JOURNAL OF MATERIALS SCIENCE 11 (1976) 1200–1206

The Rockwell C hardness of quenched high-purity iron-carbon alloys containing 0.09 to 1.91% carbon

A. LITWINCHUK[†], F. X. KAYSER, H. H. BAKER
Ames Laboratory ERDA and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa, USA

A. HENKIN
Mechanical Engineering Department, Iowa State University, Ames, Iowa, USA

The Rockwell C hardnesses of thirteen high-purity iron–carbon alloy specimens that had been brine-quenched from temperatures in the austenite region to room temperature were measured. The hardness versus wt % C curve exhibits a maximum value of ~65.5 R_c near 0.9% C. The decrease in hardness at carbon concentrations >0.9% is the result of a rapid increase in the volume fraction of retained austenite. Attention is called to the desirability of using these or similar data in materials texts to illustrate this structure–property relationship.

1. Introduction

Nearly eighty years have passed since Brinell first demonstrated the importance of quantitative measurements of the indentation hardness of steels [1]. Even today, however, reliable hardness data do not exist for plain-carbon steels quenched to microstructures of martensite and retained austenite (such hardnesses to be referred to hereafter as H(Q)) and covering the entire composition range from 0 to ~2% C*. Excellent data are, of course, available over the carbon range of interest in commercial steels, that is from about 0.1 to 0.7% [2–6]. Moreover, qualitatively correct representations of the shape of the H(Q) versus wt % C curve have been in the literature for years [7–9]. Unfortunately, still other sources report hardness values that are incorrect in magnitude and/or misrepresent the shape of the curve [10, 11]. The latter problem arises if one fails to document the effect on the hardness of increasing volume fractions of the softer phase – austenite, which are retained in the higher carbon alloys. The rather shoddy treatment this subject matter is accorded in many present-day materials texts is an inevitable result of the above noted complications.

We report here Rockwell C hardness measurements that were made at 23° C on a set of brine-quenched specimens containing from 0.09 to 1.91% C. Excepting the presence of a trace amount of boron, these were otherwise high-purity iron-carbon alloys. The boron was added to enhance the hardenability of those alloys with $\gtrsim$ 1% C [4, 12, 13]. This made possible the preparation of a specimen set all of whose members could be quenched to aggregates of martensite and retained austenite while at the same time being of sufficient size to permit both precision density and hardness measurements. An obvious advantage of adding boron to improve the hardenability rather than, say, nickel is that the optimum boron concentration is so small as to leave the hardness and density unaffected. For the sake of uniformity, an identical amount of boron was added

---

*All carbon concentrations are given in weight percent.

[†] Present address: Supervisor of Special Analytical Services at the Detroit Diesel Allison Division of General Motors Corp., Detroit, Michigan 48228, USA.

to each of the alloys. Density measurements made on spheroidize-anneal specimens prepared from most of these same alloys have been given elsewhere [14]. The density data obtained from the as-quenched specimens will be presented in a separate paper [15].

2. Alloy and specimen preparation, metallographic examination

Specimens were prepared from thirteen rods of various iron–carbon alloys. Alloy preparation began with multiple arc-meltings (under helium) of preweighed quantities of arc-melted electrolytic iron† and spectroscopically pure carbon. A 20 ppm charge addition of 99.4% pure boron was made to each alloy in the next-to-last melt sequence. The shape of the final mould cavity was such as to produce a 16 cm long bar with a nearly circular cross-section that was approximately 1.5 cm in diameter. Each bar was given a vacuum homogenizing anneal then rotary swaged directly from the homogenizing temperature to a 1.1 cm diameter rod. The homogenizing anneals were as follows: alloys with $<1\%$ C were held at 1000° C for 72 h; those with $>1\%$C were held at 1150° C for 72 h.

Several specimens, 5 cm long and with the diameters listed in Table I, were lathe turned from each rod. The specimen diameters were (i) small enough to permit cooling from the austenite region of sufficient rapidity to suppress bainitic and pearlitic transformations and also (ii) in the case of alloys containing from 1.1 to 1.4% C, small enough to minimize, if not prevent, the formation of macroscopic quench cracks. Their surfaces were polished through 600 grit paper then electro-polished in a perchloric acid bath at −70° C. The polished specimens were placed in individual quartz tubes which were in turn filled with argon, evacuated, then sealed. Each capsule was heated to the austenitizing temperature listed in Table I and held at that temperature for one hour after which it was removed from the furnace, broken and the specimen allowed to fall into an agitated brine-quench bath at 23° C. The quenched specimens were cleaned in a solution composed of equal parts of HNO_3, HCl and water. Their densities were determined within two hours of the time of quench following a procedure that has been described elsewhere [14].

A 1.2 cm long piece was acid-saw cut from one end of each density specimen and placed in a close fitting hole bore on the centreline and through a 1.2 cm high by 3.18 cm diameter mild-steel cylinder. The latter served the dual purpose of support fixture during hardness testing and metallographic mount. The flat faces of the specimen-mount assembly were lapped parallel and planar. The cut face of the specimen was polished and etched for metallographic examination. Several pieces were also cut from each density specimen for carbon analysis. The latter results are given in Table I.

3. Hardness testing and results

Rockwell C hardness measurements were made on the specimen end opposite that prepared for metallographic examination, that is on what had been an external and flat surface of the density specimen.* A series of certified test blocks were used at regular intervals to check the instrument. The hardness results are summarized in Table I.

4. Discussion

4.1. Metallography

The microstructures of seven of the quenched specimens are shown in Figs. 1 to 4. The morphological transitions evident here, and first seen by the pioneers of metallography and their successors [16–22], have been discussed recently by Marder and Krauss [23], Speich [24], Kelley [25], and Kennon [26]. As regards the present specimen set, the lath martensite structure, shown in Fig. 1, was observed in the samples containing 0.09, 0.19 and 0.39% C. Lath and plate martensite co-existed in the specimens containing from 0.56 to about 1% C (see Fig. 2a) the fraction

---

[†] The concentrations of the major substitutional impurities in the arc-melted iron (in ppm by weight where 1 ppm $= 10^{-4}$ weight percent) were as follows: 55 Ni, 40 Si, 30 Al, 20 Cu, 20 W, 12 Mo, 12 Mn, 10 Cr, 10 S and 10 P. It also contained 200 ppm of oxygen, 4 ppm of nitrogen and 2 ppm of hydrogen. With the addition of carbon, the oxygen concentration in the alloys was reduced to < 10 ppm.

[*] Vickers diamond pyramind hardness measurements were ultimately made on the metallographically prepared surfaces. These results will be published later in context with a review article written by one of us (FXK) on the H(Q) of steels cooled to room temperature at rates comparable to those experienced in commercial heat-treating practice.

TABLE I Alloy Compositions, Austenitizing Temperatures, Specimen Diameters, Austenite Grain Boundary Area/Volume and Hardness Data

Alloy* wt. %C	Aust. temp. (°C)	Specimen diameter (mm)	Austenite G.B. area (cm² cm⁻³)	Rockwell C hardness†		
				Mean	High	Low
0.09	940	4.57	140	33.8	+2.2	−2.8
0.19	900	6.35	–	42.7	+0.4	−0.2
0.39	850	6.35	200	56.6	+0.4	−0.6
0.56	825	4.57	–	61.6	+0.4	−0.4
0.76	800	4.57	–	64.5	+0.7	−0.5
0.96	880	4.57	–	65.5	+0.4	−0.4
1.13	950	3.05	56	64.0	+0.6	−0.9
1.35	1010	3.05	38	58.7	+1.3	−1.6
1.59	1070	4.57	30	51.4	+1.1	−2.2
1.65	1100	4.57	–	48.9	+2.6	−1.4
1.79	1130	4.57	18	43.2	+1.9	−2.4
1.84	1150	4.57	16	35.0	+1.0	−3.0
1.91	1160	4.57	–	30.8	+3.2	−3.8

*The nitrogen contents of the first five alloys listed above were as follows (in ppm by weight); 3, 4, 5, 3, 6.

†The average of four impression except for the 0.56% C alloy where only three impressions are included.

occupied by the laths appearing to diminish toward zero near the upper end of this concentration range. The martensite in the higher carbon alloys was entirely plate-like. From its appearance in Figs. 3 and 4, it was of the $(259)_\gamma$ type in samples with 1.59%C and greater. The volume percentage of retained austenite increased from zero, or near zero, in the 0.19%C samples to about 85% in those with 1.91%C.

Micro-cracks in and around plate martensite crystals were observed in all specimens containing 0.76%C and greater. From visual estimates, the crack frequency per unit sample volume was greatest in the 1.13 and 1.35%C specimens.

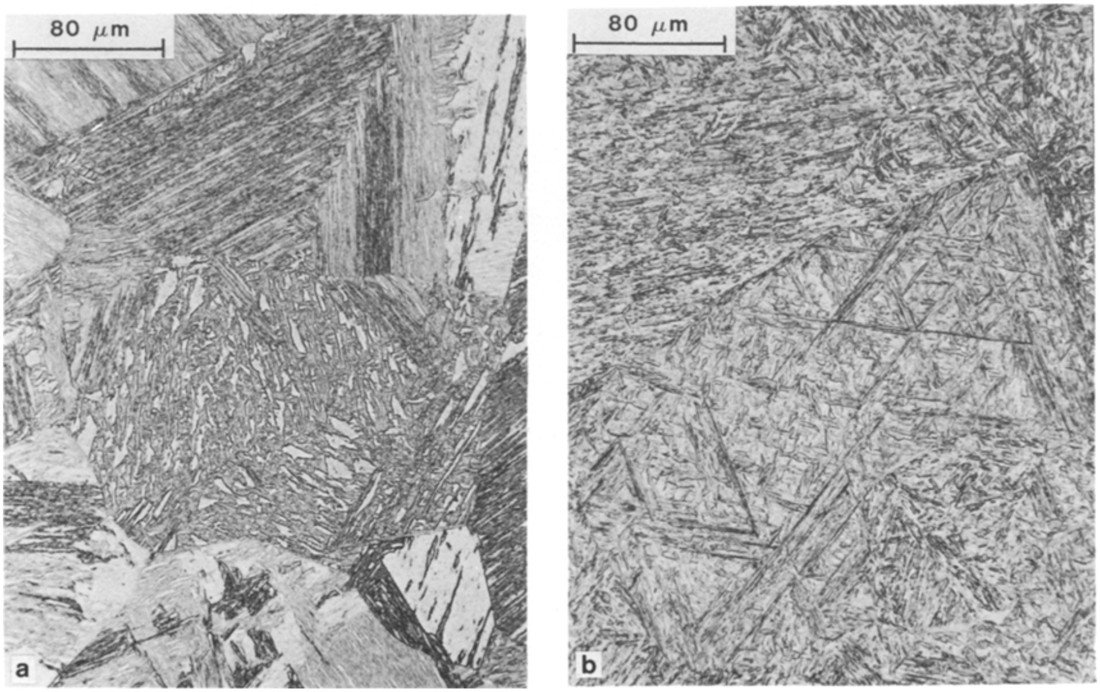

Figure 1 Light micrographs of (a) a 0.09%C sample brine-quenched from 940° C and (b) a 0.39%C sample brine-quenched from 850° C.

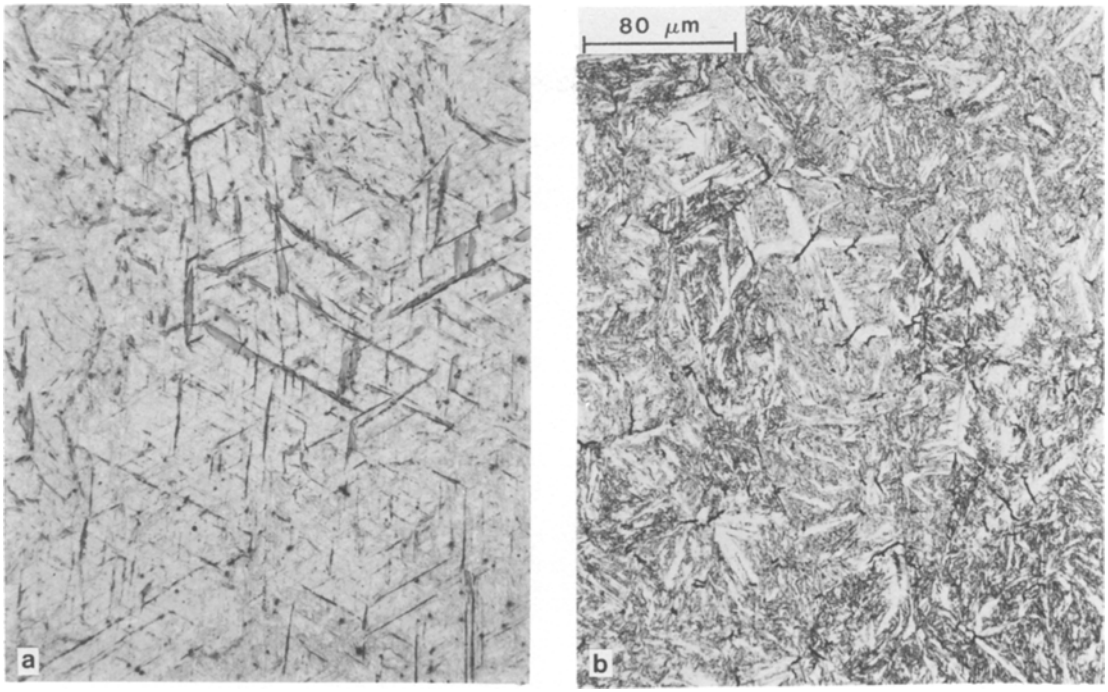

Figure 2 Light micrographs of (a) a 0.76%C sample brine-quenched from 800° C (scale as in b) and (b) a 1.13%C sample brine-quenched from 950° C.

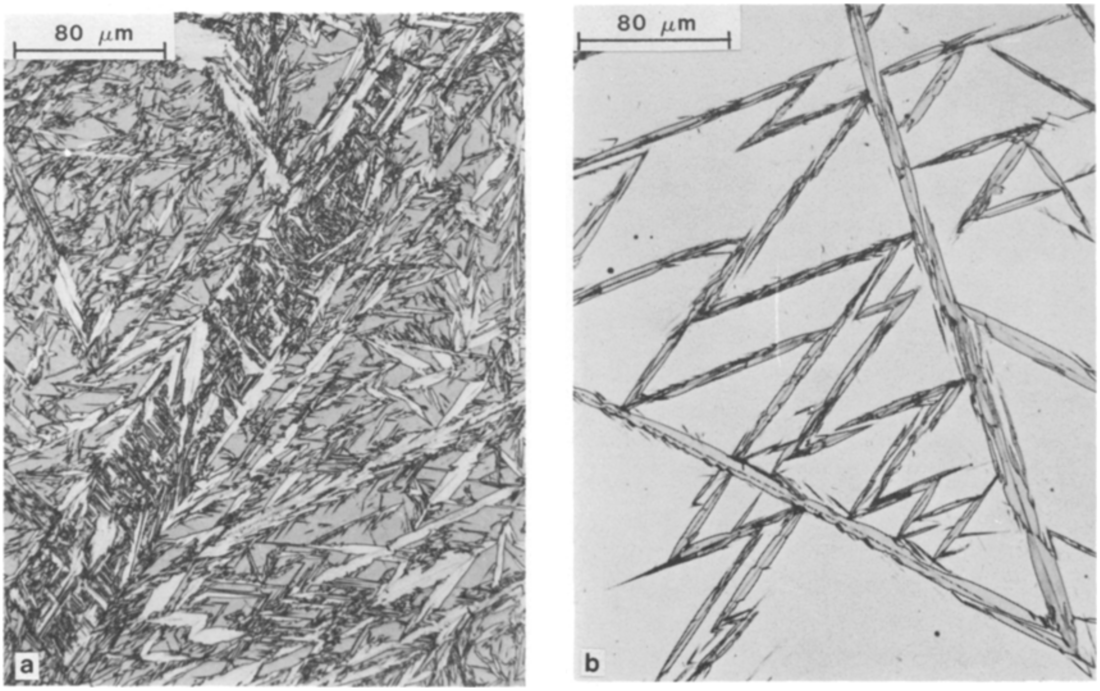

Figure 3 Light micrographs of (a) a 1.59%C sample brine-quenched from 1070° C and (b) a 1.91%C sample brine-quenched from 1160° C. Note presence of the austenite annealing twin in (a).

These observations are in good agreement with the results of recent investigations [27, 28]. Although the frequency and length of micro-cracks in the 0.76%C alloy were such that their detection was more difficult, several may be seen in the central area of Fig. 2a. The plates in the 0.56%C sample were sufficiently sparse that there were few plate-on-plate impingements. We were unable, by light microscopical methods, to obtain incontrovertible evidence for the existence of micro-cracks in this alloy.

A discontinuous grain-boundary reaction product, like that shown in Fig. 4, was observed in the 1.79, 1.84 and 1.91% specimens. It was confined to the immediate central areas of the sections prepared for metallographic examination and was probably proeutectoid cementite. Its presence should have no effect on the hardnesses and only a small effect on the densities of these alloy.

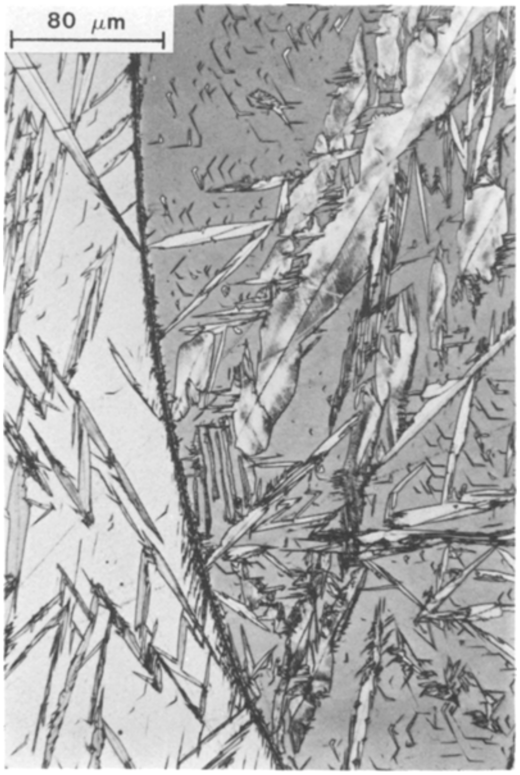

Figure 4 Light micrograph of a 1.84%C sample brine-quenched from 1150° C. This was taken very near the centre of the specimen. Note the reaction product at the austenite grain boundary.

4.2. Hardness

The hardness data are plotted in Fig. 5. The H(Q) versus wt %C curve may be regarded as the summation of variation independent and interactive factors. These include (i) the nature and volume fraction of martensite and austenite in each sample, (ii) the morphology, (iii) the micro-cracks present and (iv) changes which occur during the test such as stress-assisted transformation of retained austenite into martensite, the propagation of micro-cracks, the fracture of martensite plates, etc.

It is well established that the extreme hardness of quenched steels derives from the presence of martensite [16]. Moreover, it has long been known that H(Q) increases rapidly with increasing carbon in low and medium carbon steels [1–11, 24, 25, 29–31]. Fig. 5 clearly demonstrates that a maximum hardness, ~65.5 Rockwell C, occurs near 0.90%C in the H(Q) versus wt %C curve for high-purity iron–carbon alloys. The ensuing decrease in H(Q) with respect to increasing carbon stems primarily from a rapid increase in the volume fraction of retained austenite. The magnitude of the decrease is accentuated by the fact that the hardness of the martensite phase apparently increases little (particularly as measured on the Rockwell C scale), if at all, after reaching a high value near 0.90%C [25, 30].

The scatter in the data, first apparent near 1.3%C and which becomes progressively greater with increasing carbon, is a consequence of the microstructural coarseness in the high-carbon samples in relation to the indentation area. The higher austenitizing temperatures required for alloys with >1.3%C, coupled with the purity of the materials, led to large austenite grain sizes (see values for the austenite grain boundary area per unit volume for these samples listed in Table I) and correspondingly large martensite plate sizes. The existence of micro-cracks, particularly in the 1.35%C alloy, may also contribute to the scatter.

It is important to point out that were this same experiment repeated using as specimen-material alloys like SAE 13XX, 81XX, 23XX, etc., the maxima in the various H(Q) versus wt %C curves would appear in each case at carbon concentrations lower than the 0.90% observed here [4]. This is because the alloy grades have lower M_s temperatures and correspondingly higher retained

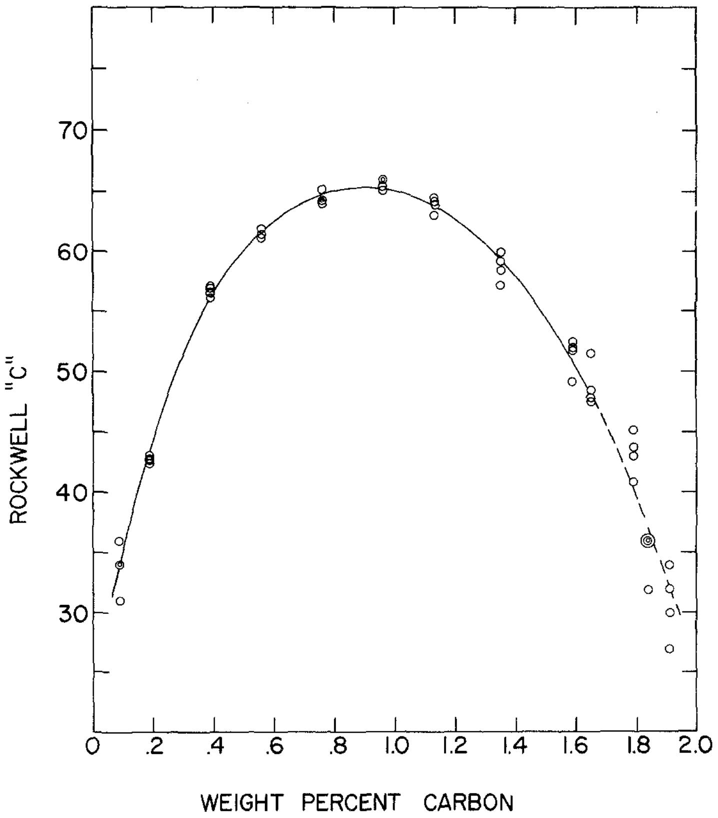

Figure 5 The Rockwell C hardness versus wt%C curve for iron-carbon alloys brine-quenched to room temperature from temperatures in the austenite region.

austenite concentrations. Even so, for carbon concentrations below about 0.7%C, the H(Q) values for the commercial steels should be the same, or very nearly the same, as those reported here. That this is so is born out by the good agreement (over the carbon concentration range 0.2 to 0.7%) between the present results and those obtained by Parker [2], Hodge and Orehoski [3], and Kayser, Thomson and Boegehold [4] from a number of commercial steels.

One might expect that by extending the present methods, the H(Q) versus wt %C curve could be established up to the maximum concentration of carbon in austenite, 2.11% [32], thereby establishing the hardness of high-carbon austenite. This supposes that somewhere in the composition interval 1.91 to 2.11%C the M_s versus composition curve passes below room temperature.* In fact we attempted to do this with the following results: (1) even for a 2.0%C alloy specimen the M_s temperature is a few degrees above room temperature, thus 4 to 5% martensite formed in specimens of this alloy quenched to room temperature, (2) the precipitation at the austenite grain boundaries became an increasingly severe problem and we concluded that better quenching methods (and probably different specimen configurations) than those used here were needed to minimize the effects of this reaction, and (3) the progressive decrease in the temperature range available for austenitizing very high carbon specimens ultimately surpassed the capability of our equipment to maintain the temperature limits demanded. An alternative method for approximating the hardness of a high carbon steel corresponding to 100% austenite and 100% martensite is one first carried out by Tamaru [8]. It consists of quenching a series of, say, 1.91%C specimens from 1160°C to various temperatures from 23 to −196°C, determining the hardness and austen-

---

*The M_s temperature of the 1.91%C alloy as determined by metallographic quench and temper methods was 50 ± 10°C the upper limit corresponding to the temperature at which martensite cyrstals first appeared in the larger grains, the lower, the temperature at which they first appeared in the smaller grains. That several investigators have been able to quench high-carbon foils to all austenite for use in Mössbauer studies [33] must be due to the M_s temperature dependence on the grain size of these alloys.

ite volume fractions of each then plotting the data (that is hardness versus vol % austenite) and extending the curve to its limits. We are presently carrying out this experiment.

Acknowledgements

The authors would like to thank Gaylord Stowe who prepared the alloys used in this investigation, Les Reed who homogenized and swaged the arc-cast bars, and Bob Bachman, Gary Austin and Nile Beymer who performed the chemical analyses. Work performed for the U.S. Energy and Development Administration under Contract No. W-7405 eng-82.

References

1. A. WAHLBERG, *Jernk. Ann.* **85** (1901) 79; *J. Iron Steel Inst.* **59** (1901) 243 and **60** (1901) 234; *Stahl and Eisen* **21** (1901) 382 and 465.
2. C. M. PARKER, "The National Emergency Steels NE 8000 Series", AISI Contribution No. 7, 1942; see also J. FIELD, *Metals Prog.* **43** (1943) 402.
3. J. M. HODGE and M. A. OREHOSKI, *Trans. Met. Soc. AIME* **167** (1946) 627.
4. F. X. KAYSER, R. F. THOMSON and A. L. BOEGEHOLD, *Trans. AMS* **45** (1953) 1056.
5. K. J. IRVINE, F. B. PICKERING and J. GARSTONE, *J. Iron Steel Inst.* **196** (1960) 66.
6. G. T. BROWN and B. A. JAMES, *Met. Trans.* **4** (1973) 2245.
7. L. GUILLET, "La Trempe et la Revenue des Produits Métallurgiques" (Gaston Dion Paris, 1921). See also P. OBERHOFFER, "Das Technische Eisen" (Julius Springer, Berlin, 1925) p. 66.
8. K. TAMARU, *Sci. Rpts.*, Sendai, Tohoku Imp. Univ. (1st Ser.) **15** (1926) 829.
9. E. C. BAIN, "Alloying Elements in Steel" (ASM, Cleveland, Ohio, 1939) p. 36.
10. J. L. BURNS, T. L. MOORE and R. S. ARCHER, *Trans. ASM* **26** (1938) 1.
11. M. A. GROSSMANN, "Principles of Heat Treatment" (ASM, Cleveland, Ohio, 1935) p. 50.
12. R. A. GRANGE, "Boron in Iron and Steel" (John Wiley, New York, 1957).
13. A. BROWNRIGG, *J. of Austr. Inst. Metals* **18** (1973) 124.
14. F. X. KAYSER, A. LITWINCHUK and G. L. STOWE, *Met. Trans.* **6A** (1975) 55.
15. A. LITWINCHUK and F. X. KAYSER, to be published.
16. F. OSMUND, "Microscopic Analysis of Metals", edited by J. E. Stead (Charles Griffin, London, 1904).
17. H. LE CHATELIER, *Mém. Sci. Rev. de Met.*, **1** (1904) 207.
18. F. ROBIN and P. GARTNER, *Mem. Sci. Rev. de Mét.* **8** (1911) 224.
19. N. J. WARK, *Metallurgie* **8** (1911) 731.
20. B. H. ENLUND, *Jernk. Ann.* **106** (1922) 389.
21. H. HANEMANN and A. SCHRADER, *Trans. Am. Soc. for Steel Treat.* **9** (1926) 169.
22. J. M. ROBERTSON, Carnegie Scholarship Memoires of Iron and Steel Inst. **20** (1931) 1.
23. A. R. MARDER and G. KRAUSS, *Trans. ASM Quart.* **60** (1967) 651.
24. G. R. SPEICH, *Trans. Met. Soc. AIME* **245** (1969) 2553.
25. P. M. KELLEY, "Electron Microscope and the Strength of Crystals", edited by G. Thomas and J. Washburn (Interscience, New York, 1973) p. 917.
26. N. F. KENNON, *J. Austr. Inst. Metals* **19** (1974) 3.
27. A. R. MARDER, A. O. BENSCOTER and G. FRAUSS, *Met. Trans.* **1** (1970) 1545.
28. R. G. DAVIES and C. L. MAGEE, *Met. Trans.* **3** (1972) 307.
29. D. T. LLEWELLYN, *Steel Times*, **198** (1970) 243. See also BROWNRIGG [13] p. 134.
30. W. S. OWEN, E. A. WILSON and T. BELL, "High-Strength Materials", edited by V. F. Zackay (John Wiley, New York, 1965) p. 167.
31. R. H. RICHMAN, "Deformation Twinning", edited by R. E. Reed-Hill, J. P. Hirth and H. C. Rogers (Gordon and Breach Science Publishers, New York, 1964) p. 237.
32. J. C. CHIPMAN, *Met. Trans.* **3** (1972) 55.
33. M. LESOILLE and P. M. GIELEN, *Met. Trans.* **3** (1972) 2681.

Received 31 December 1975 and accepted 15 January 1976