

## MICROALLOYED BAKE-HARDENING STEELS

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### Abstract

A variety of bake-hardenable steels have been developed in the past two decades and implemented by automakers, to achieve good dent-resistance with formability. The evolution of these products is reviewed here as alloy compositions, annealing (and coating) processes, and performance expectations have changed over the years through the progression from traditional low-carbon grades to hot-dip coated “bake-hardenable interstitial-free” type steels, to Advanced High Strength Sheet Steels. The role of microalloying is especially highlighted, with some emphasis on effects of Nb. Mechanistic effects are discussed, and some thoughts are presented related to areas or opportunities for improved understanding in the future.

### Early Bake-Hardening Steels

Effects of carbon and nitrogen strain-aging are well known, and nitrogen aging provided strengthening in ingot-cast rimmed steels of the past. Bake-hardening (BH) steels were developed later, where control of solute carbon levels was sufficient to provide a strengthening increment during the paint baking cycle (at elevated temperature) after stamping, while maintaining resistance to room temperature aging during lengthy periods associated with shipping and storage. These steels have evolved over the years, in terms of their processing routes, metallurgical characteristics, and applications, and this evolution continues today. Bake-hardening steels have become ubiquitous in exposed automotive applications, although the baking increment of strengthening is also employed in some unexposed components.

Early bake-hardening steels were developed over 20 years ago, based on simple low-carbon steel compositions, processed using continuous annealing facilities that incorporated low-temperature overaging whereby recrystallization after cold-rolling is accomplished at high temperature, and the overaging section provides a means to carefully control dissolved carbon levels, so that bake-hardening is achieved without ambient aging [1]. While there are detailed issues related to nucleation and growth kinetics during overaging, control of solute carbon in these steels can be thought of simply in terms of the temperature dependence of carbon solubility in ferrite, whereby lower carbon levels are soluble at reduced temperature. Nitrogen aging is suppressed in these Al-killed steels via precipitation of aluminum nitrides. The maximum coil widths that could be processed in these continuous annealing facilities were frequently less than the widths required by automotive customers for exposed body-panels, and batch-annealed bake-hardening steels were developed to provide a wider product range, as well as a viable production route for steelmakers without continuous annealing lines. These early bake-hardening steels were frequently used in the uncoated condition, or with electroplated zinc (or zinc-alloy) coatings.

Batch-annealed bake-hardening low-carbon steels involve some different metallurgical characteristics than the continuous annealed versions where it is easy to control solute carbon via overaging. Very slow cooling associated with the batch-annealing process makes it more difficult to retain carbon in solution, although it is found that significant bake-hardening can be achieved if the intercarbide particle spacing is sufficient, as illustrated for a range of batch-annealed low-carbon steels in Figure 1 [2]. If the carbide particles are sufficiently spaced, then the diffusion distance for solute carbon atoms becomes too great to remove all of the carbon from solution in the ferrite even under slow cooling conditions. In practice, the wide intercarbide spacing is usually obtained by using a very low carbon level ( $\sim 0.010$  wt. %), so that all of the cementite is dissolved during annealing (in contrast to the widely distributed spheroidal carbides found in typical low-carbon steels), and precipitation at ferrite grain boundaries during subsequent cooling ensures that the carbides are coarse and widely spaced. A small niobium addition ( $\sim 0.010$  wt %) has been used for grain refinement in the batch-annealed low-carbon bake-hardening grades, in order to reach desired strength levels, albeit with a small reduction in the plastic anisotropy ratio (e.g.  $r_{ave}$ ) [3]. These steels have been successfully employed for several years in many locations.

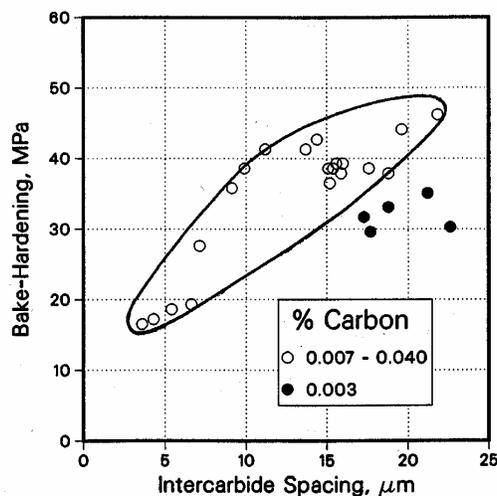


Figure 1. Influence of intercarbide spacing on bake-hardening of low-carbon batch-annealed steels [2].

### Interstitial-Free Steels and Bake-Hardening Variants

Installation of modern hot-dip coating lines capable of producing sheet steels with surface quality suitable for exposed applications created a substantial shift in composition/processing approaches. These coating lines essentially involve high temperature recrystallization annealing, followed by hot-dip coating in molten zinc at a temperature of approximately  $500^{\circ}\text{C}$ , followed by a galvannealing heat treatment in some cases. The temperatures associated with galvanizing/galvannealing are higher than would be desired for a suitable overaging treatment, and a separate overaging section is not usually available. Consequently, the processing of conventional low-carbon steels through such facilities results in a product with inferior aging resistance [e.g. 4]. Aging is problematic for exposed parts due to the potential formation of strain-lines during forming, and for unexposed parts due to diminished ductility or formability. Consequently, interstitial-free (IF) steels, where carbon is “stabilized” (removed from solution in ferrite) by addition of strong carbide forming elements, were developed and implemented for exposed hot-dip applications. Microalloying with Nb, Ti, and in some instances V, is of obvious importance in these steels, as it provides the fundamental character of carbon stabilization.

(Nitrogen stabilization is also important in these steels, and is accomplished either by microalloy nitride forming additions, or by aluminum.) This trend led to a substantial increase in vacuum-degassing capability to produce the ultra-low carbon (ULC) levels (less than approximately 0.005 wt. %) desired in IF sheet steels, corresponding to the increase in modern hot-dip coating line capacity.

Expanded use of IF sheet for exposed applications, driven primarily by expanded capability for production of exposed-quality hot-dip coated sheet, was accompanied by some benefits as well as some concerns. The yield strength of these steels is relatively low, while the ductility is high, when compared to conventional low-carbon sheet steels. Formability of these steels is correspondingly excellent, while the dent-resistance in service is of concern, particularly in regions of parts where forming strains are low, and the substantial work-hardening rates associated with these steels are not able to be used advantageously. Stronger versions of the IF steel family were developed to enhance dent-resistance and structural performance when necessary. Strengthening is based particularly on P, Mn, and sometimes Si additions, due to their potent solution strengthening effects. These effects have been quantified by several investigators. The effects are usually considered to be independent and additive, although one study [5] suggests interactions between Mn and either Si or P, whereby the interaction leads to lower strength; this interaction was attributed to different characteristics of the atomic size mismatch between iron and the substitutional additions.

Higher-strength IF steels led to the natural development of bake-hardening versions of interstitial-free steels containing small amounts of solute carbon.<sup>1</sup> The strengthening contribution available from carbon strain aging provides enhanced dent-resistance. Furthermore, the presence of some solute carbon mitigates a potential concern for “secondary work embrittlement” (SWE) that is sometimes encountered in solution strengthened IF steels whereby intergranular fractures occur when the work hardened ferrite matrix becomes stronger than the grain boundaries. The ferrite grain boundary cohesive strength is diminished by the presence of some elements such as phosphorus, and increased by the presence of other elements such as carbon or boron; which explains the susceptibility of P-strengthened IF steels to the SWE phenomenon, and the beneficial influence of small levels of solute carbon (and boron).

The physical metallurgy of bake-hardenable IF steels are complicated, interesting and largely controlled by microalloying effects, so represents the primary aspect of this overview. These grades have been investigated for several years, with much interest and activity occurring in approximately the late 1990’s, when development and application of these steels became more widespread. Products have been widely commercialized, and review of the literature indicates that research activity has subsided, although some good reviews have been published recently [6,7]. The essential character of a bake-hardenable IF steel is that it has an ultra-low carbon level along with Nb and/or Ti (and sometimes V) microalloying similar to conventional IF sheet steels, along with slight modifications in alloying and processing to ensure the presence of small amounts of dissolved carbon.

The carbon and nitrogen levels in bake-hardenable IF steels are similar to conventional IF steels, and the differences are largely associated with the microalloying strategy. In conventional IF steel, carbon and nitrogen are fully stabilized by adding amounts of Ti and Nb that are in excess of stoichiometric levels needed to form TiN, TiC and/or NbC. Ti-only, Nb-only, and Ti-Nb

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<sup>1</sup> The common terminology “bake-hardenable interstitial-free steel” is perhaps a misnomer, since it implies at the same time, both the presence and the absence of interstitials in solution in ferrite. While “nearly interstitial-free” may be a better description, we will employ the common terminology here, despite its oxymoronic character.

approaches are most common. In the Ti-only approach, titanium combines with carbon, nitrogen, and sometimes sulfur, while in the Ti-Nb approach, titanium is added to stabilize nitrogen and niobium to stabilize carbon. In the Nb-only approach, aluminum is used for nitrogen stabilization, while niobium is added for carbon stabilization. Hot strip mill processing can influence the precipitation kinetics and degree of stabilization in the hot-band, which is reported to influence texture development, but sufficient Nb/Ti additions usually lead to continuous yielding and aging resistance in the final product. The different microalloying approaches are all practiced successfully, with the choice often based on proprietary and producer-specific preferences. High levels of solute-Ti are reported to adversely influence coating surface quality and galvannealing reaction behavior [8], and consequently the Ti-only approach is less common for exposed-quality hot-dip applications. Vanadium is also reported to offer potential for full carbon stabilization in IF steels [9], although other investigators have suggested that vanadium is not a potent carbon stabilizer [10]. To the authors knowledge V-containing fully-stabilized IF steels remain at developmental stage.

In bake-hardenable versions of IF steel, solute carbon is obtained by a variety of approaches. First, the carbon-stabilizing microalloying addition can be reduced so that it is inadequate for full stabilization. Such behavior can be accomplished by the so-called partially stabilized variants, or could theoretically be achieved in unstabilized steels if the total carbon level could be controlled at sufficiently low (ppm) levels. Second, fully stabilized compositions can be annealed at sufficiently high temperatures such that the microalloy carbides are partially dissolved, whereby interstitial carbon is “destabilized” by processing. Third, the addition of weaker carbide-forming elements such as vanadium [11,12], chromium, or molybdenum [13] can provide or contribute to incomplete stabilization. In each of these approaches, alloying and processing are carefully controlled to achieve a narrow window of solute carbon, and provide the requisite balance between aging resistance and bake-hardening response.<sup>2</sup> Again, a variety of approaches have been used with commercial success, based on local preferences. However, the approaches are slightly different in bake-hardening IF than in the fully-stabilized IF steels. Batch-annealed bake-hardenable IF steels have also been produced [11,15], although these products are somewhat less important as they do not apply to modern hot-dip coated products produced on continuous galvanizing lines with in-line annealing, and alternative low-carbon varieties with sufficient aging resistance after batch-annealing are readily available.

Pioneering work in the partially stabilized or “destabilized” IF steels is exemplified by the work of Satoh *et al.* [16], which provides a good background to the subject. Solute carbon levels in Nb and Ti containing steels having a variety of “stoichiometric ratios” (the Nb/C or Ti/C atomic ratios relate to the degree of stabilization that is possible) are illustrated over a range of annealing soak temperatures in Figure 2. The fully stabilized (Ti-containing) compositions can be “destabilized” at high enough temperatures, but partially stabilized steels provide solute carbon and bake-hardening at lower soak temperatures, and are preferred for practical reasons associated with processing ease, if sufficient control of chemical composition is available. Differences in plastic anisotropy ratios (r-values) between steels reflect differences in solute carbon prior to cold rolling, which are well known to influence texture development. Rapid cooling after annealing is preferred to suppress carbide formation during cooling, and thereby maintain desired levels of carbon in solution. Models of NbC dissolution and precipitation generally confirm these effects [4,17], and also indicate that the reprecipitation behavior is not influenced substantially within the time/temperature regime associated with hot-dip coating (e.g. in the zinc

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<sup>2</sup> An additional approach is to carburize (via atmosphere control) a fully-stabilized IF steel after recrystallization, thereby introducing solute carbon, providing bake-hardening and resistance to secondary-work embrittlement. This approach has been studied [e.g. 14], but suffers from composition gradients and controllability issues.

pot). While the carbide spacing also influences kinetics of reprecipitation in microalloyed BH steels, the details are by nature much different than presented earlier for low-C steels (Figure 1), since microalloy precipitation/dissolution is controlled by diffusion of the substitutional microalloying species, rather than carbon interstitials.

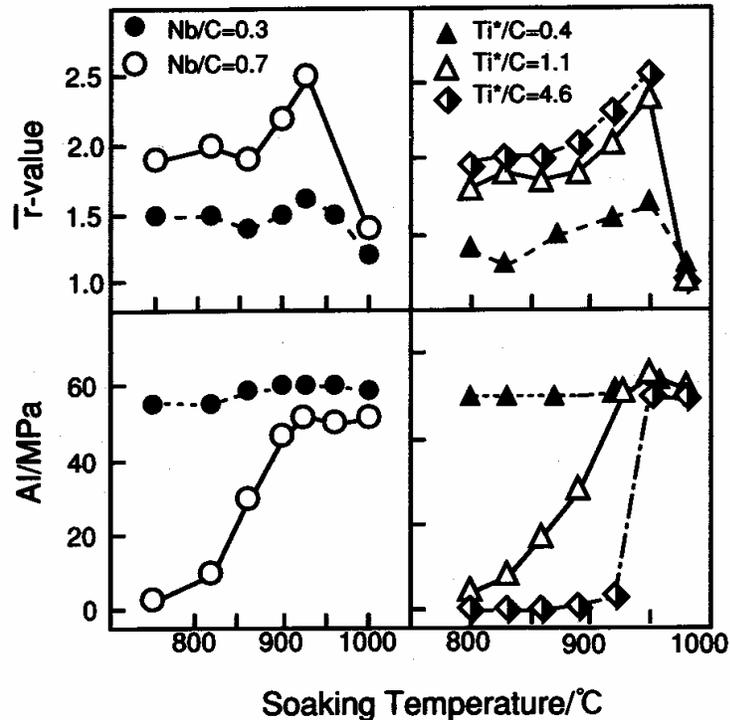


Figure 2. Influence of soaking temperature on bake-hardenability (indicated here as AI) and average  $\bar{r}$ -value in Nb or Ti added ultra-low carbon steels [18].

In Ti-containing ULC steels,  $\text{TiS}$  and  $\text{Ti}_4\text{C}_2\text{S}_2$  can form along with  $\text{TiN}$  and  $\text{TiC}$  (and  $\text{MnS}$ ), depending on composition and processing [19,20]. In fully stabilized IF steels, excess Ti is always present in the Ti-only steels, and so the sulfide and carbosulfide are commonly reported, as they are somewhat more stable than even  $\text{TiC}$ . Precipitation of titanium carbosulfide ( $\text{Ti}_4\text{C}_2\text{S}_2$ ) is considered beneficial in fully stabilized IF, as carbon is removed from solution at high temperature, thus contributing to the stabilization of carbon. In BH-IF steels the situation is very different, since precise control of solute carbon levels is needed. Any variation in the tendency to form  $\text{TiS}$  or  $\text{Ti}_4\text{C}_2\text{S}_2$  influences the Ti level available for stabilization of remaining carbon, as does the amount of nitrogen in the steel, since  $\text{TiN}$  is the first precipitate to form. Since Ti interacts with both N and S prior to stabilizing carbon, precise control of solute control is difficult with a partially stabilized Ti-only approach, which is not recommended for bake-hardening IF products [6,16,18], despite its success in fully-stabilized IF products. Consequently, Nb appears to be the most frequently used approach for partial stabilization of carbon, while either titanium or aluminum [4,16] is used to stabilize nitrogen. An alternative Ti-V approach has also been employed successfully for some years [3,11], whereby titanium stabilizes nitrogen and sufficient vanadium is added to provide partial stabilization of carbon.

In the Nb-containing BH-IF steels, composition and processing details again reflect local preferences based on operating practices and customer requirements. Hot-rolling practices influence mechanical behavior and texture evolution, and the degree of NbC precipitation is well known to be influenced by coiling temperature. Figure 3 shows the effects of coiling temperature and Nb/C ratio on the degree of stabilization (and hence precipitation), along with related yield strength properties, which are also influenced largely by differences in NbC

precipitation behavior. Clearly, completion of the precipitation process is promoted by both high coiling temperature, and high Nb/C ratios, as expected. Plastic anisotropy ratios are usually considered to benefit from lower solute levels in the hot-band, so higher coiling temperatures are preferred from this perspective, although lower coiling temperatures are preferred by some producers for reasons related to uniformity of properties along the coil length. These differences in hot-band properties can be reflected in the final properties after subsequent cold-rolling and annealing [21,22]. Specific effects of coiling temperature related to bake-hardening response may be somewhat more complicated, as bake-hardening is influenced by both solute carbon and ferrite grain size, and final solute carbon level is influenced by the extent of precipitation in the hot-band, as well as the precipitate size and distribution, which influence the reprecipitation and then dissolution behavior during heating, as well as reprecipitation during subsequent cooling. Some investigators have reported that the bake-hardening increment is insensitive to coiling temperature [22], while others have reported some sensitivity to coiling temperature [21]. Finish-rolling temperature, as well as reduction ratios and rolling speeds may also influence properties [21,23].

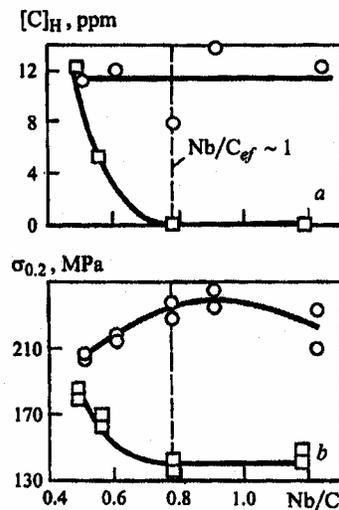


Figure 3. Dissolved carbon level (and yield strength) in ULC Nb-containing steels, for different Nb/C ratios and coiling temperatures (squares represent 770°C coiling temperature, while circles represent 650°C coiling temperature) [21].

Other studies have suggested some additional interesting solute-related effects in Nb-containing BH-IF steels. In one instance, a quite small addition of Nb is suggested [24] to increase the yield strength of recrystallized sheet at the temperature of hot-dip coating, thereby aiding resistance to undesired strains in the coating process. In addition, a boron addition is reported [25] to increase the stability of NbC, and suppress its redissolution. Such behavior would presumably not reflect solubility-related influences, but rather interfacial effects related to boron segregation. While boron also improves resistance to secondary-work embrittlement, the solute carbon present in BH-IF grades makes the SWE phenomenon less likely in comparison to fully-stabilized IF grades.

### Advanced High Strength Steels

The term “Advanced High Strength Sheet Steels” (or AHSS) is currently used to describe dual phase (DP) steels with ferrite+martensite microstructures, transformation-induced plasticity (TRIP) steels containing substantial quantities of metastable retained austenite, and “complex-phase” steels that may contain all of the above microconstituents, along with some pearlite and bainite. Greater levels of bake-hardening are found in these steels than in conventional ferritic

bake-hardening grades, due in part to the local stress/strain fields in the multiphase microstructures. However, the development of microalloyed AHSS varieties has been more recent, and attention has not yet focused on bake-hardening effects, because these high strength steels are usually applicable to structural and crash-relevant components, rather than exposed applications where bake-hardening steels are more typically used. Nonetheless, the influence of Nb on strain-aging characteristics of dual-phase steels has been examined recently [13]. Figure 4 shows that a 0.05 wt. % Nb addition increases the bake-hardening increment in galvanized and galvanized steels. This effect is believed to be related to grain refinement associated with the Nb addition [13], whereby finer grained materials are known exhibit slightly enhanced baking response [7,26]. The decrease in aging index that apparently accompanies the increased bake-hardening is quite interesting, but less well understood at this time.

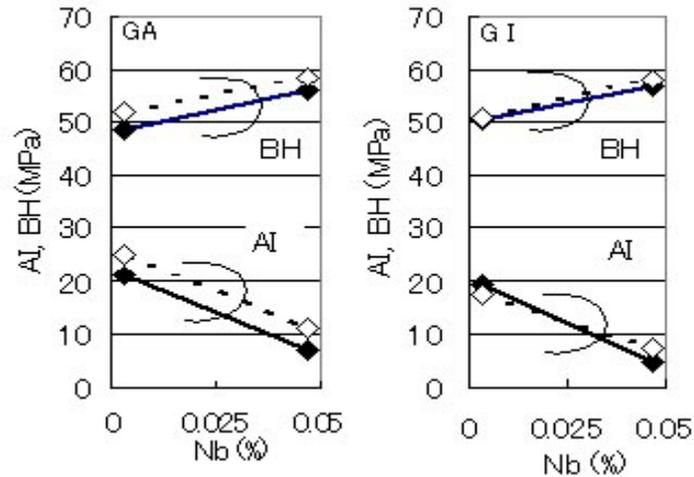


Figure 4. Influence of a 0.05 wt. % niobium addition on the bake hardening index and aging index of galvanized (GA) and galvanized (GI) dual-phase (590MPa) sheet steels. The solid symbols represent an annealing soak temperature of 850°C, while the open symbols represent a soak temperature of 900°C.

Bake-hardening is useful for unexposed structural components typical of many AHSS applications, as well as exposed applications that may be contemplated for these steels. For safety-critical applications where high strain-rate properties are important, recent work on conventional low-carbon BH and Nb-stabilized IF grades indicates that the bake-hardening increment of strengthening is diminished at elevated strain rates (while work hardening is retained), and may not contribute substantially at strain rates above  $10^2 \text{ s}^{-1}$ , as shown in Figure 5. Additional work is needed and underway to examine the baking response under high-rate conditions for DP and TRIP grades.

### Discussion and Concluding Remarks

This overview has provided a perspective on the development of different families of bake-hardening steels, which have contributed to cost and quality improvements in automotive manufacture. These steels have been successfully implemented, with different details of composition and processing adopted by producers based on local mill preferences and customer requirements. The underlying physical metallurgy principles are reasonably well understood, although a number of areas/opportunities remain where further understanding would be helpful. For example, details of the solubility relationships and precipitation behaviors which control the solute levels in the various families of steels, and thereby the baking response, is a further opportunity to understand these behaviors.

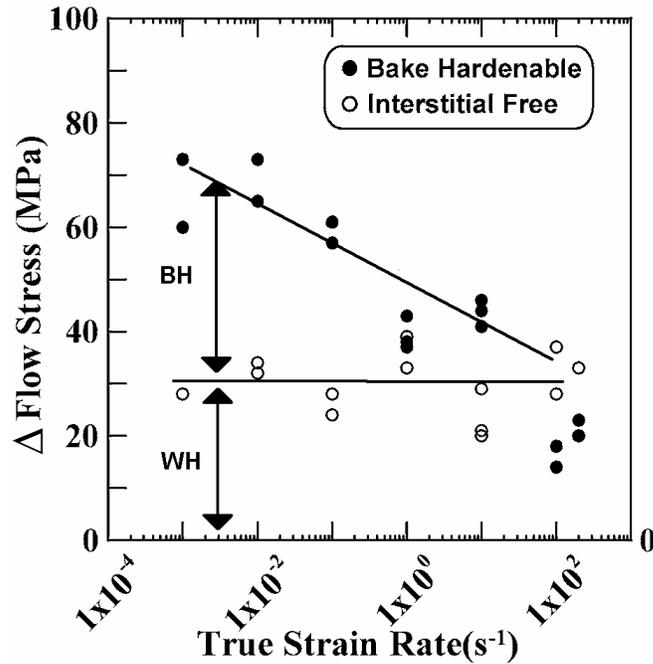


Figure 5. Difference between yield strength as-received yield and after 2% prestrain and baking for low-C BH and Nb stabilized IF steels [27].

For example, the sulfide and carbosulfide formation behaviors in Ti-containing steels remain incompletely understood, and can influence carbon levels in solution. In V-containing steels, it has been mentioned earlier that there are different perspectives on the effectiveness of vanadium as a carbon stabilizer in ULC sheet grades. Similarly, in Nb-containing steels where aluminum is used for stabilization of nitrogen, it is usually presumed that niobium forms carbides (rather than carbonitrides), and that all of the nitrogen is combined with aluminum. However, it is reasonable to expect that under some conditions, some nitrogen could be combined with niobium, thereby influencing the amount of niobium effectively available for carbon stabilization. These effects are subtle, but may be important especially in BH-IF grades, where control of solute carbon via microalloy precipitation behavior needs to be very precise.

Recent work to understand NbC and VC solubility products in ULC ferrite has also shown some interesting effects of holding time on the levels of dissolved carbon in the ferrite matrix. Figure 6 shows carbon Snoek peaks obtained during internal friction testing of a Ti-Nb ULC steel, and similar results were obtained in Ti-V steels (at higher V levels). The figure shows that some solute carbon remained in the hot band. During annealing the solute carbon levels increased, and subsequently decreased, reaching very low values after very long annealing times at 845°C. While attractive levels were achieved at annealing times typical of commercial processing, the non-equilibrium effects are interesting and perhaps important, and indicate that the use of the equilibrium solubility product in ferrite may not suitably represent the important characteristics of these steels. It is well known that the carbon Snoek peaks measured by internal friction detect only carbon in solution in the ferrite matrix, whereas carbon is also understood to segregate to ferrite grain boundaries (28-30). In ULC steels, this carbon segregation to grain boundaries may be quite important (and is suggested to be responsible for the reduced solute levels shown in Figure 6 at longer annealing times), although experimental verification of the grain boundary carbon levels is difficult. Nonetheless, a better understanding of these effects is needed to optimize control of solute carbon levels in BH-IF steels.

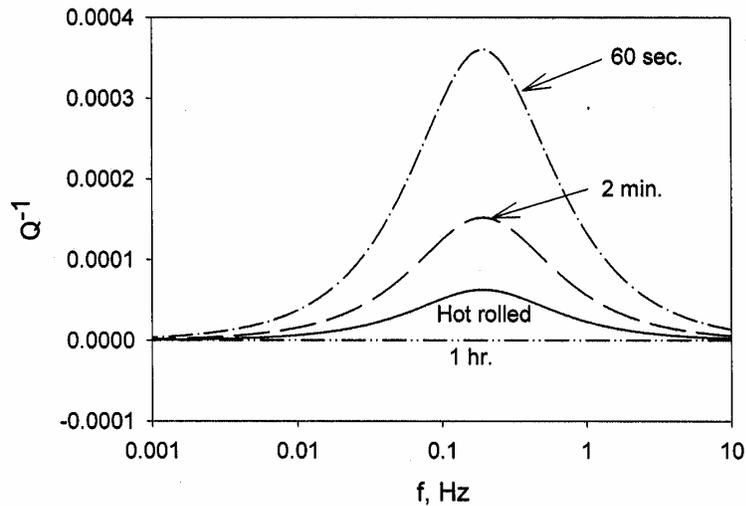


Figure 6. Internal friction (carbon Snoek peaks) vs. pendulum frequency at room temperature, for Ti-Nb BH-IF steel (0.003C, 0.018Nb) in the hot-rolled condition, and after cold-rolling and annealing at 845°C for various lengths of time [28].

Some interesting effects associated with induction annealing response have also been observed in a “fully stabilized” Ti-stabilized ULC steel. The steel contained 0.0035 C, 0.11 Mn, 0.007 P, 0.007 S, 0.035 Al, 0.057 Ti, and 0.002 N (in wt.%), and was induction annealed using a 12 kV, 2.2MHz power source by heating at a rate of 480°C/s to a maximum temperature of 865°C (determined by pyrometry), followed by holding for 2 s and then air cooling [31]. The resulting tensile test curves are shown in Figure 7, up to a strain of about 15%. Considerable yield point elongation is evident, and the yield strength was also higher than observed for samples of the same alloy “conventionally” annealed in a laboratory molten salt bath. Since the degree of stabilization should be substantial due to the high Ti level, these results are counterintuitive and would benefit from replication. Nonetheless, the results raise interesting questions related to the potential for rapid annealing in the production of BH-IF grades. While the results in Figure 7 are not fully understood, one possibility is that carbon present at grain boundaries is released during rapid heating, and remains in solute form as insufficient time is available for precipitation during heating, holding, or cooling.

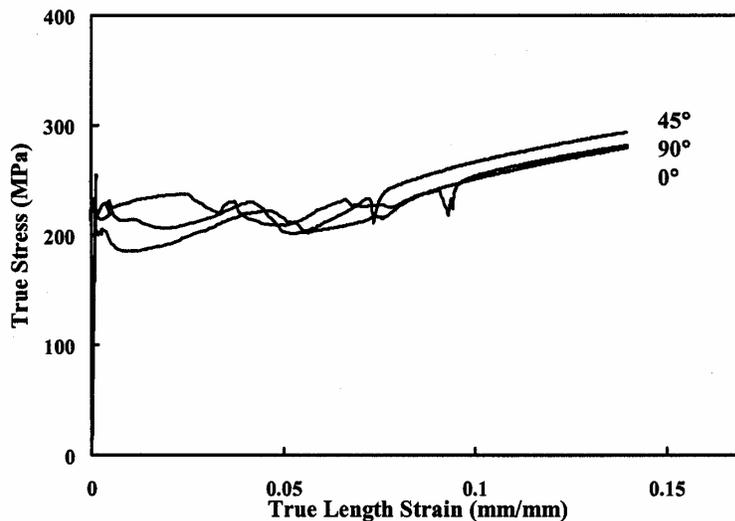


Figure 7. Tensile test results for Ti-IF sheet in longitudinal, transverse and diagonal specimen orientations, after induction annealing at a heating rate of 480°C/s to a soak temperature of 865°C [31]. Courtesy of J.S. Barrett and J.S. Blanzky.

Microalloy solubility in ferrite is thought to control solute carbon levels after annealing of BH-IF grades. This presumption is reasonable, as austenite formation is expected at quite high temperatures in ULC grades, and the intercritical ( $\alpha + \gamma$ ) temperature regime is quite limited. Nonetheless, austenite effects related to microalloy carbide solubility are worthy of consideration. For example, austenite formation during annealing would allow enhanced carbide dissolution (i.e. increased solute carbon levels) because of 1) increased microalloy carbide solubility in austenite compared to ferrite, and 2) the possibility of “reversion” which is known [32] to occur as a result of different precipitate/matrix orientation relationships in ferrite and austenite.<sup>3</sup> Conversely, it is interesting to speculate that processing which leads to fine precipitation in austenite during hot rolling prior to cold rolling and annealing, might conceivably lead to reduced carbide stability at the annealing temperature, relative to precipitates formed in ferrite, as a result of the difference in interfacial energy associated with differences in orientation relationship. This factor could be relevant to BH-IF steels, although it does not seem to have been considered in previous studies of these grades, and perhaps represents an area of future investigation.

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<sup>3</sup> Reversion is promoted in austenite because precipitates formed in ferrite (with a Baker-Nutting orientation relationship) have an unfavorable orientation relationship in the austenite after transformation during heating, with higher interfacial energies driving precipitate dissolution, subsequently followed by reprecipitation in austenite with a more favored cube-cube orientation relationship [32].

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