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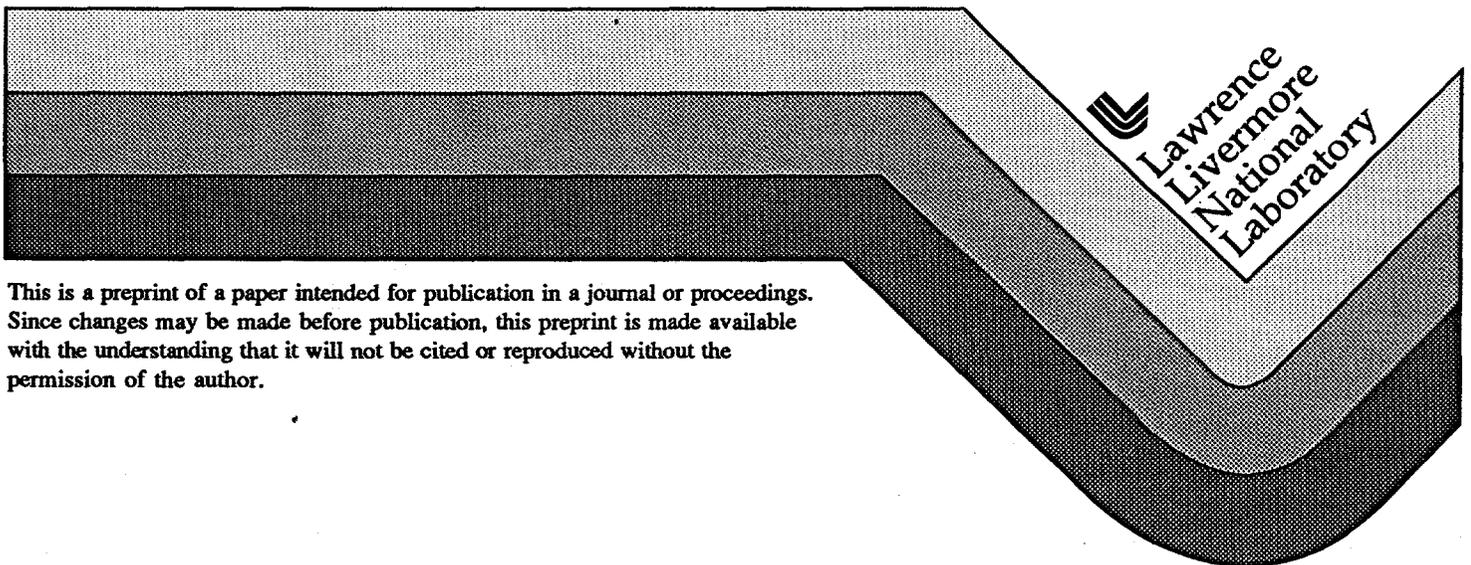
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PROCESSING AND MECHANICAL BEHAVIOR OF  
HYPEREUTECTOID STEEL WIRES

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Abstract

Hypereutectoid steels have the potential for dramatically increasing the strength of wire used in tire cord and in other high strength wire applications. The basis for this possible breakthrough is the elimination of a brittle proeutectoid network that can form along grain boundaries if appropriate processing procedures and alloy additions are used. A review is made of work done by Japanese and other researchers on eutectoid and mildly hypereutectoid wires. A linear extrapolation of the tensile strength of fine wires predicts higher strengths at higher carbon contents. The influence of processing, alloy additions and carbon content in optimizing the strength, ductility and fracture behavior of hypereutectoid steels is presented. It is proposed that the tensile strength of pearlitic wires is dictated by the fracture strength of the carbide lamella at grain boundary locations in the carbide. Methods to improve the strength of carbide grain boundaries and to decrease the carbide plate thickness will contribute to enhancing the ultrahigh strength obtainable in hypereutectoid steel wires.

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## Introduction

High strength materials can reduce weight in load-bearing structures and thus provide improvements in both energy conservation and performance as well as pollution abatement. This is especially true of wires and fibers that are used as reinforcement in composite materials. A good example is the ultrahigh strength steel wire that is used in tires for automobiles and light trucks. This ultrahigh strength wire is the primary component that defines the structural performance of the tire as well as its weight and rolling resistance. Both U.S. and foreign tire companies have invested heavily in development studies to increase the strength of steel tire cord. The primary approach for increasing wire strength has been to increase incrementally the carbon content used in high carbon steels for tire cord [1-5]. Only limited work has been done, however, on steel wire with carbon concentrations above the eutectoid composition (0.76% C). Practical application of these steels has been avoided, because, if appropriate processing steps are not followed, then a brittle continuous carbide network can form along grain boundaries with deleterious effects on properties. A typical continuous carbide network is shown in Fig. 1 for a hypereutectoid steel containing pearlite. Work by research groups in Japan and the United States has shown that this network can be eliminated. The Japanese approach, pioneered by work at Nippon Steel [2-4], has involved carbon contents up to 1.3% C and has shown that network formation can be suppressed by rapid cooling from the austenite phase field [2-4] or by small cobalt additions [1]. The United States approach, pioneered by work at Stanford University and Lawrence Livermore National Laboratory [6-12], has involved ultrahigh-carbon steels (UHCSs), which contain 1 to 2.1% C. Work by these researchers has shown that the carbide network can be broken up in steels containing high carbon concentrations (up to 1.8% C) with thermo-mechanical processing procedures [6].



*Fig. 1. Hypereutectoid steel containing a continuous carbide net-work and pearlite. The network, which is deleterious to properties, can be broken up by thermo-mechanical processing procedures or alloying additions.*

There are compelling reasons for studying hypereutectoid steels with no carbide network at grain boundaries. These higher carbon contents should produce higher strength wire and thus the potential for dramatically lowering the weight and rolling resistance of tires. The potential for increasing the strength of wires used in tires is illustrated in Fig. 2, which shows wire strength as a function of carbon content. The wire diameter (0.28 mm) and the amount of cold work is constant for all data points given as solid circles. Of special note are the UHCSs, which are projected to have wire strengths in excess of 4000 MPa. These ultrahigh strength UHCS wires are expected to be significantly stronger than the 3400 MPa wire currently used in premium tires. It should be mentioned that Nippon Steel has recognized the value of

hypereutectoid carbon contents ( $>0.8\%$  C) for increasing the tensile strength of steel wires [2-4]. Specifically, as shown in Fig. 2, they have recently developed a wire with a tensile strength of 3700 MPa at 0.93% C. The possibility of obtaining even higher strengths with smaller diameter wires (and thus more highly worked materials), is shown in Fig. 3 for a steel containing 0.96% C. This work was done by Ochiai et al [2-4] and shows that with decreasing wire size a strength of over 5500 MPa is possible at 0.04 mm.

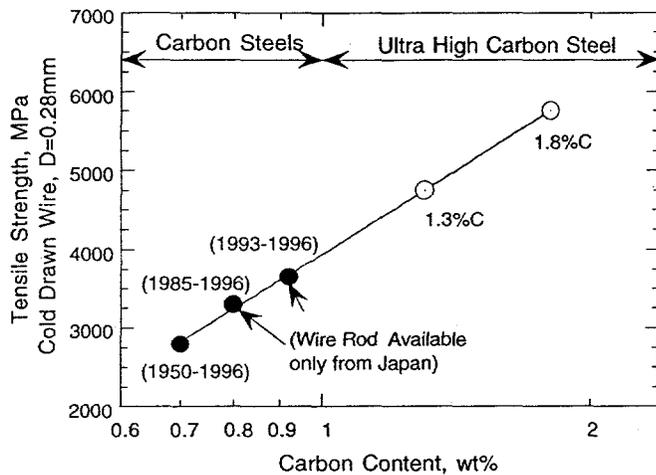


Fig. 2. Influence of carbon content on the strength of steel wires. Current premium radial tires use high carbon steel wire with a strength of 3400 MPa.; the projected strengths for ultrahigh carbon steels containing 1.3% and 1.8% C are shown in the figure by the open circle symbols.

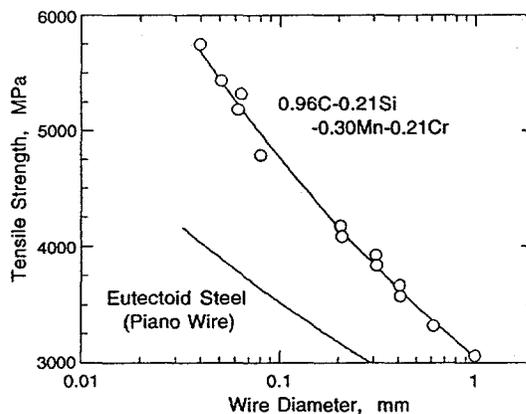


Fig. 3. Tensile strength versus wire diameter for a Japanese hypereutectoid steel containing 0.96% C[3].

The potential energy savings in passenger vehicle and trucks resulting from this increased wire strength are substantial in the U. S. and can have a major influence on national initiatives such as the Partnership for a New Generation of Vehicles (PNGV) [13]. The stated goal of the PNGV program is to produce an affordable, family-sized sedan that achieves 80 miles/gallon within ten years. Fuel efficient tires can have a major impact on achieving these goals.

Previous work in eutectoid and hypereutectoid steels has led to a quantitative understanding of the relationship between microstructure and tensile properties [7-9, 14-18]. Most of the relations developed are based on the Hall-Petch equation [19, 20]. Thus, the yield strength was shown to be proportional to the inverse square root of the barrier spacing, involving grain size and intercarbide spacing in spheroidized steels [6-8, 14, 17], and pearlite colony size, plate spacing and plate orientation in pearlitic steels [2-4, 9, 14-18]. Wire drawing experiments of nominally pure iron by Langford and Cohen [21] showed the importance of subgrain formation and the elongation of subgrains on enhancing the strength of iron. This work is a valuable starting point for understanding processing-structure-strength correlations in

hypereutectoid steel wires. In the present paper we review recent work that has been done on hypereutectoid steels and analyze existing data for structure-property correlations.

### Work Done at Nippon Steel

Ochiai et al [2-4, 22] have performed an extensive investigation on the metallurgical factors influencing the strength of eutectoid and low level hypereutectoid steel wires. The factors they investigated included alloying elements, patenting methods, transformation kinetics and microstructure, segregation behavior and deformation and failure characteristics. They were able to establish clear correlations between the composition, processing, microstructure, and strength in these steels.

The influence of alloying elements (mostly Cr, Si, Mn, and of course C) on the transformation temperature and kinetics, microstructure, and strengthening effects are summarized in Table 1. As is clear from Table 1, substitutional alloying elements (such as Cr, Si, Mn, and as well as other element (such as V and Co) will retard the kinetics of carbide dissolution or precipitation during patenting. The resulting slow kinetics during patenting will, in turn, slow down the wire drawing productivity. These alloying elements also tend to segregate and promote formation of stringers and proeutectoid carbide networks. In addition, it is known that some of the elements form oxides that bond strongly to the surface of wire rods and make the descaling of the surface oxide difficult prior to the wire drawing process.

Table 1. Effects of Alloying Elements

Element	Eutectoid Steel	Hypereutectoid Steel
Cr	-Raises the nose temperature of TTT curve. -Delays transformation. -Refines lamellar spacing	-Refines lamellar spacing.
Si	-Raises the nose temperature. -Raises optimum patenting temp. -Increases lamellar spacing. -Delays transformation. -Dissolves in ferrite and strengthens it. -Reduces descalability.	-Suppresses proeutectoid carbide formation.
Mn	-No effect on nose temperature. -Delays transformation. -Promotes lamellar formation at low content (0.3-0.5%).	
C		-Refines lamellar spacing.
Co		-Suppresses proeutectoid carbide formation.

Ochiai et al were aware of the common perception that an increase of carbon content into the hypereutectoid range will lead to the inevitable genesis of proeutectoid carbide network along grain boundaries. Network formation results in a reduction in the strengthening effect of carbon addition beyond the eutectoid composition compared to that observed in the hypoeutectoid steels. Based on these observations, Ochiai et al studied the influences of alloy additions and cooling rate during patenting on this proeutectoid carbide network. They limited the non-carbon alloying elements to the necessary minimum amounts and searched for the optimum patenting condition which produces network-free microstructures with enhanced drawability and increased strength. They mapped out the range of cooling rates as a function of carbon content where the precipitation of grain boundary proeutectoid was suppressed as

shown in Fig. 4. While most of the cooling rates were achieved by lead patenting, they concluded that hypereutectoid steels with carbon content up to 1.10% could be patented by industrial cooling equipment which can achieve cooling rates of 10-15°C/s.

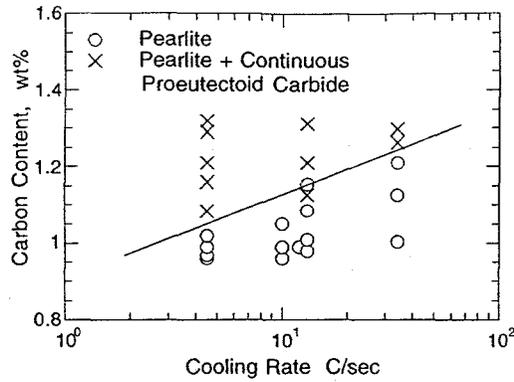


Fig. 4. Effect of cooling rate on the formation of grain boundary proeutectoid carbides in hypereutectoid steels.

Ochiai et al investigated the relationships between the patented microstructure, tensile strength, reduction of area and drawing limits as a function of the transformation temperature in both eutectoid and hypereutectoid steels. They concluded that the optimum transformation temperature is 575°C, which leads to the optimum pearlitic microstructure for drawability and enhanced strength in both eutectoid and hypereutectoid steels.

Ochiai et al observed that the tensile strength of the patented wire at 1.70 mm diameter increased with carbon content. In

Fig. 5, their tensile strength data for hypereutectoid and eutectoid steels are plotted as a function of carbon content. It can be seen that the tensile strength of the patented wire increases almost linearly with the carbon content. These patented wires of 1.70 mm diameter were drawn to 0.3 mm diameter. The tensile strength increment from wire drawing (defined as the strength at 1.70 mm diameter minus the strength at 0.3 mm diameter) is plotted as a function of carbon content in Fig. 6. The data show that the tensile strength increment, i.e., the work hardening rate, increases with increasing carbon content. The increase in tensile

strength and work hardening rate with

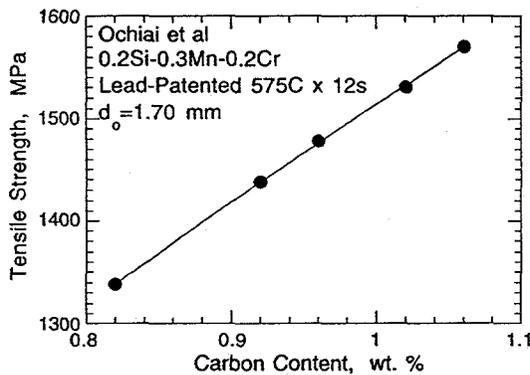


Fig. 5. Tensile strength vs. carbon content in lead-patented eutectoid and hypereutectoid steel wires.

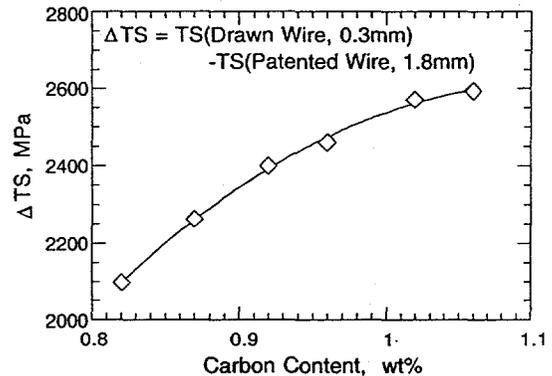


Fig. 6. Tensile strength increment vs. carbon content in wire drawing from 1.8 mm to 0.3 mm in eutectoid and hypereutectoid steels.

carbon content was attributed to the increasing refinement of lamellar spacing and cementite thickness in pearlite. The researchers also observed that the stress for delamination (known as threshold strength) was increased with increasing carbon content. For example, the threshold strengths of the 0.3 mm wire were about 3600 MPa and 3900 MPa at a drawing strain of 3.79

for 0.82% C eutectoid and 0.92% C hypereutectoid steels, respectively. This indicates that drawability will increase as the carbon content increases.

They also studied the segregation of alloying elements (mainly Mn, C, and P) in the core regions of the initial continuously cast blooms and their evolution into microsegregations and stringers in the rods and drawn wires [22]. They observed that the microsegregations and stringers had phase transformation and deformation/fracture characteristics that differ from those of the homogeneous matrix. They showed that there was a good correlation between the mean size of large segregations in the bloom and billets and the drawing limit of wire rods prepared from the segregated areas of the blooms and billets. As the segregation size became smaller, the drawing limit increased. They concluded that the segregation of Mn, C, and P lead to the formation of brittle martensite, proeutectoid carbide networks, or phosphides along grain boundaries. These brittle phases then instigated premature fracture during the wire drawing process resulting in reduced drawability and productivity. The Nippon Steel researchers have also developed technologies [2] to suppress and/or minimize segregation and the size of these segregated regions by electromagnetic stirring of the melt in the casting mold and light compression of the crater end of the cast ingots.

#### Work Done at Kobe Steel

Kanetsuki et al [1] noted that the strength of carbon steel depends mainly on the carbon content, and therefore a hypereutectoid steel will have a higher strength than a eutectoid steel. They further noted that the hypereutectoid steels tend to have lower drawability because of proeutectoid carbide formation on grain boundaries. In an attempt to suppress the formation of the grain boundary proeutectoid carbides, the Kobe researchers have studied the influence of Co (up to 3.05%) on the formation of the proeutectoid carbide network in steels containing 1.01 to 1.48% C. Kanetsuki et al found that the grain boundary proeutectoid carbide can be prevented during patenting in hypereutectoid steels with carbon contents up to 1.3%, by Co addition. They found that the lamellar spacing in the pearlitic structure was reduced with increasing carbon content and reduced further by the Co additions. They tested the drawing characteristics of the hypereutectoid steels and concluded that the drawability was as good as the eutectoid steel, and the work hardening rate and tensile strength increased with increasing carbon content. Such improvements in strength are additive to the strengthening resulting from decreasing lamellar spacing with carbon content and Co additions. Their data on a 1.15% C-0.98% Co hypereutectoid steel are compared with other data for other hypereutectoid steels in a later section.

#### Work Done at Pohang Steel

At Pohang Steel Company, Pohang, Korea, one of the largest steel companies in the world, researchers are working on hypereutectoid steels, with the objective of going into production on wires for tires with a carbon level in the order of 0.93%. In a recent publication, Choi and Park [5] describe microstructure-property relations of four composition steels with increasing carbon content (0.83, 0.94, 1.01 and 1.12% C). Utilizing 7 mm diameter rods as starting material, they have examined the microstructure of these steels following different cooling rates (5, 15 and 25°C/sec), and have obtained fully pearlitic structures for the three lowest composition materials. They showed that the initial strength and strain-hardening rate of the

0.94%C hypereutectoid steel increased with an increase in cooling rate. An analysis of all their data with a Hall-Petch type relation led the authors to the surprising conclusion that the Hall-Petch parameter,  $k_y$ , was solely a function of the volume fraction of pearlitic cementite, and not on the interlamellar spacing.

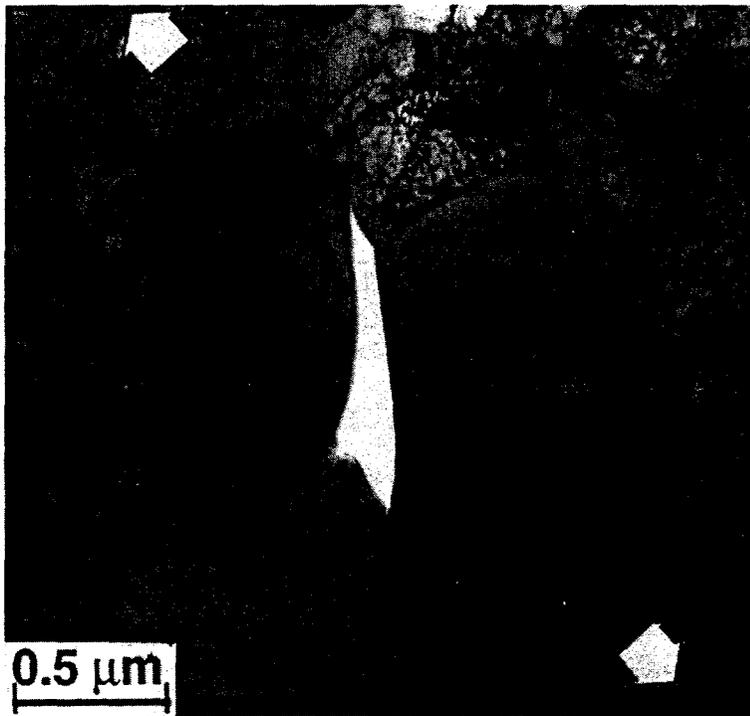
### Work Done at Lawrence Livermore National Laboratory

Work at Lawrence Livermore National Laboratory has centered on a study of the yield and fracture behavior of spheroidized and pearlitic ultrahigh carbon steels (UHCSs) [7-9]. In addition, some studies on the transformation kinetics in wires of ultrahigh carbon steel were made in order to establish some guidelines on the kinetics of phase transformations producing desired microstructures during wire processing.

#### Fracture of hypereutectoid steels.

Previous work has established that the strength of high carbon and ultrahigh carbon steels is limited by the fracture strength of the carbides [8]. Therefore knowledge defining the influence of composition and microstructure on the strength of these carbides in hypereutectoid steels should be highly useful for developing the appropriate composition and processing steps for achieving ultrahigh strength wires.

SEM and TEM studies by Lesuer, Syn and Sherby [8] have shown that failure in a spheroidized UHCS-1.8%C material occurs along grain boundaries in the coarse carbide particles. An example of a carbide particle that was fractured into two parts is shown in the TEM photomicrograph presented in Fig. 7. Fracture is clearly at a grain boundary because



*Fig. 7. TEM of a large carbide particle fractured in the UHCS-1.8% C during tensile test. Arrows represent the tensile axis.*

both ends of the crack meet at obvious triple points. Diffraction patterns identified that a large misorientation existed between the two separated carbide grains. It was concluded that failure in spheroidized hyper-eutectoid steels is the result of a crack-nucleation dominated process which is dependent on a critical fracture stress [8].

Fig. 8 illustrates the importance of crack nucleation on fracture. The figure shows that fracture strength data for hyper-eutectoid steels follow a Hall-Petch type relation when plotted as a function of the reciprocal square root of the

average coarse carbide particle size. The results indicate that fracture of the composite occurs when a critical stress is reached which is solely a function of the average coarse spheroidized carbide particle size (typically found at ferrite matrix grain boundaries). These data can be used to estimate the strength that may be expected in an oriented pearlitic UHCS steel wire with ultrafine layers of the iron carbide phase. Remarkable fracture strengths are calculated by extrapolation. If the carbide thickness is  $0.017 \mu\text{m}$ , a typical thickness observed in a hypereutectoid pearlitic steel [5], a fracture strength of 5000 MPa is predicted. The prediction does require that the pearlite plates be oriented in the direction of testing. This is expected because the extensive wire drawing done commercially in making fine wires leads to a highly oriented carbide plate morphology.

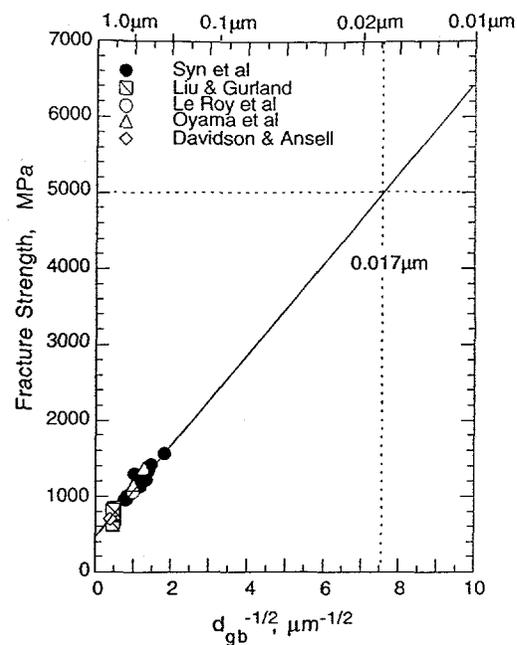


Fig. 8. Fracture strength of spheroidized hypereutectoid steels as a function of average carbide size [8]. Extrapolation of data predicts high fracture strength at ultrafine carbide sizes.

Another important variable influencing the fracture strength of spheroidized hypereutectoid steels is the intrinsic fracture strength of the carbide. In detailed analyses of the data shown in Fig. 8, Lesuer, Syn and Sherby [8] developed a fracture model based on the concept that the ferrite matrix applies stress to the carbide particle and thus the stress in the ferrite matrix is the driving force for crack initiation at the grain boundaries within the coarse carbides. The authors calculated the ferrite matrix fracture stress by averaging the ferrite stress using upper and lower bound concepts. In order to fulfill the fracture mechanics requirement that the ferrite matrix fracture strength must be zero at infinite carbide (crack) size, Lesuer et al made the discovery that the strength of the carbide was a function of composition of the hypereutectoid steels studied. This discovery is graphically illustrated in Fig. 9 where three groups are shown according to composition differences. The unalloyed and low alloyed hypereutectoid steels show higher values of carbide strength than the more extensively alloyed steels. It would appear that elements that dissolve in the carbide decrease the grain boundary strength. Thus, it is postulated that chromium and

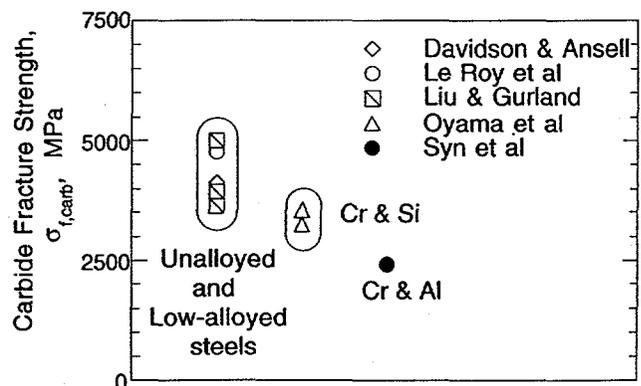


Fig. 9. Predicted carbide fracture strength as a function of composition for spheroidized hypereutectoid steels.

aluminum, which dissolve in iron carbide and distort the carbide lattice (or form carbide of a different structure), decrease the grain boundary carbide strength. On the other hand, silicon, which does not dissolve in the carbide, does not influence the grain boundary carbide strength (Le Roy et al's material). Manganese is known to produce an  $M_3C$  type carbide, as does iron, and therefore may behave in an indistinguishable way from iron in influencing the grain boundary strength.

We conclude that there is considerable optimism in being able to produce exceptionally strong wires with hypereutectoid steels. The composition must be selected so that the following requirements are met: (1) no carbide network is developed during processing, (2) ultra thin layers of carbides are formed, (3) an intrinsically high grain boundary carbide strength is achieved, and (4) a high volume fraction of wire-oriented pearlitic carbides are produced.

#### Transformation kinetics in ultrahigh carbon steel wires

The patenting process, used in processing eutectoid composition wires, depends on the rapid transformation of eutectoid steels to austenite upon heating followed by a second rapid transformation to pearlite on cooling.

An ultrahigh carbon steel containing 1.8% C and 1.6% Al was processed into a wire, 1.22 mm in diameter, by a series of cold-drawing steels. Following the earlier work on the fracture of spheroidized hypereutectoid steels, the initial structure of the UHCS material consisted of fine spheroidized carbides. Short term austenitizing treatments were given to the wires. The times were 10, 30 and 60 seconds at 810°C, which was followed by air cooling. The temperature of 810°C was selected as 40°C above the critical transformation temperature. Tensile tests were performed on the austenitized-and-air-cooled wires. The ultimate tensile strength and the tensile ductility

are shown in Fig. 10. As can be seen, there is a strong influence of austenitizing time on the resulting strength and ductility indicating the rapid change of structure during the heat treating procedure. With an increase in austenitizing time there is a decrease in ductility and an increase in the ultimate tensile strength. The change in properties is related to a change in microstructure from a divorced eutectoid transformation (DET) spheroidized microstructure at short austenitizing time to a mixture of pearlite-DET microstructure at longer austenitizing times. The results are encouraging in that transformations occur rapidly and can be controlled. Related transformation studies to achieve fully pearlitic structures in sheet form of the same UHCS-1.8% C material are described elsewhere [9].

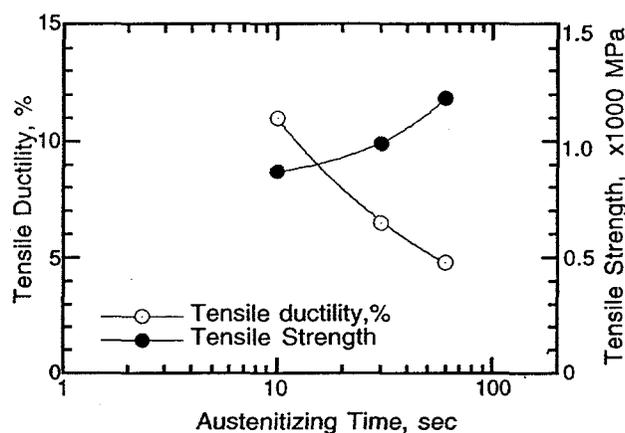
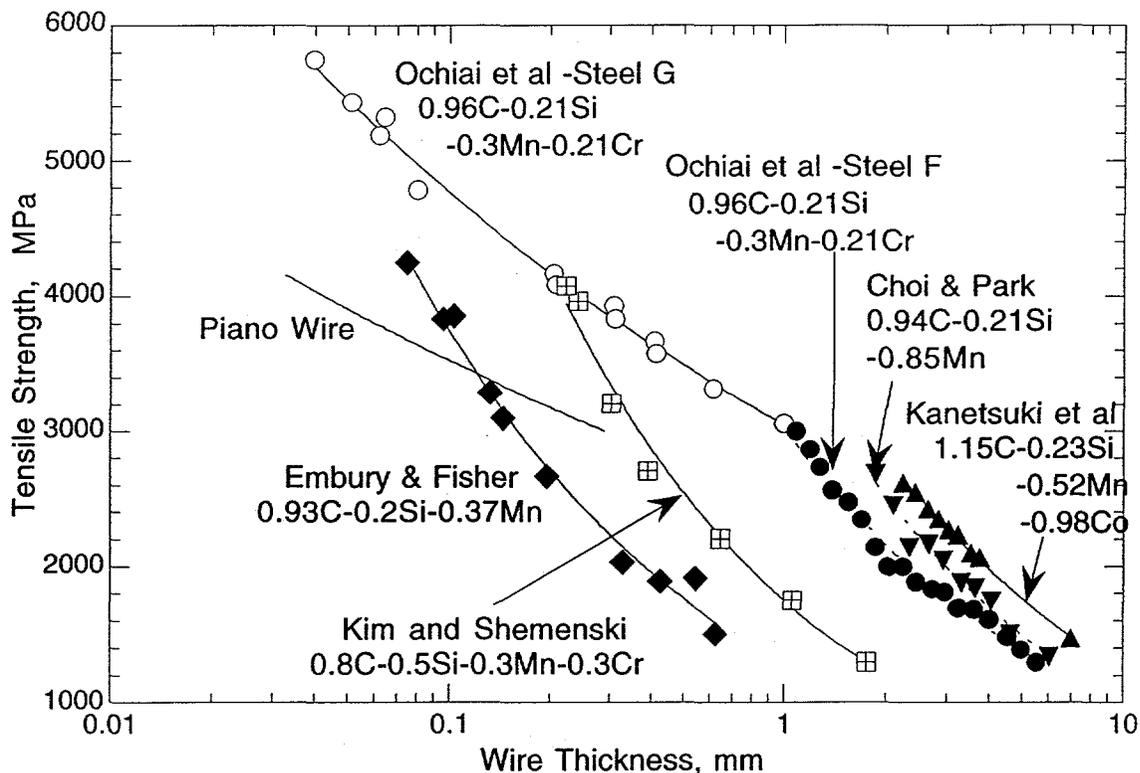


Fig. 10. Tensile ductility and tensile strength as a function of austenitizing time at 810°C in a UHCS containing 1.8% C.

Our review on the mechanical behavior of hypereutectoid steels, with emphasis on wire applications, revealed that very high strengths can be produced. The work of Nippon Steel, led by Ochiai and his colleagues, has resulted in the strongest available steel wires for tire applications. A tensile strength approaching 6000 MPa has been achieved (Fig. 3).

As a way of summarizing wire drawing data on the strength of eutectoid and hypereutectoid steels, Figure 11 illustrates the tensile strength of cold-drawn wires as a function of wire diameter. Five of the curves are for hypereutectoid composition wires and two of the curves are for eutectoid composition wires (data of Kim and Shemenski [23] and piano wire). Significant differences exist between the data sets shown in Fig. 11. The basis for this scatter is the different starting diameters before wire drawing to the diameters indicated in



*Fig. 11. Tensile strength as a function of wire diameter during wire drawing process for eutectoid and hypereutectoid steels. Choi and Park's initial wire strength was estimated by extrapolating the presented data.*

the figure. These different starting diameters represent sizes at which different investigators performed their last patenting operation. Order is introduced into these data when they are analyzed in terms of the incremental increase in strength from wire drawing. Fig. 12 illustrates the result of plotting the data for hypereutectoid steels of nominally the same composition as a function of the drawing strain. All the data are seen to fall on the same curve even though the initial wire sizes are an order of magnitude different (Wire diameter of Embury and Fisher was 0.6 mm, of Ochiai et al was 1.75 mm and of Choi and Park was 7 mm). The data appear to fall on a common curve with gradual upward curvature. The correlation indicates that the mechanism of hardening by wire-drawing is the same irrespective of the initial wire diameter.

With the success shown by calculating the strength increment from cold-drawing, given in Fig. 12 for a single composition hyper-eutectoid steel, it was decided to plot all the data in Fig. 11 in the same way. The result is shown in Fig. 13. Although more scatter in the data is observed than shown previously for the same composition hyper-eutectoid steels (Fig. 12), it would appear, in general, that compositions with higher carbon contents tend to have slightly higher hardening increments for a given amount of drawing strain.

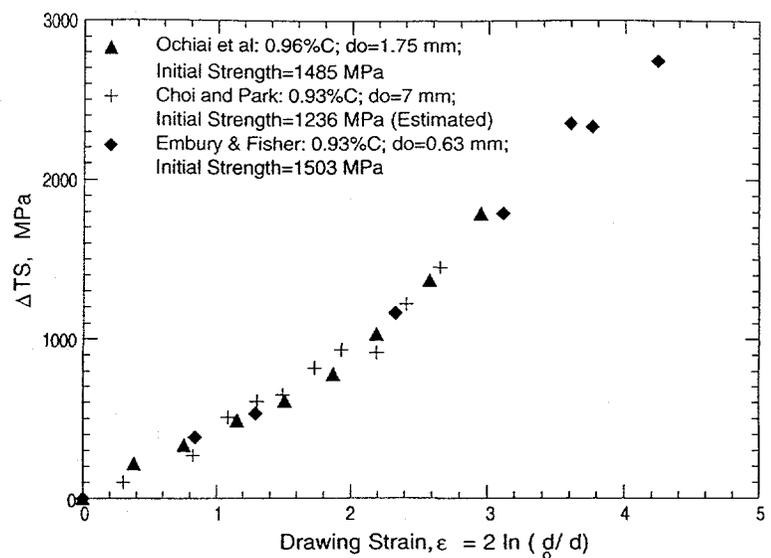


Fig. 12. Strength increment as a function of wire drawing strain in hypereutectoid steels with similar carbon contents.

In summary, we conclude that the basis for achieving excellent mechanical properties in hypereutectoid steels is the control of microstructure. It is clear that the normal continuous carbide network needs to be eliminated. This is done either by thermal-mechanical processing

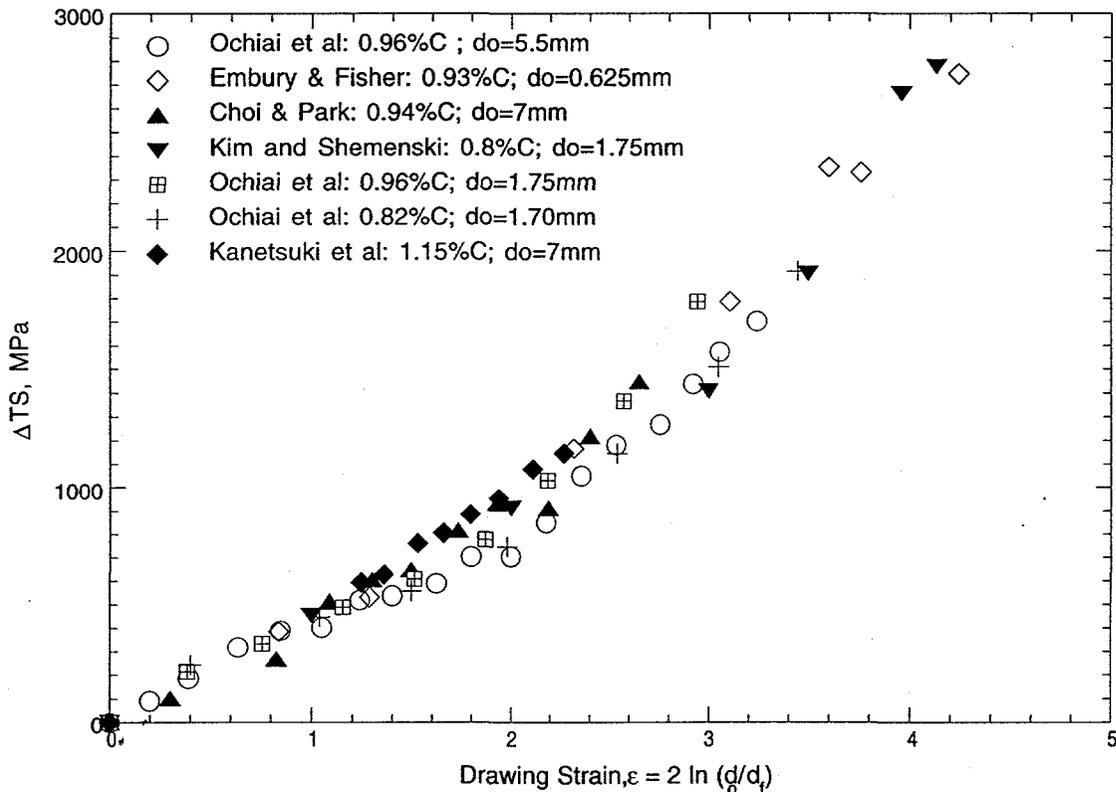


Fig. 13. Strength increment as a function of wire drawing strain for eutectoid and hypereutectoid steels with different compositions, initial wire diameters and initial strengths.

steps, by alloy additions or by control of transformation from austenite to a fully pearlitic structure. In addition, the thickness of the cementite phase in pearlite should be as fine as possible, and the cementite should be optimally oriented in the direction of the wire.

It is proposed by the authors that the tensile strength of pearlitic wires is dictated by the fracture strength of the carbide lamella, at grain boundary locations in the carbide. Methods to improve the strength of cementite grain boundaries, for example by solute alloy additions, should improve the fracture strength of hypereutectoid steel wires. The grain boundary size is an important variable dictating the fracture strength since the grain boundary thickness can be viewed as the crack size. Thus, methods of decreasing the cementite plate thickness is another important objective.

#### Acknowledgment

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