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PROSPECTS FOR MAKING CARBIDE-FREE BAINITIC THICK STEEL PLATE BY MEANS OF CONTROLLED QUENCHING: A FIRST ESTIMATE

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ABSTRACT

Materials used for the shells of pressurized railroad tank cars must be strong and inexpensive, yet also easily weldable and resistant to fracture. The high costs associated with special alloy compositions have made it difficult in the past to find improved materials that attain all of these goals. Recent advances in steel making research indicate that commercial grade low alloy steels have the potential to offer improved properties at moderate cost in thicknesses suitable for tank car construction, if modern thermomechanically controlled processing methods are applied. Results are presented from a heat transfer analysis of controlled quench schedules for 12.7 and 25.4 mm thick plate. The calculated cooling curves are compared with an isothermal transformation diagram for a medium carbon low alloy steel. The results suggest the possibility that interrupted water spray quenching might produce carbide-free bainite, a microstructure now associated with the combination of high strength, high fracture toughness, and good weldability.

INTRODUCTION

Railroad tank cars provide carriage for most bulk liquid chemicals and a significant share of liquefied gas products in North America. The small profit margins on these commodities force the railroads and tank car builders to keep costs low, in order to retain market share. On one hand, this puts a high priority on strong but inexpensive material to help reduce car tare weight and construction cost. On the other hand, safe year-round carriage of pressurized hazardous commodities requires weldable materials with good low-temperature fracture resistance. Improvement in all technical aspects is desirable but has been difficult to achieve in the past without high cost.

In the 1960s the material most commonly used for pressure car construction was A-515 Grade 70, a plain medium carbon steel with strength and weldability adequate for general service conditions. However, analysis of pressure shell failure incidents and accidents in that era pointed to brittle fracture of A-515 at low temperature. Such fractures generally appeared to have been triggered by the action of normal service loads on cars that had been cold soaked in ambient temperatures below 0 °F (-18 °C). The car building industry responded by changing specifications from A-515 to A-516, achieving a modest gain in weldability at low cost. This change reduced the potential for weld defects that could become fracture origins in service, but there was no corresponding improvement in the material fracture resistance. More ambitious improvements were later attempted but were not successfully brought to market.

In the 1970s the Association of American Railroads sponsored development of TC-128, a micro-alloyed high strength low alloy (HSLA) carbon steel with a fine-grained ferrite-pearlite microstructure. TC-128 is stronger, somewhat more weldable, and fracture resistant to temperatures much lower than A-515/A-516 (see Table 1). However, the relatively high cost of making a specialty product in small heats prevented TC-128 from coming into wide use.

In the 1980s the industry revisited the topic of micro-alloyed steels in a study of design options (Phillips, et al., 1987) in which the authors concluded that: *"The controlled-rolled HSLA steels have significant advantages in weldability and low temperature toughness, and will be attractive for use in all pressure cars."* This led to the so-called A-8XX project, under which a trial heat of a commercial grade HSLA steel was produced and tested for mechanical properties. The A-8XX steel was found to be comparable to TC-128 in strength, but the project was terminated after other tests showed that its fracture toughness was inferior to that of TC-128 (Hicho, 1991).

In the 1990s developments in other sectors of the steel making industry have led to better understanding of thermomechanically controlled processing (TMCP) of micro-alloyed steels. Recent research suggests that a tank car steel with improved properties might now be within reach at moderate cost. This paper examines some possibilities for applying TMCP to plate in the range of thicknesses required for pressure cars.

TABLE 1. TANK CAR STEEL PROPERTIES [a]

Property	Strength (ksi) [b]		Elong.	Charpy impact energy (ft. lb.) [c]		Trans. temp.
Alloy	yield	ultimate	(%)	upper	lower	(° F)
A-515/516 Gr 70	38	70	21	31	3	+30
TC-128B normalized	50	81	22	55	3	-30

[a] Phillips, et al., 1987

[b] Minimum values; 1 ksi ≈ 6.9 Mpa

[c] Approximate values; 1 ft.lb. ≈ 1.4 J

THERMOMECHANICALLY CONTROLLED PROCESSING

TMCP encompasses a variety of on-line quenching treatments, often preceded by a final stage of hot working at relatively low temperature, in the recrystallization part of the austenite phase field. Broadly stated, the goals of TMCP are to reduce the austenite grain size, to maximize the density of ferrite nucleation sites thus producing a highly refined grain size in the finished product, and to limit the adverse effects of precipitated carbon diffusion (see Krauss (1989) for comprehensive discussion).

Carbon strengthens steel by precipitating to form carbides (Fe_3C), but carbides also lower resistance to fracture unless grain size is refined and carbon diffusion is restricted. Lowering the workpiece temperature before the start of the austenite - ferrite phase change achieves both effects. The ferrite morphology changes, first from equiaxed to acicular grains, and finally to a lath microstructure (bainite). Restricting diffusion decreases the size of carbon-rich regions, and their morphology also changes from Fe_3C networks (cementite) to isolated cementite regions, and then to carbide particles. If elements such as niobium, titanium, or vanadium are micro-alloyed in the composition, they tend to preferentially combine with the carbon, leading to a finely dispersed phase in the ferrite laths. This type of microstructure, termed carbide-free bainite, offers the best combination of strength and fracture toughness.

The thin sheet stock used for auto manufacturing now includes HSLA steels with ultra-low carbon content for high ductility and good weldability. Thin, low strength HSLA sheet is relatively easy to quench to a carbide-free bainite microstructure because a virtually uniform cooling rate can be maintained through the entire thickness (typically 1 to 3 mm), and also because the other alloy elements can scavenge most of the carbon.

Conversely, either greater strength requirements or greater thicknesses increase the challenge of making fracture tough bainitic products. Greater strength requires more carbon and, consequently, more effort to disperse or eliminate carbides. Greater thickness means more carbon diffusion because thermal conductivity will tend to limit the internal cooling rate.

In spite of these difficulties, recent work has included investigations of plate stock subjected to TMCP by means of interrupted water spray quenching. Studies of 13 mm thick trial plates for two candidate pipeline steels showed that increased cooling rates produced, higher yield strength, equal ultimate strength, and equal or better fracture toughness in comparison with air cooling (Ruddle, et al., 1993), with acceptable weldability (Bowker, et al., 1994). Similar experiments conducted with 13 mm thick X70 pipeline steel and 19 mm thick commercial grade HSLA steel showed increases in both yield and ultimate strength, lower toughness in the pipeline steel, and equal toughness with a lower transition temperature in the HSLA steel (Stachowiak, 1994). The microstructures observed in the spray-cooled specimens were mixed, with greater bainite content for higher spray-cooling rates (Ruddle, et al., 1993), and a transition from coarse banded pearlite (air cooled) to a mixture of fine-grained acicular ferrite and upper bainite (Stachowiak, 1994).

The similarity of strength, weldability, fracture toughness, and minimum thickness requirements for tank cars to the requirements for pipeline steels make these investigations relevant. Even though the results obtained in the foregoing studies might not be considered satisfactory for application to tank car construction, they at least suggest that it might be possible to find a moderately priced micro-alloyed commercial grade steel which will be suitable for thick section TMCP. The use of interrupted cooling is a key factor in the application of TMCP to produce fracture tough bainitic microstructure in thick sections.

INTERRUPTED COOLING

For thin sheet, a continuous water spray can depress the temperature through the entire thickness quickly enough to produce a non-equilibrium transformation far enough below the austenite - ferrite equilibrium range, thus retarding the diffusion of carbon precipitated from the austenite phase and promoting fine ferrite grain size. It is only necessary to terminate the quench in time to keep the sheet temperature above the martensite start line (M_S) until the austenite - ferrite phase change is completed.

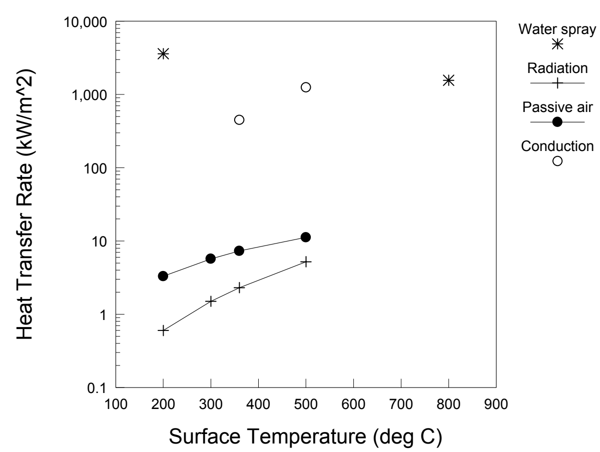

FIGURE 1. COMPARISON OF HEAT TRANSFER RATES (AMBIENT TEMPERATURE 20 °C)

Conversely, quenching establishes a temperature gradient in thick plate and must be interrupted in order to keep the surface temperature above the M_S while allowing enough time to cool the interior. A comparison of estimated heat transfer rates (Fig. 1) illustrates the rationale for interrupted cooling. These estimates are based on: the reported range of water spray heat transfer coefficients from 2 kW/m^2 °C at 800 °C to 20 kW/m^2 °C at 200 °C (Liscic, et al., 1992, and Totten, et al., 1993); radiative transfer at an emissivity of 0.26, which is the median for the range of 0.2 to 0.32 reported for steel at surface temperatures between 300 and 1000 °C (White, 1994); a passive air cooling heat transfer coefficient of 5 W/m^2°C$^{5/4}$ loosely based on buoyant convection; and thermal conductivity from 30 to 50 W/m^2 °C with a quarter-thickness-average approximation of the near-surface temperature gradient in the plate. Water spray quenching evidently removes heat from the surface much faster than it can be replaced by conduction from the interior. Passive air and radiative cooling remove heat much more slowly, however, allowing conduction from the interior to raise the surface temperature when the water spray is interrupted.

It follows that the surface temperature can be quickly brought close to the M_S, but that more time is needed to decrease the interior temperatures to a similar extent. Therefore, alloying is essential in order to delay the phase change long enough to develop a bainitic microstructure in thick plate. The isothermal transformation characteristics of EN17 steel will be used as an example. EN17 has a carbon content somewhat higher than desirable for a tank car steel and is alloyed with molybdenum rather than the typical micro-alloy components of HSLA steels (see Table 2). It is used as an example in the work reported here only for convenience. EN17 has a moderate transformation rate with earliest time to bainite start about 10 s (Fig. 2), as compared with 2 to 4 s for quick transforming steels.

TABLE 2. COMPARISON OF ALLOY COMPOSITIONS [a]

Wt % Alloy	C	Mn	Si	Al	Cu	Mo	Nb	Ni	V
A-515 A-516	0.31 0.28	1.30 1.30	0.45 0.45						
TC-128B	0.29	1.46	0.45						0.08
A-8XX trial heat	0.16 max	1.00 to 1.75	0.15 to 0.50				0.06 max [b]		0.11 max [b]
Pipeline steels [c]	0.08 to 0.09	1.90	0.25 to 0.35	0.025 to 0.035	0.00 or [d] 0.20		0.045 to 0.055	0.00 or [d] 0.11 [e]	0.07 to 0.08
EN17 [f]	0.38	1.49	0.25			0.41			

[a] As reported in Phillips, et al., 1987 except where indicated otherwise

[b] Nb + V 0.16 max

[c] Ruddle, et al., 1993

[d] Two trial compositions

[e] Ni 0.09 min

[f] American Society for Metals, 1977

HEAT TRANSFER MODEL

Simplified transient heat transfer analyses were conducted with a two-dimensional finite element model to simulate interrupted water spray cooling of thick plates. The schematic in Fig. 3 illustrates the relation of the model to a hypothetical plate. The two-dimensional model ABCD has no lateral conduction. Edges AB, BC, and CD are insulated; quenching, radiative, and convective cooling boundary conditions are applied along edge DA. Altogether the model represents the central region (no edge effects) and upper half-thickness of the plate, with conduction accounted for from the mid-plane BC to the surface DA but neglected along the rolling direction. Interrupted cooling was simulated by switching between quenching and passive cooling boundary conditions. For either condition, the appropriate heat transfer coefficients were assigned as constants both in time and along edge DA. Quenching was simulated by combining a heat transfer coefficient of 3 or 3.5 kW/m^2 °C with radiation to a 20 °C ambient background. (Assuming 100% vaporization of the water spray, 3 kW/m^2 °C would be equivalent to flow rates of 0.7 l/m^{2}s at 800 °C plate surface temperature or 0.1 l/m^{2}s at 200 °C for each face.) Passive cooling was simulated by combining the radiation term with the approximation of 5 W/m^2 °C$^{5/4}$ from buoyant convection.

The effect of latent heat, which evolves during the phase change from austenite to ferrite, was also investigated. A rough estimate of 65 kJ/kg (or 5.1x10^5 kJ/m^3 based on the 7861 kg/m^3

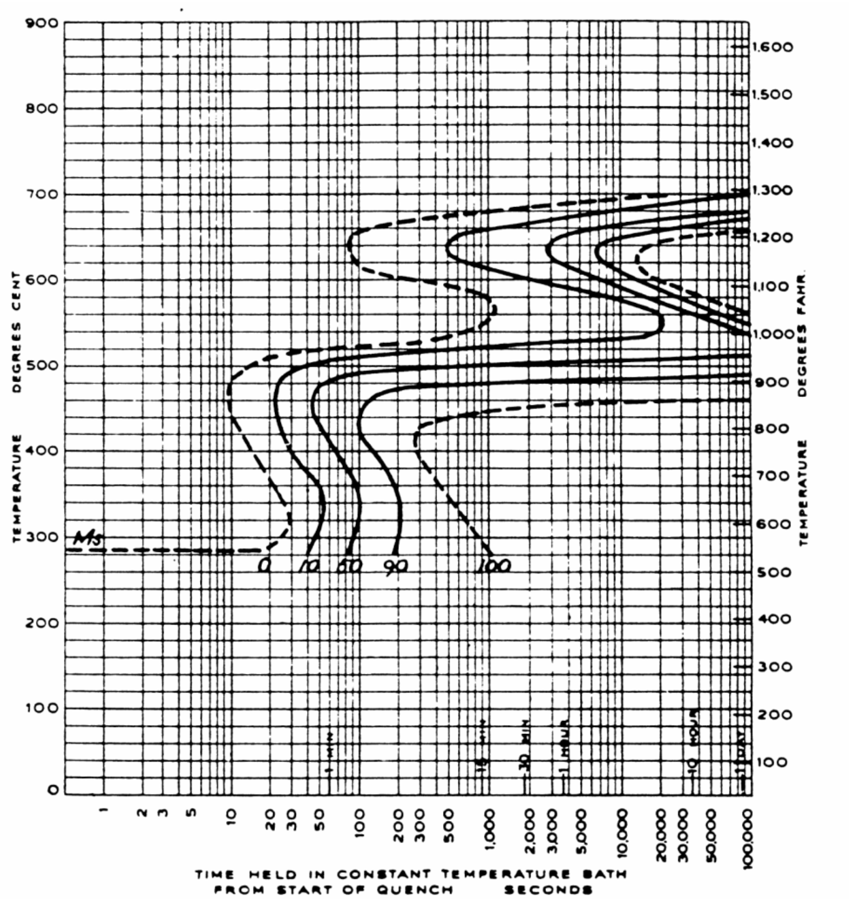

FIGURE 2. EN17 STEEL ISOTHERMAL TRANSFORMATION DIAGRAM
(USED WITH PERMISSION FROM ASM INTERNATIONAL, ATLAS OF ISOTHERMAL
TRANSFORMATION AND COOLING TRANSFORMATION DIAGRAMS, 1977)

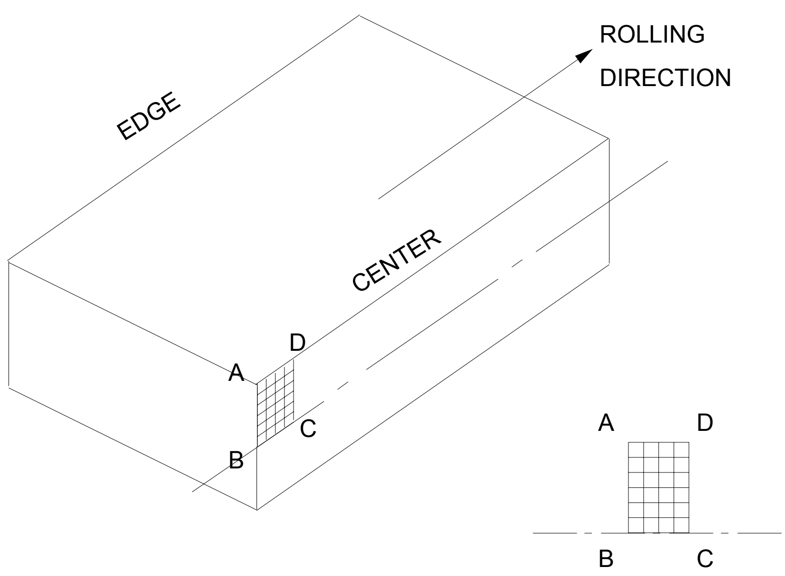

FIGURE 3. RELATION OF FINITE ELEMENT MODEL TO PLATE

density of steel) was obtained by taking the area under the spike in a plot of steel heat capacity versus temperature used by others to simulate rim quenching of a locomotive wheel (Kuhlman, et al., 1988). When eutectoid composition items such as wheels or rails are quenched, latent heat evolution has a significant effect on both temperature - time history and residual stress because the phase change occurs over a narrow temperature range and a short time. In the present case, the goal was to distribute the heat evolution in time, in proportion to the percentage of transformed material as determined from the tracks of cooling curves across the transformation diagram. This was empirically done by first using the plate model to calculate cooling curves with latent heat neglected and then re-calculating in stages to adjust the cooling curve tracks with latent heat accounted for. Comparison of the two kinds of results showed the effect to be insignificant, a consequence of the fact that the phase change typically extends over times on the order of 250 to 1000 s in the present case.

EXAMPLE RESULTS

Analyses were carried out for plates of 12.7 and 25.4 mm thickness. A few trials were necessary in each case to establish an interrupted cooling schedule that would bring the entire thickness to nearly uniform temperature in the lower part of the austenite - bainite region without cooling the surface below the M_S.

Fig. 4 summarizes the result for the 12.7 mm thick plate, for which a water spray heat transfer coefficient of 3 kW/m^2 °C was assumed. Cooling curves for the mid-point, quarter-thickness point, and surface are superimposed on a reproduction of the bainite nose portion of the EN17 transformation diagram (Fig. 1). From left to right the transformation contours are the bainite start, 10, 50, 90, and 100% transformation; the dashed line indicates the M_S. In this case the treatment schedule consisted of water spray quenching from 845 °C for 10 s, passive cooling for 2.5 s another quench for 2.5 s, and passive cooling thereafter. Note that the re-heating from conduction during the first passive cooling interval is effective in reducing the temperature gradient; the entire thickness enters the austenite - bainite region in the 300 - 400 °C range, and the temperature gradient virtually disappears before 10% transformation. However, in the final passive cooling period, the plate temperature crosses below the M_S before bainite completion, indicating that the finished product would include at least a small percentage of martensite.

Pulsed re-heating was also investigated as a means to prevent martensite formation. This was simulated by periodically increasing the ambient temperature, to represent external radiators, starting at the M_S crossing time of 300 s. Fig. 5 summarizes the results obtained for two cases: (a) four 60 s on/off cycles with radiators set at 700 °C; and (b) five 60 s on/off cycles with radiators set at 540 °C. Only the surface temperature curves are shown, since the interior gradient remains small. In the first case, the re-heating appears to be too intense, and the result suggests some coarse grained bainite, as well as additional opportunity for diffusion to produce aggregated carbide particles. The second re-heating schedule appears to be as close to ideal as possible in practice, maintaining the surface temperature within 50 °C above the M_S until bainite completion.

Fig. 6 summarizes the similar results obtained for the 25.4 mm thick plate, for which a water spray heat transfer coefficient of 3.5 kW/m^2 °C was assumed. The schedule in this case consists of a 20 s quench, 2.5 s passive cooling, 2.5 s quench, 5 s passive cooling, and 2 s quench before the long passive cooling period. Most of the bainite transformation occurs in the 300 - 400 °C range, but the interior enters the austenite - bainite region at about 500 °C. The extra thickness also results in a later M_S crossing time (600 s), so only three 60 s on/off cycles of re-heating at 540 °C are needed to maintain the transformation in the lower bainite region. In this case, one would expect the finished microstructure to include about 10% coarse grained bainite in the interior, with aggregated carbides. This is a consequence of the high interior temperatures at entry into the austenite - bainite transformation.

DISCUSSION

The candidate pipeline steels investigated by Ruddle et al. (1993) are quick transforming steels with a minimum start time at about 4 s. Stachowiak (1994) reported neither the full compositions nor the transformation diagrams for the X70 pipeline and HSLA steels he investigated but did cite the significant alloy elements: Cr, Mo, Nb, Ni, Ti for the X70 steel; and Mo, Ti, V for the HSLA steel. One may surmise that the additions of Cr, Mo, and Ni produced, among other effects, steels with moderate transformation rates similar to that of the EN17 steel used as the example in the present work. Thus, although EN17 is an unlikely candidate for tank car construction, its transformation diagram still provides a useful basis for assessing the prospects of making thick plate with lower carbon content and a carbide-free bainite microstructure.

Other heat treatment schedules are possible beside those considered above. For example, the work of Ruddle et al. (1993) showed that the cooling start temperature affects the location of the entry point on the transformation start line. The cooling start temperature could be reduced from 845 to perhaps 800 °C, in the present case, to further decrease the temperature gradient and bring the entire thickness within 50 °C above the M_S before the start line. Increasing the water spray flow rate would be an alternative. However, the rates quoted earlier should be treated with caution because of the complex relation between mass flow rate, surface temperature, other factors, and actual heat transfer coefficient (Liscic, et al., 1992, and Totten, et al., 1993). Also, different flow rates would be required to achieve the same cooling rate at the top surface and underside.

Calculations are thus useful for screening options, but testing is obviously required to verify the type of microstructure produced by interrupted cooling. It is also essential to test thoroughly in order to establish confidence that the desired properties can be achieved for the range of compositions

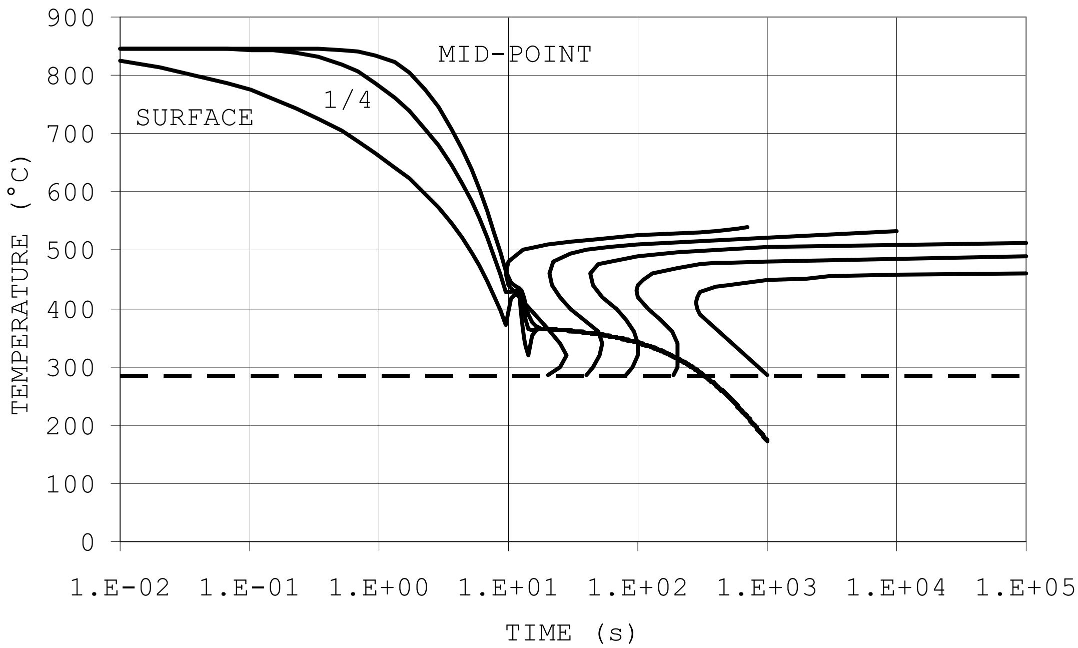

FIGURE 4. INTERRUPTED COOLING OF 12.7 MM PLATE

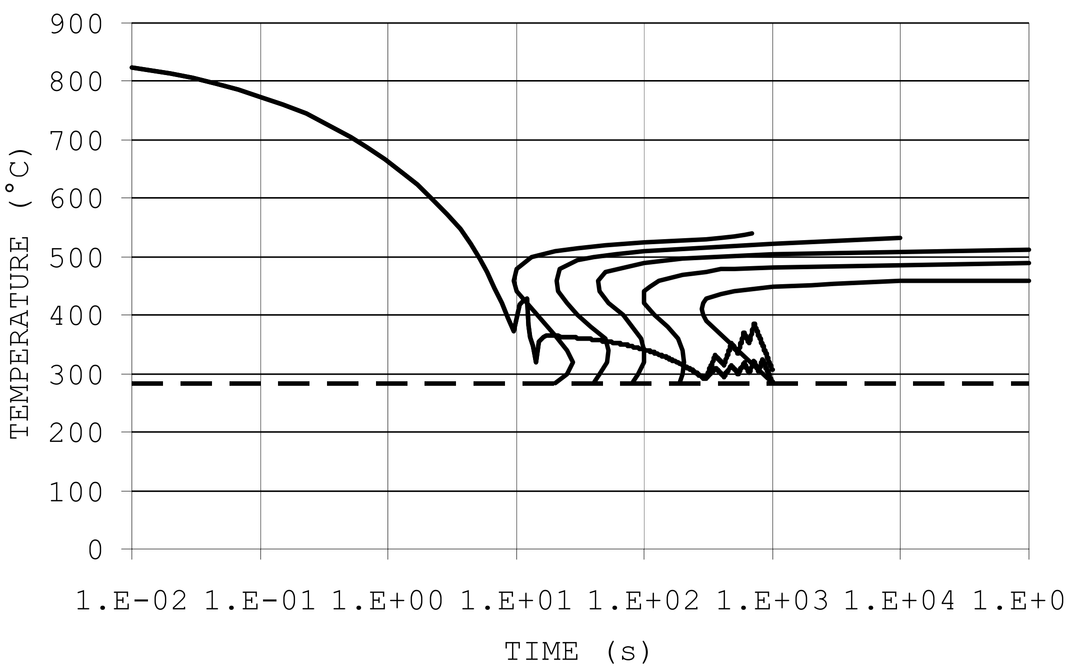

FIGURE 5. EFFECT OF PULSED REHEATING

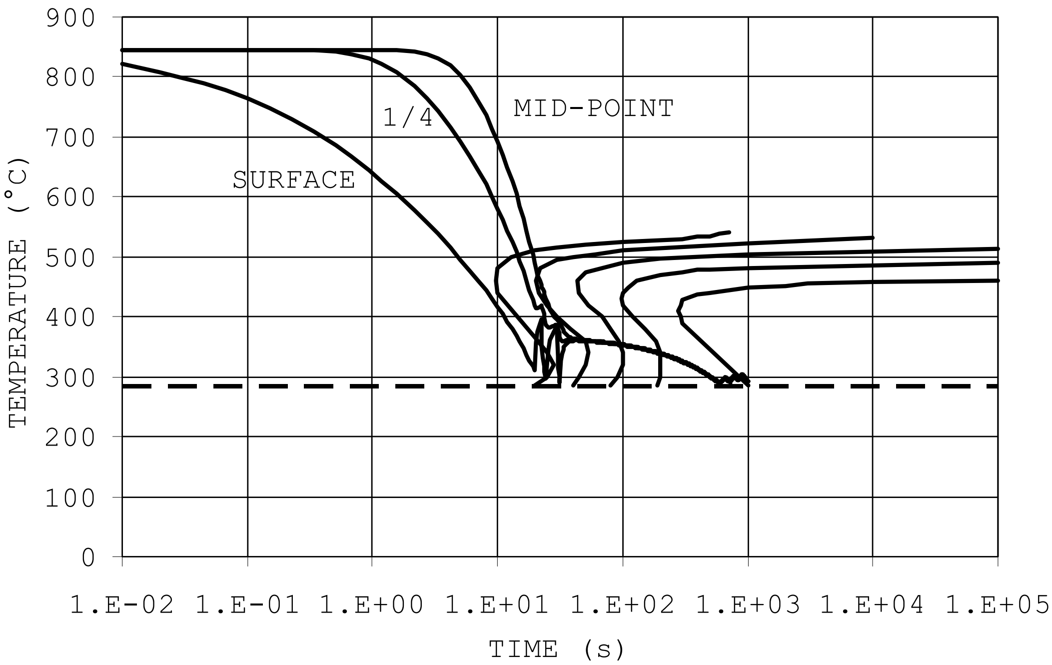

FIGURE 6. INTERRUPTED COOLING AND RE-HEATING OF 25.4 MM PLATE

allowed by specifications for ladle analysis. The sensitivity to composition is illustrated by comparison of the older EN17 steel (American Society for Metals, 1977) and its modern counterpart (Vander Voort, 1991) which has additions of 0.14% Cr and 0.24% Ni, essentially the same bainite nose, but for which the M_S has increased from 285 to 325 °C. Questions of suitability for practical construction and welding must also be answered before carbide-free bainites can be seriously considered for tank car construction. Plate stock is cold-formed to sector shape and butt welded to fabricate the pressure shell, which is then subcritically heated for stress relief. Suitability for welding is likely to be of most concern because the weld metal and heat affected zone will briefly reach austenitizing temperatures. The details of micro-alloy composition can then be of great concern if accelerated cooling is needed to avoid undesirable microstructure. For example, the vanadium addition in a late 1970s commercial grade HSLA steel was associated with underbead quench cracking at welds made to fabricate the underframe structure of an urban bus, and fatigue crack propagation reduced the service life of the structure by a factor of ten (Orringer and Tong, 1985).

A similar issue arises with regard to the numerous attachment welds that are made to the completed pressure shell. The design constraints on these welds often require endings or corners which create local stress concentrations in the shell. Approximate estimates of the stress concentration effect (Orringer et al., 1988) have been experimentally verified (Larson et al., 1992) and refined (Hicho et al., 1995). Although these stresses are partially relieved in service (Larson et al., 1992, and Shen and Clayton), it is obviously advisable to avoid heat affected zone microstructure that might be susceptible to early fatigue cracking. Work toward this end, in progress at the Volpe Center, has as its goal the development of a heat transfer and stress analysis model for simulation of effects near attachment welds and for use in screening candidate post-weld heat treatments.

CONCLUSIONS

Manufacture of carbide-free bainitic plate in thicknesses appropriate for railroad tank car pressure shells appears to be technically feasible from the viewpoint of requirements for accelerated cooling. Interrupted cooling followed by pulsed re-heating is a practical strategy for keeping the material within 50 °C above the martensite start line during the entire austenite - bainite transformation.

Candidate materials can certainly be found, among the modern HSLA steels, with suitable transformation characteristics. Whether such materials will also be suitable for car construction at an attractive price remains to be seen.

Simplified heat transfer analysis, in which the effect of phase change latent heat is neglected, provides a useful means for custom design of heat treatment schedules to fit the characteristics of candidate steels. Similar analyses of typical weld details are possible and should be equally useful in assessments of suitability for welding.

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