JOURNAL OF MATERIALS SCIENCE 27 (1992) 2048–2052

Absence of external E-field effects on transformations in steels

P. J. COTE, L. V. MEISEL, T. HICKEY
Benet Laboratories, Watervliet Arsenal, Watervliet, NY 12189, USA

Large hardness increases were recently reported for an ASTM A723 steel and a tool steel when a 1 $kV\,cm^{-1}$ external electric field was applied during the post-austenitization quench. The increased hardness was attributed to a field-induced order-of-magnitude decrease in the austenite decomposition rate during the quench. The results of an extensive study of austenite decomposition kinetics in the same A723 steel and a similar tool steel in the presence and absence of electric fields of magnitudes up to 3 $kV\,cm^{-1}$ during post-austenitization cooling are reported here. Differential thermal analysis and thermomagnetic analysis were employed to directly monitor the austenite decomposition processes in both steels. Supplementary hardness measurements in the tool steel are also reported. No effects of external electric fields on austenite transformations were detected.

1. Introduction

Cao *et al.* [1] recently reported remarkable hardness increases in steel specimens resulting from the application of external electric fields during heat treatment. They found hardness increases as large as a factor of two within the bulk of quenched, 1.6 to 3 mm diameter specimens when an electric field of 1 $kV\,cm^{-1}$ is applied between the sample and a pair of parallel plates during the quench. A small additional hardness increase is observed when the field is also applied during austenitization. They attribute these hardness increases to a field-induced order-of-magnitude reduction in austenite decomposition rates (i.e. increased hardenability) during quenching.

The alloys used by Cao *et al.* [1] were an O2-type tool steel* and a 4340-type steel. Larger hardness increases were reported for the tool steel and that was explained as a consequence of the higher inherent hardenability of 4340. More detailed studies of the tool steel were published in the proceedings of a recent Army Research Office Workshop on Field Effects on Materials [2].

The work reported here principally employed differential thermal analysis (DTA) and thermomagnetic analysis (TMA) to quantitatively test the reports regarding external electric field effects on transformation rates. DTA and TMA offer the advantage of *in situ* monitoring of phase transformations, as a given specimen is cycled with and without an externally applied E-field, thereby eliminating effects of variations among samples. Since the major E-field effect is reported on austenite decomposition rates during cooling, this is emphasized; however, results on the influence of E-fields on the austenite transformation on heating are also included. Hardness measurements, which supplement the transformation data, are also presented for the tool steel.

Specimen and electric field configurations similar to those used by Cao *et al.* [1] were investigated for both types of steel. No E-field effects were detected on the austenite transformations of the tool steel or the 4340-type steel, which indicates that the explanation for the reported E-field effects should be sought elsewhere.

2. Experimental procedure

The thermal analysis data were obtained using a modified Mettler TA1 thermal analyser which provides simultaneous digital recordings of DTA and thermogravimetric analysis (TGA) signals. Alumina sample holders of 9 mm diameter were used for sample and reference. High-purity copper rods of the same dimensions as the specimen were used as references.

Helmholtz coils were placed around the furnace so that the TGA system emulates a thermomagnetic analyser. The coils produce a uniform and a gradient H-field which yield a force on a magnetic specimen that is registered as an apparent change in sample weight. The austenite transformations in these steels are accompanied by changes in magnetic state, so TMA data complement the DTA data in the present study. Reaction rates were thus determined by thermal means (austenite transformation exotherms) and by magnetization changes (paramagnetic austenite-to-ferromagnetic bainite and paramagnetic austenite-to-ferromagnetic pearlite/ferrite).

The system was also modified to produce an electric

*At the time of final submission of this paper we were informed by H. Conrad that the specimen which they labelled as O2 tool steel is now believed to contain less than half the amount of Mn of commercial O2 tool steel. This does not materially affect the contents of this paper since the hypothesis in question is implied to be a universal phenomenon.

0022–2461

field configuration similar to that of Cao *et al.* [1] within the smaller sample space of the DTA apparatus. Platinum electrodes (5 mm × 20 mm) served as the negative parallel plates and were held inside the sample holder at an approximate 7 mm separation with a mica insert. A platinum connector for the positive lead was spot-welded directly to the 3 mm specimens, which were positioned midway between the plates. With the 2 mm gap between the specimen and each of the two negative plates, a voltage of 600 V produces a mean field of roughly 3 kV cm^{-1} in the gap region. This compares with the gap field given by Cao *et al.* [1] as 1 kV cm^{-1} with larger (25 cm × 10 cm) parallel plates maintained at a 2 cm separation. Typical currents ranged from 60 μA at the 830C austenitization temperature to 20 μA or less during the cooling of the sample.

Specimen protection against decarburization was usually provided with an He–10% H_2 gas mixture. Additional protection against decarburization was obtained by copper plating (2 mils = 51 μm) of the steel samples. Plated and unplated samples were used in the present experiments. The specimens were in the form of rods 3 mm in diameter and 19 mm long. The rods used by Cao *et al.* [1] ranged from 1.6 to 3 mm in thickness and were 25 to 45 mm in length.

The 4340-type steel used by Cao *et al.* [1] was supplied to them by the current authors. Material from the same block was used in our study. It is more properly designated as an ASTM A723 steel which is essentially a 4340 steel, refined by electroslag remelting and modified by addition of 0.1% V and with 3.18% Ni rather than the 1.8% Ni they assumed. We will use the ASTM designation in the remainder of this paper. The O2 tool steel samples were obtained from standard machine shop stock. The compositions of the steels are given in Table I.

3. Results and discussion

3.1. Transformation–time path

The thermal cycles employed for the steels were selected to provide the clearest demonstration possible of E-field effects on the austenite transformations during cooling, while accommodating the large differences in the transformation rates (hardenability) of the two steels and the cooling-rate limitations of the apparatus.

The hardenability is sufficiently high in the ASTM A723 steel that a full isothermal transformation at the bainite transformation region (i.e. below B_S and above M_S) can be obtained after cooling from the austenitizing temperature at 20 °C min^{-1}. Thus, the entire bainite transformation at a given temperature can be monitored in our apparatus.

The high hardenability is demonstrated in Fig. 1, which shows DTA and TMA data obtained by cooling ASTM A723 steel from the austenitization temperature at only 10 °C min^{-1}. The thermal and magnetic data show the classic martensite transformation beginning at M_S (the martensite start temperature), which is approximately 280 °C, with no transformation in the bainite region above M_S. Fig. 2 shows the corresponding path on the CCT (continuous-cooling–transformation) diagram obtained by examining transformations in a 3.0 wt % Ni specimen at various cooling rates.

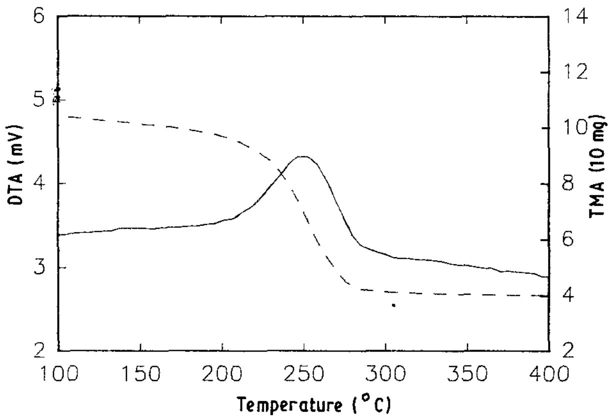

Figure 1 (——) DTA and (– – –) TMA data illustrating high hardenability of the 3.18% Ni composition ASTM A723. Both measurements show the martensite transformation beginning at about 280°C with no detectable bainite. In this case the zero magnetic force corresponds to 4 units on the TMA axis. The magnetic force increases monotonically with the amount of (ferromagnetic) martensite transformed from (paramagnetic) austenite. Cooling rate 10 °C min^{-1}.

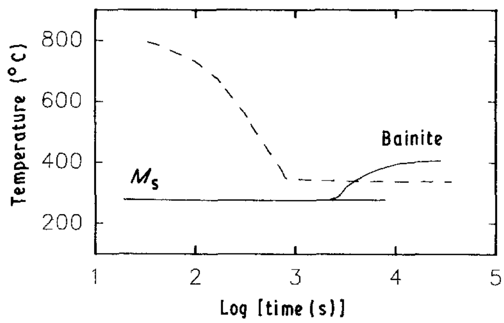

Figure 2 Approximate CCT diagram for the high-Ni composition used in the present measurements. The dashed line shows the cooling path used in the isothermal studies of the bainite transformation.

TABLE I Steel compositions

Steel	Composition (wt %) C	Mn	Si	Ni	Cr	Mo	V	P	S	Al	W	Co
ASTM A723	0.34	0.62	0.16	3.18	1.02	0.48	0.10	0.008	0.004	0.005	–	–
O2 Steel	0.88	1.4	0.45	0.03	–	0.18	0.08	0.009	0.003	–	0.10	0.28

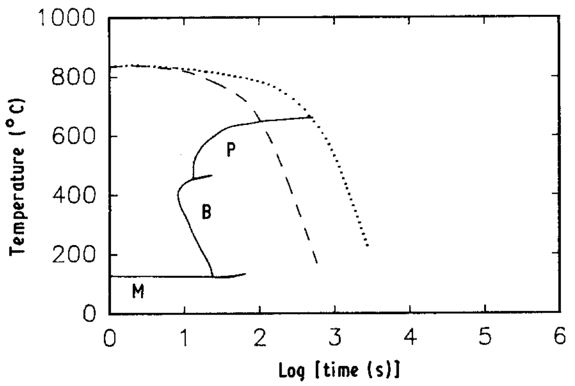

Figure 3 Main features of CCT diagram for O2 tool steel. Broken lines show cooling paths used in the present field-effect studies: (---) 50 °C min^{-1}, (. . .) 15 °C min^{-1}.

Since the much higher austenite decomposition rates (lower hardenability) and instrumentation limitations precluded the use of isothermal transformations for studies of possible field effects in the tool steel, several convenient continuous cooling paths through the pearlite/ferrite and bainite transformation zones on the O2 CCT diagram were selected as shown in Fig. 3 (CCT data reproduced from Cao *et al.* [1]).

3.2. ASTM A723 steel

The following thermal cycles were used for the ASTM A723 steel:

(i) Heat to an austenitization temperature (837 °C) at 25 °C min^{-1}.

(ii) Hold for 15 min at 837 °C.

(iii) Cool to the selected temperature, in the bainite region, at 25 °C min^{-1}.

(iv) Hold (isothermal) at the selected temperature for 1 h.

Figs 4 and 5 show the bainite transformation data under E-field-on and E-field-off conditions, respectively, for a coated specimen during isothermal annealing at 355°C. The data were obtained in consecutive runs on as-received material. The E-field-on

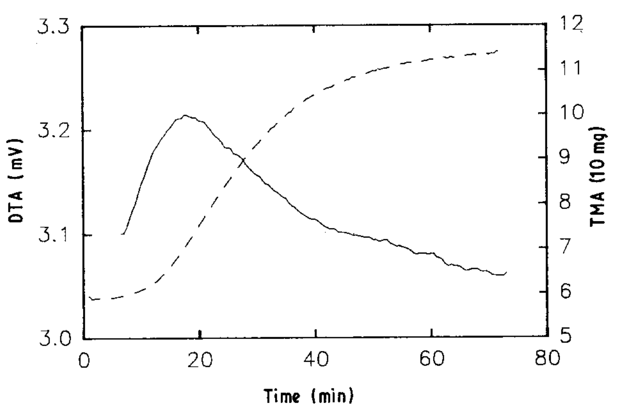

Figure 4 (——) DTA and (---) TMA data for the 355 °C isothermal bainite transformation with an applied external electric field of 3 kV cm^{-1}. As the transformation progresses from austenite (paramagnetic) to bainite (ferromagnetic), the magnetic force increases from zero (6 TMA units) to its full value (11.5 TMA units). The specimen was copper-plated.

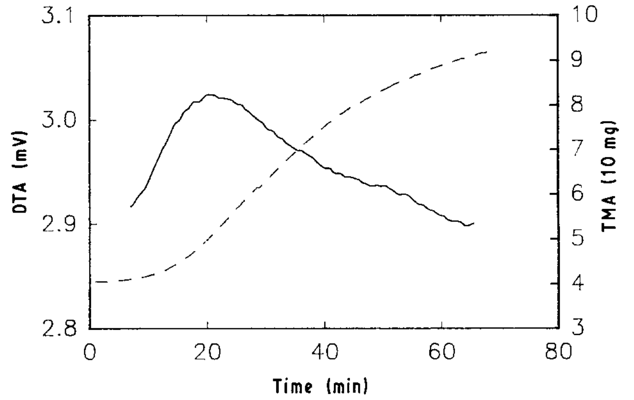

Figure 5 (——) DTA and (---) TMA data for the 355 °C isothermal bainite transformation with no applied field. The magnetic force varies from zero (4 TMA units) to its full value (9.5 TMA units) as the transformation progresses from (paramagnetic) austenite to (ferromagnetic) bainite. The specimen was copper-plated.

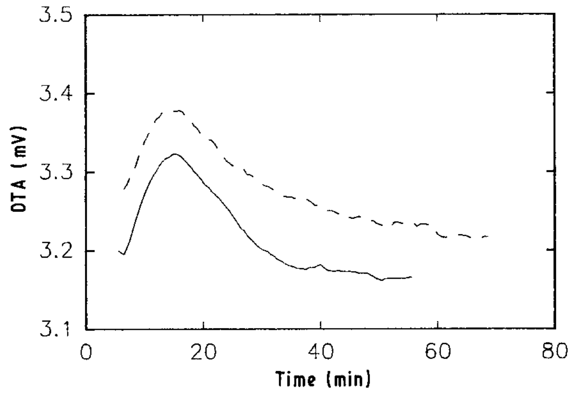

Figure 6 DTA output for the isothermal transformation of bainite in ASTM A723 at 337 °C using an uncoated specimen under (——) field-on (3 kV cm^{-1}) and (---) field-off conditions.

preceded the E-field-off case. The reaction-rate peaks (the DTA peaks) are slightly different: the E-field-off peak occurs at slightly longer time and has a reduced height indicating a more sluggish bainite transformation for the field-off run. The TMA data reflect the same effect with the magnetization increasing at a slower rate for the field-off case.

Essentially the same small changes were obtained for subsequent cycles with no E-fields. Thus, Figs 4 and 5 demonstrate the effect of prior heat treatment; they do not indicate a marginally poorer hardenability for the E-field-on case. The E-field-on first pair are shown to preclude the possibility that prior heat treatment vitiates the E-field effects. Had there been the claimed order-of-magnitude shift in hardenability with field, the peak position would be shifted an order of magnitude in time.

An uncoated sample of ASTM A723 was also tested to allay concerns that copper coating might interfere with the E-field effect. The results are presented in Fig. 6. The isothermal hold temperature was 337 °C in this case. The smaller amplitude of the field-off run in this case is due to a combination of the thermal cycling effect and the premature transformation of a small amount of austenite to bainite in the outermost decarburized layers of the specimen prior to initiation of the isothermal hold. As in the coated case, the peak maxima occur at approximately the same time. Thus, no difference between the field-on and field-off cases is observed. (Obviously, no order-of-magnitude shift can be supported.)

3.3. Tool steel

The results of the continuous cooling experiments following a 15 min austenitization at 837 °C on the O2 tool steel specimen are given in Figs 7 and 8. The cooling paths of 15 and 50 $°C\,min^{-1}$ are shown in Fig. 3. The austenite-to-pearlite/ferrite and austenite-to-bainite transformations are manifested by distinct DTA peaks. The relative quantities of pearlite/ferrite and bainite can be deduced from the relative areas under the peaks. Here, the slower cooling rate of Fig. 7 is seen to yield a preponderance of pearlite, while the faster rate of Fig. 8 yields a more equal mix of the two austenite decomposition products.

The close similarity of the E-field-on and E-field-off cases at both cooling rates demonstrates the absence of E-field effects on austenite transformations. Furthermore, the large difference in transformation response at the two rates demonstrates the sensitivity of the present experiments to changes in transformation kinetics.

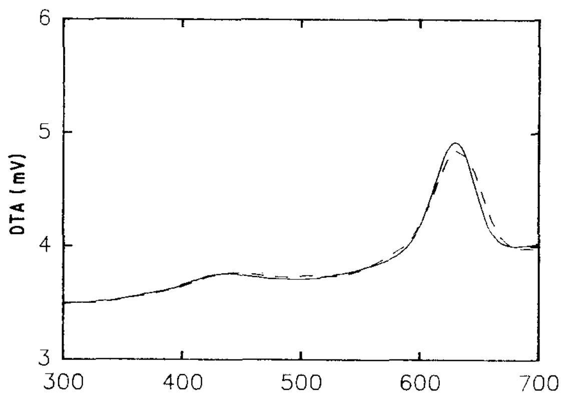

Figure 7 DTA output for continuous cooling of O2 tool steel at a rate of 15 $°C\,min^{-1}$ for (——) field-on and (– – –) field-off conditions. Only a vestige of the bainite peak remains at this slow cooling rate, indicating the preponderance of pearlite in the microstructure.

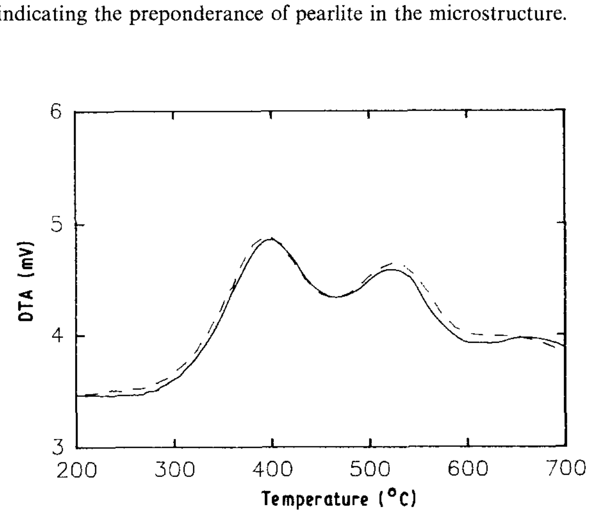

Figure 8 DTA output for continuous cooling of O2 tool steel at an average rate of 50 $°C\,min^{-1}$ for (——) field-on and (– – –) field-off conditions. The two peaks reflect a roughly equal mix of pearlite and bainite.

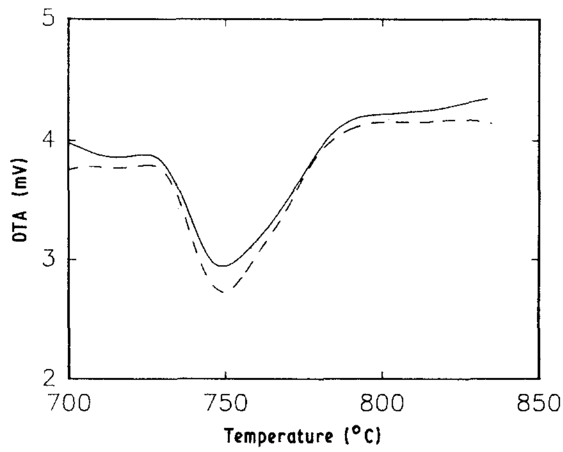

Figure 9 DTA output for the formation of austenite on heating O2 tool steel at 25 $°C\,min^{-1}$ under (——) field-on (3 kV cm) and (– – –) field-off conditions.

Hardness measurements on the tool steel specimen cooled under E-field-on and E-field-off conditions at a cooling rate of 50 $°C\,min^{-1}$ are in complete accord with the transformation data cited above. The Knoop hardnesses (deduced from 20 points along the length of sectioned specimens) were identical (425 $\pm$ 1 $kg\,mm^{-2}$) for E-field on and off.

Cao *et al.* also concluded [1] that the transformation to austenite, which occurs on heating, is significantly accelerated by the application of an external field. We examined this transformation for numerous heating runs for both ASTM A723 and tool steel and found no evidence of an E-field effect. Fig. 9 shows the typical null result we obtained.

3.4. Comments on the procedures and results of Cao *et al.*

The reported order-of-magnitude increase in steel hardenability with an external E-field is difficult to understand. The main explanations suggested by Cao *et al.* [1] require E fields within the bulk of the metal. In their experiments, the sample is the centre positive electrode separated from two negative plates by an insulating medium (air/oil). The measured electric current through the quenching media (silicone and mineral oil) during the quench, where the major effect occurs, is only 200 μA, implying that $E \approx 10^{-9}\ V\,cm^{-1}$ within the metal. The magnitude of the current is many orders of magnitude less than any previously reported [2] to produce significant effects on material properties. Thus, it seems that an alternative explanation of their observations is needed.

There is a problem with the quench procedure employed for the tool steel by Cao *et al.* [1]. The treatment which yields the largest field effect involves a quench into silicone oil maintained at 145 °C. As indicated in the CCT diagram they assume for their tool steel (reproduced in Fig. 3), this is at or above M_S (the martenisite start temperature), which indicates that their process is actually designed for an interrupted quench with an isothermal hold in the lower bainite region. The amount of bainite formed in such a thermal process depends on the hold time, which is not given.

A key question in this matter is the origin of the unusual softness (300–400 VHN) of the field-off case since this is, in effect, the standard quench procedure. The high hardness (800–900 VHN) of the field-on cases is actually the rule with quenched, small specimens of tool steel.

Another mystery is their observation [1] of bainite in the 2×3 mm rod specimens of ASTM A723 at the cooling rates of their experiments: at cooling rates of approximately $30\,°C\,s^{-1}$, bainite is reported to form without the field, while no bainite forms when the field is applied. They also observe bainite after air quenches, for which the quench rate is given as approximately $5\,°C\,s^{-1}$. The issue here is that the hardenability of this steel is much too high to form appreciable amounts of bainite at these cooling rates in the absence of E-fields. The 3.18% Ni in this steel produces an order-of-magnitude shift in the bainite knee to longer times relative to 4340 steels. The data in our Fig. 1 shows that cooling this steel at $10\,°C\,min^{-1}$ (i.e. $0.17\,°C\,s^{-1}$) is sufficient to bypass the bainite knee. Therefore, the possibility of bainite in oil-quenched 2 mm × 3 mm rods of this ASTM A723 steel is essentially precluded.

In addition to the improper quench procedure, a factor in the surprising findings of Cao *et al.* [1] may be the lack of any specimen protection during their heat treatments. Their experiments were conducted in air where oxidation and decarburization at high temperatures (up to 870 °C in their experiments) is rapid and will significantly alter the chemistry of thin samples. (We observed serious decarburization and oxidation when we tried experiments in air.) An assessment of the surface condition of their specimens might provide a clue to the source of the reported phenomena.

4. Conclusions

The present work establishes that external E-fields of magnitude as large as $3\,kV\,cm^{-1}$ produce essentially no changes in austenite transformation kinetics for ASTM A723 and O2 tool steel. Further, identical hardness values were obtained for O2 tool steels that were quenched with and without E-fields. The present results therefore refute the hypothesis [1] that external electric fields produce order-of-magnitude reductions of austenite decomposition rates in such steels. The problems evident in the procedures used by Cao *et al.* [1] may be obscuring the true origins of their mysterious observations.

Acknowledgements

We appreciate the assistance of Mr Christopher Rickard who performed the hardness measurements and the metallography. We thank Mr Paul Croteau for his assistance in specimen preparation and Mr Julius Frankel for his critical reading of this manuscript.

References

1. W. D. CAO, X. P. LU, A. F. SPRECHER and H. CONRAD, *Mater. Lett.* **9** (1990) 193.
2. Proceedings of US Army Research Office Workshop on High Intensity Electromagnetic and Ultrasonic Effects on Inorganic Materials Behavior and Processing, July 1989, edited by H. Conrad and I. Ahmad. (North Carolina State University, N.C., 1989)
3. H. CONRAD, Private Communication.

Received 25 September 1990
and accepted 26 July 1991