JOURNAL OF MATERIALS SCIENCE **32** (1997) 5005–5010

Superhardening behaviour of titanium treated Cr–Mo steel

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The effect of titanium on the hardening behaviour of medium carbon steel alloyed with chromium and molybdenum has been studied. It has been shown that the superhardening could be produced without superheating. The optimum titanium content for superhardening is between 0.03–0.05 wt%, and above this optimum level the hardening decreases with increasing titanium content. By dilatometry, it is shown that the optimum titanium content results in large hardness increases due to a strong retardation of the ferrite/pearlite and bainite transformations, this being particularly noticeable for the bainite transformation. However the superhardening behaviour weakens as the melting temperature is increased from 1550 to 1650 °C, and the superhardening effect completely disappears after a spheroidization annealing treatment.

1. Introduction

It is well known that the hardening behaviour of steels is related to their chemical compositions and austenite grain size [1–3]. However the use of deoxidants such as titanium and aluminium has been reported to have no marked effect on the hardening behaviour [1]. Brown and James [4] however have reported a remarkable increase in the hardness after superheating of the melt to 1650 °C. This phenomenon, called superhardening, has been shown to be dependent on the concentration of alloying elements in the steel. There exists a threshold alloying content which must be exceeded before the superhardening effect can be observed. In addition to superheating, Brown and James also reported that the superhardening effect only occurred at high deoxidant concentrations i.e., Al $\geqslant$ 0.05 wt %, or Ti $\geqslant$ 0.03 wt %.

Mostert and Van Rooyen [5] made a quantitative assessment of the hardness increase resulting from a superhardening treatment in terms of a superhardening multiplying factor. The value of this superhardening multiplying factor can be higher than 3 if the calculated critical diameter (D_I base) is larger than 170 mm (D_I base is the critical diameter calculated using the prediction system developed by Grossman [1]). This is larger than the multiplying factor obtained from boron treated steels [6–11]. In other words the superhardening treatment is a more powerful method to enhance the hardness of steel than boron additions.

Several attempts to describe the mechanism of superhardening have been reported in the literature [5, 12–14]. It has been proposed that a retardation in the ferrite growth rate or bainite transformation rate is largely responsible for the hardness increases resulting from a superhardening treatment. Superheating produces a more uniform distribution of alloy atoms in the solidifed steel. Carbon diffusion would be retarded by the randomly distributed carbide forming elements. The aluminium and titanium are considered to scavenge nitrogen and oxygen and prevent the segregation of nitrogen to the grain boundaries.

Although titanium has been shown to play an important role in superhardening, the investigated titanium content was *circa* 0.03 wt % [4]. In the present study, a wider titanium content, up to 0.2 wt % is investigated in order to elucidate the effect of higher titanium contents on the superhardening. In addition the effect of spheroidization annealing on the superhardening is also studied, since the Cr–Mo steel investigated in this study is extensively used in the cold forging industry. In general, before cold forging the steel must be softened by spheroidization annealing, and the effect of spheroidization annealing on superhardenability has not be investigated.

2. Experimental procedure

All the steels investigated in this study were melted in a vacuum induction furnace and cast into 110 × 110 mm square billets of 50 kg weight. The casts were either heated to 1550 °C or superheated to 1650 °C. They were forged into 30 mm diameter bars after being soaked at 1250 °C. Before the standard 25 mm Jominy hardness test specimens were made, the bars all underwent the same thermal treatment (normalizing) of 1 h at 870 °C followed by an air cooling. Jominy end quench tests were carried out after the samples had been austenitized at 845 °C. In addition to the Jominy end test curves, the hardness values were compared by reference to the distance from the quenched end to the HRC 43 position which will be referred to in future as J_{HRC} 43.

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The chemical compositions of the investigated steels were determined using the combustion method for carbon and sulphur, whilst the concentrations of all the other elements were obtained using a spark optical emission spectrometer. The samples used in the analysis were taken from the Jominy bars used in the hardness measurements.

The heating pattern for spheroidization annealing was a 2 h soak at 780 °C followed by cooling to 730 °C at a cooling rate of 240 °C h^{-1}, cooling to 680 °C at a cooling rate of 10 °C h^{-1} and finally a cool to room temperature at a cooling rate of 200 °C h^{-1}.

3. Results and discussion

3.1. Hardening without superheating

A series of casts were made to investigate the effects of titanium on the hardening behaviour. The base chemical composition (in wt %) is listed in Table I: C $\sim$ 0.41, Si $\sim$ 0.18, Mn $\sim$ 0.98, Cr $\sim$ 1.16, Mo $\sim$ 0.20 with titanium increasing from trace amounts to 0.22. All the 12 casts were made at a maximum melt temperature of *circa* 1550 °C, i.e., without superheating.

Three typical Jominy hardness curves are compared in Fig. 1 which illustrate that there is a highly significant increase in the hardness obtained by control of the titanium content. However it should be noted that the hardness does not always increase with titanium content, steel 12 with the highest titanium level of 0.22 wt % has a hardness value that is inferior to that of steel 7 that has a titanium content of 0.039 wt %. Fig. 2 shows the relationship between titanium content and hardening index (J_{HRC} 43) which as previously mentioned is the distance from the quenched end to the HRC 43 position on the Jominy end test bar. It is clear that the optimum titanium content for maximum hardenability is around 0.04 wt %, and that the hardness decreases if the titanium content exceeds this level. The maximum hardness obtained through control of the titanium content is remarkable in that from Fig. 2, the multiplying factor based on J_{HRC} 43 is near to 3.0 at a titanium content around 0.04 wt %. It is reported in the literature [4, 5, 14, 15] that in order to obtain superhardening, three essential conditions must be simultaneously satisfied: (a) the base composition must be such that a threshold level of

TABLE I Chemical compositions for the steels that did not undergo superheating

Steel number	Composition (wt %)								ASTM grain size
	C	Si	Mn	P	S	Cr	Mo	Ti	
1	0.41	0.20	0.96	0.014	0.011	1.14	0.20	–	7–8
2	0.42	0.19	0.97	0.015	0.011	1.15	0.20	0.011	7–8
3	0.41	0.20	0.96	0.014	0.011	1.14	0.20	0.017	7–8
4	0.41	0.20	0.97	0.014	0.010	1.15	0.20	0.024	8–9
5	0.41	0.18	0.98	0.014	0.010	1.16	0.20	0.026	8–9
6	0.41	0.18	0.99	0.014	0.010	1.16	0.20	0.031	8–9
7	0.41	0.18	0.98	0.014	0.011	1.16	0.20	0.039	8–9
8	0.41	0.18	0.98	0.014	0.010	1.15	0.20	0.050	8–9
9	0.42	0.19	0.99	0.016	0.010	1.17	0.21	0.077	8–9
10	0.42	0.19	0.99	0.015	0.011	1.17	0.21	0.120	8–9
11	0.42	0.18	0.98	0.015	0.010	1.17	0.20	0.170	8–9
12	0.42	0.18	0.98	0.015	0.010	1.17	0.21	0.220	8–9

(Fe balance)

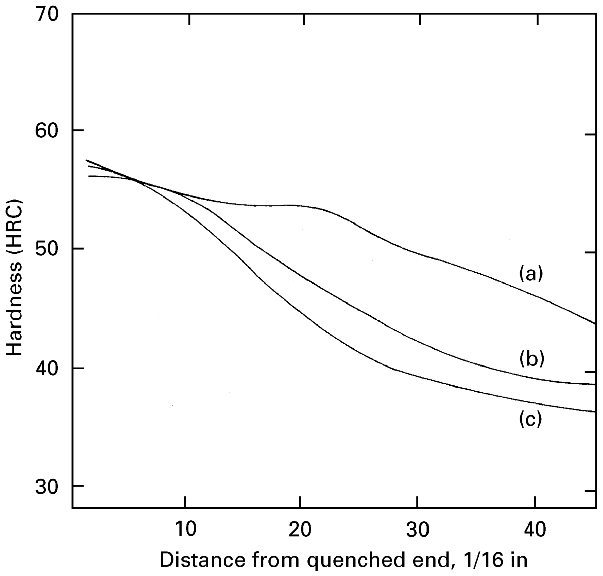

Figure 1 Jominy end test curves for Ti contents of (a) 0.039 wt %, (b) 0.22 wt % and (c) 0.011 wt %.

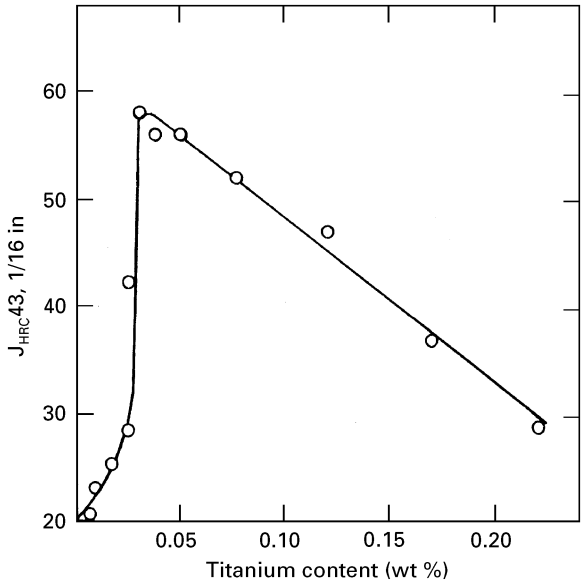

Figure 2 The relationship between the titanium content and the HRC43 distance on Jominy curve. (Without superheating).

TABLE II Chemical compositions for the steels that were superheated

Steel number			Composition (wt %)						ASTM grain size
	C	Si	Mn	P	S	Cr	Mo	Ti	
1	0.42	0.26	0.95	0.015	0.013	1.15	0.20	0.022	8–9
2	0.42	0.26	0.95	0.014	0.012	1.15	0.20	0.031	8–9
3	0.42	0.26	0.95	0.014	0.012	1.16	0.20	0.035	8–9
4	0.41	0.26	0.95	0.015	0.015	1.15	0.20	0.038	8–9
5	0.41	0.25	0.96	0.015	0.012	1.15	0.20	0.042	8–9
6	0.41	0.25	0.96	0.015	0.013	1.16	0.20	0.063	8–9
7	0.41	0.25	0.96	0.014	0.011	1.16	0.20	0.110	8–9
8	0.41	0.26	0.97	0.015	0.012	1.15	0.20	0.180	8–9

(Fe balance)

hardening is exceeded (b) the melt must be superheated above 1650 °C (c) the Al or Ti content must be higher than that needed solely for deoxidation, i.e., Ti > 0.03 wt %. However in this study, the superhardening phenomenon is observed without superheating at titanium contents of *circa* 0.04 wt % (see Fig. 2). Mangonon [16] has studied the effect of titanium addition on the hardening of vanadium modified AISI 4330, and reported that the addition of 0.04–0.05 wt % titanium lowered the hardening in alloys containing only vanadium, but raised the hardening when both Mo and V were present. Garbaz and Pickering [17] and Pickering [18] have reported that the addition of 0.04 wt % Ti to a 0.24 wt % C–0.21 wt % V–1.7 wt % Mn–0.4 wt % Si steel considerably increased the hardness and proposed that the increase in the hardness was created by pinning grain boundaries or the retardation of grain boundary movement during austenitization.

Fig. 2 indicates that the superhardening effects observed in the present study have two features that have not been previously reported [4, 5, 12–15]. These features are (a) superhardening can be obtained without superheating and (b) the degree of superhardening decreased as the titanium content exceeded 0.04 wt %. The steels used in the previously published papers had generally been aluminium treated [5, 13–15] whilst Brown and James [4] investigated steels containing ~ 0.04 wt % titanium. Thus the superhardening characteristics of steels with titanium levels above 0.04 wt % was not discussed in the work of Brown and James.

It has been suggested that superhardening may result from very fine carbide/nitride preciptates existing at the austenite grain boundaries before the transformation [5, 15]. The superhardening effect decreases at higher titanium contents (Ti > 0.04 wt %) as is shown in Fig. 2 which is probably related to the particle size distribution of the TiN and TiC precipitates. There should be an optimum particle size distribution for the TiN/TiC which is favourable for grain boundary pinning and/or retardation of the transformation.

3.2. Hardening with superheating

We have so far discussed the hardening of steels at the normal melting temperature of 1550 °C. In order to investigate the effect of a high melting temperature, i.e., superheating, on hardening, a series of casts were made at a melt temperature of 1650 °C. The analysed chemical compositions are listed in Table II and comparison of these results to those contained in Table I shows that the basic chemical compositions are very similar.

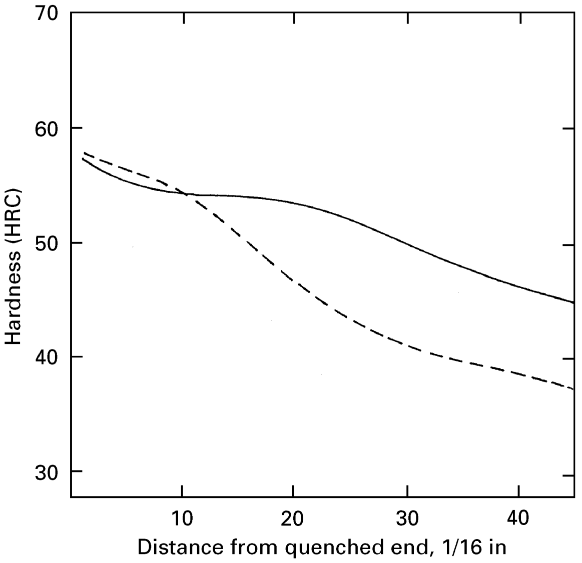

Figure 3 Jominy end test curves of two steels having Ti contents of 0.031 wt % melted at; (—) 1550 °C and (---) 1650 °C.

The result of a Jominy end hardness test performed on steel no 2 which has a titanium content of 0.031 wt % is plotted in Fig. 3 (dotted line), the solid line represents the result for steel No. 6 in Table I which has the same titanium content but did not undergo the superheating. From Fig. 3 it is obvious that after the superheating treatment, the hardness decreased. Fig. 4 shows the relationship between titanium content and J_{HRC} 43 and the dotted line represents the results obtained without superheating that were previously plotted as Fig. 2. From Fig. 4 two conclusions may be drawn. (a) the maximum hardness values are obtained at titanium contents of *circa* 0.04 wt % (b) there is a significant decrease in the hardening behaviour after superheating a result which differs to all other previously reported investigations [4, 5, 12–15] in which superheating significantly increased the hardness. On the basis of the experimental

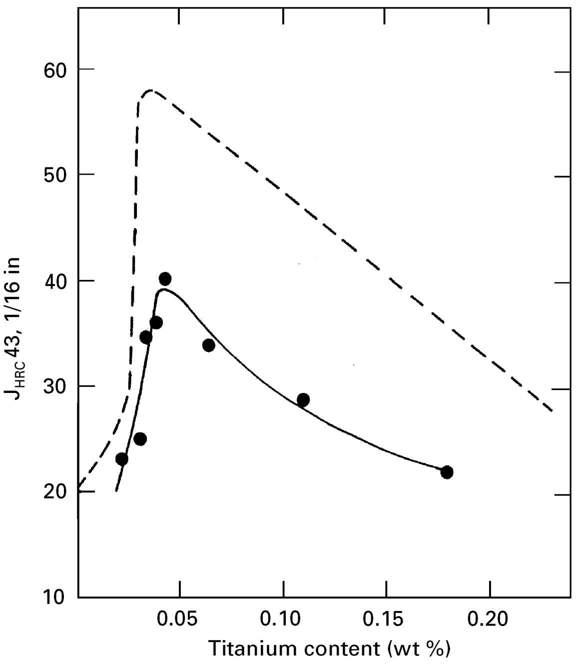

Figure 4 The relationship between the titanium content and HRC43 distance on the Jominy curve. (With superheating). Melted at ● 1650 °C and --- 1550 °C.

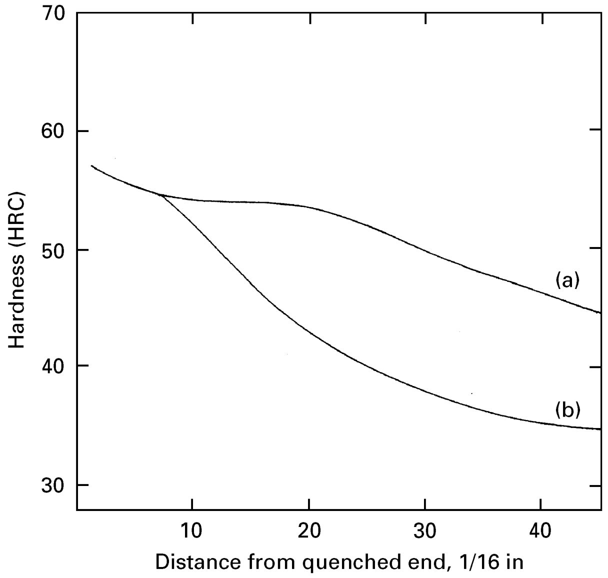

Figure 5 Jominy end test curves for steel with a titanium content of 0.031% (a) without and (b) with spheroidization annealing.

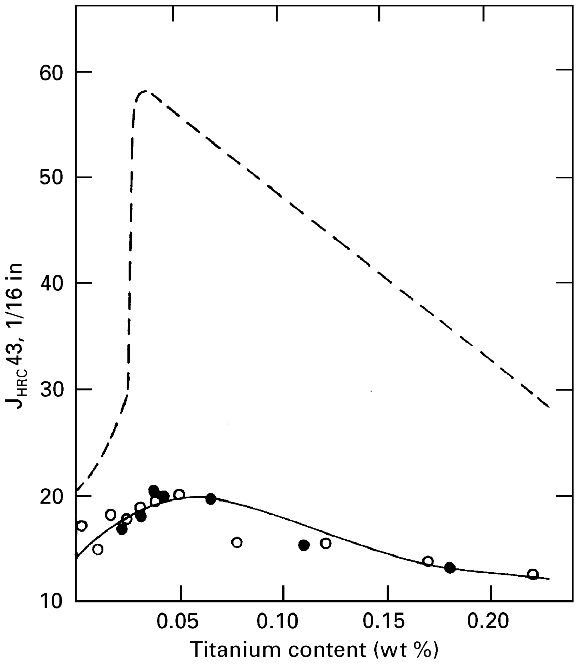

Figure 6 The relationship between titanium content and HRC43 distance on Jominy curve for (—) with and (---) without spheroidization annealing. ● With superheating, ○ without superheating.

results in the present study that suggest that superheating results in a decrease of the hardness, it is proposed that the presence of some specific type of TiC/TiN precipitates, and also a specific size distribution of these precipitates is a necessary prerequisite for the superhardening phenomenon. Superheating itself is not a necessary condition for superhardening.

3.3. Hardening after spheroidization annealing

In order to investigate the effect of spheroidization annealing on the superhardening, all the steels listed in Tables I and II were spheroidized after normalization and then the samples were investigated using Jominy end tests. The heating pattern for the spheroidization annealing has been discussed at an earlier point in this paper.

The results of Jominy end tests on samples both with and without spheroidization annealing (SA) for steel no. 6 in Table I are displayed in Fig. 5. The hardening is significantly decreased after the spheroidization annealing. In detail, Fig. 6 shows the relationship between the titanium content and $J_{HRC}43$, open circles representing steels without superheating. Clearly, in Fig. 6, whether the steels are superheated or not the superhardening phenomenon completely disappears if the steels are spheroidization annealed before the Jominy end test is performed. Fig. 7(a and b) displays the optimal microstructure of steel no. 6 in Table I in the as normalized and spheroidized states, respectively. In Fig. 7a, the results after normalization, the microstructures mainly consist of bainite and martensite with a hardness value HRC 41. In Fig. 7b, which shows the sample after spheroidization annealing, the microstructure mainly consists of ferrite and spheroidized carbides, with a hardness value HRB 85. In general, a spheroidization treatment is related to the diffusion of carbon thus some carbides will dissolve and/or coarsen after treatment [19]. The suppression of superhardening after spheroidization is probably associated with the dissolution and/or coarsening of TiC/TiN precipitates which results in some precipitate morphology or particle size distribution which offset the effectiveness of grain boundary pinning.

3.4. Continuous cooling transformation diagrams

The influence of superhardening on the transformation characteristics was also investigated. A continuous cooling transformation (CCT) diagram of steel

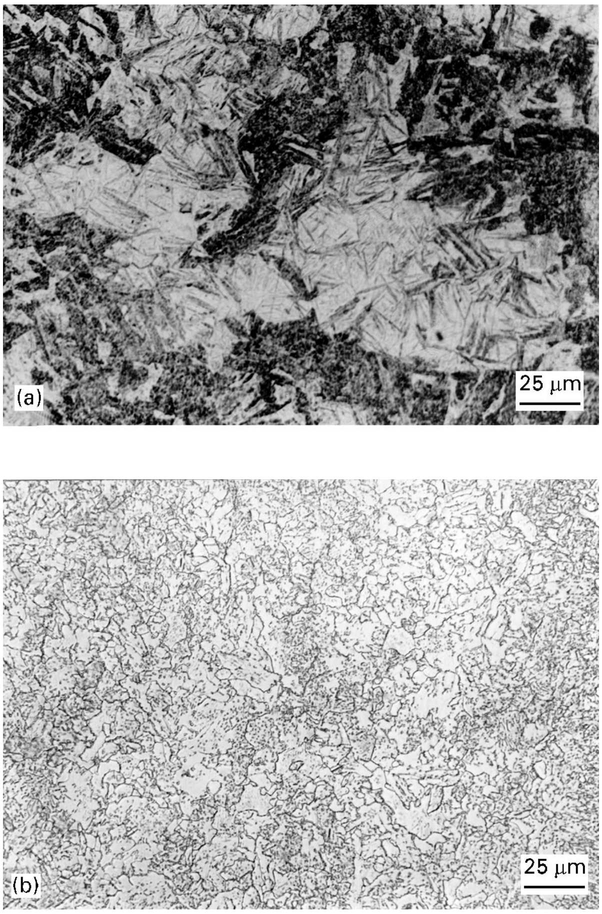

Figure 7 Optical microstructures, (a) as normalized (b) as spheroidized.

6 in Table I (with a Ti content of 0.031 wt %) having the maximum observed hardening was compared to that of steel 1 in Table I (with no Ti addition) by using a dilatometer. The samples for this investigation were hollow cylinders with an outside diameter of 4.9 mm, an inside diameter of 3.5 mm and 13 mm in length. The samples were austenitized in a vacuum chamber at 850 °C for 15 min followed by cooling to room temperature at various cooling rates.

Fig. 8 shows the results obtained using the dilatometer where the dotted line is the steel without any titanium addition and the solid line is the steel with a 0.031 wt % titanium content. It appears that the superhardening produced by the titanium addition displaces the ferrite bay and bainite bay to longer times, e.g., the critical cooling rate for ferrite start nose being about 0.5 °C s^{-1} for the steel without any titanium is retarded to 0.9 °C s^{-1} for the steel with the 0.031 wt % Ti content. The critical cooling rate for bainite start nose is also retarded from 2.6 to 11.0 °C s^{-1} by the superhardening. It is clear from Fig. 8 that the retardation of the transformation is more pronounced in bainite than in ferrite which is probably related to the point that a certain level of calculated hardenability is required for superhardening. Grolbler and Rooyen [13] have, through a comparison of isothermal time–temperature-transformation (TTT) diagrams, reported that the bainite transformation is retarded to a greater extent than that of the ferrite transformation. On the other hand a study of Sachs *et al.* [12] indicated that a retardation of the ferrite growth rate is primarily responsible for the superhardening effect.

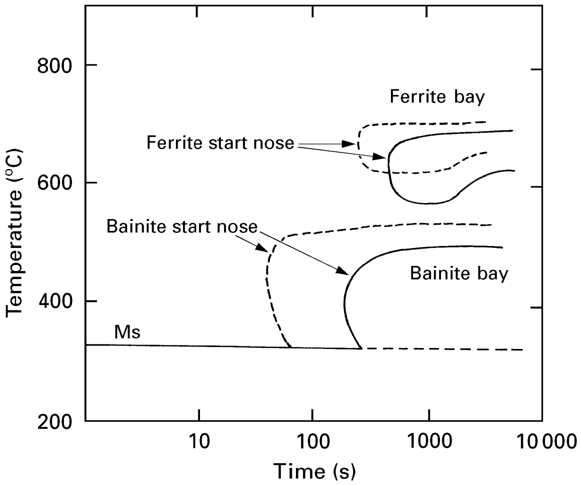

Figure 8 Continuous cooling transformation curves for titanium contents of (- -) trace amounts and (—) 0.031 wt %.

Fig. 8 also shows that superhardening does not change the basic shape of the CCT diagram, it merely displaces the curve to longer times. Also a slight lowering of the ferrite and bainite transformation temperatures are observable, with that for the bainite transformation being greater.

4. Conclusions

An attempt has been made to investigate the effect of additions of titanium on the hardening behaviour of medium carbon Cr–Mo steel. The following conclusions can be drawn:

(1) Superhardening occurs at an optimum titanium level of *circa* 0.04 wt %.

(2) If the titanium content exceeds 0.04 wt %, then the superhardening effect gradually decreases.

(3) Superheating drastically decreases the hardening of Ti treated Cr–Mo steels which differs to all other previously reported investigations that suggest that superheating is a necessary condition for superhardening.

(4) The superhardening behaviour completely disappears after spheroidization annealing.

(5) The retardation of the bainite transformation produced by the titanium addition is more noticeable than the retardation of the ferrite transformation.

Acknowledgement

The author is grateful to the China Steel Corporation for permission to publish this paper.

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Received 4 January 1995
and accepted 21 October 1996