Effect of Titanium Carbide Precipitates on the Ductility of 30 mass% Chromium Ferritic Steels

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The effect of morphology of Ti carbides on the ductility of 30 mass%Cr ferritic steels containing C and Ti was investigated by tensile test at low temperatures. C and Ti contents were varied from 0.011 to 0.071 mass%, and from 0.094 to 0.60 mass%, respectively. The ratio Ti/C was about nine. Two kinds of heat treatments were adopted to obtain different types of morphology of Ti carbide precipitates, namely numerous fine grain boundary Ti carbide precipitates about 0.05 μm in diameter and coarse globular Ti carbide particles in the 1.5 μm size range. The tensile ductility was evaluated by transition temperatures in reduction of area. The numerous fine grain boundary Ti carbide precipitates lead to an increase in the transition temperature more than uniformly dispersed coarse globular Ti carbide particles. The former brings about the increase in the amount of intergranularly fractured surface in dimple and brittle fracture more than the latter. Cluster-like coarse globular Ti carbides at grain boundaries cause a scatter band of the transition temperature. Microfractographic examinations reveal that initiation of microcracks for brittle fracture is considered to be caused by intergranular fracture cracks which are promoted by decohesion at the interface between the matrix and many grain boundary Ti carbide precipitates and by decohesion at the interface between the matrix and cluster-like coarse globular Ti carbides at grain boundaries.

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1. Introduction

In Fe–Cr alloys, it is known that impurity elements such as C and N are responsible for the decrease of toughness and ductility.^{1–4)} The variation in the degree of the embrittlement associated with heat treatments such as water quenching, air cooling and furnace cooling has been related to the amount of carbide and nitride precipitates.^{5,6)}

In the previous papers, the author reported that an increase in the volume fraction of carbide and nitride precipitates resulted in an increase in the ductile-brittle transition temperature (DBTT) determined by impact tests and a decrease in the strain at fracture in tensile test,⁷⁾ and also reported that the DBTTs for reduction of area (RA) determined by tensile tests depended on the volume and morphology of Cr carbide and Cr nitride precipitates.^{8,9)} That is, Cr carbide, Cr nitride and Ti carbide precipitates at grain boundaries lead to more remarkable increase in the DBTT for RA 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.

The purpose of the present study is to clarify the effects of the morphology of Ti carbide precipitates on the DBTT for RA, fracture mode, and brittle fracture mechanism in tensile tests.

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 C and Ti contents, different amounts of Fe–4%C mother alloy and sponge titanium were added in the molten 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
T1	29.4	0.011	0.001	0.003	0.094
T2	29.8	0.025	0.001	0.004	0.21
T3	29.4	0.037	0.001	0.003	0.32
T4	29.3	0.071	0.001	0.002	0.60

Table 1. C and Ti contents were varied from 0.011 to 0.071 mass%, and from 0.094 to 0.60 mass%, respectively. The ratio Ti/C was about nine.

Cast round ingots of 50 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 treatments were selected to obtain different morphology of Ti carbide precipitates. 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 “SFA” (Solution treatment, Furnace cooling, and Aging), cold rolled specimens were solution treated at 1423 K for 300 s followed by furnace cooling at a mean cooling rate of $8.8 \times 10^{-2} \text{ K}\cdot\text{s}^{-1}$ to 1123 K, and aged at 1123 K for 900 s followed by quenching into iced water.

Tensile tests were carried out at temperatures ranging from 77 K to room temperature (RT) at a strain rate of $4.9 \times 10^{-4} \text{ s}^{-1}$ using an Instron machine. Microstructures of the specimens, heat treated by the processes SA or SFA were observed by means of a transmission electron microscope (TEM). Thin foils for TEM observations were first mechanically polished to about 200 μm thick and then

electrolytically thinned at 278 K in a mixed solution of 20% perchloric acid and 80% ethanol. A transmission electron microscope (JEM-2000EX) operating at 200 kV was used. The fracture surfaces after tensile tests were observed by means of two scanning electron microscopes (SEM) (Hitachi-Akasi MSM-101 and JSM-6320F).

3. Results

3.1 Microstructures

Figure 1 shows a typical electron micrograph of the specimen T2 (0.025%C), heat treated by the process SA. Numerous fine spheroidal Ti carbide precipitates were observed at grain boundaries. Their size was about 0.05 μm . In the specimens T3 and T4 (which contain above 0.037%C), heat treated by the process SA, Ti carbide precipitates at grain boundaries were observed as in the specimen T2 shown in Fig. 1, and coarse globular Ti carbide particles within the grains were also observed. The size of the coarse globular Ti carbide particles was about 1 μm .

Figure 2 shows typical electron micrographs of the grain boundary (a) and Ti carbide (b) in the specimen T2

(0.025%C), heat treated by the process SFA. Majority of coarse globular Ti carbide particles were observed predominantly within the grains, and their size was about 1.5 μm (Fig. 2(b)). Fine spheroidal Ti carbide precipitates were not observed at grain boundaries (Fig. 2(a)). The coarse globular Ti carbide particles were uniformly dispersed in the specimens with below 0.025%C.

Figure 3 is given an instance of some coarse globular Ti carbide particles forming a cluster (which is called to cluster-like Ti carbides) at the grain boundary in the specimen T4 (0.071%C), heat treated by the process SFA. Their size was about 1.5 μm . Majority of coarse globular Ti carbide particles located within the grains, however the cluster-like Ti carbides were rarely observed at grain boundaries in the specimens T3 and T4 (which contain above 0.037%C), heat treated by the process SFA. In the case of the process SFA, fine Ti carbide precipitates at grain boundaries, as shown in Fig. 1 were not observed independent of C content.

Figure 4 shows an electron micrograph of the specimen T4 (0.071%C), heat treated by the process SFA. Some coarse Ti carbide particles on the wavy grain boundary were observed. This phenomenon suggests that grain boundary migration occurred during furnace cooling from 1423 to 1123 K, and

Fig. 1 Transmission electron micrograph of titanium carbides in specimen T2 (0.025%C), heat treated by the process SA.

Fig. 3 Transmission electron micrograph of titanium carbides in specimen T4 (0.071%C), heat treated by the process SFA.

Fig. 2 Transmission electron micrograph of titanium carbides in specimen T2 (0.025%C), heat treated by the process SFA. (a) At grain boundary. (b) Within grain.

Fig. 4 Transmission electron micrograph of wavy grain boundary in specimen T4 (0.071%C), heat treated by the process SFA.

that the grain boundary was pinned by some coarse Ti carbide particles. Therefore, it should be considered that the cluster-like Ti carbides at grain boundaries shown in Fig. 3 were produced during grain boundary migration.

Despite the fairly similar heat treating temperatures, the differences between the microstructures produced by the two processes remarkably appeared in the location, number and size of the Ti carbide precipitates. That is, the process SA gave rise to grain boundary precipitation of numerous fine Ti carbides, while the process SFA produced uniformly dispersed coarse globular Ti carbide particles in the specimens with below 0.025%C and rarely produced the cluster-like Ti carbides at the grain boundary in the specimens with above 0.037%C.

The volume fraction of Ti carbide precipitates in the specimen, heat treated by the processes SA or SFA was calculated to clarify the relationship between the volume fraction of Ti carbide precipitates and DBTT. The volume fraction of Ti carbides after quenching from 1123 K was calculated by using the solubility of C at 1123 K and the densities of the matrix and Ti carbide. The solubility of C at 1123 K of Fe–30%Cr alloy (which does not contain Ti) has been determined experimentally as 0.002%C.⁷⁾ The solubility of C of Fe–30%Cr–Ti alloy is estimated smaller than that of Fe–30%Cr alloy, because the affinity of Ti for C is larger than that of Cr for C. Therefore the solubility of C at 1123 K of Fe–30%Cr–Ti alloy is estimated to negligible small. The densities of the matrix and Ti carbide are 7.7 Mg/m³ and 4.9 Mg/m³, respectively.^{7,10)}

Grain size measurement of the specimens after two heat treatment processes was carried out on the etched specimens. In the specimens T1, T2, T3 and T4 (which contain from 0.011 to 0.071%C), heat treated by the process SA, their grain size decreased from 125 to 80 μ m with increasing C content. In those, heat treated by the process SFA, their grain size decreased from 135 to 82 μ m with increasing C content. Variations in their grain size between the processes SA and SFA were scarcely recognized.

3.2 Tensile tests

In the specimens T1, T2, T3 and T4 (which contain from 0.011 to 0.071%C), heat treated by the process SA, their lower yield stress at RT increased from 242 to 268 MPa with increasing C content. In those, heat treated by the process SFA, their lower yield stress at RT increased from 221 to 266 MPa with increasing C content. The variations in their lower yield stress between the processes SA and SFA were scarcely recognized.

Figures 5, 6 and 7 illustrate the change in the RA of the specimens T1 (0.011%C), T3 (0.037%C) and T4 (0.071%C) in tensile tests conducted at temperatures ranging from 77 K to RT respectively. Microfractographic examinations have been carried out on fractured specimens. Marks D, B, and IG in these figures indicate fracture appearance. Further details will be described later.

In the specimen T1 (0.011%C), heat treated by the process SA (open diamonds in Fig. 5), the RA remained unchanged in the temperatures above 200 K. The RA at 153 K was slightly lower than that at 200 K, and then the RA decreased to zero at 77 K. On the other hand, the RA for the specimen

Fig. 5 Relation between reduction of area and testing temperature for specimen T1 (0.011%C), heat treated by the processes SA or SFA. *—SFA. **—SA.

Fig. 6 Relation between reduction of area and testing temperature for specimen T3 (0.037%C), heat treated by the processes SA or SFA. *—SFA. **—SA.

T1 (0.011%C), heat treated by the process SFA (open double circles in Fig. 5) remained unchanged in the temperatures between RT and 153 K, and then rapidly decreased to zero at 77 K. The DBTT were defined at the point where RA was equal to one-half of the upper shelf in RA. The DBTT for the specimen T1 (0.011%C), heat treated by the process SFA was lower than that for specimen T1 (0.011%C), heat treated by the process SA.

Fig. 7 Relation between reduction of area and testing temperature for specimen T4 (0.071%C), heat treated by the processes SA or SFA. *—SFA. **—SA.

The RA for the specimen T3 (0.037%C), heat treated by the processes SA or SFA (Fig. 6) showed similar behavior to that for specimen T4 (0.071%C), heat treated by the processes SA or SFA (Fig. 7) in the temperatures between RT and 77 K, respectively. The RA for the specimen T3 (0.037%C), heat treated by the process SA remained unchanged in the temperatures above 200 K. The RA at 153 K was lower than that at 200 K, and then that decreased to zero at 77 K. The DBTT for the specimen T3 (0.037%C) was higher than that for the specimen T1 (0.011%C), heat treated by the process SA. The RA for the specimen T3 (0.037%C), heat treated by the process SFA remained unchanged in the temperatures above 200 K. The RA values at 153 K scattered suddenly. Majority of RA values remained unchanged showing the values with above 80%, but the lowest RA value was similar to that for the specimen T3 (0.037%C), heat treated by the process SA. The RA for the specimen T4 (0.071%C), heat treated by the process SFA (Fig. 7) also scattered at 153 K, while the RA values for the specimens T1 (0.011%C) and T2 (0.025%C), heat treated by the process SFA did not scatter either at same temperature.

The relationship between the RA and morphology of Ti carbide precipitates is summarized as follows. (1) The DBTT for the specimen containing numerous fine Ti carbide precipitates at grain boundaries was higher than that for the specimen containing uniformly dispersed coarse globular Ti carbide particles. (2) The cluster-like coarse globular Ti carbides at grain boundaries caused a scatter band of the DBTT.

Marks D, B, and IG in Figs. 5, 6 and 7 indicate 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.

In the specimen T1 (0.011%C), heat treated by the process SA, the fracture mode at RT was typically of dimple-type, and that at 200 K was of dimple fracture containing ductile intergranular fracture.¹¹⁾ In the fracture mode at 153 K, the ductile intergranular fracture, brittle fracture and dimple fracture were recognized to coexist together. The fracture mode at 77 K was of brittle fracture containing brittle intergranular fracture.¹¹⁾ On the other hand, in the specimen T1 (0.011%C), heat treated by the process SFA the fracture modes in the temperatures above 200 K were typically of dimple-type, and that at 153 K is of dimple fracture containing a small part of ductile intergranular fracture. That at 77 K was of brittle fracture.

The fracture mode of the specimen T3 (0.037%C), heat treated by the process SA was similar to that of the specimen T4 (0.071%C), heat treated by the process SA, in the temperatures between RT and 77 K. The fracture mode of the former specimen is described. That at RT was typically of dimple-type, and that at 200 K was of dimple fracture containing ductile intergranular fracture. That at both 153 and 77 K was of brittle fracture containing brittle intergranular fracture.

On the whole, the numerous fine grain boundary Ti carbide precipitates bring about the increase in the amount of intergranularly fractured surface in dimple and brittle fracture more than the uniformly dispersed coarse globular Ti carbide particles.

Figure 8 shows a scanning electron micrograph of the fracture surface observed in the specimen T1 (0.011%C), heat treated by the process SA and tensile tested at 153 K. The brittle fracture and brittle intergranular fracture are recognized to coexist together, and the river pattern also appears.

Figure 9 gives high magnification details of the brittle intergranular fracture surface observed in the specimen T3 (0.037%C), heat treated by the process SA and tensile tested at 153 K. The numerous fine Ti carbide precipitates corre-

Fig. 8 Scanning electron micrograph of specimen T1 (0.011%C), heat treated by the process SA and tensile fractured at 153 K.

Fig. 9 Scanning electron micrograph showing numerous fine grain boundary Ti carbide precipitates on intergranular fracture surface of specimen T3 (0.037%C), heat treated by the process SA and tensile fractured at 153 K.

sponding to Fig. 1 are recognized on the brittle intergranular fracture surface. Convex surfaces of traces of the Ti carbide precipitates and concave those are not mixed in Fig. 9 but only the former is recognized.

The fracture mode of the specimen T3 (0.037%C), heat treated by the process SFA was similar to that of the specimen T4 (0.071%C), heat treated by the process SFA, in the temperatures between RT and 77 K. The fracture mode of the latter specimen is described. That in the temperatures above 200 K was typically of dimple-type, and that at 153 K presented two types of fracture modes, namely dimple-type and brittle-type. That is, the fracture mode of the specimen showing the higher RA value was of dimple fracture containing a small part of ductile intergranular fracture and that of the specimen showing the lower RA value was of brittle fracture containing brittle intergranular fracture. The fracture mode at 77 K was of brittle fracture.

Figure 10 shows the scanning electron micrograph of the fracture surface observed in the specimen T4 (0.071%C), heat treated by the process SFA, tensile tested at 153 K, and showing lower RA value. The brittle fracture and brittle intergranular fracture are recognized to coexist together in this figure. The cluster-like Ti carbides were observed on the

Fig. 10 Scanning electron micrograph of specimen T7 (0.071%C), heat treated by the process SFA and tensile fractured at 153 K.

Fig. 11 Relation between the volume fraction of titanium carbide and transition temperature in Fe-30%Cr-C-Ti alloys, heat treated by the processes SA or SFA.

brittle intergranular fracture surface. The river pattern also appears in this figure.

Figure 11 shows the relation between the DBTT and calculated volume fraction of Ti carbides in a series of C containing alloys. In the case of the process SA (open triangles) the DBTT increased with increasing Ti carbide up to 0.3 vol% of Ti carbide and then it remained unchanged over 0.3 vol% of Ti carbide. On the other hand in the case of the process SFA (open double circles), the DBTT did not increase with increasing Ti carbide below 0.2 vol% of Ti carbide, while it scattered above 0.3 vol% of Ti carbide. It is obvious that numerous fine carbides on grain boundaries caused the increase in the DBTT more than the uniformly dispersed coarse globular carbides below 0.2 vol% of Ti carbide.

4. Discussion

The brittle fracture mechanism in the case of the process SA is discussed. In general, it is well known that the appearance of the river pattern is brought about by the movement of a cleavage crack across a grain boundary and a subgrain boundary.^{12,13)} However, the photograph in Fig. 8 shows that the appearance of the river pattern may be brought about by the intergranular fracture crack, and suggests a strong possibility that the microcrack for brittle fracture is initiated by the intergranular fracture crack. This present intergranular fracture shown in Fig. 8 may be caused by the decohesion at the interfaces between the matrix and many Ti carbide precipitates at grain boundaries, since the author proposed that such decohesion may be caused by a dislocation pile-up at the Cr carbide and the Cr nitride precipitates at grain boundaries.^{8,11)}

Next, the specimens T3 and T4 (which contain above 0.037%C), heat treated by the process SFA and fractured at 153 K showed two types of fracture modes which were of ductile dimple-type and brittle fracture-type. In spite of

absence of numerous fine Ti carbide precipitates at grain boundaries in those specimens, the brittle fracture occurred. The photograph shown in Fig. 10 also suggests the strong possibility that the microcrack for brittle fracture is initiated by the intergranular fracture crack, since the appearance of the river pattern may be brought about by the intergranular fracture. This present intergranular fracture shown in Fig. 10 may be also caused by the decohesion at the interfaces between the matrix and cluster-like coarse globular Ti carbides at grain boundaries. It is considered that when a plane axis direction of the grain boundary surface containing the cluster-like Ti carbides is nearly at right angles to the plane axis direction of maximum shear stress against the tensile stress direction,¹⁴⁾ the brittle fracture may be caused by such brittle intergranular fracture.

In determining a heat treatment condition for the lower DBTT, we must keep in mind to obtain a microstructure in which second phase particles are as possible as dispersed within the grains.

5. Conclusions

The effect of the morphology of Ti carbide precipitates on the ductility of 30 mass% Cr ferritic steels containing C and Ti has been investigated. The different types of the morphology of Ti carbide precipitates were obtained by two kinds of heat treatment processes. Tensile tests were carried out at temperatures ranging from 77 K to RT. The tensile ductility was evaluated by transition temperatures in RA.

The results obtained are summarized as follows:

- (1) Aging after water quenching from the solution treating temperature gave rise to grain boundary precipitation of numerous fine Ti carbides, whereas furnace cooling from the solution treating temperature to the aging temperature produced uniformly dispersed coarse globular Ti carbide particles in the specimens with below 0.025%C, and also produced cluster-like coarse globular Ti carbides at grain boundaries in the specimens with above 0.037%C.
- (2) The DBTT for the specimen containing uniformly dispersed coarse globular Ti carbide particles is lower than that for the specimen containing numerous fine grain boundary Ti carbide precipitates.
- (3) The cluster-like coarse globular Ti carbides at grain boundaries caused the scatter band of the DBTT.
- (4) Initiation of microcracks for brittle fracture is considered to be caused by the intergranular fracture which is promoted by the decohesion at the interface between the matrix and many grain boundary Ti carbide precipitates and by the decohesion at the interface between the matrix and cluster-like globular Ti carbides at grain boundaries.

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