The effect of alloying elements on the structure and mechanical properties of ultra low carbon bainitic steels

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Microalloying with Nb and B leads to a granular bainite microstructure which is composed of a bainitic ferrite matrix and a uniformly distributed martensite/austenite-constituent in the as-rolled condition. Due to this transformation strengthening mechanism, high strength and toughness could be achieved even though the C content was extremely low. It was found that both dissolved Nb in austenite and free B are prerequisites for granular bainite formation. Furthermore, there is a critical B content to achieve the complete bainitic transformation strengthening effect. The critical B content increases with C content. C thus diminishes the effect of B in promoting bainite transformation, due to the formation of boron carbides or the depletion of dissolved Nb in austenite. The effect of Mn, Mo and Ni on the decomposition of austenite is similar. A parameter "*Mneq*" which relates the effect of these alloying elements on the Bs temperature was derived. It was confirmed that the strength of bainitic steels is inversely proportional to the *Bs* temperature.

1. Introduction

With the discovery of huge energy resources in the Arctic region, the demand for large diameter pipelines to transport oil and gas through severe environments is increasing. Furthermore, in order to improve the transportation efficiency, larger diameter pipelines operating at higher pressures are desired. As a result, the specification for linepipe steels, including strength, low temperature toughness, weldability and resistance to hydrogen-induced cracking, becomes more and more critical. Consequently, the conventional microalloyed ferrite and pearlite steels are unable to achieve these requirements [1]. On the other hand, the potential effect of minute additions of B on the decomposition of austenite and the associated strengthening mechanism could provide an effective way to improve the properties of steels. During the last two decades, a series of ultra low C bainitic steels (ULCB) have successfully been developed with the application of controlled rolling and microalloying technology [2–6]. Due to their high strength, high toughness, good weldability and superior resistance to hydrogen-induced cracking, these kinds of steels have been successfully applied not only in the construction of transmission pipelines but also in some other critical applications, such as the HY-80 alternative for warship construction [7] and automobile bumpers and frames [8, 9].

Basically, these steels were microalloyed with 0.045 wt% Nb and 15 p.p.m. B. Accompanied with a high Mn content, the granular bainite structure can be obtained in the as-rolled condition. In order to protect B from the formation of BN, Ti was added to fix nitrogen as TiN. The matrix structure then consists of bainitic ferrite laths with a very high dislocation density, which is introduced due to the plastic relaxation of invariant plane strain associated with the bainitic transformation [10]. Besides, the high C second phase is mainly composed of a martensite/austenite constituent (M/A-constituent) [2–6]. As a result, a significant strengthening effect arises due to these transformation structures. This type of structure has been named granular bainite by Habraken *et. al.* [11] due to the granular morphology of the M/A-constituent or carbide free bainite designated the B1 structure by Ohmori [12].

As described above, the strengthening mechanism is attributed to the amount of bainite and the dislocation density within the bainitic ferrite matrix. This is quite different from the conventional ferrite–pearlite steels which rely mainly on ferrite grain refinement and precipitation hardening. Therefore, the effects of rolling processes and chemical composition on the properties of ultra low C bainitic (ULCB) steels may be different from that of conventional ferrite–pearlite steels. The major purpose of the present work was to evaluate the effect of chemical composition on the decomposition of austenite and the resultant microstructure and properties of ULCB steels.

2. Experimental procedure

The experimental steels were prepared from 250 kg vacuum melts and cast as 160 × 160 mm square ingots.

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The chemical compositions are listed in Table I. Steels A–D varied in B and Nb content and were used for evaluation of their effect on the decomposition of austenite. Steels E–L varied in B content and were designed to evaluate the effect of B content on the properties of steels. Steels M–P, Q–T, U–V and W–X varied in C, Mn, Mo and Ni contents, respectively.

Before rolling, the steels were heated at 1150 °C for 2 h. During rolling the temperatures were measured using an optical pyrometer. The finish rolling temperature was controlled to around 780 °C. This was achieved by adjusting the slab temperature when the thickness was reduced to 45 mm. The rolling reduction per pass was around 20 % and the final plate thickness was 15 mm.

In order to measure the continuous-cooling-transformation (CCT) diagram of the experimental steels, 12 mm long tube specimens with 3 mm inside diameter and 5 mm outside diameter were machined along the longitudinal direction of the plates. The specimens were heated at 950 °C for 5 min and then cooled down to ambient temperature at various cooling rates ranging from 0.15 °C s^{-1} to 30 °C s^{-1} in a dilatometer. From the transformation points of each cooling curve and observation of the transformed microstructure, the CCT curves of experimental steels can be obtained.

The specimens used for microstructural evaluation, including optical microscopy and scanning electron microscopy (SEM), were mechanically polished and etched in a 3 % nital solution.

For the tensile test, the specimens were sectioned in both the transverse and longitudinal directions of the plates. The tensile specimens were 12.5 mm in diameter in reduced area and 50 mm long in gauge length.

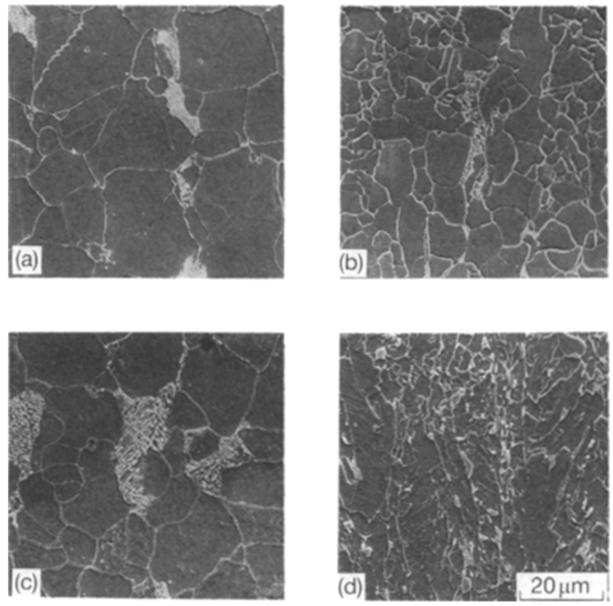

Figure 1 SEM micrographs of as-rolled steels: (a) steel A, Nb, B-free steel; (b) steel B, microalloyed with 0.053% Nb; (c) steel C microalloyed with 17 p.p.m. B; (d) steel D, microalloyed with 0.046 Nb and 17 p.p.m. B.

For toughness evaluation, the standard V-notch Charpy impact test specimens were sectioned in the longitudinal direction of the plates. The impact transition temperatures (ITT), defined as the temperatures where the absorbed energy equals 100 J were also determined.

3. Experimental results and discussion

Fig. 1 shows the SEM micrographs of as-rolled steels with similar base compositions but different Nb and B

TABLE I. The chemical compositions of experimental steels (wt %)

Steel	C	Si	Mn	P	Al	Ti	Nb	Mo	Ni	S[a]	B[a]	N[a]
A	0.029	0.16	1.84	0.013	0.019	0.016	-	-	-	25	0	32
B	0.028	0.15	1.80	0.010	0.008	0.008	0.053	-	-	33	0	50
C	0.026	0.16	1.81	0.015	0.020	0.018	-	-	-	44	17	33
D	0.021	0.16	1.77	0.014	0.020	0.020	0.046	-	-	34	17	28
E	0.038	0.15	1.78	0.012	0.025	0.017	0.054	-	-	43	9	34
F	0.038	0.15	1.80	0.011	0.017	0.017	0.053	-	-	43	14	34
G	0.040	0.17	1.84	0.014	0.017	0.020	0.048	-	-	42	30	24
H	0.040	0.17	1.84	0.014	0.017	0.020	0.048	-	-	42	49	24
I	0.022	0.17	1.87	0.011	0.022	0.021	0.052	-	-	42	9	32
J	0.022	0.16	1.84	0.011	0.015	0.020	0.053	-	-	42	13	32
K	0.019	0.16	1.83	0.011	0.024	0.021	0.053	-	-	45	28	23
L	0.019	0.17	1.84	0.011	0.019	0.021	0.051	-	-	45	50	23
M	0.030	0.16	1.82	0.013	0.009	0.016	0.046	-	-	45	16	27
N	0.039	0.17	1.82	0.013	0.009	0.018	0.047	-	-	50	15	28
O	0.050	0.16	1.83	0.014	0.034	0.020	0.046	-	-	50	16	25
P	0.056	0.17	1.84	0.014	0.034	0.021	0.047	-	-	47	17	28
Q	0.029	0.17	1.71	0.011	0.016	0.020	0.049	-	-	46	17	26
R	0.029	0.16	1.62	0.011	0.019	0.020	0.049	-	-	46	18	26
S	0.029	0.16	1.52	0.013	0.022	0.018	0.049	-	-	44	16	36
T	0.029	0.16	1.41	0.013	0.021	0.018	0.044	-	-	44	18	35
U	0.034	0.16	1.46	0.011	0.024	0.018	0.054	0.15	-	56	22	34
V	0.034	0.16	1.44	0.011	0.017	0.017	0.053	0.35	-	42	17	26
W	0.029	0.17	1.45	0.011	0.011	0.020	0.052	-	0.15	42	20	30
X	0.029	0.17	1.45	0.011	0.011	0.019	0.052	-	0.30	42	20	30

[a] S, B and N in p.p.m.

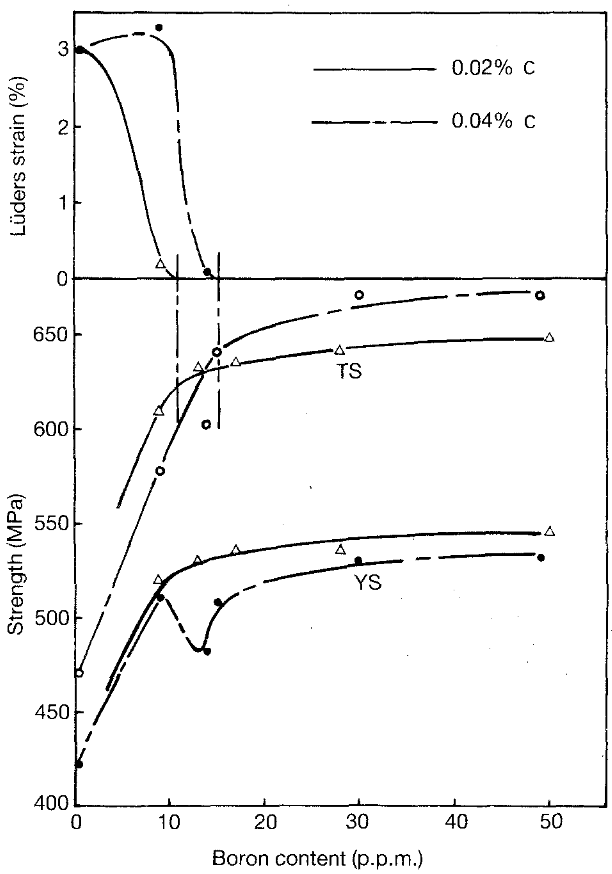

Figure 2 Variation of tensile properties of as-rolled experimental steels with B content.

contents. When neither Nb nor B was added, the structure was found to be ferrite and pearlite. With 0.053 wt % Nb (Fig. 1b), no change in the structure was found except for ferrite grain refinement. Similarly, when 17 p.p.m. B was added without Nb (Fig. 1c), the matrix structure remained ferritic but the morphology of pearlite degenerated. The possible mechanism for this change in pearlite morphology could be that B displaces the Acm line significantly to the lower C side because the solubility of B in cementite is higher than that in austenite [13]. Consequently, cementite formation in austenite would be accelerated, whereas the rate of ferrite nucleation is reduced by B. As a consequence, the cooperative growth of lamellar cementite and ferrite is depressed. Therefore (Fig. 1c), the morphology becomes that of degenerated pearlite. Only when both 0.046 % Nb and 17 p.p.m. B were added together was the desired granular bainite structure obtained (Fig. ld). This consists of a bainitic ferrite matrix and a uniformly distributed small granular-shaped light etching phase, which was identified as a constituent composed of martensite and austenite [13–15]. In addition, several straight markings arrayed along the rolling direction, which are considered to be prior austenite grain boundaries (PAGB), can easily be visualized in the structure. The shape of the prior austenite grains is pancaked because the recrystallization of deformed austenite was retarded by Nb(C, N) [14].

There is therefore a synergistic effect between Nb and B for granular bainite formation. It has been proposed [2] that a certain amount of dissolved Nb in austenite is required to enhance the hardenability effect of B. Several possible mechanisms have been proposed to account for the prominent synergistic effect of Nb and B. First, Nb can retard the recrystallization of deformed austenite and thus stabilize the austenite grain boundaries by preventing fresh boundary formation during recrystallization. B then has sufficient time to diffuse to the austenite grain boundaries and prevent the formation of ferrite [15]. Secondly, Nb can decrease the diffusivity and activity of C in austenite. Therefore, the dissolved Nb in austenite might protect B from the formation of B carbide, such as Fe_{23} (C, B)$_6$ [16]. Thirdly, dissolved Nb in austenite itself has a profound effect in the prevention of ferrite formation [16, 17]. More work is needed before the real mechanism can be clarified.

Fig. 2 shows the effect of B content on the tensile properties of two series of steels with different C content. It can be seen that the strength level of B-free steel is very low due to its ferrite–pearlite structure and extremely low C content. However, when the steels were slightly microalloyed with B, a significant strengthening effect resulting from bainitic transformation can be observed. Moreover, the Lüders strain decreases dramatically with B content. Besides, there were obvious transition points on the strength versus B content curves and these points are essentially close to the B content where the Lüders strain is completely eliminated. For greater B contents, the strengthening effect is saturated. A concentration just high enough to eliminate the Lüders strain (Fig. 2) may be judged as the critical B content to achieve the desired bainitic transformation and the associated strengthening effect. The critical B content is dependent on the C content of steel. It is around 11 p.p.m. when the C content is 0.02 wt %, and increases to 15 p.p.m. when the C content increases to 0.04 wt %. The mechanisms for the reduced B effect at higher C contents could be attributed to the formation of boron carbides, such as Fe_{23} (C, B)$_6$, which consume B. Alternatively, the high C content may promote Nb(C, N) precipitation and thus reduce the dissolved Nb in austenite. Therefore, the synergistic effect of dissolved Nb and B must decrease.

Fig. 3 shows the variation of upper shelf energy and ITT with B content. The ITT of B-free steel is lowered to − 120 °C due to its extremely low C content. When the steels are microalloyed with B, a significant strengthening effect associated with bainitic transformation is obtained, while the toughness is only slightly reduced. However, the deterioration in toughness becomes serious when the B content is over 40 p.p.m. The reason for this remarkable deterioration in toughness is probably boron carbide precipitation along the PAGB.

Fig. 4 shows SEM micrographs of steels microalloyed with a similar level of Nb and B but with different carbon contents. Again, an adverse effect of C on the hardenability of granular bainite transformation can be found. When the C content increases, the amount of polygonal ferrite increases dramatically. This polygonal ferrite mainly resides at

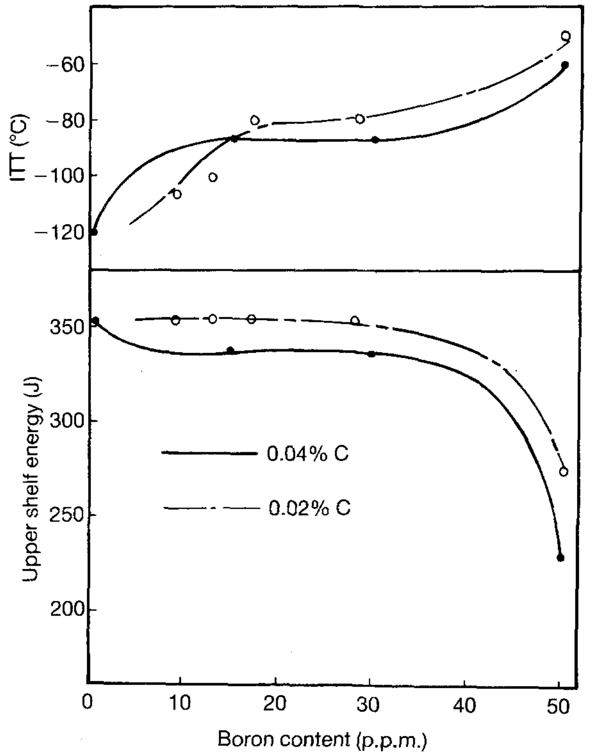

Figure 3 Variation of upper shelf energy and ITT with B content.

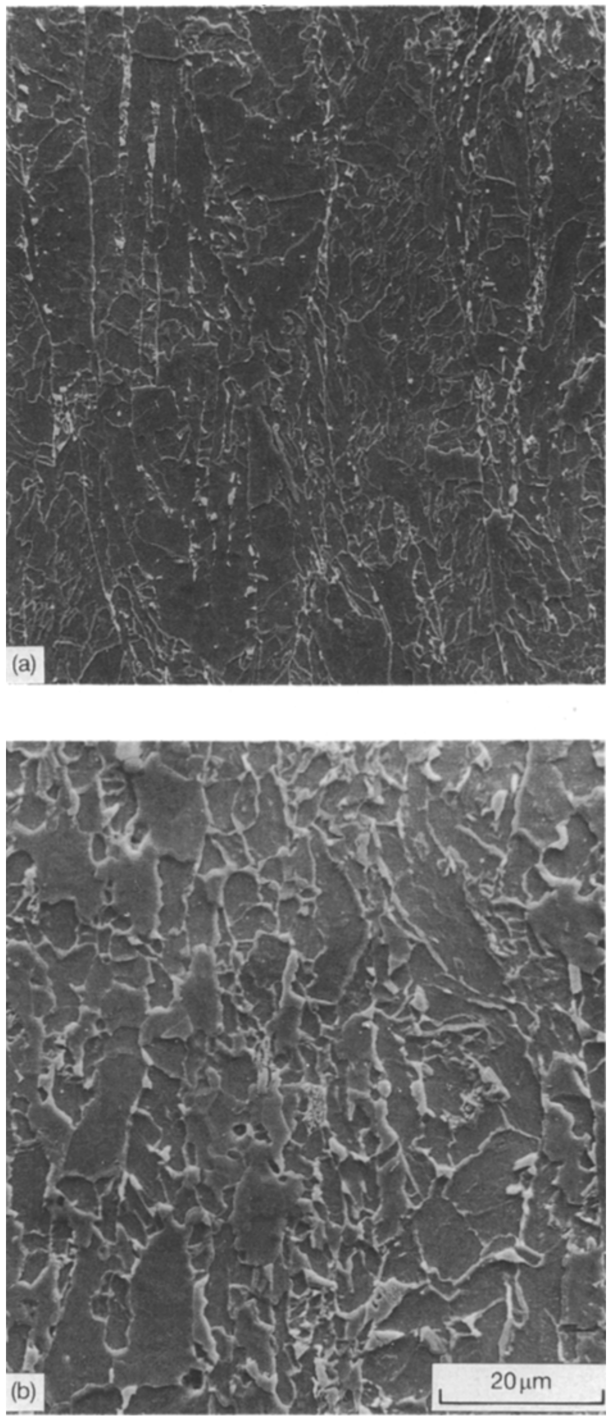

Figure 4 SEM micrographs of as-rolled experimental steels D and N with 0.021 % C and 0.039 % C, respectively. (a) steel D; and (b) steel N.

the PAGB where the stored strain energy due to rolling was larger. Therefore, the straight markings of PAGB gradually disappear with increasing C content. Furthermore, the M/A-constituent gradually degenerates into pearlite with increasing C content.

Fig. 5 shows the effect of C content on the mechanical properties of steels with similar Nb and B contents. The yield strength decreases with increasing C content due to the decrease in hardenability and the consequent larger amount of allotriomorphic ferrite. However, the tensile strength increases with C content. This is attributed to the increment in the amount of second phase. A decreasing C content results in a significant beneficial effect on the impact toughness (Fig. 5).

Other alloying elements which can delay ferrite formation, such as Mo, Mn and Ni, are also needed to achieve granular bainite. These elements can alter the transformation temperature and consequently the mechanical properties of granular bainite. Fig. 6 shows the CCT diagrams of three experimental steels with different Mo contents. It is clear that in these three steels ferrite and bainite have their separate transformation C-curves. When the Mo content is increased, the C-curve associated with ferrite transformation is delayed to longer times. On the other hand, the Bs temperature decreases significantly with increasing Mo content.

Fig. 7 shows the variation of Bs temperature and critical cooling rate, determined from CCT diagrams, as a function of Mn, Mo and Ni content. Mo is the most effective in decreasing the Bs temperature and the critical cooling rate to avoid ferrite transformation. A parameter "Mn equivalent" (*Mneq*) which relates the effect of various alloying elements to Bs can be derived as

$$Mneq\,(\%) = \mathrm{Mn} + 3.43\mathrm{Mo} + 0.56\mathrm{Ni}$$

and the decrement in Bs temperature can be related to the increment in *Mneq* as

$$\mathrm{Bs}\,(^{\circ}\mathrm{C}) = -\,36.6(Mneq)$$

It is well known that both yield strength and tensile strength of bainitic steels are closely related to their transformation temperature [18–20]. Fig. 8 shows the effect of decrement in Bs temperature by alloying on the increment of tensile and yield strengths, and a good linear relation can be found. Every 10 °C decrease in the Bs temperature results in 15.1 and 15.7 MPa increments in yield and tensile strengths, respectively. This increment in strength by depressing the bainitic transformation temperature is independent of alloying element. Therefore, the effect of alloy content on the strength of steels with granular bainite structure can be related to their effect on the Bs temperature, i.e. the parameter *Mneq*. For every 1 wt % increment in *Mneq*, the increment in yield and tensile strengths is 55.3 and 57.5 MPa, respectively.

Although the contribution of Mn, Mo and Ni to the Bs temperature and strengthening effects of granular bainite steel can be correlated by a single parameter *Mneq*, their effect on the toughness is quite different. Fig. 9 relates the change in ITT to the increment in tensile strength due to alloying with various elements. It can be seen that Mn has no effect on ITT. The effects of Mo and Ni on toughness are opposite. Although the effect of Mo on the strengthening of steels is about 3.4 times that of Mn, the deterioration in toughness is remarkable. The strengthening effect of Ni is comparatively minor, but it is beneficial to toughness.

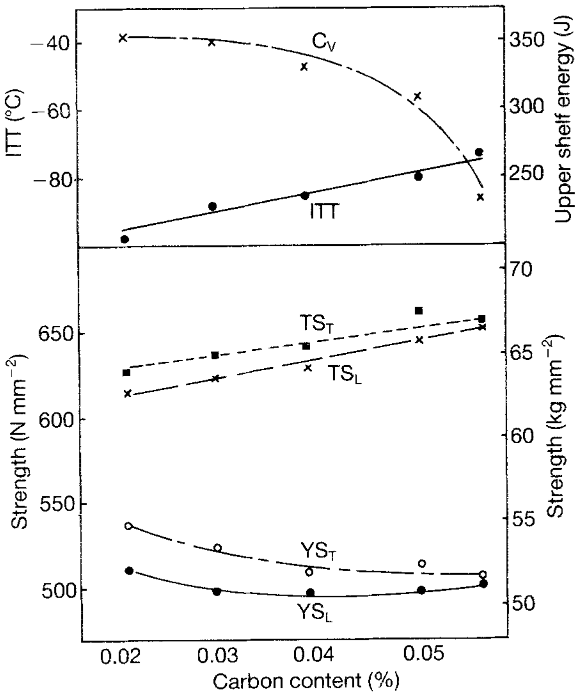

Figure 5 Variation of mechanical properties with C content.

4. Summary and conclusions

Microalloying with Nb and B gives a granular bainite microstructure composed of dislocated bainitic ferrite and a M/A-constituent in the as-rolled condition. High strength and toughness could be achieved with this granular bainite structure, even at low C content. It was found that both dissolved Nb in austenite and free B are prerequisites for granular bainite formation. Furthermore, there is a critical B content to achieve the desired bainitic transformation and the associated strengthening effect. The critical B content increases with increasing C content. On the other hand, C was found to promote polygonal ferrite formation for

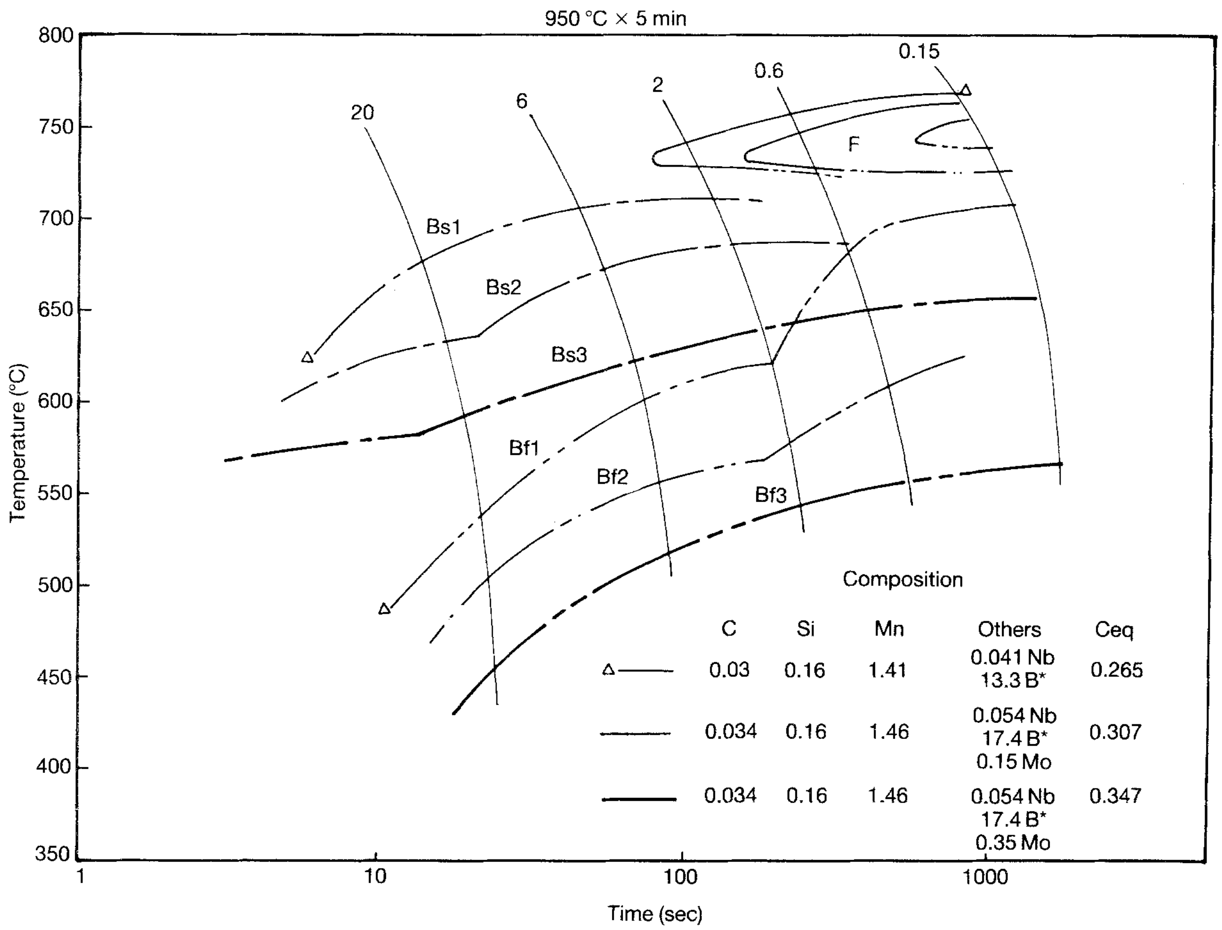

Figure 6 The continuous cooling transformation diagram of steels with different Mo content.

* Parts per million.

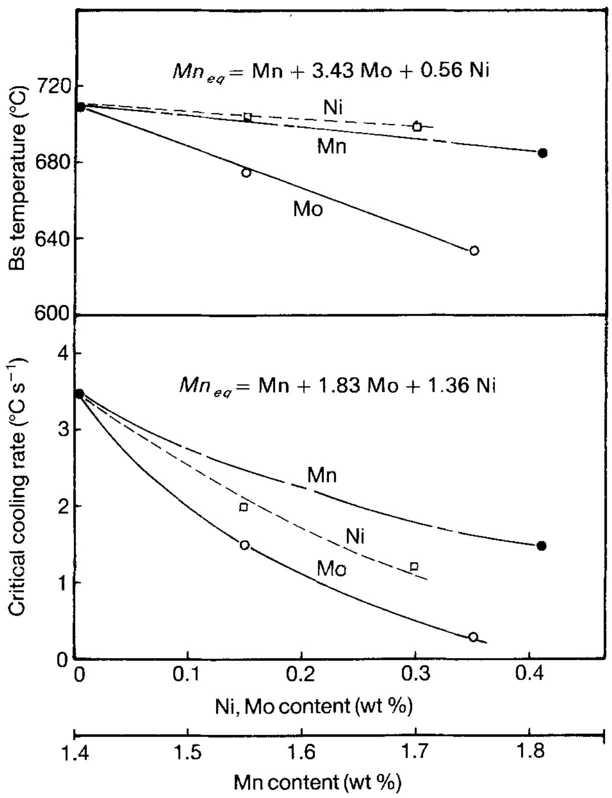

Figure 7 Variation of critical cooling rate to avoid ferrite formation and Bs temperature with Mn, Mo and Ni content.

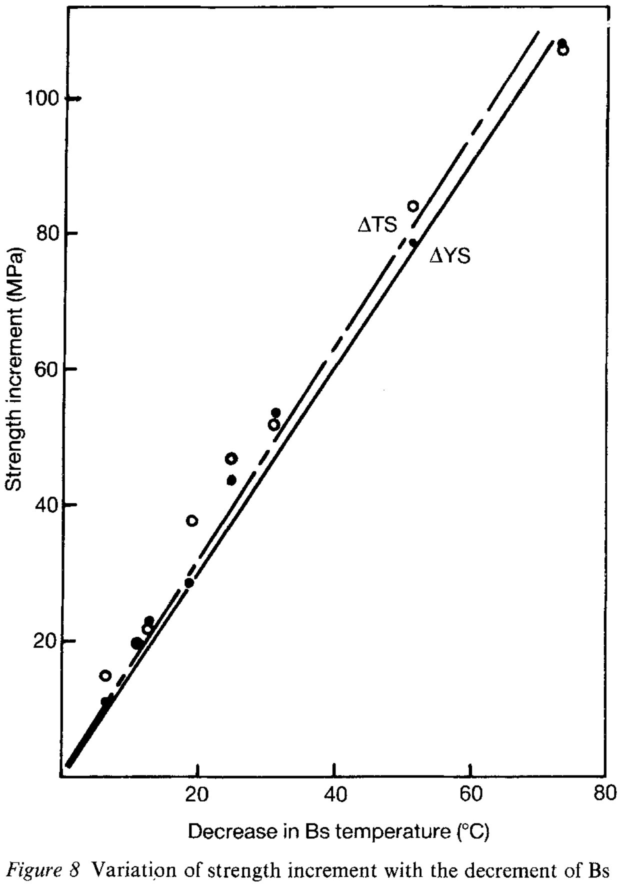

Figure 8 Variation of strength increment with the decrement of Bs temperature due to alloying with Mn, Mo and Ni.

steels with a similar Nb and B content. Consequently, the yield strength of steels decreases with increasing C content. These results indicate that C might diminish the effect of B for bainitic transformation due to the

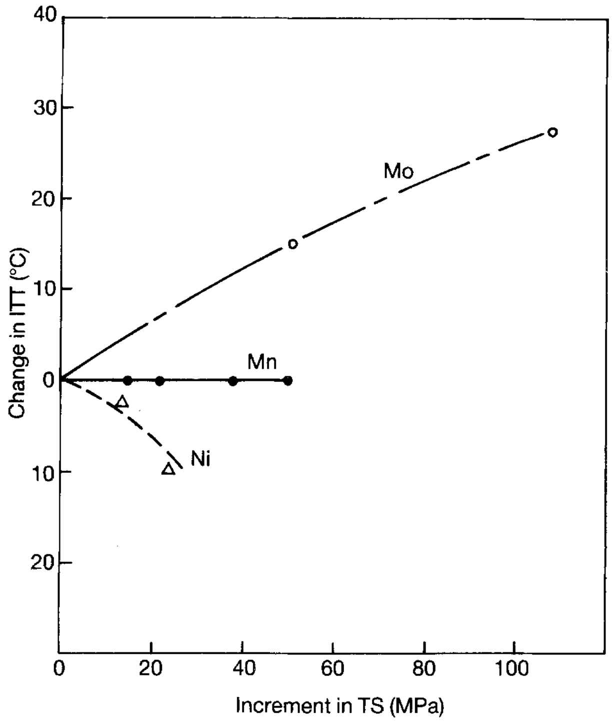

Figure 9 Variation of change in ITT with tensile strength increment due to alloying with Mn, Mo and Ni.

formation of boron carbide and/or the depletion of dissolved Nb in austenite. The effects of Mn, Mo and Ni on the decomposition of austenite are similar. They were found to delay the polygonal ferrite transformation and depress the transformation of bainite to a lower temperature. A parameter *Mneq* was proposed to relate the effect of these alloying elements to the Bs temperature. The strengthening contribution from these alloying elements was found to be linearly proportional to the resulting decrement in Bs temperature. Every 1% increment in *Mneq* resulted in a 36.6 °C decrement in Bs temperature, and consequently 55.3 and 57.5 MPa increments in yield and tensile strengths, respectively. These alloying elements had different effects on toughness. Mn exhibited no effect on the toughness, whereas Mo decreased and Ni improved the toughness of ULCB steels remarkably.

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