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OVERVIEW

Enhanced Phenomena in Metals with Electric and Magnetic Fields: I Electric Fields

Hans Conrad

Materials Science and Engineering Department, North Carolina State University, Raleigh, NC 27695-7907 USA

The effects of an externally-applied electric field on the equilibria and kinetics of solid state transformations in metals and alloys are reviewed. Regarding equilibria, electric fields have been found to affect the solubility of solutes and the composition as well as volume fraction of phases present. Regarding kinetics, electric fields have been shown to affect recovery and recrystallization, precipitation, phase coarsening, hardenability and sintering. Electric fields thus offer an additional means of controlling microstructure and in turn properties. Our understanding of the effects of an electric field on solid state transformations in metals and alloys is very meager. It appears that most of the observed effects on kinetics are through its influence on vacancies.

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1. Introduction

The external parameters generally considered in materials science are the temperature, pressure (or stress), time and environment (solid, liquid or gas). Usually neglected are the effects of externally-applied electric or magnetic fields. However, in many cases such fields can have a significant influence. In this paper we review the effects of an electric on the equilibria and kinetics of solid state transformations in metals. The influence of a magnetic field by Prof. M. Enomoto is presented in the companion paper.

Most of the studies on the effects of an electric field on solid state transformations in metals have been performed on Al and Fe alloys, with much less on other metals or alloys. Since interstitial carbon plays a major role in the Fe alloys, the discussion to follow will consider the effect of a field on ferrous alloys separately from those on non-ferrous alloys.

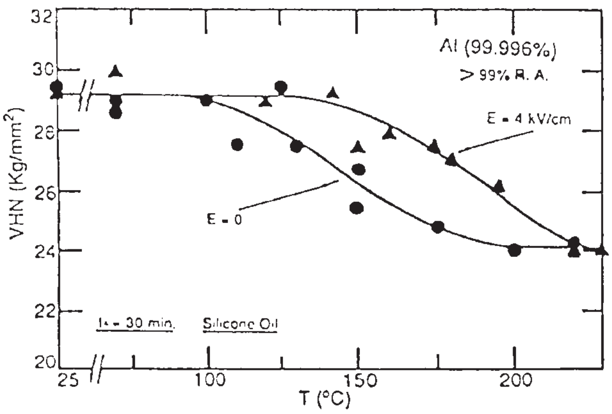


Fig. 1 Vickers hardness vs. isochronal (30 min) annealing temperature for cold drawn high purity Al wire without and with an electric field $E = 4\,kV/cm$. From Conrad *et al.*[1)]

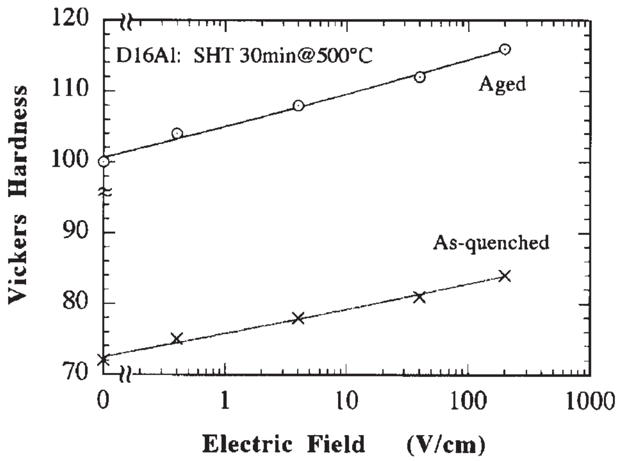


Fig. 2 Effect of electric field strength applied during the solution heat treatment at 500°C of the Soviet Al alloy D16 on the hardness: (a) following quenching and (b) after natural aging. Data from Klypin and Soloviev.[2)]

2. Non-Ferrous Metals and Alloys

2.1 Recovery and Recrystallization

Conrad and coworkers[1)] were the first to report that the application of an external dc electrostatic field during the isochronal annealing of high purity Al retarded the recovery and recrystallization process; see Fig. 1. They also found a retarding effect for commercial purity Cu, the magnitude of the effect in this metal increasing with the amount of cold work prior to the annealing. It was suggested by these authors that the field retarded the rates of dislocation glide and climb and subgrain coalescence in the recovery and recrystallization process.

2.2 Solid Solution and Precipitation

Klypin and coworker Soloviev[2,3)] were the first to report that an electric field can influence the age hardening response of Al alloys. They reported that a modest external dc electric field $E = 100$–$500\,V/cm$ applied during the solution heat treatment (SHT) and subsequent aging of several Al alloys gave an increase in their hardness; see for example Fig. 2. In the case of the Soviet Al alloy V65, they found employing replica electron microscopy that a field $E = 100\,V/cm$ applied during the SHT of this alloy reduced the size of the secondary undissolved phases, *i.e.* more complete solution had occurred. This was supported by resistivity measurements, which gave a higher resistivity for the SHTs with a field compared to without. Their resistivity measurements gave that the effect of the field on solubility was equivalent to a temperature increase of ~60°C. Further, there occurred a polarity effect of the field, a greater effect occurring when the specimen was connected to the positive terminal of the power supply compared to the negative terminal. These authors also established by hardness measurements that the effects of the field were not simply at the outer surface of the specimen but extended to at least 0.1 mm below the surface. Klypin and Soloviev[2,3] attributed the effect of an electric field applied during SHT to the change in the chemical potential of the phases that are present so that their solution is enhanced.

A number of investigators subsequently confirmed that an electric field can not only influence the SHT and aging of Al alloys,[4–9] but can also have an effect on such phenomena as homogenization of the cast ingot[10,11] and superplasticity,[12–15] including in the latter an influence on the chemical composition adjacent to the grain boundaries. That an electric field can affect the microstructure in Al alloys was reported by Liu and Cui.[11] They determined the influence of an electric field $E = 2\,\text{kV/cm}$ applied during the homogenization at 570°C of 2091 Al–Li cast ingots on the microstructure (TEM) which subsequently occurred following rolling, SHT and then aging at 180°C. The field produced changes in the precipitate structure, which in turn led to increases of 10–16% in the yield and tensile strengths. However, a decrease in elongation occurred for long homogenization times. They attributed the observed effects of the electric field on the microstructure and properties through its influence on the diffusion rates of Cu and Mg, especially Cu.

That an electric field can increase the solubility of solutes in Al alloys was supported by the studies of Jung and Conrad.[7–9] They found that the application of a dc electric field $E = 5\,\text{kV/cm}$ during the SHT of Al–Mg–Si alloys (AA6022 and AA6111) gave an increase in the resistivity ρ_w and hardness H_w of subsequently water-quenched specimens; see for example Fig. 3. No effect of a field during SHT was however observed for the AA6061 alloy. Comparing the composition of the three 6000-series alloys, one finds that an effect of electric field occurred for the alloys with either the presence of excess Si (AA6022) or the addition of Cu (AA6111).

A thermodynamic analysis of the results on AA6022 and AA6111 gave that the field reduced both the enthalpy ΔH_s and entropy ΔS_s of solution of Mg_2Si in the Al matrix, but the magnitudes of the changes were such that there still occurred a reduction in the Gibbs free energy $\Delta G_s = \Delta H_s - T\Delta S_s$ for the SHT temperature range investigated. The reduction in ΔG_s in turn gives an increase in solubility c_s according to the well-known relation

$$c_s = \exp(-\Delta G_s/\text{kT}) \qquad (1)$$

The effect of electric field on the solubility of Mg_2Si in AA6111 is shown in Fig. 4.

The studies by Jung and Conrad[7–9] gave that the increases in ρ_w and H_w which resulted from application of an electric field during SHT were maintained throughout the subsequent natural aging, there being no detectable effect on the kinetics of the aging process. In contrast, Liu and Cui[5] reported that by applying an electric field $E = 4\,\text{kV/cm}$ during the aging of the 2091 Al–Li alloy at 150° to 170°C the time t_p to reach

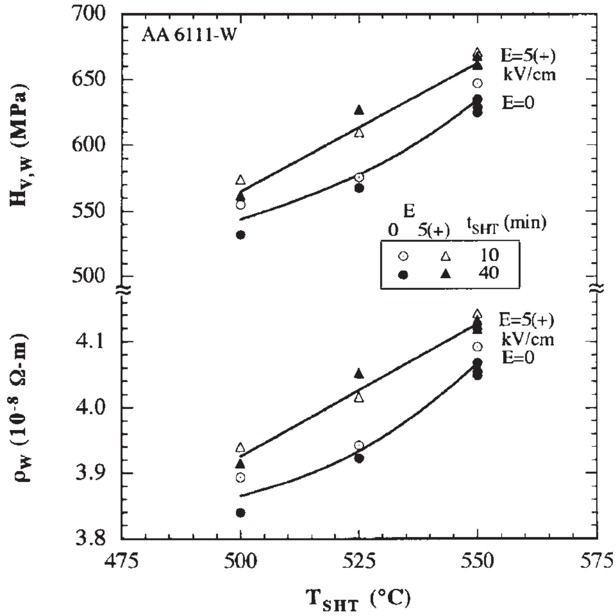


Fig. 3 Resistivity ρ_w and hardness H_w of as-quenched AA6111 Al alloy vs. the solutionizing temperature T_{SHT} without and with an electric field $E = 5\,\text{kV/cm}$ for solutionizing times of 10 and 40 min. From Conrad and Jung.[7]

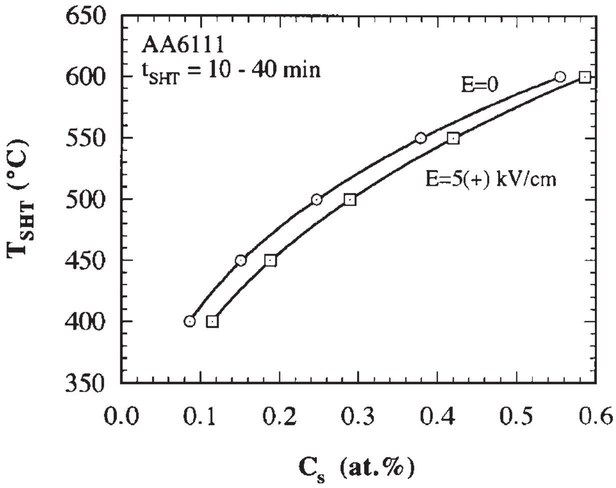


Fig. 4 Effect of an electric field on the solubility of Mg_2Si (presumably Al–Mg–Si–(Cu) complexes) in AA6111 Al. From Conrad and Jung.[7]

the peak strength at each temperature was increased, *i.e.*, the aging rate was retarded by the field. Taking an equation of the form $t_p/T = A\exp(Q/\text{kT})$, these authors obtained $Q = 0.25$ eV for $E = 0$ and $Q = 0.45\,\text{eV}$ for $E = 4\,\text{kV/cm}$. Thus, the field increased the apparent activation energy for the aging process. TEM observations of the aged specimens revealed that the δ' precipitates were less numerous and somewhat larger for aging with the field compared to without.

2.3 Phase Coarsening

Jung and Conrad[16] reported that an electric field retarded the coarsening of the Pb-rich and Sn-rich phases in the commercial 60Sn40Pb solder alloy; see Fig. 5. They attributed this effect of the electric field to its influence on the vacancy concentration in the specimen interior. In a

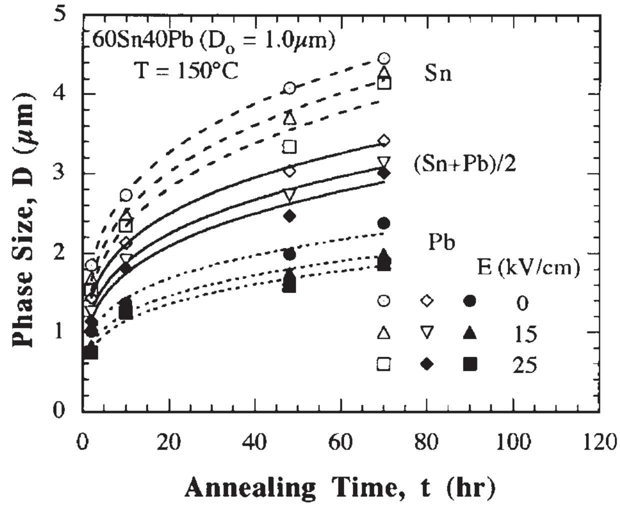


Fig. 5 Effect of an external electrical electric field on the coarsening of the Pb-rich and Sn-rich phases in a 60Sn40Pb solder joint annealed at 150°C. From Jung and Conrad.[16)]

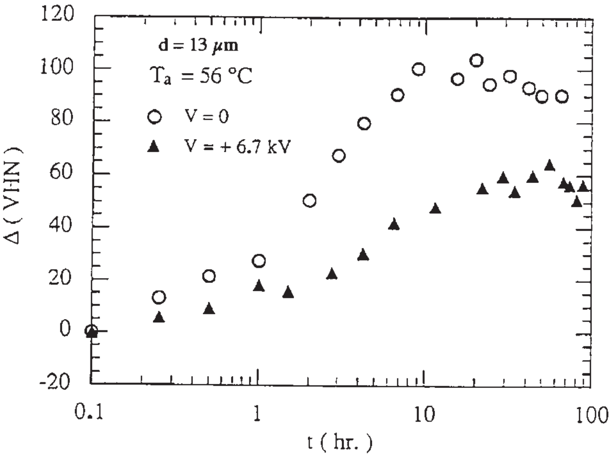


Fig. 7 Hardness of a quenched low-carbon steel vs. aging time at 56°C with and without an external electric field $E = 14\,\mathrm{kV/cm}$. From Lu and Conrad.[19)]

subsequent paper[17)] these authors determined that in the annealing with field there had occurred a gradient in the phase sizes from the surface of the cylindrical specimen to its center, the size of each phase increasing as one progressed from the surface to the center. Moreover, the volume fraction of the Sn-phase at the center was above the equilibrium value. To explain this, it was proposed that the field may have changed the electrochemical potential of the phases to give the higher-than-equilibrium volume fraction of the Sn phase.

3. Ferrous Alloys

3.1 Sintering

Fahmy and Conrad[18)] found that the application of an electrostatic field during the sintering of iron powder compacts reduced the porosity, Fig. 6. These authors proposed that the reduction in porosity resulted from the migration of vacancies from the internal pores to the surface.

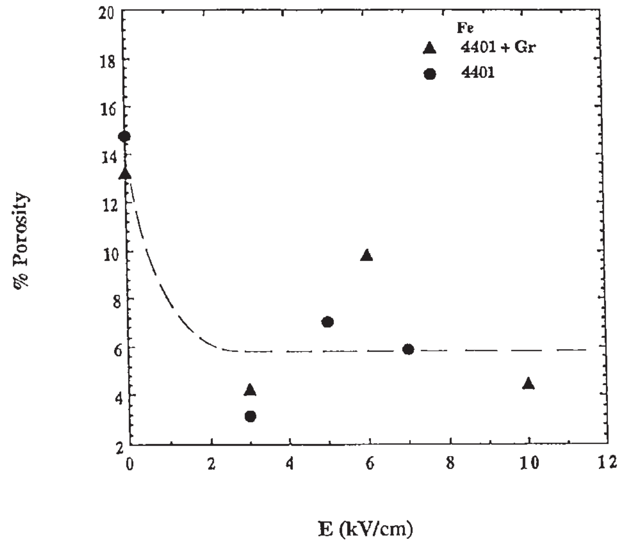


Fig. 6 Effect of electric field strength on the porosity of iron powder compacts sintered at 1100°C. From Fahmy and Conrad.[18)]

The experimental variation of porosity as a function of depth below the surface agreed with that calculated based on the assumption that the migration of vacancies was the controlling process. It was found that the specimens sintered with the field could be surface carburized, whereas those sintered without a field could not.

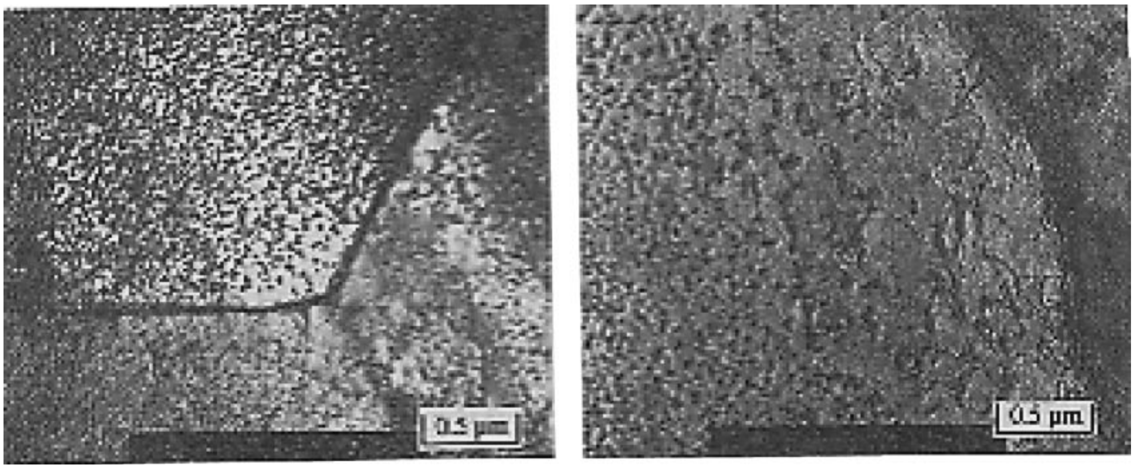
3.2 Quench Aging

Similar to the Al–Li alloy,[5)] the quench aging of a low-carbon steel was found to be retarded by an electric field, see Fig. 7. To be noted, the field not only increased the time t_p to obtain maximum hardness but also reduced the hardness value. An Arrhenius plot of $\log(t_p/T)$ vs. $1/T$ gave $Q = 0.68\,\mathrm{eV}$ for $E = 0$ and $Q = 0.85\,\mathrm{eV}$ for $E = 14\,\mathrm{kV/cm}$. The effect of the field on the microstructure of a quench-aged specimen is shown in Fig. 8. The field increased the size of the precipitate-free zone (PFZ) adjacent to the grain boundaries and increased the size and spacing of the Fe_3C precipitates in the vicinity of the boundary. By considering the microstructure to consist of a duplex structure and that the hardness obeyed a linear rule of mixtures with respect to the volume fraction of each structure, it was shown that the decrease in hardness with field was in qualitative accord with the observed microstructure.[20)]

Since the major nucleation sites for Fe_3C precipitates are vacancies or vacancy clusters, the observed changes in microstructure with field can be attributed to a depletion of vacancies by the field in the manner illustrated in Fig. 9. Under the influence of the field the vacancies migrate from within the grain to the grain boundary and then move rapidly along the grain boundaries to the specimen surface. A similar mechanism could apply for the effect of electric field on the sintering of iron powder compacts[18)] and during the superplasticity of Al alloys.[12–15)] An important factor in this model would be the presence of an oxide film on the surface.

3.3 Quench Hardening (Hardenability)

Klypin[3)] was the first to report that an electric field applied during the austenitizing of steels increased their hardness following cooling. He attributed this to the influence of the



E=0 E=13.7 kV/cm

Fig. 8 TEM micrographs showing the effect of an external electric field $E = 14\,\text{kV/cm}$ on the nature of the precipitates adjacent to the grain boundaries in quenched low-carbon steel aged 80 h at 56°C. From Lu and Conrad.[19)]

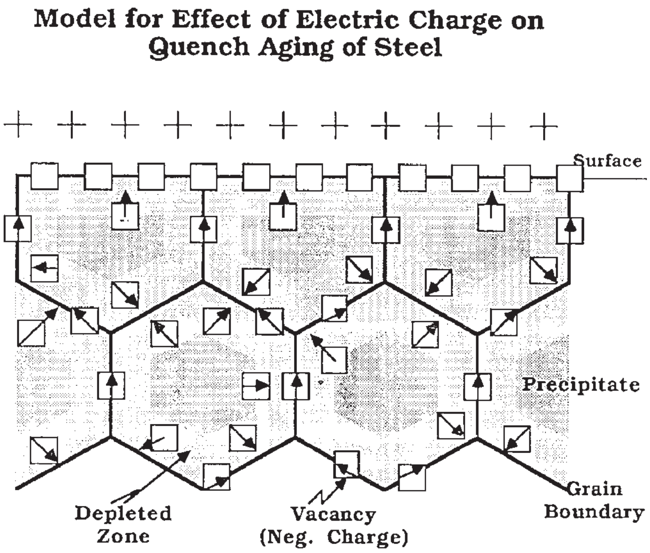


Fig. 9 Schematic of the proposed model for the effect of an electric field on the quench-aging of low-carbon steel. From Conrad.[21)]

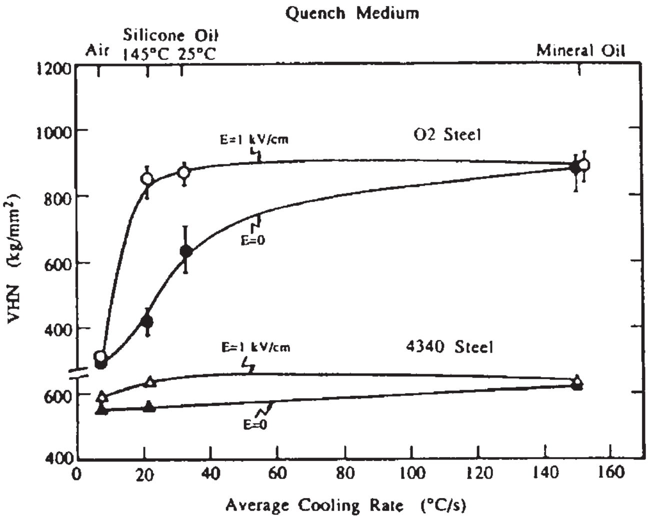


Fig. 10 Effect of an electric field applied during austenitizing and quenching on the Vickers hardness vs. average cooling rate between 800° and 500°C for unalloyed high-carbon (02) and alloyed medium-carbon (4340) steels. From Cao *et al.*[22)]

field on the electrochemical potential of the coexisting phases. Stimulated by the results obtained by Klypin, Conrad and coworkers[22,23)] subsequently investigated in more detail the effects of an electric field applied during both austenitizing and quenching on the hardenability of steels. For insulating purposes during quench, and to obtain different cooling rates, the quench media were either silicone oil at various temperatures or mineral oil. The influence of an electric field on the hardness of an unalloyed high-carbon (0.9 mass%C) steel and an alloyed medium-carbon steel (4340) as a function of the cooling rate during quenching is shown in Fig. 10. It is seen that the effect of the field depends on the cooling rate and the composition of the steel. The significant effect of a field on the hardenability of the unalloyed high-carbon steel as measured by a simulated Jominy end-quench test is shown in Fig. 11. To be mentioned is that with the field the hardness at the quench-end of the specimen ($x = 0$) in Fig. 11 is of the same magnitude as was obtained by quenching the steel in water at 25°C.

In subsequent work Zheng *et al.*[23)] found an effect of a field on the hardenability of a high-carbon steel similar to that in Fig. 11, but the quench media was silicone oil at 25°C rather than at 145°C. Moreover, they determined by optical microscopy that the increased hardness with the field at each location along the simulated Jominy curve corresponded to a microstructure representing a higher cooling rate. For example, the microstructure without field at $x = 3\,\text{mm}$ from the end face of the Jominy specimen consisted of 20 vol% pearlite and 80 vol% martensite while that with the field was 100 vol% martensite. Zheng *et al.*[23)] also measured the temperature-time profiles (cooling curves) along the Jominy test specimens and from these constructed the cooling–transformation (C–T) diagrams shown in Fig. 12. To be noted is that the field has shifted the C–T curves to longer times (or lower temperatures), *i.e.*, the field has retarded the austenite-to-pearlite transformation. These authors proposed

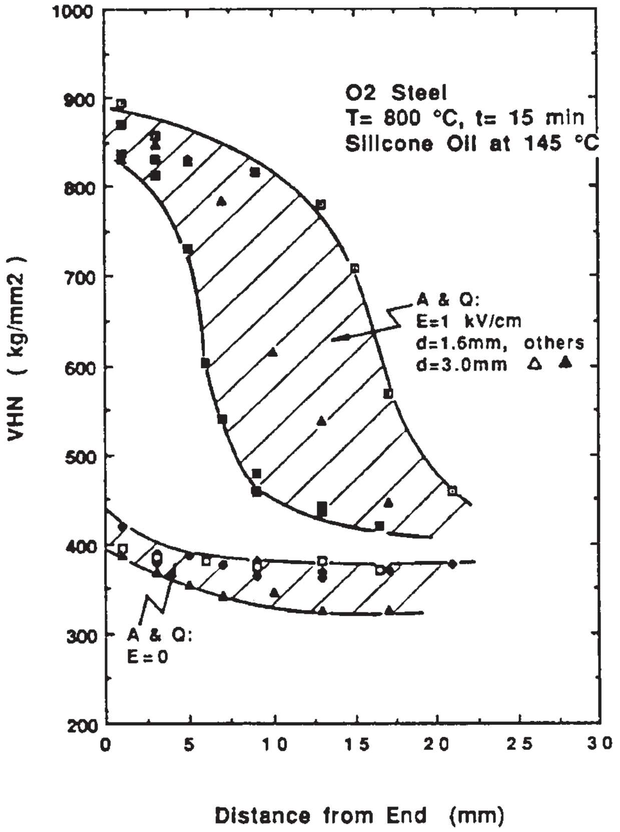


Fig. 11 Effect of an electric field $E = 1\,\mathrm{kV/cm}$ on the hardenability of an unalloyed high-carbon steel quenched in silicone oil at 145°C as measured by a simulated Jominy end-quench test. Field was applied during both austenitizing (A) and quenching (Q). From Cao *et al.*[22]

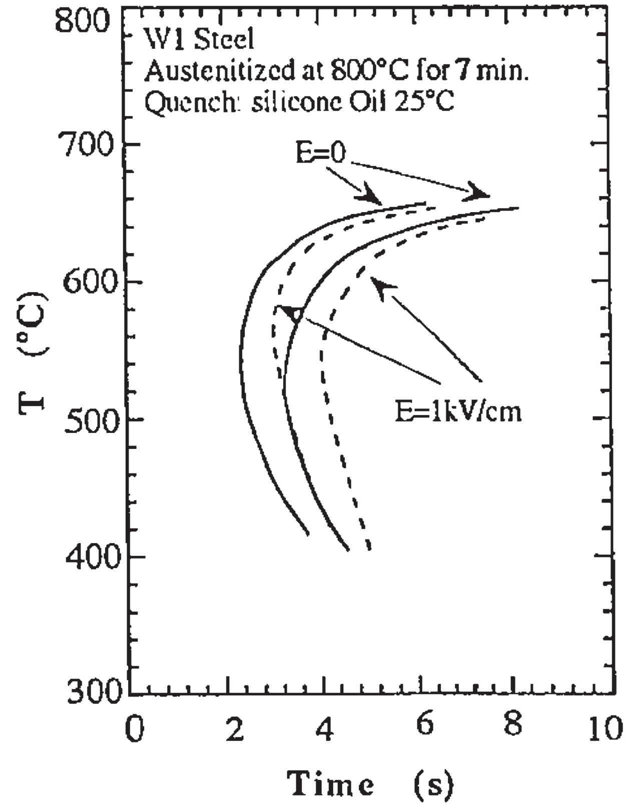


Fig. 12 Effect of an electric field on the C–T curve for a high-carbon steel. From Zheng *et al.*[23]

that the effect of the field on the hardenability was through its influence on the vacancy concentration. This suggests that vacancies play a role in the diffusion of carbon in iron, as has been reported.[24]

4. Summary and Conclusions

The application of an external dc electric field can have a significant influence on solid state transformations in metals. The effect can be on equilibria (solubility, volume fraction and composition of phases) or on kinetics (recrystallization, precipitation, phase coarsening, sintering and hardenability). Electric fields thus provide an additional means for managing the microstructure of metals and in turn their properties. This provides the potential of producing metals and alloys with improved properties at a lower cost.

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