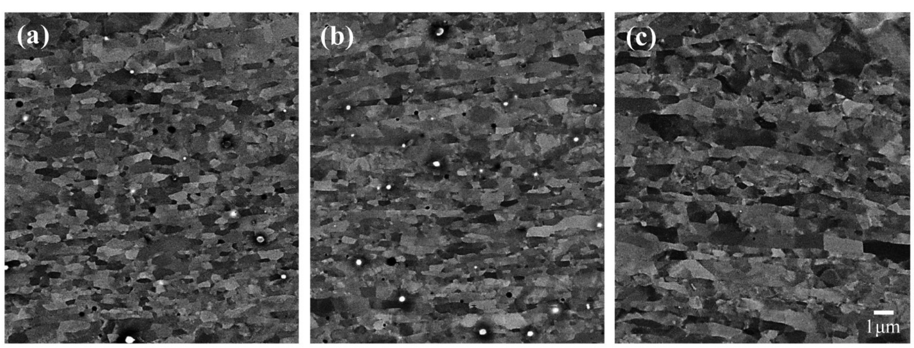

Fig. 4. Microstructures of ODS Ferritic Steels Milled in (a)Ar, (b) Ar-H_2 Mixture Gas, and (c) He Atmospheres.

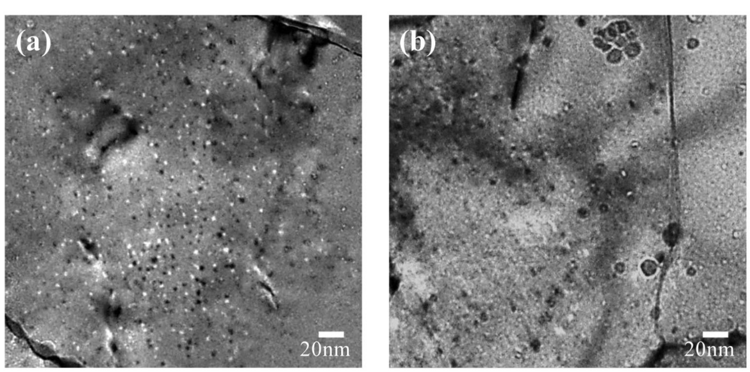

Fig. 5. TEM Bight Field Images Showing nano-oxide Particles of ODS Ferritic Steels Milled in (a) Ar and (b) He.

from the extraction carbon replica method showing nano-oxide distribution of ODS steels are presented in Fig. 6. ODS steel milled in Ar had fine and homogeneous oxide particles below 10nm in diameter. ODS steels milled in Ar-H_2 mixture gas and He also had very fine oxide particles below 5nm in diameter However, the distributions of oxide particles were not so uniform, and coarse oxide particles co-existed and agglomerated. Analysis results of the chemical composition by the TEM-EDS revealed that the fine oxide particles below 10nm in diameter were Y-Ti-O complex oxides. On the contrary, coarse oxide particles of Ar-H_2 and He milled ODS steels over 20nm in a diameter consisted of Cr or Ti and O, which means they are to be Cr_2O_3 and TiO_2. Thus, microstructural inhomogeneity of these ODS steels is attributed to coarse oxide particles with diameters of several tens of nm cause by a high oxygen concentration in ODS steels.

3.3 Tensile and Creep Properties of ODS Ferritic Steels Milled in Different Atmospheres

Microstructural observation revealed that different MA atmospheres affected the powder morphology and oxygen concentration of ODS ferritic steels. MA in Ar gas showed the lowest excess oxygen concentration, while MA in Ar-H_2 mixture gas had the highest excess oxygen concentration. This corresponded to nano-oxide particle morphologies such as diameter and distribution homogeneity. Tensile tests of the ODS ferritic steels milled in different atmospheres were carried out at room temperature and 700 ºC. Significant tensile property changes at room temperature were not observed in spite of an increase of excess oxygen, as shown in Fig. 7. At the high temperature of 700 ºC, however, excess oxygen concentrations of ODS ferritic steels significantly affect both the tensile strength and the total elongation. ODS ferritic steel with low excess oxygen of 0.12% showed the highest tensile strength and total elongation, while higher excess oxygen made the tensile properties deteriorate; and the ODS steel milled in Ar-H_2 which has the highest excess oxygen showed the lowest total elongation at the high temperature. This different behavior of tensile properties at the high temperature can be correlated with the different grain and oxide particle distribution. According to the Orowan strengthening mechanism, hard dispersoids like Y_2O_3 are bypassed through the formation of Orowan loops. When this occurred, finer diameter and a higher number density of oxide particles gives higher Orowan stress. Uniform

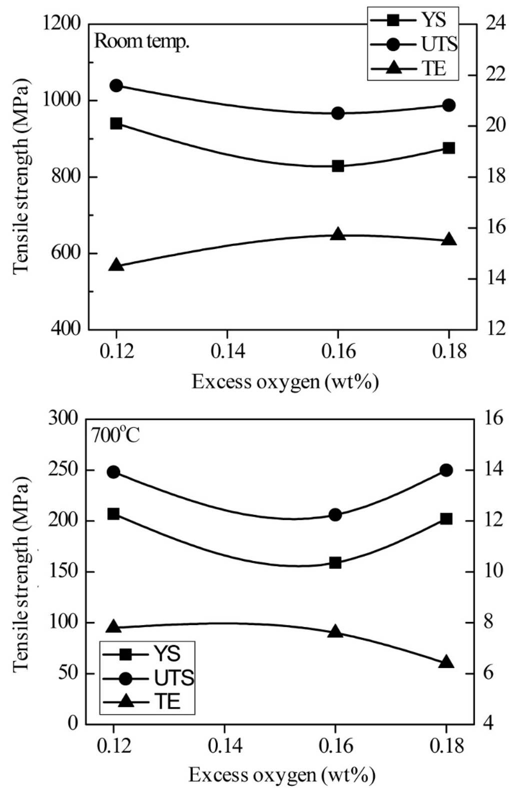

Fig. 7. Change in Tensile Properties of ODS Ferritic Steels as a Function of Excess Oxygen Concentration.

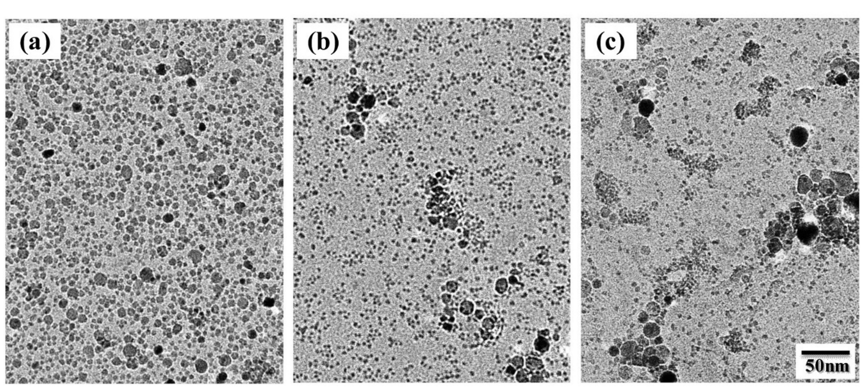

Fig. 6. Carbon Replica Images Showing nano-oxide Particle Distribution of ODS Ferritic Steels Milled in (a) Ar, (b) Ar-H_2 Mixture Gas, and (c) He Atmospheres.

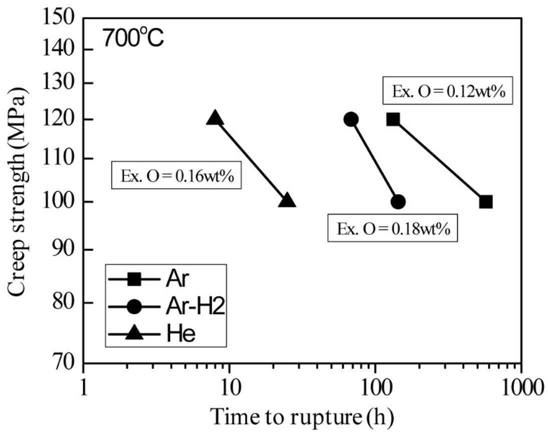

Fig. 8. The Creep Strength of ODS Ferritic Alloys Milled in Various Atmospheres with Excess Oxygen.

distribution of grains and oxide particles also affect the ductility of ODS steels. High excess oxygen concentration gives inhomogeneous microstructure with a co-existence of fine and coarse oxide particles as well as grains as shown in Fig. 4. An area partially concentrated with oxide particles had insufficient ductility. Coarse particles can also be an initiation site of the micro-crack when the alloy deforms. As shown in Fig. 4 and 6, inhomogeneous oxide particle distribution makes grains to grow partially, and this corresponded to the deterioration of the tensile properties at high temperature. Creep rupture tests of the ODS ferritic steels with different inert gas atmospheres were also performed at 700 ºC in a stress range between 100 and 120MPa. The test results are plotted on log-log scale in Fig. 8. The creep strength of Ar milled ODS ferritic steel was higher than that of the He milled ODS steel. This also coincides with the results of the microstructural analysis described above. Consequently, the mechanical alloying atmosphere mainly affects the oxygen concentration and powder particle size of ODS steels. Under the argon atmosphere, the ODS ferritic steel with lower excess oxygen generated a homogenous distribution as well as nano-oxide particles with a fine diameter as shown in Figs. 5 and 6. These microstructural features lead to excellent creep rupture strength at the high temperature.

4. CONCLUSIONS

ODS ferritic steels were fabricated through mechanical alloying in different atmospheres and HIP processes to investigate the effects of MA atmospheres on the microstructures and mechanical properties. MA powder milled in Ar was fine with an irregular particle shape, while the powders milled in an Ar-H_2 mixture and He gases were coarse and spherical in shape with a smooth surface. Moreover, ODS ferritic steels milled in Ar showed a lower excess oxygen concentration than those milled in the Ar-H_2 mixture and He gases. This led to a microstructural homogeneity with a fine oxide particle distribution. Low excess oxygen under 0.12wt% is favorable to form a homogeneous microstructure including fine grains and oxide particle distributions, and to generate excellent creep strength.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2012M2A8A1027872).

REFERENCES

[1] P. Yvon and F. Carré, “Structural Materials Challenges for Advanced Reactor Systems.” *J. Nucl. Mater.*, **Vol. 385**, pp. 217-222 (2009).

[2] S. Ukai, T. Okuda, M. Fujiwara, T. Kobayashi, S. Mizuta and H. Nakashima, “Characterization of High Temperature Creep Properties in Recrystallized 12Cr-ODS Ferritic Steel Claddings.” *J. Nucl. Sci. Technol.*, **Vol. 39**, pp.872-879 (2002).

[3] T.K. Kim, C.S. Bae, D.H. Kim, J. Jang, S.H. Kim, C.B. Lee and D. Hahn, “Microstructural Observation and Tensile Isotropy of an Austenitic ODS Steel.” *Nucl. Eng. Technol.*, **Vol. 40**, pp.305-310 (2008).

[4] H.S. Cho, H. Ohkubo, N. Iwata, A. Kimura. S. Ukai and M. Fujiwara, “Improvement of Compatibility of Advanced Ferritic Steels with Super Critical Pressurized Water Toward a Higher Thermally Efficient Water-cooled Blanket System, ” *Fusion Eng. Design*, **Vol. 81**, pp.1071-1076 (2006).

[5] S. Yamashita, N. Akasaka, S. Ukai and S. Ohnuki, “Microstructural Development of a Heavily Neutron-Irradiated ODS Ferritic Steel (MA957) at Elevated Temperature.” *J. Nucl. Mater.*, **Vol. 367-370**, pp.202-207 (2007).

[6] S. Ohtsuka, S. Ukai and M. Fujiwara, “Nano-mesoscopic Structural Control in 9CrODS Ferritic/martensitic Steels.” *J. Nucl. Mater.*, **Vol. 351**, pp.241-246 (2006).

[7] Z. Oksiuta and N. Baluc, “Effect of Mechanical Alloying Atmosphere on the Microstructure and Charpy Impact Properties of an ODS Ferritic Steel.” *J. Nucl. Mater.*, **Vol.386-388**, pp.426-429 (2009).

[8] N.Y. Iwata, T. Liu, P. Dou, R. Kasada, A. Kimura, T. Okuda, M. Inoue, F. Abe, S. Ukai, S. Ohnuki and T. Fujisawa, “Effect of MA Environment on the Mechanical and Microstructural Properties of ODS Ferritic Steels.” *J. Nucl. Mater.*, **Vol. 417**, pp.162-165 (2011).

[9] S. Ukai, M. Harada, H. Okada, M. Inoue, S. Nomura, S. Shikakura, K. Asabe, T. Nishida and M. Fujiwara, “Alloying Design of Oxide Dispersion Strengthened Ferritic Steel for Long Life FBRs Core Materials.” *J. Nucl. Mater.*, **Vol. 204**, pp.65-73 (1993).

[10] S. Ohtsuka, Ukai, M. Fujiwara, T. Kaito and T. Narita, “Improvement of 9Cr-ODS Martensitic Steel Properties by Controlling Excess Oxygen and Titanium Contents.” *J. Nucl. Mater.*, **Vol. 329-333**, pp.372-376 (2004).