Effect of Mo on the microstructure and thermal expansion of high Si ferritic heat-resistant ductile iron

Kyeong-hwan Choe[1,a *], Kyong-whoan Lee[1,b] and Myung-ho Kim[2,c]

[1]Korea Institute of Industrial Technology, 156, Gaetbeol-ro, Yeonsu-gu, Incheon, 406-840, Repubic of Korea

[2]Inha University, 100 Inha-ro, Nam-gu, Incheon, 402-751, Repubic of Korea

[a]tankchoe@kitech.re.kr, [b]whoan@kitech.re.kr, [c]mhkim@inha.ac.kr

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Abstract. The effect of molybdenum (Mo) on the microstructure and thermal expansion of heat-resistant ductile iron having ferrite matrix was investigated. Microstructure of heat-resistant ferritic ductile iron consists of ferrite, eutectic carbide at eutectic cell boundaries, precipitated carbide in grain and graphite. Pearlite was found around eutectic carbide in some specimens, however, all pearlite was decomposed by the annealing treatment. As Mo content was increased, the fraction of pearlite and the number and size of carbide increased and the number of graphite decreased. After annealing, a pearlite decompsed to Fe and C atoms. The size of precipitated carbide increased by the effect of particel coarsening. As Mo contents increased, the contraction by ferrite-austenite transformation decreased. The growth at high temperature exhibited different patterns between 900 and 1,000^{o}C. It is considered to be due to the differences in the fraction of transformed austenite.

Introduction

Conventional heat-resistant ferritic ductile iron has a composition of 4.0~6.0wt% of Si and 0.4~2.0wt% Mo and is used for automotive components of exhaust system such as turbine housing of turbocharger and exhaust manifold. To cope with environmental regulations and fuel consumption restrictions on automobiles in recent years, the exhaust gas temperature of the engine is gradually raised, and thus the heat resistance of exhaust system components is required to be higher. So a lot of research is underway to improve the heat resistance through the alloy design and optimization of the ferritic heat-resistant cast iron. [1-3] The properties required for automobile exhaust system is as follows; Oxidation resistance, Structural stability, high temperature strength, resistance to repeated heating and cooling. [4] For the improvement of heat resistance, Mo is added to the ferritic ductile iron. However, Mo promotes the formation of pearlite and carbide. Pearlite can be decomposed in high temperature, so the specimen having a pearlite matrix expands during cyclic heating and cooling. In this study, we investigated the effect of Mo contents on the microstructures and thermal expansion of ferritic heat resistant ductile iron having high Si content.

Experimental Procedure

The chemical compositions of ferritic DCI prepared for this study are presented in Table 1. The cast samples were obtained by melting steel scrap, pig iron, Fe-75 wt pct Si and Fe-60 wt pct Mo in a high frequency induction furnace. Spheroidizing and inoculation practices were performed in a conventional sandwich method by the addition of Fe-Si-5% Mg and Fe-Si-4% Ba alloy, simultaneously. The melt was poured into Y-shaped CO_2 sand molds with a 25mm thickness of bottom section. The cast specimens were austenized at 930^{o}C for 3 hours, cooled at furnace up to 600^{o}C and then air cooled for the investigation of the annealed microstructure. The specimens for metallographic investigation were obtained from the bottom section of the Y-shaped block. The general microstructure and constituent phases were investigated by the optical microscopy (EPIPHOT 200, Nikon).

Table 1. Chemical compositions of test specimens

Sample			C	Si	Mn	P	S	Mg	Mo		Remarks
0.0Mo	Aimed		3.00	5.20	0.55	<0.07	<0.02	0.04	0.00		CE=4.7
	Analyzed		2.60	5.20	0.23	0.03	0.01	0.07	0.01		CE=4.3
0.4Mo	Aimed		3.00	5.20	0.55	<0.07	<0.02	0.04	0.50		CE=4.7
	Analyzed		2.79	5.33	0.55	0.08	<0.02	0.04	0.38		CE=4.6
0.7Mo	Aimed		3.00	5.20	0.55	<0.07	<0.02	0.04	0.80		CE=4.7
	Analyzed		2.88	5.37	0.56	0.08	<0.02	0.03	0.69		CE=4.7

The specimen to evaluate the thermal expansion was a cylinder shape with 6mm diameter and 25mm length. The test was conducted with a dilatometer to conform to the ASTM E831 standard. Using DIL 402PC (NETZSCH, France), the temperature was raised to 950^{o}C and 1,000^{o}C in the N_2 atmosphere and then, maintained at that temperature for 120 minutes to evaluate the change of the length of the specimens. The microstructure of the specimens was observed before and after the test to check the change of the microstructure by dilatometric test.

Results and discussion

Figure 1 shows the change of as-cast microstructures according to the Mo content and the result of image analysis was shown in figure 2. In the case of 0.0 Mo specimen, pearlite couldn't be found in matrix and the fraction of pearlite in matrix increased as Mo content increased.Nodularity of graphite is almost same in all specimen, however, the size of graphite was larger in Mo added specimens. The number of graphite was also reduced to half by Mo addition. Mo is the element that retards graphitization and promote the formation of carbide and pearlite, thus the nucleation of graphite in eutectic reaction was inhibited. Also because of the stability of carbide, the fraction of pearlite increased.[6, 7]

Figure 3 shows the phases that exist at the eutectic cell boundary of Mo added specimens. It is found that white phases sized several to tens of μm existed at the eutectic cell boundary. They have shape similar to ledeburite in white cast iron. It seems that they are complex carbide of Fe and Mo. In graphite-austenite eutectic reaction, Mo, Fe and C atoms segregated from austenite to residual liquid due to the difference of solubility and then, they form complex carbide at austenite cell boundry in the final stage of eutectic reaction. Adjacent to these carbides, lamellar phase and fine spherical phase were also found. It seems that lamellar phase is pearlite and spherical phase is precipitated carbide when cooling. EDX analysis of these phases are shown in figure 4. It is confirmed that lamellar phase is pearlite and the fine spherical phase is a complex carbide of Fe and Mo. However, the stoichiometric ratio of precipitated carbide was different to its of eutectic carbide. Black and et al. reported that in the Si-Mo ductile iron, the stoichiometric ratio of eutectic carbide is (Fe+Mn) : (Mo+Si) : C = 0.9:1.0:0.4 and the raito of (Fe+Mn) and (Mo+Si) in precipitated carbide is about 2.2:1. [7]

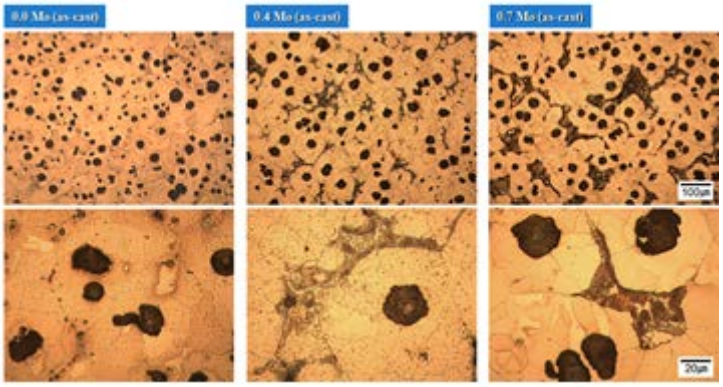


Fig. 1 Representative as-cast microstructure of specimens having various Mo contents.

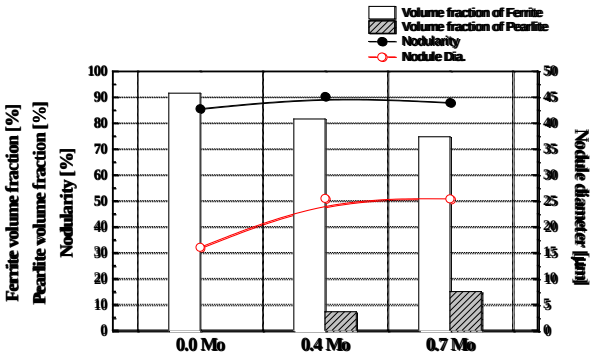


Fig. 2 Image analysis of microstructures.

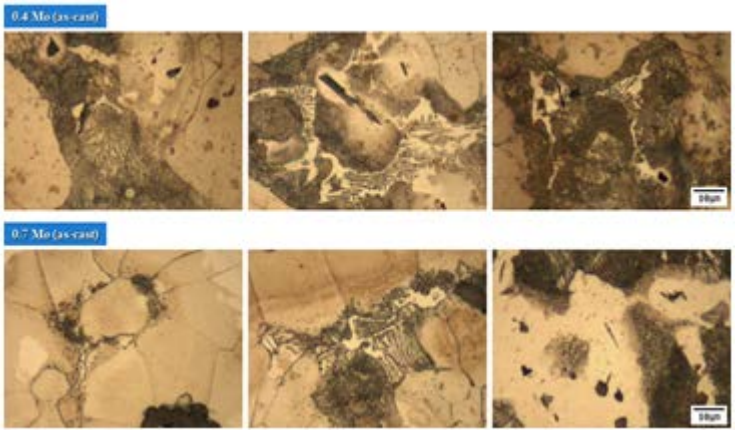


Fig. 3 The morphology of carbides precipitated at grain boundaries in as-cast microstructures.

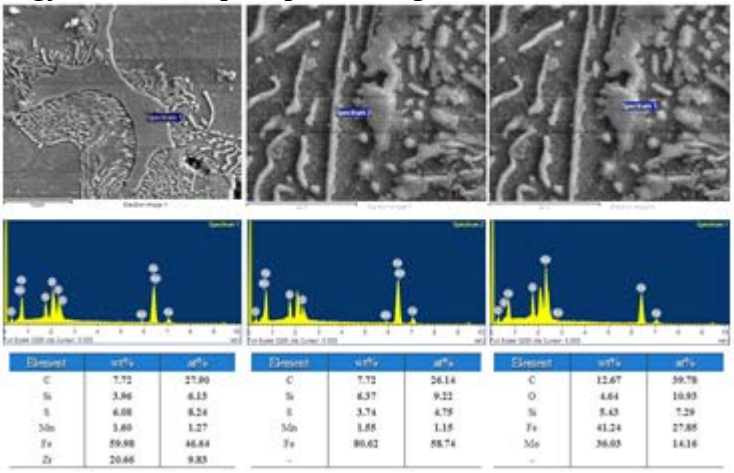


Fig. 4 The EDX analysis of eutectic and precipitaed carbide in as-cast microstructures.

Figure 5 shows the annealed microstructure of specimens having various Mo contents. Pearlite found in Mo added specimen decomposited completely by annealing. The size of eutectic carbide at cell boundary decreased slightly, however, was not decomposed by annealing treatment. On the other hand, in the case of precipitated carbide adjacent to eutectic carbide, the size increased and the number decreased. When ferritic cast iron is heated into autenite temperature range, cementite in pearlite and carbide are decomposed to (Fe, M)+C. Since the solubility of carbon in austenite is higher than in ferrite, decomposed carbon atom was dissolved into matrix, and then, it is educed to graphite during cooling.

Figure 6 shows the carbides which exist in austenite cell boundary. In as-cast microstructures shown in figure 3, fine carbide coexists with pearlite adjacent to eutectic carbide at grain boundary, however, after annealing, the size of carbide increased slightly. According to K. R. Williams et al., using the steel or other general alloys at a high temperature can seriously change the microstructure, and the change of size, spacing and type of precipitate can mean that the resistance to creep and fracture of multiphase alloy at the high creep environment can differ. [8] The secondary phase in a

multi component alloy are coarsened to minimize the interfacial energy by reducing the interface area. The coarsening speed increases according to the temperature. The specimens containing Si and Mo have some pearlites and micro carbides around the grain boundary at as-cast condition. When they are heated to a high temperature, the nearby pearlites are decomposed to (M+C) to be educed into the graphites while the micro carbides are bonded with each other to be coarsened during cooling. For the spherical precipitates, the concentration of the solute in the matrix near the particles increases when the radius of curvature decreases by the Gibbs-Thompson effect. Therefore, the concentration of the matrix around the small particles is higher than the concentration of the matrix around the large particles. Therefore, the solutes diffuse from the side of small particles to the side of large particles and thus the small particles become extinct while the large particles grow. As the result, the particles are coarsened and the total number of particles decreases. [9]

Using ThermoCalc software, Fe-C phase diagram in the composition of test specimens was calculated and the results are shown in figure 7. With the addition of Mo, MC phase are precipitated in the ferrite temperature range and the precipitation temperature of MC rises as Mo content increases.

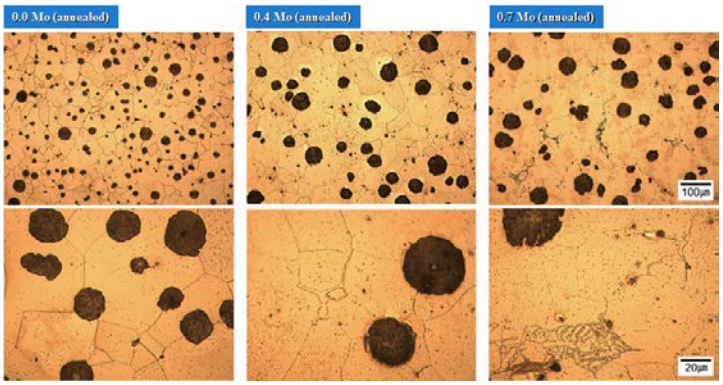


Fig. 5 Representative Annealed microstructures of various specimens.

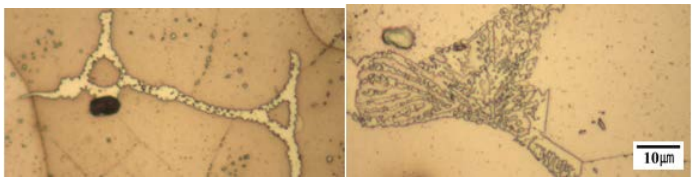
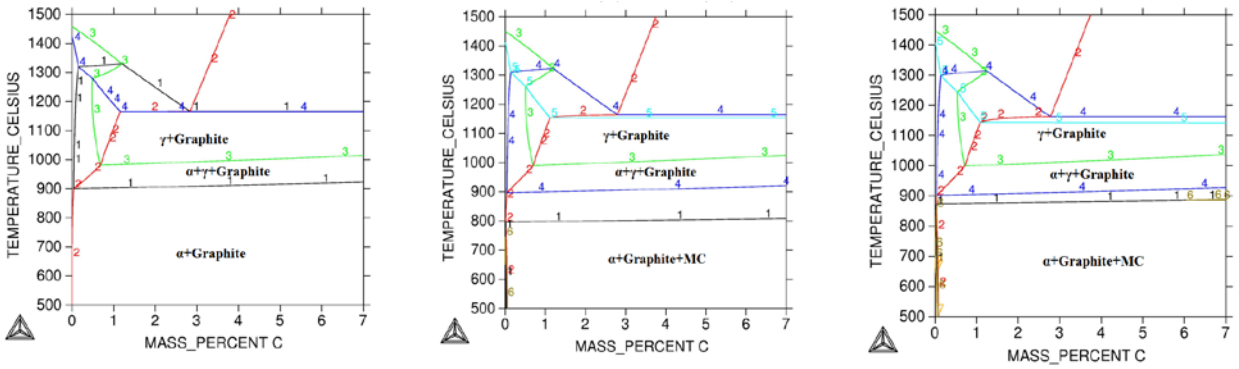


Fig. 6 The morphology of carbides precipitated at grain boundaries in annealed microstructures.



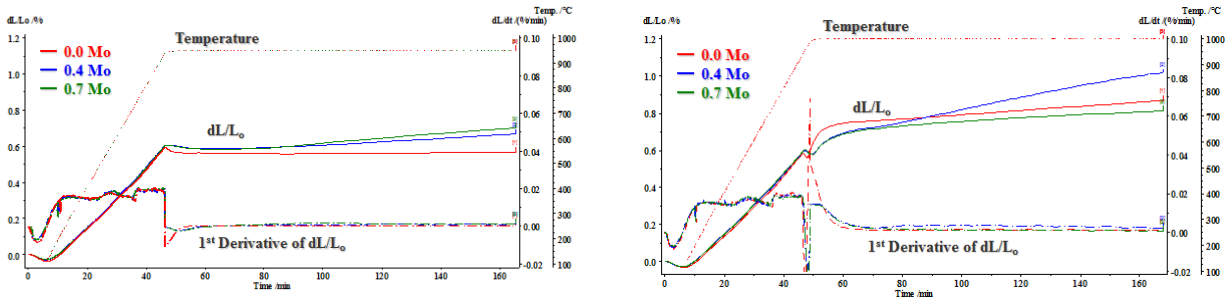
(a) C 2.60wt%-Si 5.20wt%-Mn 0.23wt% (b) C 2.79wt%-Si 5.33wt%-Mo 0.38wt%-Mn 0.55wt% (c) C 2.88wt%-Si 5.38wt%-Mo 0.69wt%-Mn 0.56wt%

Fig. 7 Fe-C Phase diagram calculated by ThermoCalc software

Figure 8 shows the result of change of length when the specimens are maintained at 950°C and 1,000°C for 2 hours in dilatometric test. Thermal expansion during heating was almost same

regardless of Mo content. At 1st derivative curve, the point of inflection was found around 700 °C. It is considered as the decomposition of pearlite, however, in 0.0 Mo specimen having no pearlite, same inflection was also found. Thus it seems the expansion due to carbon migration from graphite occurred below transformation temperature, however, further investigation was needed. In figure 9 (a), a contraction by A_1 transformation was found in all specimen and a contraction in 0.0 Mo specimen was larger than in other specimens. Figure 10 shows the equilibrium Phase fraction calculated by ThermoCalc software. As Mo contents increases, the co-existence region of ferrite and austenite got larger. If the rate of phase transformation are constant in the co-existence region of ferrite and austenite, it is predicted that the progress of phase transformation in 0.0 Mo specimen was more rapid than in Mo added specimens.

Mean while, the expansion when held for 2hours exhibited a different pattern in 950 and 1,000°C. In 950°C, the specimen more expanded as Mo content increased. In heating, pearlite in matrix was decompsed to Fe and C atoms and C atoms were dissolved into austenite. The dissolution of C atoms expanded the austenite matrix, thus 0.7Mo specimen having the highest fraction of pearlite expanded larger than other specimens. On the other hand, 0.4Mo specimen expanded larger than other specimen in 1,000°C. It is considered to be due to the differences in the fraction of transformed austenite. On the calculated equilibrium phase fraction in figure 10, the temperature range of the coexistence of ferrite and austenite in the composition of 0.4Mo specimen is from 905 to 1,001°C, and that in 0.7Mo specimen from 911 to 1,011°C. If the specimens were heated to same temperature, the fraction of austenite in 0.4Mo was higher than in 0.7Mo.Ferrite has low solubility of carbon, so the expansion by carbon migration is low at high temperature. Therefore, it is considered that the specimen having higher fraction of austenite expands larger. It can be confirmed from the microstructures after dilatometric test in figure 11. Unlike as-cast condition, 0.4Mo specimen had highiest fraction of pearlite after dilatometric test. It means that more ferrite transformed to austenite in dilatometric test.



(a) 950 °C (b) 1,000 °C

Fig. 9 Thermal expansion when held for 2 hours at 950 and 1,000 °C

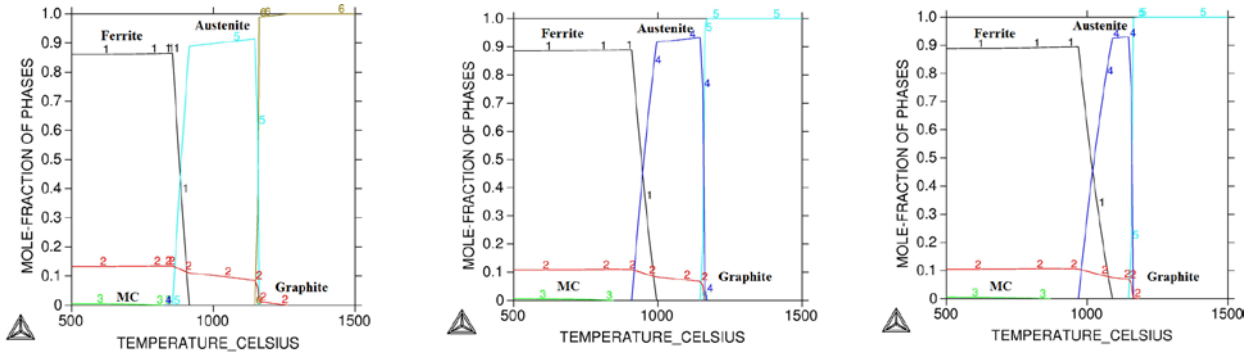


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Fig. 10 Equilibrium Phase fraction calculated by ThermoCalc software

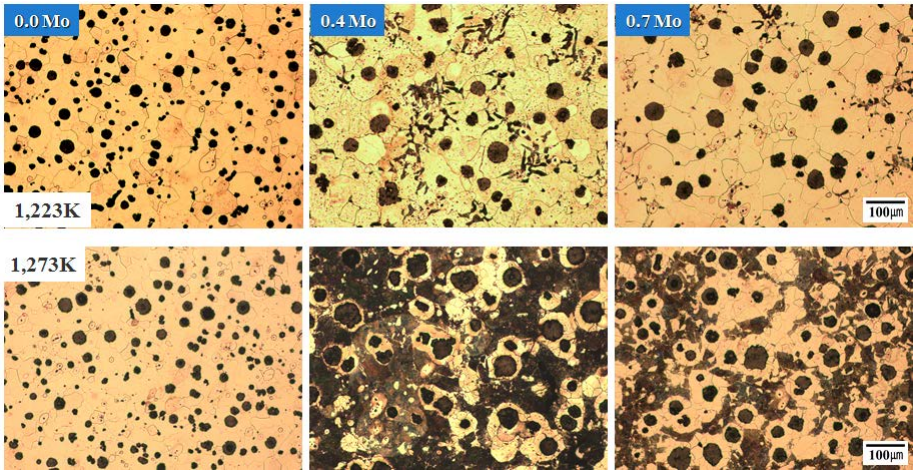

Fig. 11 Microstructures of various specimens after dilatometric test

Conclusions

Study of effect of Mo content in the high Si ferritic heat-resistant ductile iron on microstructure and thermal expansion obtained following conclusion:

1) As Mo contents increased, the size of eutectic carbide at cell boundary increased, and pearlite and fine precipitated carbide also increased
2) After annealing, pearlite decompsed to Fe and C atoms. The size of precipitated carbide increased by the effect of particel coarsening.
3) As Mo contents increased, the contraction by ferrite-austenite transformation decreased. The growth at high temperature exhibited different patterns between 900 and 1,000^{o}C.

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