Nitrogen strain aging in ferritic steels

Several approaches to reducing or eliminating nitrogen strain-aging effects are presented, including the potential advantages of using micro alloying.

By Robert J. Glodowski

With the advent of Electric Arc Furnace (EAF) steelmaking in North America over the last 50 years, ferrous wiredrawing operations went through a learning curve with respect to understanding and tolerating the higher nitrogen levels inherently resulting from this melting practice. Today, virtually all wire rod manufactured in North America is from EAF steel. Steel and wire producers have been able to make the adjustments necessary in both steelmaking control[1] and wiredrawing practices to accommodate these changes in steel chemistry.

The disadvantages of high nitrogen levels in steel used in wiredrawing are almost always attributed to the effects of interstitial, or "free" nitrogen in ferrite. It is well known that free nitrogen, along with interstitial carbon (the carbon in solution in ferrite), play a significant role in the strain aging effect in steel[2,3,4]. The result of strain aging during wiredrawing is an increase in the strain-hardening rate and a decrease in drawn wire ductility. The usefulness of the wire is reduced because of increased breakage during fabrication of finished products, inability to meet drawn wire ductility test requirements such as torsion tests and, in the worst cases, it can result in reduced service life. Nitrogen strain aging is a problem that exists throughout the carbon range, from low carbon (0.05%) to high carbon (0.82%) steel rods.

Nitrogen has a number of beneficial effects that are often overlooked[3]. The usefulness of nitride-forming elements, primarily vanadium, aluminum and titanium, are dependent on the presence of nitrogen. Vanadium nitrides are effective strengtheners and are useful for grain refinement during heat treatment processes. Aluminum is totally ineffective for austenite grain refinement during heat treatment without a sufficient amount of nitrogen present. Titanium can be very effective at controlling austenite grain growth at high temperatures, but must have nitrogen available to form the very stable titanium nitride. Columbium (niobium) will form various versions of carbonitrides, Cb(C,N), depending on composition and processing. However, the N-rich version of Cb(C,N) is not considered the most desirable form of niobium precipitate. In addition, boron additions have been used to effectively lower the strength of low-carbon rods and reduce strain aging through the formation of BN. Select approaches used today to neutralize the negative effects of nitrogen, as well as utilize the positive aspects of nitrides, are reviewed in this work.

Background

The negative aspects of nitrogen in steel are almost entirely associated with the presence of dissolved, or free, interstitial nitrogen in ferrite. Measurement of this free nitrogen can be done in many ways. Numerous chemical analysis techniques are available[5], but are generally tedious and subject to uncertainty. Internal friction measurement is also an accepted method, but can be subject to interpretation difficulties, particularly with high manganese[6]. As a result, most researchers have chosen to use a strain aging index method to quantify free nitrogen. J. D. Baird described the strain age index test method in detail in 1963[2]. This method is shown schematically in Fig. 1 as drawn by Baird. The strain age index, ΔY, is the increase in flow stress caused by aging, usually at 100°C, after a given amount of pre-strain. This measurement is then related to free nitrogen. The normal aging temperature used is 100°C because it has been shown that carbon strain aging requires temperatures above that level.[2]

Fig. 2 shows the published[3,4] relationship between the strain age index and free nitrogen content. The free nitrogen must be less than 5 ppm to achieve a strain age index, ΔY, less than 10 MPa. Above 60 ppm, ΔY becomes insensitive to the N content. This relationship is important because it states that: 1) free nitrogen levels must be extremely low to eliminate strain aging; and 2) above 60 ppm, additional free nitrogen would not have any additional effect on strain aging, since the maximum amount of

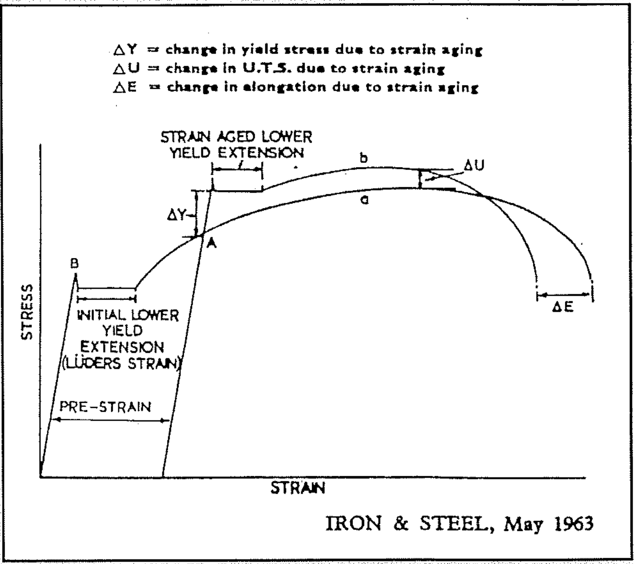

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Fig. 1. Stress-strain curve for steel strained to A, unloaded, aged, then restrained, curve b.[2]

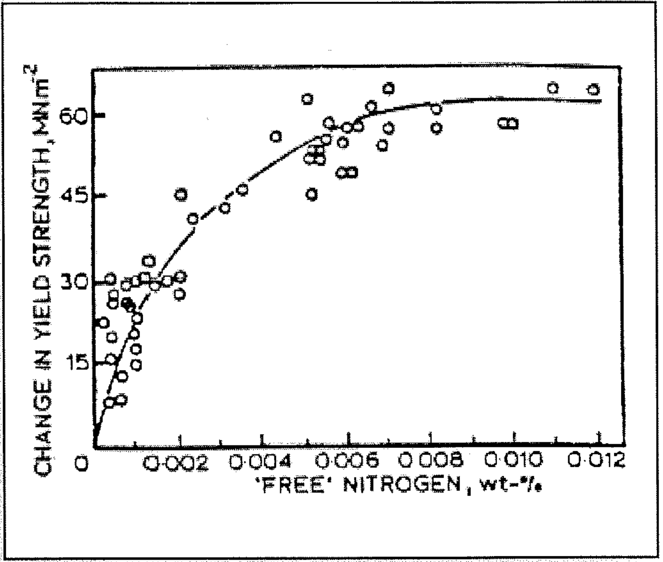
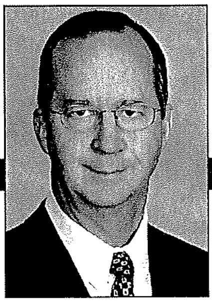


Fig. 2. Influence of free nitrogen content on the magnitude of strain aging.[3]

hardening is achieved with 60 ppm N. Based on this relationship, one might conclude that there is no advantage in limiting nitrogen when the level exceeds 60 ppm. Any level above 60 ppm would have no additional impact on strain aging, at least as measured by strain aging index. Also, this relationship suggests that it is virtually impossible to eliminate strain aging by limiting total nitrogen. Even the best of today's steelmaking practices would find it impossible to keep nitrogen levels below 10 ppm. Based on this type of measurement, the only practical way to reduce the susceptibility to strain aging is to eliminate free nitrogen by combining the nitrogen with another element.

If the combination of another element with nitrogen produces other desirable results, then the microalloy addition provides dual benefits. Available nitride forming elements are aluminum, niobium, titanium, vanadium and boron. Of these, only vanadium nitrides readily provide the potential for both increased strength and a reduction of strain aging susceptibility. Titanium has been shown to reduce free nitrogen, but the nitrides of titanium tend to be relatively large. As a result, they do not strengthen and the large precipitates can have negative effects on the drawability of the steel rods. Niobium is relatively ineffective in reducing free nitrogen because of its affinity for carbon. In medium- and high-carbon grades, the low solubility of NbC can also result in large precipitates detrimental to wiredrawing. Aluminum nitrides, while remaining small, do not strengthen effectively and aluminum nitride formation is very sluggish when cooling from rolling temperatures. The presence of aluminum in as-rolled steel products, unless purposely slow-cooled, does not provide assurance that nitrogen has been effectively combined to reduce aging. Interestingly, boron has been shown to effectively lower the tensile strength of low-carbon rods while significantly reducing strain aging characteristics.

Extensive production experience of high-carbon rods has shown somewhat different effects of nitrogen levels than the previous discussion would suggest. Production performance of silicon-killed steels without any significant nitrogen binding elements present indicate a strong negative effect of nitrogen level when increased from 60 ppm to 120 ppm. The criteria for these observations was not the strain aging index as shown in Fig. 1, but rather torsion (twist to failure) testing that has become a standard test for evaluating drawn wire ductility. The strain aging index test, when used to evaluate nitrogen aging, includes holding the sample from one to two hours at 100°C (212°F) after prestraining. This allows sufficient time for the free nitrogen available to effectively



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migrate to dislocations for the pinning effect. As stated previously, the maximum strengthening from aging (ΔY) in this test appears to be around 60 MPa, achieved with 60 ppm N. However, higher free nitrogen levels may either increase the driving force for nitrogen diffusion or lower the nitrogen diffusion distance necessary to reduce ductility. For a given situation where the diffusion time and temperature is less than optimized for maximum aging, higher free nitrogen levels above 60 ppm may increase the tendency for partial aging. For example, during wiredrawing, the cold work and friction contribute to a significant increase in the temperature of the wire. Peak wiredrawing temperatures may exceed 150°C, but usually only for a very short time. While the maximum ΔY may be achieved at 60 ppm N after complete aging, the sensitivity of partial aging to limited time at temperature may continually increase with higher levels of free nitrogen. In other words, a given drawing practice may provide adequate drawn wire ductility with 60 ppm free nitrogen steel, but will be unacceptable at 120 ppm free nitrogen. The critical wiredrawing temperature where nitrogen aging adversely affects ductility may decrease with increasing free nitrogen content.

This observation suggests that *any* reduction of free nitrogen with nitrogen binding elements can be beneficial, even if the free nitrogen level remains at significant levels. In wiredrawing applications, it may not always be necessary to eliminate free nitrogen, but only to control it to reasonable levels appropriate for a given wiredrawing practice. Reducing free nitrogen to near zero, however, would provide the maximum protection.

Microalloying choices

The question then becomes one of which nitrogen binding alloy element is the appropriate choice for reducing free nitrogen. The answer will be dependent on the processing variables and on the effect of each element on final properties. Different elements may be appropriate in different situations.

Aluminum. Aluminum can be effective as a nitrogen-scavenging element in carbon steels because its affinity for nitrogen is much larger than for carbon. However, the precipitation kinetics of AlN are very sluggish[6]. Because of this, AlN does not form to any significant degree during normal rod processing, even with reduced cooling rates. Aluminum can be very effective for austenite grain growth control when AlN is formed upon a subsequent reheat operation, such as during spheroidize annealing or austenitizing for quenching. When high-carbon wire is patented, nitrogen can be effectively tied up as AlN. However, for critical high-carbon operations like tire-cord manufacturing, the use of aluminum is specifically discouraged because of the tendency to form non-deformable Al_2O_3 inclusions. Most wire applications do not involve reheating after rolling, so the effectiveness of aluminum for reducing nitrogen strain aging is limited. Also, most steelmaking operations producing wire rod in North America use billet casters with metering nozzles. The reoxidation potential of aluminum makes casting difficult in these operations, further reducing the viability of aluminum as a microalloy of choice.

Titanium. For cases where minimum strengthening is desired, titanium additions can be effective, as long as the amount added is stoichometric with the nitrogen content[7]. TiN is the most stable of the nitrides, forming during solidification of the steel and remaining stable during the billet reheat operation. Any additional Ti can, if not tied up with sulfur, form TiC precipitates after rolling and during transformation to ferrite, adding strength to the steel. The primary disadvantage of using Ti for tying up nitrogen is that large non-deformable TiN precipitates will form, which are detrimental for the high cold-working deformation in wiredrawing. Also, the potential for reoxidation during steelmaking, and the potential for precipitation strengthening from dissolved Ti during rolling, make the effect of titanium additions on strength quite unpredictable. The presence of TiN may be acceptable in cold-heading applications where there is less overall deformation, and would provide some grain refinement if subsequently heat-treated.

Columbium. Columbium (niobium) additions have been suggested[8] for tying up nitrogen at lower carbon levels. One concern is that the stoichiometric ratio of CbN is 6.6:1 in weight %, meaning that for a typical low carbon steel with 80 ppm N, 0.053% Cb would have to be present to tie up all of the available nitrogen. This assumes that carbon would not interfere, which is not the case. CbC has a similar solubility as CbN[9], but the amount of carbon present in typical low C steels is 10 times the nitrogen level. Analysis of Cb(C,N) precipitates in hot-rolled 0.06% C strip steels, even with high nitrogen, has shown that depending on processing the precipitate may contain as much as 4 times more carbon than nitrogen[10]. In addition, the Cb(C,N) precipitates contribute to significant strengthening, something not usually desirable in low carbon steels intended for wiredrawing. In high-carbon steels, only a very low percentage of Cb will be in solution at normal reheat temperatures. For example, at 0.40%C, only 0.01% Cb will be in solution at 1180°C (2150°F). Because of this, very little Cb is available to tie up nitrogen, or to provide additional strengthening as Cb(C,N) precipitates in ferrite.

Boron. Boron has been extensively used to reduce strain aging in low-carbon rod steels, especially electric furnace steels[11,12,13]. Boron is unique in that it will actually lower the as-rolled tensile strength, reported to be as much as 40 MPa (6 ksi). So, for applications where lower starting rod strength is desired, along with reduced strain aging during wiredrawing, boron has a significant advantage. Boron has also been proposed for use in medium-carbon cold-heading grades, where it may be possible to eliminate spheroidization treatments[14]. The application of boron to high-carbon grades for scavenging nitrogen is not yet common, but it would seem possible that there may be some good applications. One disadvantage in high-carbon rod applications is that if uncombined B is present during Stelmor cooling, the added hardenability can contribute to unwanted martensite formation. In addition, boron at high levels can contribute to hot shortness during rolling and altered scale characteristics.

It is not well understood whether the boron in the steel actually lowers the tensile strength by influencing some change in the ferrite to austenite trans-

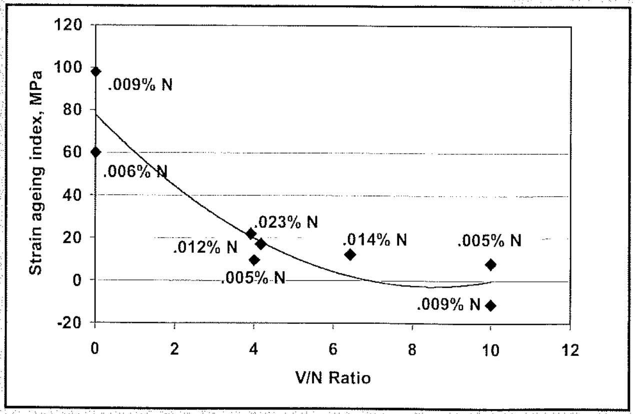

Fig. 3. Strain aging index values for Lab melted 1080 heats as a function of V/N ratio.

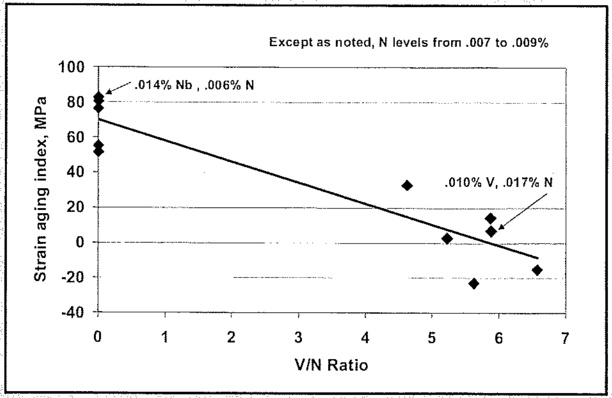

Fig. 4. Strain aging index values for production 1080 rod heats as a function of V/N ratio.

formation mechanism or that the removal of the interstitial nitrogen from the ferrite is sufficient to reduce the strength. If the mechanism were nothing more than removal of interstitial nitrogen, one would expect a similar result from aluminum or titanium additions. Since aluminum and titanium additions are not seen resulting in similar tensile strength reductions, it does suggest that there is a balance of precipitation strengthening from the AlN and TiN to counteract the reduction of strength from the removal of free nitrogen.

Vanadium. For high-carbon rods where increased strength is desirable, vanadium is a logical choice. The strengthening contribution is quite linear with increasing V additions and there are few detrimental side effects of vanadium, both during steelmaking and wiredrawing.

Previously unpublished work at Armco Kansas City Works yielded some interesting results confirming the effectiveness of vanadium for reducing the strain-aging effects of nitrogen in high-carbon pearlitic steel. The premise was to study if vanadium microalloying enhanced with nitrogen could effectively increase strengthening without increasing the potential strain-aging susceptibility normally associated with higher nitrogen levels.

Both lab melted high-carbon heats simulating AISI 1080 chemistries and production high-carbon rod samples were evaluated. The base chemistry was nominally .80% C, .70% Mn, .28% Si with typical electric furnace residuals. The strain aging index, ΔY, was determined using 3% prestrain followed by 4 hr. at 100°C (212°F). Fig. 3 shows the strain-aging index for the lab melted material after hot rolling. For a wide variation in nitrogen levels, the steel still demonstrated that if the V/N ratio was higher than four, then the strain aging index was reduced from a 60 to 100 MPa range, down to 20 MPa or less.

Fig. 4 shows the strain aging index for the production rods as a function of the V/N ratio. All but one of the V heats was standard production at the time, with vanadium levels from 0.035 to 0.045%, nitrogen from 0.007 to 0.009%. In addition to the standard "coarse grain" heats (Si killed, no microalloy) for comparison, one heat with a 0.014% Cb (Nb) addition was included. The Cb bearing heat had the same strain-aging index as the coarse grain heats. At this carbon level, it is not expected that the Cb would be effective because very little would be in solution at normal rolling reheat temperatures and CbC would be the preferred precipitate for any Cb that was in solution. Again, all materials with over 4 V/N showed little or no strain aging.

While reducing the nitrogen strain aging, vanadium can also contribute substantially to strengthening. The amount of vanadium strengthening will be affected by the nitrogen level as shown in Fig. 5. In this case, the strength increased about 50 MPa for each 0.001% nitrogen increase, up to the stoichiometric level. Additional nitrogen above that level would not be expected to contribute to significant additional strengthening in the as-rolled condition, but of course it could then be available as free nitrogen to contribute to strain aging. These observations lead to the conclusion that nitrogen additions in vanadium containing high-carbon rod steels would be beneficial for cost-effective strengthening, up to the stoichiometric level. Then any additional nitrogen would contribute to strain-aging susceptibility. Nitrogen level control, with the maximum level of N dependent on the V level present, is necessary to optimize both strength and strain aging resistance.

In a separate study[15,16], strain-aging index tests were performed on low carbon Al killed sheet steel with various microalloying additions. Although not in rod or wire form, the chemistry of the steel is similar to low-carbon rods available today with the exception of being Al killed, not typical of mini-mill billet cast low-carbon rods. In this case, samples were taken from relatively thin hot- rolled sheet material, soon after the final rolling pass. In some cases, the material did not see the normal slow cool of the coiled sheet, but were cut from the sheet on the runout table before being coiled. With rapid cooling from rolling temperature, the VN precipitation may not be completed before reaching a low temperature where the V and the N stays in solution. Results from the strain aging tests on these samples are shown in Fig. 6.

The nominal chemistry for these materials was 0.06% C, 0.3 to 1.6% Mn, .01 to .40 Si, and 0.02 to 0.05% Al. The Mn and Si were added for higher strength grades. Vanadium levels ranged from 0 to 0.13%, and nitrogen levels from 0.007 to 0.020%. Strain aging

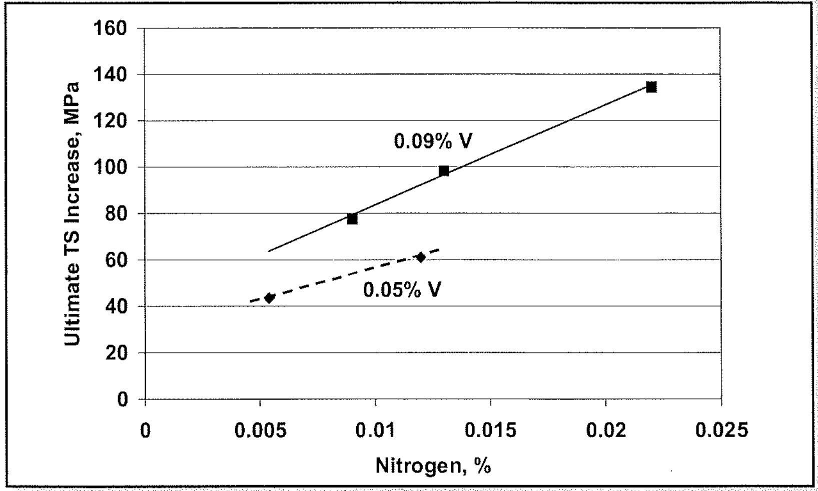

Fig. 5. Effect of nitrogen on the ultimate tensile strength increase of laboratory melted 1080 hot rolled steel for two different vanadium levels.

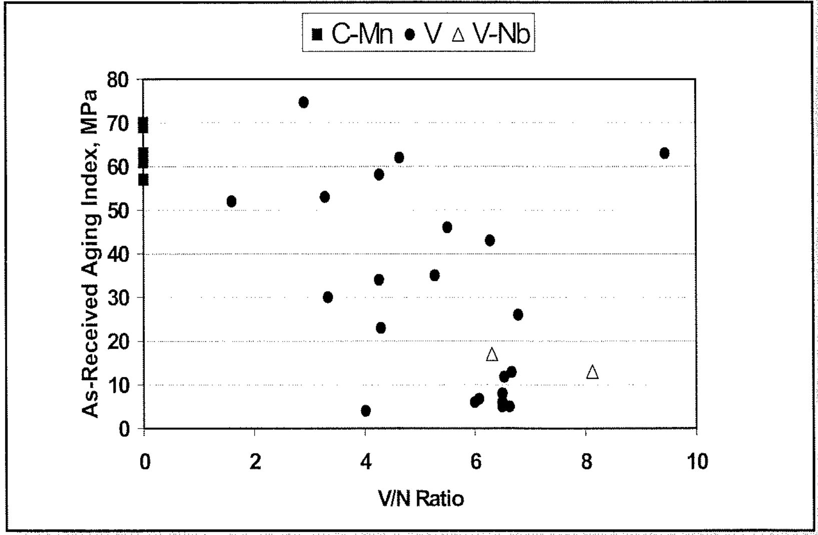

Fig. 6. Strain aging index of as-received low carbon sheet steel without slow cooling.

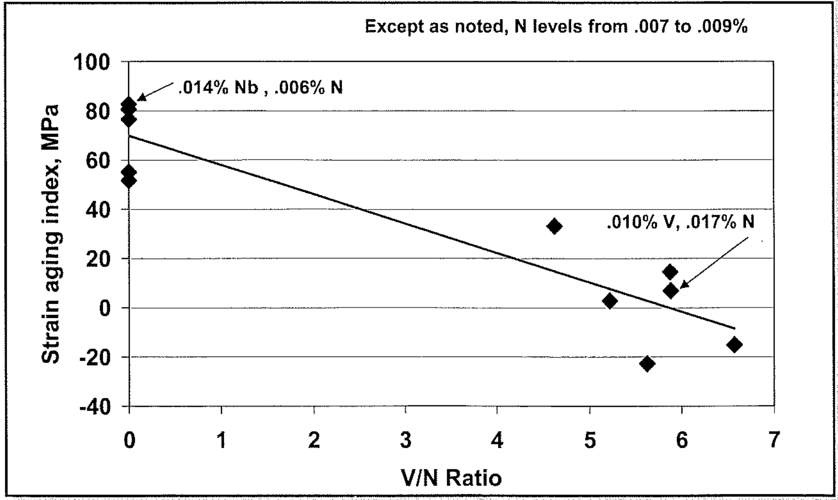

Fig. 7. Strain aging index of low carbon sheet steel after simulated coil cooling cycle.

index values were determined in the same manner as the high-carbon rod samples, except 7.5% pre-strain was used, and only 1-hour of aging at 100°C after straining. Although there is a trend to lower stain-aging index values with higher V/N ratios, it is apparent that not all samples had eliminated free nitrogen and some nitrogen aging took place.

Companion samples from the same sheet materials were subjected to reheating to 600°C (1112°F), a normal coiling temperature, for one hour then furnace-cooled for 48 hours, simulating the normal cooling cycle of a large coil. Identical strain aging tests were performed on these samples and the results shown in Fig. 7.

As can be seen in comparing Figs. 6 and 7, the effect of a reheat to 600°C (1112°F) was dramatic. The strain-aging index was reduced to essentially zero for all the vanadium-microalloyed steels. In addition, there was a corresponding increase in yield strength for those materials with significant aging index prior to the reheat. Obvious explanations include the removal of essentially all of the interstitial nitrogen by the vanadium. Aluminum alone in the plain-carbon steels did not eliminate all of the strain aging as shown, and no strength increase was noted in these steels. For those steels with higher V/N ratios, it is possible that there was also some VC precipitation, which would further reduce aging and increase strength by removing some of the carbon from the ferrite.

Summary of observations

The nitrogen strain-aging susceptibility of steel wire rod cannot be predicted from total nitrogen levels alone. Interstitial nitrogen, also know as free or uncombined nitrogen, is the controlling factor in nitrogen strain aging.

For test conditions where static aging is completed (100°C for one hour), the maximum strain-aging index is achieved with as little as 60 ppm free nitrogen.

For industrial wiredrawing situations where nitrogen aging is likely not completed, higher nitrogen levels may increase the probability of aging for a given wiredrawing practice (time at temperature).

For these industrial wiredrawing situations, even partial reduction of free nitrogen by scavenging with nitride forming elements is likely to be beneficial.

Of the available nitride formers, only boron has the advantage of lowering rod tensile strength while tying up free nitrogen. Therefore, it is used extensively in low-carbon applications. It works most effectively when added to a 1:1 atomic ratio with nitrogen.

Of the available nitride formers, vanadium offers the best properties for increasing rod tensile strength. Therefore, it is used extensively in high-carbon applications where higher strengths are desirable. Nitrogen strain aging is essentially eliminated when the V:N ratio is greater than 4:1, even when the total nitrogen approaches 200 ppm.

To optimize the strengthening affect of vanadium additions and reduce the potential for strain aging, processing of V-N steels should be controlled for maximum precipitation by considering the time at temperature necessary for full precipitation. For hot-rolled and air-cooled rods, this means maximizing the forced air-cooling rate through the austenite ferrite transformation (below 600°C (1112°F)), then halting the accelerated cooling. This provides the optimum processing to complete the austenite to ferrite transformation, and to ensure maximum V(C,N) precipitation to minimize nitrogen strain aging and maximize precipitation strengthening.

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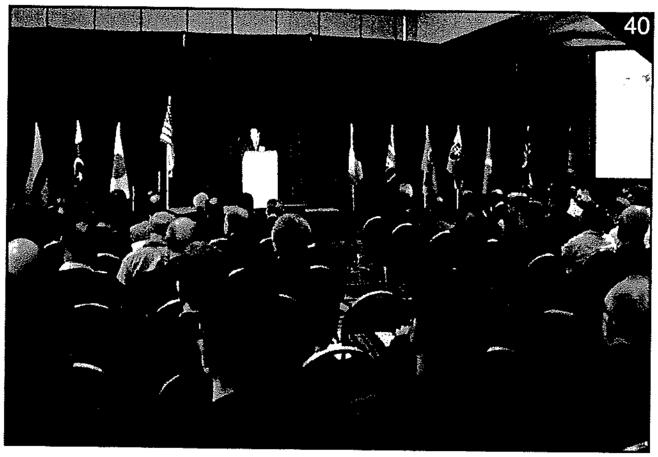

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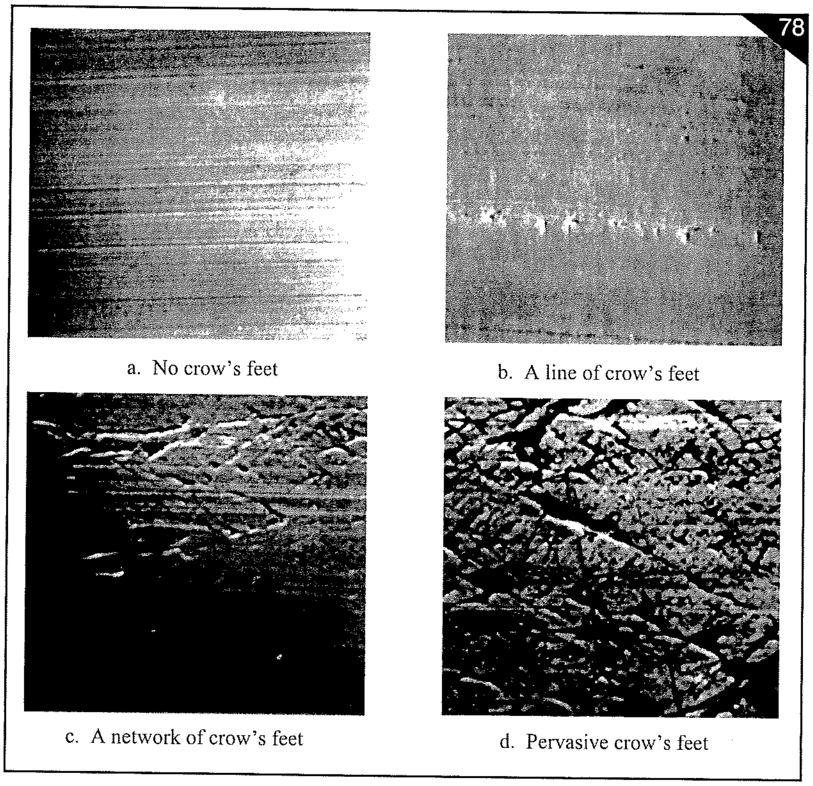

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a. No crow's feet
b. A line of crow's feet
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d. Pervasive crow's feet

(continued)

Cover: Fiber optics had it all: a glitzy image, a slew of big-time investors and hefty margins. And then telecom plummeted. Today, there are signs it may be recovering, albeit to different expectations. See p. 42.