Effect of Titanium on the Tensile Ductility of 30 mass% Chromium Ferritic Steels*

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The effect of titanium on the ductility of 30% chromium ferritic steels was investigated by tensile testing at low temperatures. Carbon content is 0.023 ± 0.002 mass%. Titanium content is varied from 0.051 to 0.26 mass%. The ratio of titanium content to carbon content, Ti/C, ranges from 2.1 to 12.4. Two kinds of heat treatment with or without solution treatment were adopted to obtain different types of morphology of carbide precipitates. Aging after solution treatment gives rise to grain boundary precipitation of coarse Cr carbides and numerous fine Ti carbides, depending on Ti/C ratio, while annealing without solution treatment produces coarse globular carbide particles within the grains. The Effect of Ti/C ratio on the ductile-brittle transition temperature (DBTT) determined by the tensile tests is not as remarkable as that on the DBTT determined by Charpy impact tests. In the case of specimens containing globular carbide particles within the grains, there is no noticeable influence of varying Ti/C ratio on fracture modes, while in the case of specimens containing grain boundary carbides, the effect of Ti/C ratio on fracture modes is remarkable and the amount of intergranular fracture first decreases with increasing Ti/C ratio up to 8 and then increases with the ratio at testing temperatures above 200 K.

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1. Introduction

In the previous papers,¹⁻⁷⁾ the author reported that the amount of Cr carbide and Cr nitride precipitates has more important effects on mechanical properties than the amount of C and N contents in 30 mass% Cr ferritic steels and reported that ductile-brittle transition temperatures (DBTTs) for reduction of area (RA) in tensile tests and the DBTT determined by Charpy impact tests depend on the volume and morphology (which means precipitation site, size, and shape) of Cr carbide, Cr nitride, and Ti carbide precipitates. That is, Cr carbide, Cr nitride, and Ti carbide precipitates at grain boundaries lead to more remarkable increase in the DBTT determined by tensile and impact tests than those precipitate particles within the grains. Fine spheroidal Cr carbide, Cr nitride, and Ti carbide particles within the grains do not exert a significant detrimental effect on the DBTT for RA. Furthermore the DBTT determined by the Charpy impact tests also remarkably depends on the ratio of Ti content to C content, Ti/C.⁸⁾

The purpose of the present study is to clarify the effects of Ti/C ratio on the DBTT for RA and tensile fracture mode, in the cases of specimens containing Ti carbide particles within the grains and grain boundary Ti carbide precipitates.

2. Experimental Procedure

Four 4 kg heats of Fe–30%Cr alloys were melted from electrolytic iron and electrolytic chromium by a high frequency vacuum induction furnace. In order to obtain specimens containing different Ti contents, different amount of sponge titanium was added in the molten Fe–30%Cr–0.02%C alloy after changing Ar into the furnace. The chemical compositions of as-cast specimens are given in

Table 1 Chemical composition of Fe–30%Cr alloys (mass%).

	Cr	C	N	O	Ti	Ti/C
TC1	29.5	0.024	0.001	0.002	0.051	2.1
TC2	29.3	0.022	0.001	0.003	0.10	4.5
TC3	29.8	0.025	0.001	0.004	0.21	8.4
TC4	29.7	0.021	0.001	0.003	0.26	12.4

Table 1. The content of C is 0.023 ± 0.002 mass%. The content of Ti is varied from 0.051 to 0.26 mass%. The ratio of Ti/C ranges from 2.1 to 12.4.

Cast round ingots of 55 mm in diameter were hot forged and hot rolled at 1273 K down to 7 mm $\times$ 13 mm square bars, shaper-finished to 5 mm in thickness, and then cold rolled to 0.5 mm in thickness. Longitudinal tensile specimens having gage sections of 17 mm long by 3 mm wide by 0.5 mm thick were prepared.

Two kinds of heat treatment were selected to obtain different morphologies of carbide and nitride precipitates.⁸⁾ In the process “SA” (Solution treatment and Aging), cold rolled specimens were solution treated at 1423 K for 300 s, quenched into iced water, and aged at 1123 K for 900 s followed by quenching into iced water. In the process “A” (Annealing), cold rolled specimens were annealed at 1123 K for 3.6 ks without solution treatment at 1423 K and quenched into iced water.

Tensile tests were carried out at temperatures ranging from 4.2 K to room temperature (RT) at a strain rate of $4.9 \times 10^{-4} \text{ s}^{-1}$ using an Instron machine. Microstructures of specimens heat treated by the process SA or A were observed by means of optical microscopy and transmission electron microscopy (TEM). Thin foils for TEM observations were first mechanically polished to about 200 μm thick and then electrolytically thinned at (273–278) K in a mixed solution of 20% perchloric acid and 80% ethanol. The fracture surfaces

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Fig. 1 Transmission electron micrograph of carbide precipitates in specimen TC1 (0.051%Ti), heat treated by the process SA.

after the tensile test were observed by means of a scanning electron microscope (SEM).

3. Results

3.1 Microstructures

When all of C atoms precipitate as TiC, Ti content calculated is necessary 4 times C content. Figures 1 and 2 show typical electron micrographs of the carbide precipitates observed in the specimens TC1 (0.051%Ti, Ti/C ratio below 4) and TC2 (0.10%Ti, Ti/C ratio above 4) heat treated by the process SA, respectively. In the specimen TC1 (0.051%Ti), coarse grain boundary carbides of 0.4 μm wide and 2 μm long are located discontinuously along the grain boundary (Fig. 1). The coarse grain boundary carbide is identified as Cr carbide consisting of $M_{23}C_6$ by analyses of electron diffraction pattern. Fine spheroidal precipitates are recognized between coarse grain boundary Cr carbides. The size of the fine precipitates is less than 0.05 μm. The composition of the fine precipitates may be considered as TiC. Electron diffraction patterns from upper and lower grains shown in Fig. 2 were analyzed as [113] and $[\bar{1}11]$ reciprocal lattice planes. In the specimen TC2 (0.10%Ti) (Fig. 2), numerous fine spheroidal Ti carbide precipitates in the 0.1 μm size range are recognized at the grain boundary. The fine spheroidal grain boundary precipitates are considered as TiC since carbide precipitates which will be showed later in Fig. 4 are identified as TiC by the analyses of electron diffraction pattern. The morphology of Ti carbide precipitates in the specimens TC3 (0.21%Ti) and TC4 (0.26%Ti) heat treated by the process SA, is similar to that in the

Fig. 2 Transmission electron micrograph of carbide precipitates in specimen TC2 (0.10%Ti), heat treated by the process SA.

specimen TC2 (0.10%Ti) heat treated by the process SA. In the case of the process SA, the specimen with Ti/C ratio of 2.1 contains coarse grain boundary Cr carbides and the specimens with Ti/C ratio above 4.5 contain numerous fine spheroidal grain boundary Ti carbides.

Figures 3 and 4 show typical electron micrographs of the carbide precipitates observed in the specimens TC1 (0.051%Ti) and TC4 (0.26%Ti) heat treated by the process A, respectively. In the specimen TC1 (0.051%Ti), coarse globular carbides are recognized within the grains (Fig. 3). The sizes of globular carbides are 0.5 to 2 μm. These carbides are identified as Cr carbide consisting of $M_{23}C_6$ by the analyses of electron diffraction pattern. In the specimen TC4 (0.26%Ti), coarse globular carbides are recognized within the grains (Fig. 4). The sizes of globular carbides are 0.5 to 1 μm. These carbide precipitates are identified as Ti carbides consisting of TiC by the analyses of electron diffraction pattern. The morphology of Ti carbide particles in the specimens TC2 (0.10%Ti) and TC3 (0.21%Ti) heat treated by the process A, is similar to that in the specimen TC4 (0.26%Ti) heat treated by the process A. In the case of the process A, the specimen with Ti/C ratio of 2.1 contains coarse Cr carbide particles within the grains and the specimens with Ti/C ratio above 4.5 contain coarse Ti carbide particles within the grains.

Grain size measurement of the specimens after two heat treatment processes was carried out on the etched specimens. The grain sizes of the specimens TC1, TC2, TC3, and TC4

Fig. 3 Transmission electron micrograph of carbide precipitates in specimen TC1 (0.051%Ti), heat treated by the process A.

Fig. 4 Transmission electron micrograph of carbide precipitates in specimen TC4 (0.26%Ti), heat treated by the process A.

heat treated by the process SA are 125 to 151 μm . The grain sizes of the specimens TC1, TC2, TC3, and TC4 heat treated by the process A are 20 to 28 μm . The grain size of the specimens heat treated by the process SA is larger than that of the specimens heat treated by the process A.

3.2 Tensile tests

The values of the lower yield stress at RT (298 K) of the specimens TC1, TC2, TC3, and TC4 heat treated by the process SA are 250 to 263 MPa and the specimen TC4 (0.26%Ti) indicates highest lower yield stress. In the specimens TC1, TC2, TC3, and TC4 heat treated by the process A, the lower yield stress of the specimen with 0.051%Ti at RT is 292 MPa and the lower yield stress of the specimens with above 0.1%Ti increases from 271 to 280 MPa with increasing Ti content. The yield stress of the specimens heat treated by the process SA is lower than that of the specimens heat treated by the process A.

Figures 5 and 6 illustrate the change in RA of the specimens TC1 (0.051%Ti) and TC3 (0.21%Ti) in the tensile test conducted at temperatures ranging from 4.2 K to RT, respectively. Microfractographic examinations were carried out on the fractured specimens. The DBTT was defined at the point where RA was equal to one-half of the upper shelf in RA. Marks D, B, and IG in Figs. 5 and 6 denote that fracture appearance is principally of dimple fracture-type (D), of brittle fracture-type (B) such as cleavage and quasi-cleavage fracture, and of intergranular fracture-type (IG), respectively. D-IG indicates the coexistence of dimple-type and intergranular-type. Similarly, the coexistence of brittle-type and intergranular-type is represented by B-IG. The number prior to IG indicates the ratio of intergranular fracture to total fracture area. The accuracy of the determination was $\pm 5\%$.

In the specimen TC1 (0.051%Ti) heat treated by the process A (open double circles in Fig. 5), the RAs remain unchanged at 90% in the temperatures between RT and 153 K, and then rapidly decrease with decreasing testing temperature. On the other hand, in the specimen TC1 (0.051%Ti) heat treated by the process SA (open diamonds in Fig. 5), the RA starts to decrease at higher temperature with decreasing testing temperature. The DBTT for the specimen TC1 (0.051%Ti) heat treated by the process SA is higher than that for specimen TC1 (0.051%Ti) heat treated by the process A.

In the specimen TC1 (0.051%Ti) heat treated by the process A, the fracture modes at testing temperatures above 153 K are of typical dimple-type and those at testing temperatures below 77 K are of brittle fracture. On the other hand, in the specimen TC1 (0.051%Ti) heat treated by the process SA, the fracture mode at RT is of dimple fracture containing ductile intergranular fracture (DIG)⁵⁾ and that at 200 K is of ductile intergranular fracture containing dimple. The fracture mode at 153 K is of brittle fracture containing brittle intergranular fracture (BIG)⁵⁾ and that at 77 K is of brittle fracture containing a small part of still brittle intergranular fracture.

After the heat treatment processes SA and A, the RA for the specimen TC3 (0.21%Ti) (Fig. 6) shows similar behavior to that for specimen TC1 (0.051%Ti) (Fig. 5).

The fracture mode of the specimen TC3 (0.21%Ti) heat

Fig. 5 Relation between reduction of area and testing temperature for specimens TC1 (0.051%Ti), heat treated by the processes SA or A.

Fig. 6 Relation between reduction of area and testing temperature for specimens TC3 (0.21%Ti), heat treated by the processes SA or A.

treated by the process A shows similar behavior to that for specimen TC1 (0.051%Ti) heat treated by the process A. On the other hand, the fracture mode of the specimen TC3 (0.21%Ti) heat treated by the process SA is remarkably different from that for specimen TC1 (0.051%Ti) heat treated by the process SA. That is, the amount of ductile intergranular fracture for the specimen TC3 (0.21%Ti) is smaller than that of ductile intergranular fracture for the specimen

Fig. 7 Relation between Ti/C ratio and ductile-brittle transition temperature in Fe-30%Cr-C-Ti alloys, heat treated by the processes SA or A. The broken lines in higher part of the figure show the results of ductile-brittle transition temperature determined by Charpy impact test for heat treatments of the processes SA and A.⁸⁾

TC1 (0.051%Ti) at testing temperatures above 200 K. However, at 153 K, the amount of intergranular fracture for the former is larger than that for the latter. In the former specimen, ductile intergranular fracture, brittle intergranular fracture, and brittle fracture coexist at 153 K, while in the latter specimen, brittle intergranular fracture and brittle fracture coexist at 153 K.

Figure 7 shows the relation between the DBTT and Ti/C ratio in a series of Ti containing alloys. The broken lines in higher part of Fig. 7 show the results of the DBTT determined by Charpy impact tests for the specimens after the heat treatment processes SA and A.⁸⁾ The DBTTs in tensile tests for the specimens heat treated by the process SA are higher than those for the specimens heat treated by the process A. Both the DBTTs first slightly decrease with increasing Ti/C ratio and then slightly increase with the ratio. The dependence of Ti/C ratio for the DBTT in tensile tests is not more remarkable than that for the DBTT determined by Charpy impact testing.⁸⁾ It is considered that the unnoticeable dependence of Ti/C ratio on the DBTT in tensile tests is due to the differences of strain rate, stress condition, and test piece size.⁹⁾

Figure 8 shows the relation between the amount of intergranular fracture and Ti/C ratio in a series of Ti containing alloys. In the case of the process A (open symbol), there is no noticeable influence of varying Ti/C ratio on the amount of intergranular fracture at testing temperatures above 153 K. On the other hand, in the case of the process SA (solid symbol), the amount of intergranular fracture is remarkably affected by Ti/C ratio. The amount of intergranular fracture at testing temperatures above 200 K is remarkably different from that at 153 K. That is, at testing temperatures above 200 K, the amount of intergranular

Fig. 8 Relation between Ti/C ratio and area fraction of intergranular fracture in Fe-30%Cr-C-Ti alloys, heat treated by the processes SA or A. Fractured at room temperature (298 K), 200 K, and 153 K.

fracture coexisting dimple first decreases with increasing Ti/C ratio up to 8 and then increases with increasing the ratio, however, at 153 K, the amount of intergranular fracture coexisting brittle fracture is first increases with increasing Ti/C ratio up to 8 and then decreases with the ratio.

4. Discussion

In the present study, the effect of Ti/C ratio on the fracture mode is remarkable. The intergranular fracture mechanism in the case of the process SA is discussed on the basis of the following two assumptions: (1) the intergranular fracture may be caused by the decohesion at the interfaces between the matrix and carbide precipitates at grain boundaries and (2) the area of the decohesion depends on the size of the grain boundary carbide precipitate. In the case of the specimens containing the grain boundary carbide precipitates, the amount of intergranular fracture first decreases with increasing Ti/C ratio up to 8 and then increases with the ratio at testing temperatures above 200 K (Fig. 8). The grain boundary precipitate of the specimen with Ti/C ratio of 2.1 is coarser than that of the specimens with above Ti/C ratio of 4.5. Hence, the amount of intergranular fracture of the specimen with Ti/C ratio of 2.1 is larger than that of the specimens with Ti/C ratio of 4.5 and 8.4. For a large amount of the intergranular fracture of the specimen with Ti/C ratio of 2.1, the previous assumptions give a consistent full explanation. However, in the specimen with Ti/C ratio of 12.4 which contains numerous fine grain boundary Ti carbides, this mechanism becomes inconsistent.

The amount of intergranular fracture takes a maximum at 8 of the ratio at 153 K. The behavior at 153 K is considerably different from that at 200 K as shown in Fig. 8. At 200 K,

ductile intergranular fracture and dimple fracture coexist. At 153 K, in the specimens with minimum and maximum ratio of Ti/C, brittle intergranular fracture and brittle fracture coexist, whereas in the specimen with Ti/C ratio of 8.4, ductile intergranular fracture, brittle intergranular fracture, and brittle fracture coexist. The specimen with Ti/C ratio of 8.4 contains the smallest amount of brittle fracture at 153 K. Therefore, at 153 K, the specimens with minimum and maximum ratio of Ti/C may more early cause brittle intergranular fracture than the specimen with Ti/C ratio of 8.4 since initiation of microcracks for brittle fracture is considered to be caused by the brittle intergranular fracture.

5. Conclusions

The effect of titanium on the ductility of 30%Cr ferritic steels was investigated by tensile testing at low temperatures. The content of C is 0.023 ± 0.002 mass%. The content of Ti is varied from 0.051 to 0.26 mass%. The ratio of Ti/C ranges from 2.1 to 12.4. Ductility was evaluated by the DBTT in reduction of area and fracture modes. The results obtained are summarized as follows:

- (1) Aging after solution treatment gives rise to grain boundary precipitation of coarse Cr carbides at Ti/C ratio of 2.1 and numerous fine Ti carbides at Ti/C ratio above 4.5. Annealing without solution treatment produces coarse globular carbide particles within the grains.
- (2) The effect of Ti/C ratio on the DBTT is slight.
- (3) The effect of Ti/C ratio on fracture modes of the specimens containing grain boundary carbides is more remarkable than that on fracture modes of the specimens containing carbide particles within the grains. In the case of the specimens containing the morphology of grain boundary carbides, the amount of intergranular fracture first decreases with increasing Ti/C ratio up to 8 and then increases with the ratio at testing temperatures above 200 K, while at 153 K it first increases with increasing Ti/C ratio up to 8 and then decreases with the ratio.

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