United States Patent [19]

Woodilla, Jr. et al.

[11] **3,895,972**

[45] **July 22, 1975**

[54] **THERMAL TREATMENT OF STEEL**

[75] Inventors: **John E. Woodilla, Jr.; Gordon W. Hunt**, both of Torrington; **Willard B. Green, Jr.**, Harwinton Heights, all of Conn.

[73] Assignee: **The Torrington Company**, Torrington, Conn.

[22] Filed: **May 9, 1974**

[21] Appl. No.: **468,497**

Related U.S. Application Data

[62] Division of Ser. No. 254,454, May 18, 1972, Pat. No. 3,826,694.

[52] **U.S. Cl.** **148/12.1**; 148/12.4; 148/144

[51] **Int. Cl.** **C21d 1/78**

[58] **Field of Search** ..... 148/12 R, 12 F, 12.1, 12.4, 148/15, 18, 134, 143, 144

[56] **References Cited**

UNITED STATES PATENTS

3,337,376	8/1967	Grange	148/143
3,663,314	5/1972	Monma et al.	148/144

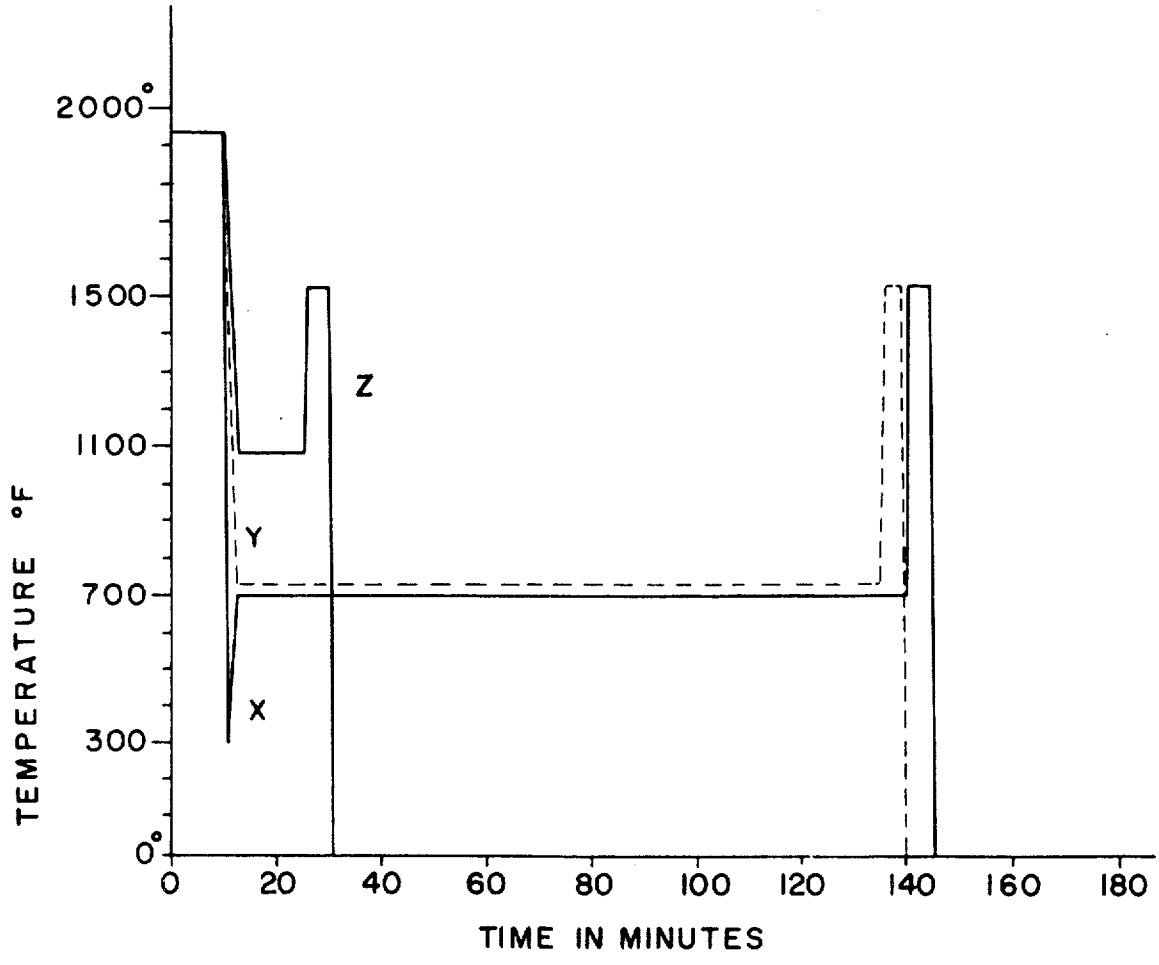
Primary Examiner—R. Dean

Attorney, Agent, or Firm—Frank S. Troidl

[57] **ABSTRACT**

A method of hardening hypereutectoid steels having less than about 10 percent total alloy content is described which results in a structure with an ultra-fine grain size (finer than ASTM No. 10) and a natural dispersion of very small excess carbides. The process includes high temperature solid solution of the carbide phase present in the material, controlled cooling through a selected area of the time temperature-transformation for the material to form pearlite (a ferrite and carbide lamellar structure) and cementite, reheating to austenitize the material, and finally, quenching to produce a structure with an ultrafine grain and a natural dispersion of very small excess carbides that results in an improvement of fatigue life and an increase in compressive yield strength.

1 Claim, 8 Drawing Figures



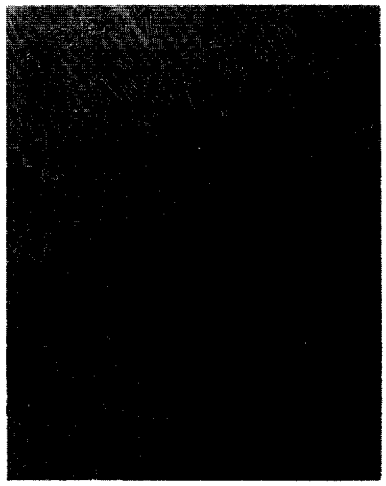


FIG. 1A (2500 X MAGNIFICATION)



FIG. 1B
(2500 X MAGNIFICATION)

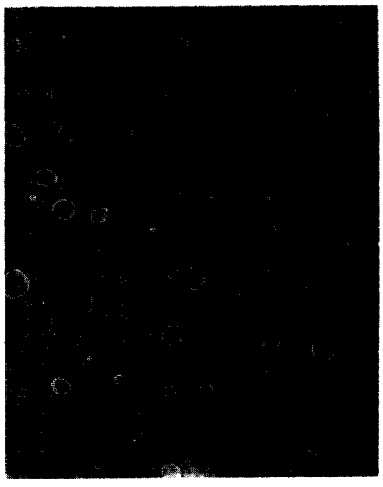


FIG. 4
(5000 X MAGNIFICATION)

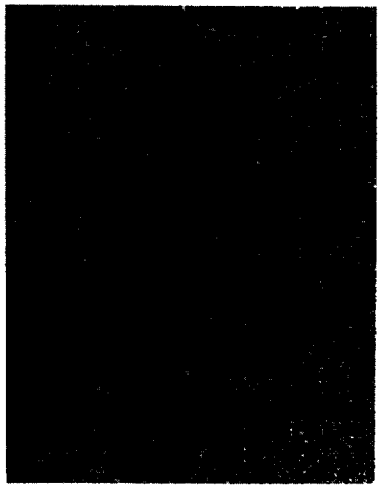


FIG. 5
(5000 X MAGNIFICATION)



FIG. 6
(5000 X MAGNIFICATION)

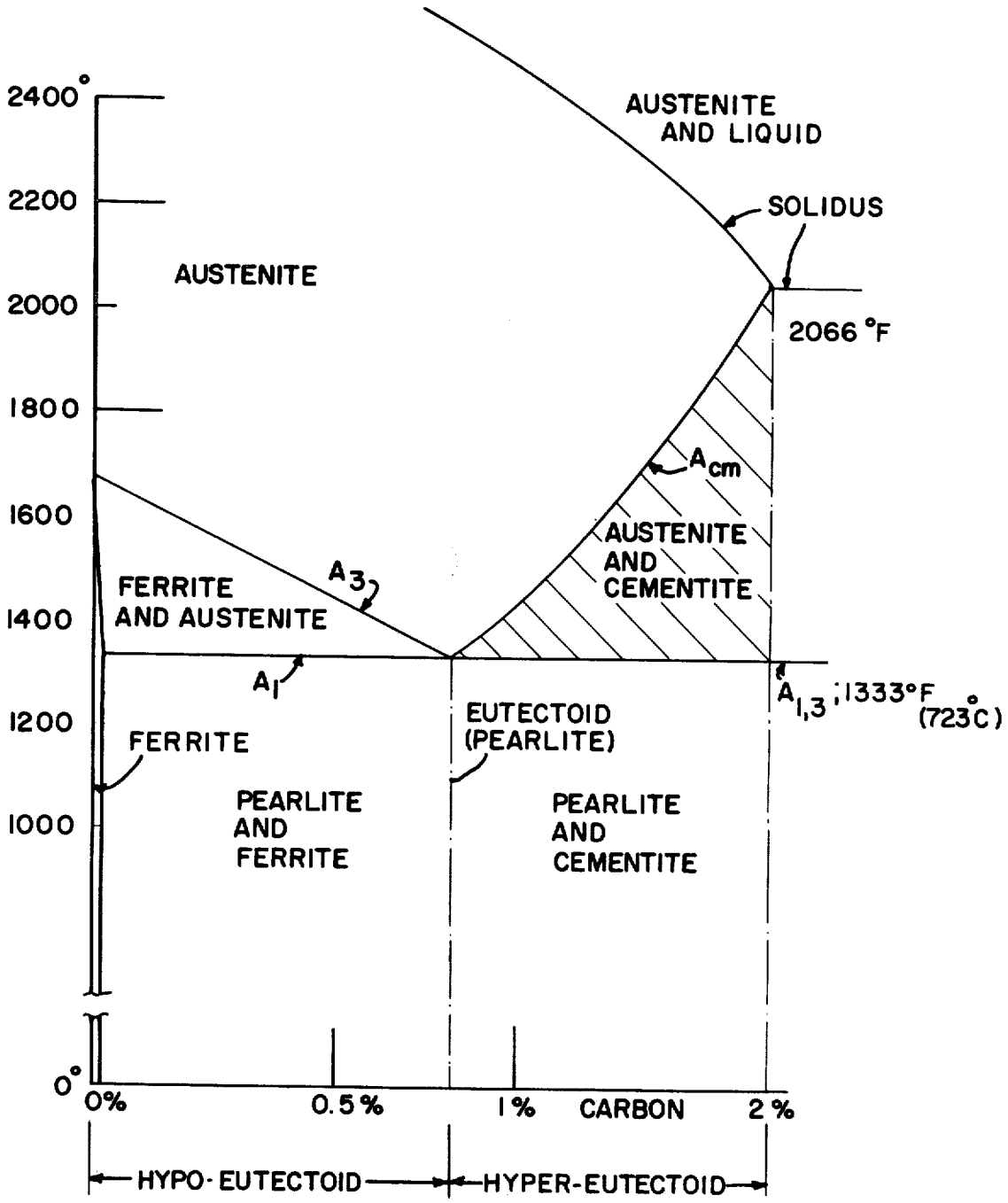

2400°
2200
2000
1800
1600
1400
1200
1000
0°
AUSTENITE AND LIQUID
SOLIDUS
AUSTENITE
2066 °F
A_{cm}
AUSTENITE AND CEMENTITE
A_3
FERRITE AND AUSTENITE
A_1
$A_{1,3}$ 1333°F (723°C)
EUTECTOID (PEARLITE)
FERRITE
PEARLITE AND FERRITE
PEARLITE AND CEMENTITE
0%
0.5%
1%
CARBON
2%
HYPO-EUTECTOID
HYPER-EUTECTOID

FIG. 2

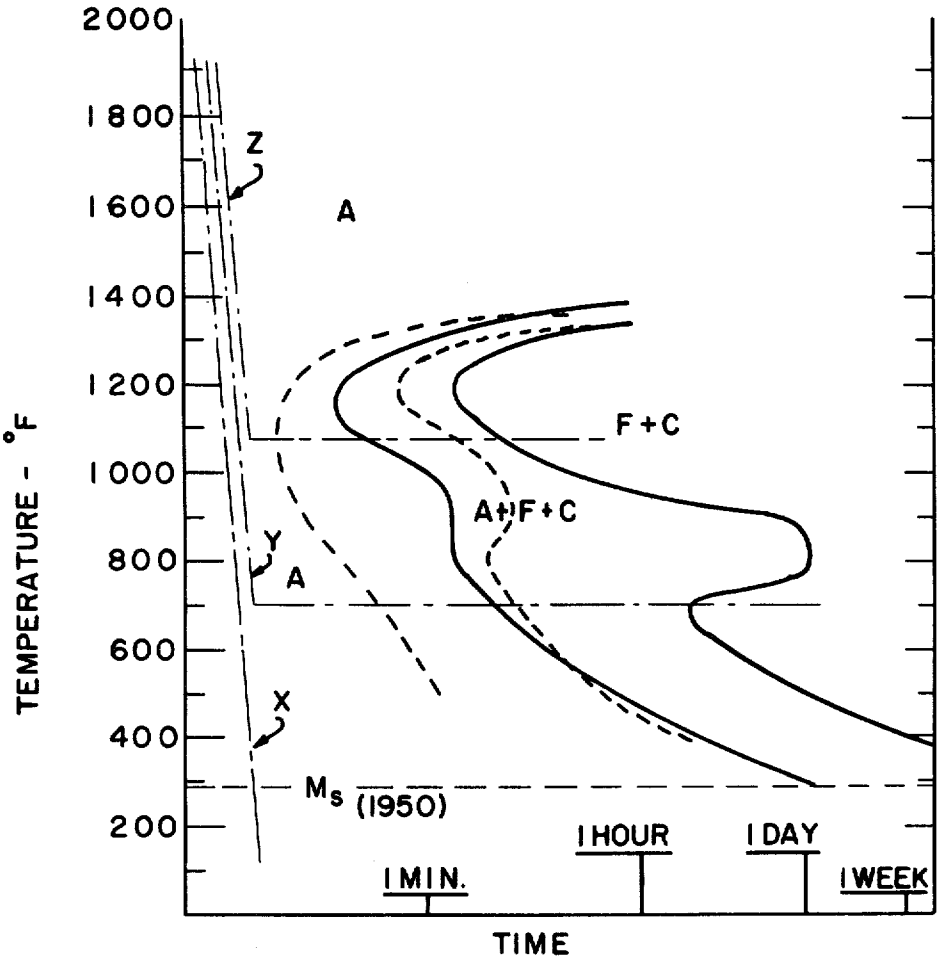


FIG. 3

Austenitized at 1950 °F
Grain Size: 3

LEGEND

A = Austenite	M = Martensite
F = Ferrite	B = Bainite
C = Carbide	P = Pearlite

Austenitized at 1550 °F
Grain Size: 9

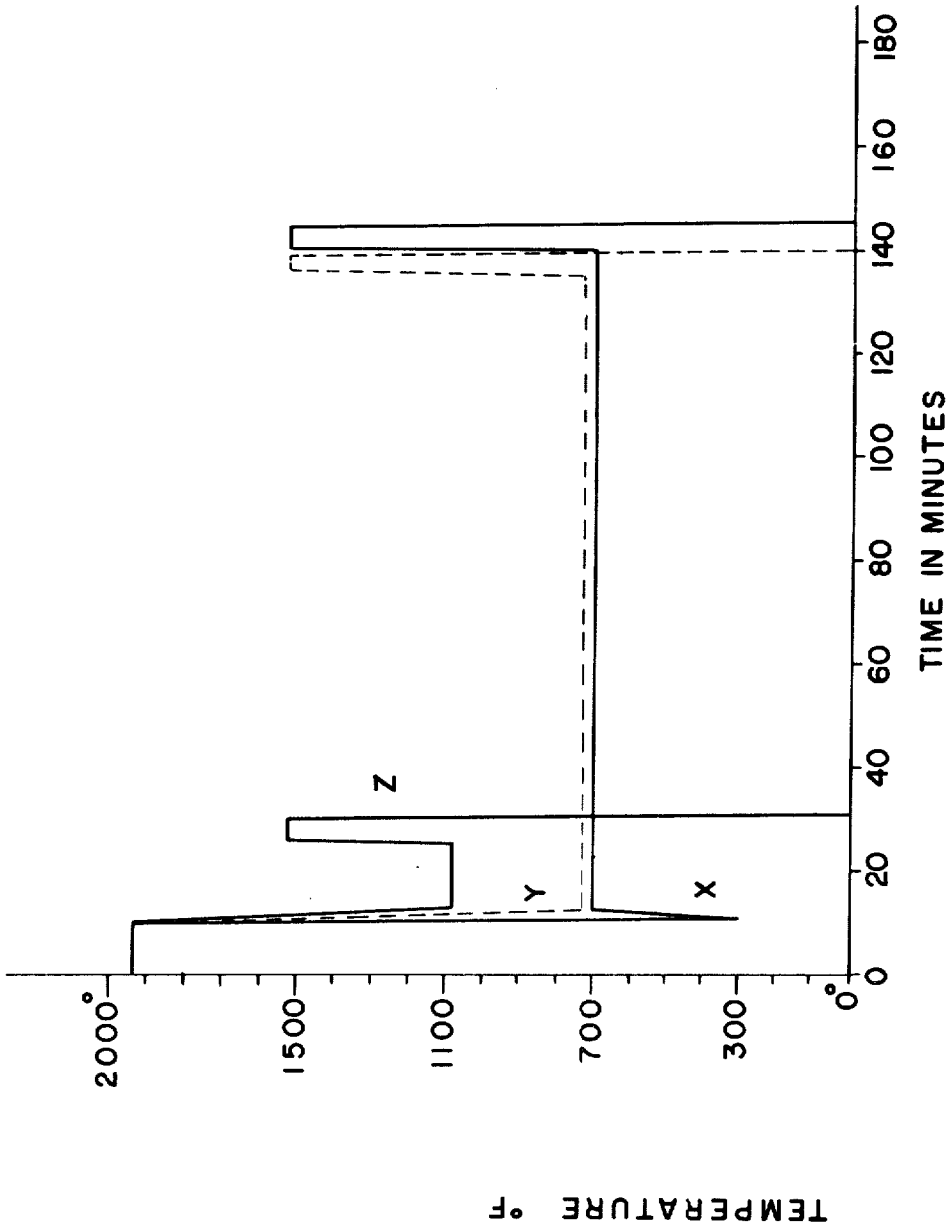

TEMPERATURE °F
2000°
1500
1100
700
300
0°
0
20
40
60
80
100
120
140
160
180
TIME IN MINUTES
Z
Y
X

FIG. 7

THERMAL TREATMENT OF STEEL

This is a division of application Ser. No. 254,454 filed May 18, 1972, now U.S. Pat. No. 3,826,694.

The present invention relates to a method of treating steel to improve mechanical properties. More particularly the invention is a heat treatment for hypereutectoid steel which develops a structure with an ultra-fine grain and a natural dispersion of predominately very small excess carbides.

The strength and wear resistance of many steels is improved by hardening them through heat treatment. For bearing applications and other uses where extended fatigue life is desirable, hypereutectoid steels (those with carbon content of **0.8** percent or more) having a low total alloy content to improve hardenability have been found superior. It is known that a refinement of grain size can improve fatigue life. Approaches to refinement of grain size are described in U.S. Pat. No. 3,337,376. Investigation has shown that one method may create microcracks, as shown in FIG. **6**, which can diminish the effect of grain refinement in improving the fatigue life of the material. A crack-free alternative method requires such long times at elevated temperatures as to make that method economically unattractive. We have developed a process for producing ultrafine grained material with refined carbides in the microstructure that is free from microcracks and which can be accomplished in minutes, thereby improving the rolling contact fatigue life and the compressive yield strength of the material. Our process comprises controlled cooling from a high austenitizing temperature through an isothermal pearlitic transformation range and rapid reheating through a critical temperature range to a lower austenitizing temperature, at which both the carbide phase and the grain size are refined. This is followed by a final quench within a short time period to near room temperature and a subsequent tempering to develop the desired properties.

The invention, as well as its advantages, may be further understood by reference to the following detailed description and drawings in which:

FIG. **1** *a* and *b* are photomicrographs showing pearlite and spheroidized carbides, respectively, in AISI 52100 steel;

FIG. **2** is the iron-carbon equilibrium diagram;

FIG. **3** is the time-temperature-transformation curve for alloy AISI 52100 steel;

FIG. **4** is another photomicrograph showing conventionally hardened AISI 52100 steel;

FIG. **5** is a photomicrograph showing the same steel heat treated according to our invention;

FIG. **6** is a photomicrograph showing two microcracks in AISI 52100 steel; and,

FIG. **7** is a time-temperature profile comparing our method with other heat treating cycles.

Carbides in low alloy compositions of steel can form platelets or spheroids as shown in FIGS. **1** *a* and *b*, respectively. One of these structures is the usual starting condition for the heat treatments to be described. The well-known iron-carbon equilibrium diagram, FIG. **2**, shows that when a hypereutectoid composition is heated and allowed to reach equilibrium at an elevated temperature, it will undergo transformations in phase from pearlite and cementite to austenite and cementite, then to austenite, a solid solution of carbon in gamma iron. Cooling slowly enough to establish equilibrium at any particular temperature will restore the phase normal to that temperature.

However, rapid cooling creates radically different changes. The time-temperature-transformation curves (commonly called "S" curves) shown in FIG. **3** vary with different composition. Those illustrated are typical for a steel designated as AISI 52100, a low alloy steel having the composition shown in TABLE **1**. They show that transformation at 700°F begins and is completed sooner if the metal is conventionally austenitized at 1550°F (the broken curves in FIG. **3**) than at 1950°F (the solid pair of curves). When quenched quickly below the M_s temperature as depicted by Path X in FIGS. **3** and **7**, and taught by U.S. Pat. No. 3,337,376, the carbon is retained in the structure and does not form a carbide. Instead, a needle-like structure, called martensite, is formed. Small patches of austenite between the martensite needles remain, and this is called retained austenite. Upon reheating to about 700°F for a prolonged time period this structure will transform to ferrite plus particles of carbide; specifically, the martensite becomes tempered and the retained austenite transforms to bainite. Reheating to the lower austenitizing temperature (1550°F) for a time sufficient to transform the ferrite to austentite and refine the excess carbides and then cooling to room temperature quickly will result in a structure similar to that shown in FIG. **5**. Structural examination with the electron microscope has shown that severe quenching below the M_s temperature on the first leg of path X may result in microcracks within the material, FIG. **6**, and these can be detrimental to fatigue life.

Modifying the cycle along path Y in FIGS. **3** and **7** (taught by U.S. Pat. No. 3,337,376) has been found to eliminate microcracks and produce the same ultrafine grain size which is desirable from a fatigue standpoint. However, the time-temperature-transformation (S) curve tells us that this transformation is about half done in less than an hour, but requires more than **2** hours for completion. Although the final product will be crack-free and look like the structure in FIG. **5**, the length of time required for this bainite producing cycle is uneconomical for the mass production of heat treated parts.

In laboratory tests, we have found that the prior history of the material influences the time and temperature necessary to dissolve the original carbides. Thus, the steel received in the spheroidized condition (FIG. **1** b) required 2100°F for **10** minutes, whereas a lower temperature or less time was found adequate to dissolve the carbides in hot-rolled stock (FIG. **1** a). Further, we have found that quenching into a suitable quench medium such as salt or lead in the approximate range 900° to 1333°F for an appropriate length of time will form pearlite, a metallurgical phase distinct both in microstructure and mechanical properties from bainite or martensite. Whereas the transformation to bainite at 700°F as taught by the prior art takes **2** to **3** hours for completion, the pearlite transformation takes less than 15 minutes at 1075°F for standard AISI 52100 steel. Besides the direct economic advantage of our cycle, path Z in FIGS. **3** and **7**, this process eliminates the possibility of microcracks that result from a severe quenching operation.

For a better understanding of the pearlite transformation range, it is helpful to refer to the iron-carbon equilibrium diagram, FIG. **2**, where it can be seen that pearlite is not stable above 1333°F (the $A_{1,3}$ line), and

therefore, will not form above this temperature. Further, the S curve shows that the time for pearlite transformation becomes unattractively long as the upper temperature limit is approached. The lower temperature limit of the pearlite forming range is more difficult to define since pearlite and bainite coexist over a range of temperatures. This range of coexistance is dependent on the amount of carbon in solution, the temperature range rising as the carbon in solution increases. In addition, for a through-hardening steel, such as AISI 52100, the amount of carbon in solution is directly dependent on the completeness of the high temperature solid solution process. For a carburizing grade of steel, the carbon content varies throughout the case and this gradient of composition correspondingly varies the range of coexistence of pearlite and bainite as one proceeds into the core region of the workpiece.

For purposes of definition, the pearlite lamellae that coexist with the bainite are very closely spaced, whereas the bainite, known as upper bainite when formed in this temperature range, is course. After the final heat treatment, the fine pearlite produces very small excess carbide particles, while the coarse bainite transforms during this heat treatment to large coarse particles (however, still smaller than the conventional spheroidized particles). The presence of upper bainite in the microstructure prior to the final heat treatment is undesirable. Thus, the lower temperature limit of the pearlite forming range can be defined as that temperature immediately below which upper bainite will form. This observation for upper bainite can be made only with an electron microscope. Since the spacing between the carbide lamellae decreases as the transformation temperature decreases, the optimum temperature for producing pearlite is near the low temperature limit. In this way, the thin carbide lamellae in the pearlite ultimately produce the finest excess carbide particles.

The remaining steps in the process are an austenitizing treatment and subsequent quench which produce a microstructure as depicted in FIG. 5, a natural dispersal of very small excess carbides in an ultrafine grained matrix. This austenitizing treatment may be performed directly after producing the pearlite, that is, reheating from the pearlite forming temperature; or, if the part is cooled to room temperature after producing pearlite, any time thereafter. The heating rate for the final austenitizing treatment is important, since there is a critical temperature range through which the parts must be heated rapidly. Failure to pass through this temperature range with rapidity will cause the pearlite lamellae to break up into excess carbides which will then grow in size, since the carbide phase is stable in this temperature range. By rapidly reaching the pure austenite region of the phase diagram (above the A_{cm} boundary), the pearlite lamellae break up into excess carbides which are unstable and will have a tendency to become smaller in size and dissolve. Proper control of temperature and time insures that the lamellae completely break up but that a large percentage of the newly formed excess carbides do not dissolve, but rather remain as excess carbides. The critical temperature range of any hypereutectoid steel lies between the $A_{1,3}$ and A_{cm} boundaries of its equilibrium diagram. For a one percent carbon alloy such as AISI 52100 these boundaries are approximately 1333° and 1440°F, respectively. The upper limit will be higher if the part has a carburized case with more than one percent carbon content. The critical temperature range has been shaded in FIG. 2 and our hardening heat treating cycle is depicted by path Z in FIG. 7.

This rapid temperature transition may be accomplished in several ways. One is by the use of a two-step heat treatment with a salt or lead bath, where the first bath is a preheat to just below the $A_{1,3}$ and the second is the final desired temperature. Other acceptable methods include induction heating and resistance heating.

FIGS. 4 and 5 are photomicrographs illustrating the microstructures produced by conventional heat treating and by the new method of heat treating, respectively. The material in both cases is AISI 52100. Rolling contact fatigue life testing has shown a 250 to 300 percent improvement in B_{10} life when material with the new microstructure, FIG. 5, is used. Also, the compressive yield strength was increased about 30 to 35 per cent. One of the primary features of this process which contributes to the extended fatigue life is the ultra-fine grain size. A substantial increase in the number of grains within a given volume of metal is believed to be a primary strengthing mechanism and an important contributor to the improved fatigue life of a material. However, grain boundaries are preferred sites for the nucleation of phase transformations, and with ultra-fine grained material, an enormous increase in the number of preferred sites results.

An undersirable transformation may occur during the quench from the final austenitizing temperature. This is the formation of an aggregate of ferrite plus carbide known as "slow quench product" which precipitates at the boundaries of the ultra-fine grained material, thereby weakening this important strengthening agent. We have found that alloying elements such as manganese and silicon, which increase the hardenability of steel, suppress the formation of the undesirable slow quench product. However, the ultra-fine grain size reduces the effectiveness of these alloying elements. Modified AISI 52100 (ASTM A485, grade No. 2) containing 1.40 to 1.70 percent manganese and 0.50 to 0.80 percent silicon, which is normally used when greater hardenability is required, has shown slow quench product formation at the center of a cross section of only three-fourths of an inch when observed with an electron microscope.

Our research has shown that the best mechanical properties are obtained when slow quench product is not present in ultra-fine grained materials. Therefore, the use of alloys with high hardenability is preferred, even for manufactured items with small cross section that under normal processing conditions might not require such hardenability.

For certain articles of manufacture it is advantageous to produce a high carbon case on the exposed surfaces of low carbon steel. Our process is applicable to the carburizing grades of steel by quenching from the carburizing furnace to the pearlite transformation temperature. The process otherwise is the same as for hypereutectoid steels and achieves the same results in the carbon enriched case.

Another modification to our process provides for the insertion of an additional step involving cold work and plastic deformation after the formation of pearlite. For example, this may involve drawing a wire through a series of dies to produce a wire of smaller cross section.

This wire would have been given the high temperature carbide solution heat treatment and the quench to the pearlite-forming temperature. Following an interruption during which the cold work is performed, the rapid austenitizing heat treatment is then performed, by which the ultra-fine grained material with refined carbides is produced. Besides wire drawing, other means of mechanical deformation which may be introduced include swaging, cold-rolling, and shaping and forming operations which must be performed before the final rapid austenitizing heat treatment, while the part is still in the unhardened condition.

It is to be understood that while the following compositions of steel have been successfully heat treated according to our process, the method is not limited to these alone. Many hypereutectoid steels having less than 10% total alloy content will respond to this method.

TABLE I

	ASTM-A295 52100 (percent)	ASTM-A485 Grade 2 (percent)	H11* (percent)	A2 (percent)
C	.98/1.10	.85/1.00	.35/.45	.95/1.05
Mn	.25/.45	1.40/1.70	.10/.40	.40/.85
P	.025 Max	.025 Max	—	—
S	.025 Max	.025 Max	—	—
V	—	—	.30/.50	.15/.50
Si	.20/.35	.50/.80	.90/1.10	.10/.40
Ni	.25 Max	.25 Max	—	—
Cr	1.30/1.60	1.40/1.80	5.00/5.50	4.75/5.25
Mo	.08 Max	.06 Max	1.20/1.50	.90/1.15
Cu	.35 Max	.35 Max	—	—

*This alloy must be carburized to be applicable.

We claim:

1. A method for producing hardened hypereutectoid steels of less than about 10 percent total alloy resulting in a structure with an ultra-fine grain size free from microcracks, and very small well dispersed excess carbides comprising the steps of:

heating the material to a temperature not exceeding the solidus for a time sufficient to dissolve the carbides present in the initial microstructure,

quenching quickly into a suitable liquid quench medium to the approximate range of 900° to 1333°F to produce pearlite,

when the pearlite transformation is complete, cooling to a suitable temperature for mechanical deformation, and mechanically deforming the material then,

rapidly heating through the $A_{1,3}$ and A_{cm} temperature range of its equilibrium diagram to the austenitizing temperature for the material for a controlled time only sufficient to convert the carbide lamellae within the pearlite into very small excess carbides and transform the ferrite to austenite, and,

quenching to harden the steel.

* * * * *