ABOUT CALCULATING THE CHARACTERISTICS OF THE MARTENSITE-AUSTENITE CONSTITUENT

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Abstract

The solid region of a linepipe steel which is influenced by the heat of welding often contains small islands which are mixtures of untempered martensite and austenite. These are sometimes referred to as the "martensite–austenite constituents" and are said to represent "local brittle zones". The purpose of this paper is to show how the development of these regions might be estimated using phase transformation theory and to examine critically whether they represent local brittle zones.

Introduction

"Local brittle zones" are small regions of relatively hard mixtures of phases which form in the heat affected zones of multipass welds. The term apparently was coined by Fairchild [1] during an Exxon project involving the construction of an offshore platform for the North Sea. Publication was delayed until 1987 [2], after which the subject began to be investigated widely. The zones usually contain untempered martensite and retained austenite and hence the term martensite—austenite ("MA") constituents. There is no doubt that if this mixture of phases in macroscopic form is studied in isolation then it would exhibit brittle behavior, but as we shall see later, this may not necessarily be the case when the MA constituent is dispersed in microscopic form. Nevertheless, in experiments where the toughness of the heat—affected zone is determined, the presence of these minute brittle regions gives rise to scatter in the measured data, because if the test specimen samples a brittle zone then the recorded value of toughness is small [3]. Scatter in mechanical property data is not only disconcerting but reduces confidence in design because of the existence of a few poor values which fall out of the desired range.

Experimental data have been interpreted to conclude that the lower bound toughness values deteriorate as the volume fraction of martensite in the form of local brittle zones increases [4]. However, the same data can be interpreted to indicate that there is a minimum in the toughness as a function of increasing fraction of martensite [5]. There is a physical expectation of the latter relation. The local zones of martensite should only be brittle if they contain a large concentration of carbon. Prior to martensitic transformation, the austenite is enriched in carbon as other forms of ferrite grow. Consequently, a larger fraction of ferrite prior to martensitic transformation is a necessary condition for the occurrence of local *brittle* zones. Otherwise, the degree of carbon enrichment will be insufficient to render the martensite brittle. Experimental work by Davis [6] has confirmed this, since localised zones of martensite were not found to cause problems with the

overall toughness of the heat-affected zone when the steel concerned had a high hardenability (and consequently a smaller amount of transformation prior to martensite).

Local brittle zones (LBZs) might be treated without a consideration of their detailed microstructure. However, from the point of view of mechanics, it is worth pointing out that insufficient work has been done to address the following questions in a quantitative manner:

- 1. How hard does a LBZ have to be in order to influence scatter in toughness? Or is it the hardness relative to the surrounding material that influences its ability to act as a brittle zone?
- 2. How big does a LBZ have to be in order to matter, relative to the size of the plastic zone in the test used to determine toughness?
- 3. Does the shape of the LBZ matter?
- 4. How many tests are required in order to establish a probability of failure-based design?

Given these deficiencies, it is not surprising that the critique by Liessem and Erdelen–Peppler [7] fails to resolve question 4 in this list, other than to suggest a change in specification. The change in essence would allow repeated testing of rejected pipes until the specification is met, which as the authors admit, does not seem to be a sensible approach. The work presented does not prove that LBZs can be neglected, but argues instead that the acceptance criteria are bizarre because the entire production of pipes contains LBZs on the longitudinal welds and luck determines whether the small–scale tests hit an LBZ.

The real issue should include a specification of an acceptable level of risk, and probabilistic testing to see whether the material and process combination manages that risk. The generation of probabilistic data is necessarily expensive. The answers to the first three questions are dealt with here after a consideration of the microstructure of the brittle zones.

Martensite/Austenite Constituent

The martensite–austenite (MA) constituent is a rather clumsy name given to what is essentially a mixture of untempered martensite embedded in carbon–enriched retained austenite. When transformations such as Widmanstätten ferrite or bainite occur at temperatures greater than that at which martensite can form (M_S) , the residual austenite is enriched in carbon and its martensite–start temperature is reduced to M_S^T . In modern low–carbon steels, the volume fraction of this residual austenite tends to be small, and some of it may partly decompose into martensite if M_S^T is greater than ambient temperature. It is this small quantity of martensite and carbon–enriched austenite that is the MA constituent.

This simple mechanism for the genesis of the MA constituent helps establish the role of alloying elements, cooling rates and austenite grain size. The ability to calculate the volume fraction and chemical composition of MA was demonstrated sometime ago in predominantly bainitic microstructures, on the basis of the detailed phase transformation theory [8, 9]; a simple numerical example is given in [10]. It relies on the fact that the bainite reaction stops when the carbon concentration of the austenite achieves that given by the T_{θ} curve; similar limiting conditions can be derived if the microstructure contains other ferritic phases.

A full description of the MA constituent should include:

- 1. The proportions of martensite and austenite in the constituent.
- 2. The chemical compositions of the martensite and austenite. This is necessary in order to estimate the hardness (see, for example, [9]). MA is formed from the residue of austenite that is left untransformed following the growth of phases such as ferrite, Widmanstätten ferrite and bainite. All of these leave the austenite richer in carbon provided the average concentration of carbon in the steel is greater than its solubility in ferrite. If the volume fraction of MA is large then its carbon concentration will be low; assuming that brittle behavior is associated with high carbon, the phase may be less harmful at sufficiently large fractions.
- 3. The shape of the MA. When MA is confined between plates of ferrite, the retained austenite within it is more stable than when it is present as blocks between differently oriented plates [8, 9]. Films of retained austenite are not considered to be damaging to toughness.
- 4. The mechanical properties of the MA region relative to its surroundings.

Some of the items listed here can be estimated by calculation, as illustrated in the calculations that follow, and indeed as attempted by Furuhara and co–workers [11]. Their Figure 6 is essentially a partial reproduction of the work described here and in [8, 9, 12] with the exception of the A_{CM} curve, which follows a procedure due to Kriesment and Wever [13]. The purpose of the A_{CM} curve is to determine whether the austenite can decompose by cementite precipitation; if the carbon concentration of the austenite exceeds that given by the A_{CM} curve then it is thermodynamically possible to form cementite. Whether it actually forms is a matter of kinetics, for example the cooling rate.

A Simple Calculation for X80 Steel

The example given here illustrates a calculation of the volume fraction (total, martensite and retained austenite) of the MA constituent, together with the chemical compositions of all the phases. The steel considered is not that encountered in pipelines, but the problem is exactly identical. A similar calculation for pipeline steels is given in [5]. Since the steel is bainitic, it is appropriate to use the T_0 curve [12], but this could be modified to be the Ae3 or other constrained equilibrium curve for other phases preceding MA.

It is interesting that the carbon concentration of MA is found to be almost independent of the average concentration in the steel [14]. This is consistent with the well–established fact that the austenite which partially decomposes to form the MA constituent, has its chemical composition limited by the T_{θ} curve. It is this T_{θ} curve which forms the basis of the calculation example presented below.

A particular X80 steel has the chemical composition [15]

When thermomechanically processed, such steels result in a microstructure which is bainitic (we assume here that "acicular ferrite" is bainite, labelled α_b) with residual phases which may, depending on the detailed processing, be the MA constituents. Because of the very low carbon concentration and the steel contains niobium, cementite precipitation does not accompany the

formation of bainite [11], so that the residual austenite prior to its partial transformation into martensite, becomes enriched in carbon.

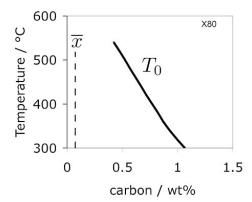


Figure 1. Calculated T_0 curve for X80 steel. \bar{x} represents the average carbon concentration of the steel at 0.073 wt%.

The calculated martensite–start temperature of the fully austenitic steel is 444 $^{\circ}$ C [16, 17]. The silicon in the steel prevents the precipitation of cementite, so that the bainite consists only of a mixture of bainitic ferrite and carbon–enriched residual austenite. The calculated T_0 curve is given in Figure 1. If it is assumed that the maximum fraction of bainite is achieved at a temperature just above 444 $^{\circ}$ C, then the transformation must stop when the carbon concentration of the residual austenite, i.e. x_{γ} reaches the T_0 curve, i.e., $x_{\gamma} = 0.66$ wt%. From mass balance,

$$V_{\alpha_b} x_{\alpha_b} + V_{\gamma} x_{\gamma} = \bar{x}$$

where V_{α_b} is the volume fraction of bainitic ferrite, V_{γ} is that of the residual austenite at the transformation temperature with $V_{\gamma} = 1 - V_{\alpha_b}$ and \bar{x} is the average carbon concentration in the alloy. Taking x_{α_b} to be 0.02 wt% (rough solubility of carbon in ferrite) and setting $x_{\gamma} = x_{T_0}$ at 444°C, gives from the lever rule applied to the T_0 curve,

$$V_{\alpha_b} = \frac{x_{T_0} - \bar{x}}{x_{T_0} - x_{\alpha_b}} \qquad \text{and} \qquad V_{\gamma} = 0.08$$

Given that $x_{\gamma} = 0.66$ wt%, its M_S^r becomes 166 °C, so that using the Koistinen and Marburger equation, the fraction of austenite retained (γ_r) in the final microstructure obtained by cooling to ambient temperature, is given by

$$V_{\gamma_r} = V_{\gamma} \times exp\{-0.011(M_S^r - 25)\}$$

= 0.08 \times exp\{-0.011(166 - 25)\} = 0.02 (1)

It follows that the amount of martensite $V_{\alpha'} = 0.08 - 0.02 = 0.06$. The final microstructure is listed in Table I. The hardness of the martensite is expected to be in the region of 700HV [10].

Table I. Summary of the Microstructure

Phase	Volume percent	Carbon content (wt%)
Bainitic ferrite α_b	92	≈ 0.02
Martensite α'	6	0.66
Retained austenite γ_r	2	0.66

One approximation made here is that the formation of bainite stops at the M_S temperature of the steel as a whole, i.e., 444° C; permitting it to proceed to an even lower temperature would reduce the $\alpha' + \gamma_r$ fraction, and increase the amount of retained austenite at the expense of martensite. It is also emphasised that the calculations are indicative of the propensity of a particular steel to form martensite–austenite constituents; the actual microstructure must of course be sensitive to the cooling rate and steel hardenability. This latter dependence can also be calculated as illustrated in Figure 2, for two steels with different hardenability; the calculations are consistent with the gradients of microstructure expected in the heat affected zone.

Some Further Discussion

The analysis above which shows that the amount of martensite that can form in a steel such as X80 when most of the austenite is allowed to transform into bainite, is really quite small. But the calculation only considers the volume fraction of martensite, not its size or shape. We therefore return to some of the questions that were posed in the introduction.

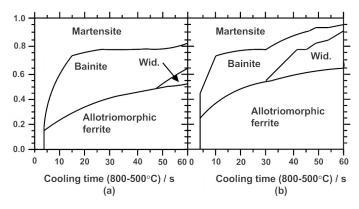


Figure 2. A small amount of martensite makes a local zone more brittle. Hence, the Fe-0.1C-1Mn wt% alloy illustrated in (a) is less susceptible to LBZ formation than the lower hardenability Fe-0.1C-1Si wt% alloy shown in (b),[5]. The vertical scale represents volume fraction and "Wid" stands for Widmanstätten ferrite.

How hard does a LBZ have to be in order to influence scatter in measured toughness? On the basis of composite theory for a two-phase mixture of $\alpha_b + \alpha'$ [18, 19], plastic flow can be estimated to begin in the martensite at a stress σ when:

$$\sigma \approx \sigma_{\alpha_b} + \frac{V_{\alpha'}}{1 - V_{\nu'}} \sigma_{\alpha'} \tag{2}$$

where $\sigma_{\alpha'}$ is the yield strength of the martensite in isolation and σ_{α_b} the stress in the majority softer phase at the point where the martensite yields. Given that linepipe steels are not particularly strong when compared with the hardness of carbon–enriched martensite, it is likely that the stress within the softer phase will never reach a value where the martensite yields, assuming that the fraction of martensite is small. This means that the MA constituent behaves essentially as a hard inclusion, in which case there is extremely good theory established to cover scatter in toughness, using for example, extreme value statistics [20, 21]. If, on the other hand, the martensite has flow properties comparable to that of the majority soft phase and is present in a sufficiently large fraction, then its influence on scatter will be dramatically reduced.

How big does a LBZ have to be relative to the plastic zone in the toughness test in order to matter? This depends on the type of toughness test. Martensite, or that which is induced by stress during testing, will behave in a brittle manner at the high strain rates associated with an impact test [22]. Occasional poor Charpy impact toughness results are inevitable in a blunt notch test where a crack must be initiated, and an island of martensite provides such an initiation site within the long–range distributed stresses at the notch. In contrast, small fractions of martensite may not be as influential when it comes to toughness tests which begin with an artificial sharp crack since the probability of finding the small region of martensite decreases.

Does the shape of a brittle zone matter? It is well known [23] that long films of hard phase tend to crack in the thickness direction whereas the crack size is related to the mean lineal intercept when it comes to equiaxed (blocky) particles. Thin films of microphases are therefore desirable relative to blocks [8, 9], and the ratio of blocky to film regions is expected to be given by

$$\frac{V_{film}}{V_{blocky}} \approx \frac{0.15V_{\alpha_b}}{V_{film} + V_{blocky} - 0.15V_{\alpha_b}}$$
 (3)

with the simple outcome that the amount of bainite in a steel such as X80 should be maximised in order to avoid blocky regions of microphases. Note that the maximum amount of bainite that can be achieved is of course dependent on the T_0 curve which can easily be calculated.

Conclusions

There is considerable literature to indicate that the presence of small regions of untempered martensite and retained austenite in the heat-affected zones of welds can lead to the deterioration of toughness. However, the wide use of the term MA constituent hides many complexities about shape, size and composition. It is unwise to claim that such regions are always detrimental. There are many steels in service where such mixtures of austenite and martensite are considered beneficial to the properties, as reviewed elsewhere [22, 24–26].

An attempt has been made in this paper to show how features of microphases might be calculated, and to identify how their shape, size and composition may influence different kinds of fracture toughness tests and scatter in the data obtained using such tests. It is hoped that some of the speculation can be converted into solid and validated theory in the years ahead.

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References

- 1. D.P. Fairchild, private communication with author, 1995.
- 2. D.P. Fairchild, "Local Brittle Zones in Structural Welds." *Welding Metallurgy of Structural Steels*, ed. J.Y.Koo, (Warrendale, Pennsylvania, USA, TMS–AIME, 1987), 303-318.
- 3. K.-H. Schwalbe and M. Koçak, "Fracture Mechanics of Weldments, Problems and Progress for Weldments." In S.A. David and J. Vitek, editors, *International Trends in Welding Science and Technology*, eds. S.A.David and J.Vitek (Ohio, USA, 1992. ASM International, 1992), 479-494.
- 4. S. Aihara and K. Okamoto, "Influence of LBZ on HAZ Toughness of TMCP Steel", *Metallurgy, Welding and Qualification of Microalloyed Steel Weldments*, eds. D.G. Howden, J.T. Hickey and M.D.Randall, (Florida, USA,1990. American Welding Society, 1990), 402-427.
- 5. S. Suzuki, G. Rees and H.K.D.H. Bhadeshia, "Modelling of Brittle Zones in the HAZ of Steel Welds", *Modelling and Control of Joining Processes*, ed. T. Zacharia, (Florida, USA, American Welding Society, 1993), 186-193.
- 6. C.L. Davis, "Cleavage Initiation in the Intercritically Reheated Coarse Grained Heat Affected Zone of Steels." (Ph.D thesis, University of Cambridge, Cambridge, U. K., 1994.)
- 7. A. Liessem and M. Erdelen-Peppler, "A Critical View on the Significance of HAZ Toughness Testing." *Proceedings of International Pipeline Conference*, (New York, NY, USA, ASME, 2004), 1-8.
- 8. H.K.D.H. Bhadeshia and D.V. Edmonds, "Bainite in Silicon Steels: A New Composition Property Approach I", *Metal Science*, 17 (1983), 411 419.
- 9. H.K.D.H. Bhadeshia and D.V. Edmonds, "Bainite in Silicon Steels: A New Composition Property Approach II", *Metal Science*, 17 (1983), 420 425.
- 10. R.W.K. Honeycombe and H.K.D.H. Bhadeshia, *Steels: Microstructure and Properties*, 2nd edition. (Butterworths–Hienemann, London, 1995).
- 11. T. Furuhara et al., "Incomplete Transformation of Upper Bainite in Nb–Bearing Low Carbon Steels." *Materials Science and Technology*, 26 (4) (2010), 392 397.
- 12. H.K.D.H. Bhadeshia and D. V. Edmonds, "The Mechanism of Bainite Formation in Steels." *Acta Metallurgica*, 28 (1980), 1265 1273.

- 13. O. Kriesment and F. Wever, "The Bainite Reaction in High Carbon Steels." *The Mechanism of Phase Transformations in Metals* (Special Report 18, London, U.K., Institute of Metals, 1955), 253-263.
- 14. F. Matsuda et al., "Review of Mechanical and Metallurgical Investigations of Martensite—Austenite Constituent in Welded Joints in Japan." Welding in the World, 37 (1996), 134 154.
- 15. S.Y. Shin et al., "Correlation of Microstructure and Charpy Impact Properties in API X70 and X80 Line-Pipe Steels." *Materials Science & Engineering A*, 458 (2007), 281 289.
- 16. H.K.D.H. Bhadeshia, "The Driving Force for Martensitic Transformation in Steels." *Metal Science*, 15 (1981), 175 177.
- 17. H.K.D.H. Bhadeshia, "Thermodynamic Extrapolation and the Martensite-Start Temperature of Substitutionally Alloyed Steels." *Metal Science*, 15 (1981), 178 150.
- 18. Y. Tomota et al., "Tensile Deformation of Two Ductile Phase Alloys: Flow Curves of α/γ Fe–Cr–Ni Alloys." *Materials Science and Engineering*, 24 (1976), 85 94.
- 19. H.K.D.H. Bhadeshia and D.V. Edmonds, "Analysis of the Mechanical Properties and Microstructure of a High-Silicon Dual Phase Steel." *Metal Science*, 14 (1980), 41 49.
- 20. H.V. Atkinson and G. Shi, "Characterization of Inclusions in Clean Steels: a Review Including the Statistics of Extremes Methods." *Progress in Materials Science*, 48 (2003), 457 520.
- 21. H.K.D.H. Bhadeshia, "Steels for Bearings," *Progress in Materials Science*, 57 (2012), 268–435.
- 22. H.K.D.H. Bhadeshia, "Nanostructured Bainite." *Proceedings of the Royal Society of London A*, 466 (2010), 3 18.
- 23. D.A. Curry and J.F. Knott. "Effects of Microstructure on Cleavage Fracture Stress in Steel," *Metal Science*, 12 (1978), 511 514.
- 24. B.C. DeCooman, "Structure–Properties Relationship in TRIP Steels Containing Carbide Free Bainite." *Current Opinion in Solid State and Materials Science*, 8 (2004), 285 303.
- 25. P.J. Jacques, "Transformation-Induced Plasticity for High Strength Formable Steels, *Current Opinion in Solid State and Materials Science*, 8 (2004), 259 265.
- 26. H.K.D.H. Bhadeshia, M. Lord, and L.-E. Svensson, "Silicon-Rich Bainitic Steel Welds." *Transactions of JWRI*, 32 (2003), 91 96.