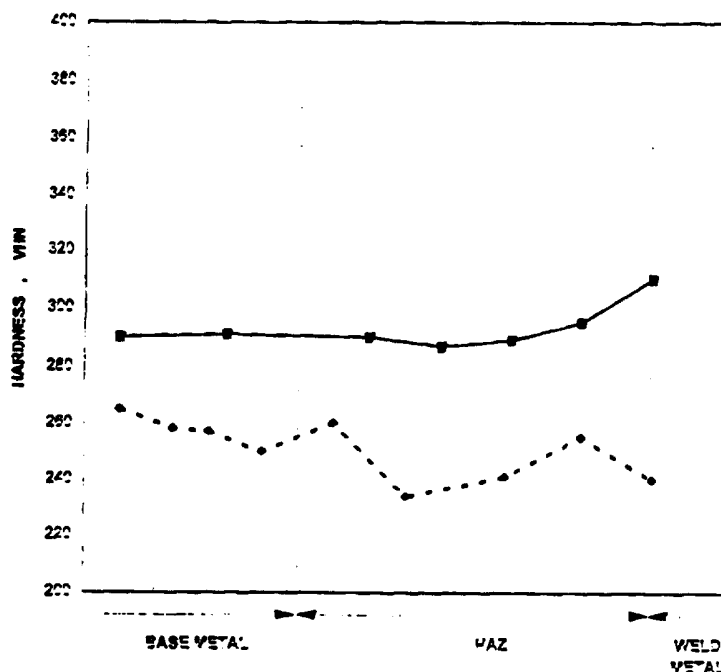




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C21D 8/02	A1	(11) International Publication Number: WO 96/17965 (43) International Publication Date: 13 June 1996 (13.06.96)
(21) International Application Number: PCT/US95/15725 (22) International Filing Date: 1 December 1995 (01.12.95) (30) Priority Data: 08/349,856 6 December 1994 (06.12.94) US (71) Applicant: EXXON RESEARCH & ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (72) Inventors: KOO, Jayoung; 10 Gateshead Drive, Bridgewater, NJ 08807 (US). HEMRAJANI, Ramesh, R.; 1580 Mountain Top Road, Bridgewater, NJ 08807 (US). (74) Agents: SIMON, Jay et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		(81) Designated States: BR, CA, CN, JP, MX, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: METHOD OF MAKING DUAL PHASE STEEL PLATE**(57) Abstract**

A high strength steel composition comprising ferrite and martensite/bainite phases, the ferrite phase having primarily vanadium and niobium carbide or carbonitride precipitates, is prepared by a first rolling above the austenite recrystallization temperature, a second rolling below the austenite recrystallization temperature; cooling between the A_{r3} transformation point and 500 °C; and water cooling to below about 400 °C.

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METHOD OF MAKING DUAL PHASE STEEL PLATE

FIELD OF THE INVENTION

This invention relates to high strength steel and its manufacture, the steel being useful in structural applications as well as being a precursor for linepipe. More particularly, this invention relates to the manufacture of dual phase, high strength steel plate comprising ferrite and martensite/bainite phases wherein the microstructure and mechanical properties are substantially uniform through the thickness of the plate, and the plate is characterized by superior toughness and weldability. Still more particularly this invention relates to the manufacture of dual phase, high strength steel which is producer friendly in its consistency, versatility and ease with which its microstructure can be established in a practical manner.

BACKGROUND OF THE INVENTION

Dual phase steel comprising ferrite, a relatively soft phase and martensite/bainite, a relatively strong phase, are produced by annealing at temperatures between the A_{r3} and A_{r1} transformation points, followed by cooling to room temperature at rates ranging from air cooling to water quenching. The selected annealing temperature is dependent on the steel chemistry and the desired volume relationship between the ferrite and martensite/bainite phases.

The development of low carbon and low alloy dual phase steels is well documented and has been the subject of extensive research in the metallurgical community; for example, conference proceedings on "Fundamentals of Dual Phase Steels" and "Formable HSLA and Dual Phase Steels", U.S. patents 4,067,756 and 5,061,325. However, the applications for dual phase steels have been largely focused on the automotive industry wherein the unique high work hardening characteristics of this steel are utilized for promoting formability of automotive sheet steels during pressing and stamping operations. Consequently,

dual phase steels have been limited to thin sheets, typically in the range of 2-3 mm, and less than 10 mm, and exhibit yield and ultimate tensile strengths in the range of 50-60 ksi and 70-90 ksi, respectively. Also, the volume of the martensite/bainite phase generally represents about 10-40% of the microstructure, the remainder being the softer ferrite phase. Furthermore, the one factor that has limited their widespread application is their rather strong sensitivity to process conditions and variability, often requiring stringent and tight temperature, and other processing to maintain their desirable properties. Outside these rather tight processing windows, most of the steels of the state of the art suffer rather dramatic and precipitous drop offs in properties. Because of this sensitivity, these steels cannot be produced in a constant fashion in practice, thus, limiting their production to a handful of steel mills worldwide.

Consequently, an object of this invention is utilizing the high work hardening capability of dual phase steel not for improving formability, but for achieving rather high yield strengths, after the 1-3% deformation imparted to plate steel during the formation of linepipe to ≥ 100 ksi, preferably ≥ 120 ksi. Thus, dual phase steel plate having the characteristics to be described herein is a precursor for linepipe.

An object of this invention is to provide substantially uniform microstructure through the thickness of the plate for plate thickness of at least 10 mm. A further object is to provide for a fine scale distribution of constituent phases in the microstructure so as to expand the useful boundaries of volume percent bainite/martensite to about 75% and higher, thereby providing high strength, dual phase steel characterized by superior toughness. A still further object of this invention is to provide a high strength, dual phase steel having superior weldability and superior heat affected zone (HAZ) softening resistance.

SUMMARY OF THE INVENTION

In conventional dual phase steels the volume fraction of the constituent phases is sensitive to small variations in start-cooling temperature.

However, in accordance with this invention, steel chemistry is balanced with thermomechanical control of the rolling process, thereby allowing the manufacture of high strength, i.e., yield strengths greater than 100 ksi, and at least 120 ksi after 1-3% deformation, dual phase steel useful as a precursor for linepipe, and having a microstructure comprising 40-80%, preferably 50-80% by volume of a martensite/bainite phase in a ferrite matrix, the bainite being less than about 50% of martensite/bainite phase.

In a preferred embodiment, the ferrite matrix is further strengthened with a high density of dislocations, i.e., $>10^{10}$ cm/cm³, and a dispersion of fine sized precipitates of at least one and preferably all of vanadium and niobium carbides or carbonitrides, and molybdenum carbide, i.e., (V,Nb)(C,N) and Mo₂C. The very fine ($\leq 50\text{\AA}$ diameter) precipitates of vanadium, niobium and molybdenum carbides or carbonitrides are formed in the ferrite phase by interphase precipitation reactions which occur during austenite ferrite transformation below the A_{r3} temperature. The precipitates are primarily vanadium and niobium carbides and are referred to as (V,Nb)(C,N). Thus, by balancing the chemistry and the thermomechanical control of the rolling process, dual phase steel can be produced in thicknesses of at least about 15 mm, preferably at least about 20 mm and having ultrahigh strength.

The strength of the steel is related to the presence of the martensite/bainite phase, where increasing phase volume results in increasing strength. Nevertheless, a balance must be maintained between strength and toughness (ductility) where the toughness is provided by the ferrite phase. For example, yield strengths after 2% deformation of at least about 100 ksi are produced when the martensite/bainite phase is present in at least about 40 vol%, and at least about 120 ksi when the martensite/bainite phase is at least about 60 vol%.

The preferred steel, that is, with the high density of dislocations and vanadium and niobium precipitates in the ferrite phase is produced by a finish rolling reduction at temperatures above the A_{r3} transformation point air cooling to between the A_{r3} transformation point and about 500°C, followed by quenching to room temperature. The procedure, therefore, is contrary to that for

dual phase steels for the automotive industry, usually 10 mm or less thickness and 50-60 ksi yield strength, where the ferrite phase must be free of precipitates to ensure adequate formability. The precipitates form discontinuously at the moving interface between the ferrite and austenite. However, the precipitates form only if adequate amounts of vanadium or niobium or both are present and the rolling and heat treatment conditions are carefully controlled. Thus, vanadium and niobium are key elements of the steel chemistry.

DESCRIPTION OF THE DRAWINGS

Figure 1 shows a plot volume % ferrite formed (ordinate) v. start-quench temperature, °C (abscissa) for typically available steels (dotted line) and the steel of this invention (solid line).

Figures 2(a) and 2(b) show scanning electron micrographs of the dual phase microstructure produced by A1 process condition. Figure 2a is the near surface region and Figure 2b is the center (mid-thickness) region. In these Figures, the grey area is the ferrite phase and the lighter area is the martensite phase.

Figure 3 shows a transmissions electron micrograph of niobium and vanadium carbonitride precipitates in the range of less than about 50Å diameter, preferably about 10-50Å diameter, in the ferrite phase. The dark region (left side) is the martensite phase and the light region (right side) is the ferrite phase.

Figure 4 shows plots of hardness (Vickers) data across the HAZ (ordinate) for the A1 steel produced by this invention (solid line) and a similar plot for a commercial X100 linepipe steel (dotted line). The steel of this invention shows no significant decrease in the HAZ strength at 3 kilo joules/mm heat input, whereas a significant decrease, approximately 15%, in HAZ strength (as indicated by the Vickers hardness) occurs for the X100 steel.

Now, the steel of this invention provides high strength superior weldability and low temperature toughness and comprises, by weight:

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0.05 - 0.12% C, preferably 0.06 - 0.12, more preferably 0.08 - 0.11

0.01 - 0.50% Si

0.40 - 2.0% Mn, preferably 1.2 - 2.0, more preferably 1.7 - 2.0

0.03 - 0.12% Nb, preferably 0.05 - 0.1

0.05 - 0.15% V

0.2 - 0.8% Mo

0.3 - 1.0% Cr, preferred for use in hydrogen environments

0.015 - 0.03% Ti

0.01 - 0.03% Al

$P_{cm} \leq 0.24$

the balance being Fe and incidental impurities.

The sum of the vanadium and niobium concentrations is ≥ 0.1 wt%, and more preferably vanadium and niobium concentrations each are $\geq 0.04\%$. The well known contaminants N, P, S are minimized even though some N is desired, as explained below, for producing grain growth inhibiting titanium nitride particles. Preferably, N concentration is about 0.001-0.01 wt%, S no more than 0.01 wt%, and P no more than 0.01 wt%. In this chemistry the steel is boron free in that there is no added boron, and boron concentration is ≤ 5 ppm, preferably < 1 ppm.

Generally, the material of this invention is prepared by forming a steel billet of the above composition in normal fashion; heating the billet to a temperature sufficient to dissolve substantially all, and preferably all vanadium carbonitrides and niobium carbonitrides, preferably in the range of 1150-1250°C. Thus essentially all of the niobium, vanadium and molybdenum will be in solution; hot rolling the billet in one or more passes in a first reduction providing about 30-70% reduction at a first temperature range where austenite recrystallizes; hot rolling the reduced billet in one or more passes in a second rolling reduction providing about 30-70% reduction in a second and somewhat lower temperature range when austenite does not recrystallize but above the A_{r3} transformation point; air cooling to a temperature in the range between A_{r3} transformation point and about 500°C and where 20-60% of the austenite has

transformed to ferrite; water cooling at a rate of at least 25°C/second, preferably at least about 35°C/second, thereby hardening the billet, to a temperature no higher than 400°C, where no further transformation to ferrite can occur and, if desired, air cooling the rolled, high strength steel plate, useful as a precursor for linepipe to room temperature. As a result, grain size is quite uniform and ≤ 10 microns, preferably ≤ 5 microns.

High strength steels necessarily require a variety of properties and these properties are produced by a combination of elements and mechanical treatments. The role of the various alloying elements and the preferred limits on their concentrations for the present invention are given below:

Carbon provides matrix strengthening in all steels and welds, whatever the microstructure, and also precipitation strengthening through the formation of small NbC and VC particles, if they are sufficiently fine and numerous. In addition, NbC precipitation during hot rolling serves to retard recrystallization and to inhibit grain growth, thereby providing a means of austenite grain refinement. This leads to an improvement in both strength and low temperature toughness. Carbon also assists hardenability, i.e., the ability to form harder and stronger microstructures on cooling the steel. If the carbon content is less than 0.01%, these strengthening effects will not be obtained. If the carbon content is greater than 0.12%, the steel will be susceptible to cold cracking on field welding and the toughness is lowered in the steel plate and its heat affected zone (HAZ) on welding.

Manganese is a matrix strengthener in steels and welds and it also contributes strongly to the hardenability. A minimum amount of 0.4% Mn is needed to achieve the necessary high strength. Like carbon, it is harmful to toughness of plates and welds when too high, and it also causes cold cracking on field welding, so an upper limit of 2.0% Mn is imposed. This limit is also needed to prevent severe center line segregation in continuously cast linepipe steels, which is a factor helping to cause hydrogen induced cracking (HIC).

Silicon is always added to steel for deoxidization purposes and at least 0.01% is needed in this role. In greater amounts Si has an adverse effect on

HAZ toughness, which is reduced to unacceptable levels when more than 0.5% is present.

Niobium is added to promote grain refinement of the rolled microstructure of the steel, which improves both the strength and the toughness. Niobium carbide precipitation during hot rolling serves to retard recrystallization and to inhibit grain growth, thereby providing a means of austenite grain refinement. It will give additional strengthening on tempering through the formation of NbC precipitates. However, too much niobium will be harmful to the weldability and HAZ toughness, so a maximum of 0.12% is imposed.

Titanium, when added as a small amount is effective in forming fine particles on TiN which refine the grain size in both the rolled structure and the HAZ of the steel. Thus, the toughness is improved. Titanium is added in such an amount that the ratio Ti/N ranges between 2.0 and 3.4. Excess titanium will deteriorate the toughness of the steel and welds by forming coarser TiN or TiC particles. A titanium content below 0.002% cannot provide a sufficiently fine grain size, while more than 0.04% causes a deterioration in toughness.

Aluminum is added to these steels for the purpose of deoxidization. At least 0.002% Al is required for this purpose. If the aluminum content is too high, i.e., above 0.05%, there is a tendency to form Al₂O₃ type inclusions, which are harmful for the toughness of the steel and its HAZ.

Vanadium is added to give precipitation strengthening, by forming fine VC particles in the steel on tempering and its HAZ on cooling after welding. When in solution, vanadium is potent in promoting hardenability of the steel. Thus vanadium will be effective in maintaining the HAZ strength in a high strength steel. There is a maximum limit of 0.15% since excessive vanadium will help cause cold cracking on field welding, and also deteriorate the toughness of the steel and its HAZ. Vanadium is also a potent strengthener to eutectoidal ferrite via interphase precipitation of vanadium carbonitride particles of $\leq 50\text{\AA}$ diameter, preferably 10-50 $\text{\AA}$ diameter.

Molybdenum increases the hardenability of a steel on direct quenching, so that a strong matrix microstructure is produced and it also gives precipitation strengthening on reheating by forming Mo_2C and NbMo particles. Excessive molybdenum helps to cause cold cracking on field welding, and also deteriorate the toughness of the steel and HAZ, so a maximum of 0.8% is specified.

Chromium also increases the hardenability on direct quenching. It improves corrosion and HIC resistance. In particular, it is preferred for preventing hydrogen ingress by forming a Cr_2O_3 rich oxide film on the steel surface. As for molybdenum, excessive chromium helps to cause cold cracking on field welding, and also deteriorate the toughness of the steel and its HAZ, so a maximum of 1.0% Cr is imposed.

Nitrogen cannot be prevented from entering and remaining in steel during steelmaking. In this steel a small amount is beneficial in forming fine TiN particles which prevent grain growth during hot rolling and thereby promote grain refinement in the rolled steel and its HAZ. At least 0.001% N is required to provide the necessary volume fraction of TiN . However, too much nitrogen deteriorates the toughness of the steel and its HAZ, so a maximum amount of 0.01% N is imposed.

The objectives of the thermomechanical processing are two fold: producing a refined and flattened austenitic grain and introducing a high density of dislocations and shear bands in the two phases.

The first objective is satisfied by heavy rolling at temperatures above and below the austenite recrystallization temperature but always above the A_{r3} . Rolling above the recrystallization temperature continuously refines the austenite grain size while rolling below the recrystallization temperature flattens the austenitic grain. Thus, cooling below the A_{r3} where austenite begins its transformation to ferrite results in the formation of a finely divided mixture of austenite and ferrite and, upon rapid cooling below the A_{r1} , to a finely divided mixture of ferrite and martensite/bainite.

The second objective is satisfied by the third rolling reduction of the flattened austenite grains at temperatures between the A_{r1} and A_{r3} where 20% to 60% of the austenite has transformed to ferrite.

The thermomechanical processing practiced in this invention is important for inducing the desired fine distribution of constituent phases.

The temperature that defines the boundary between the ranges where austenite recrystallizes and where austenite does not recrystallize depends on the heating temperature before rolling, the carbon concentration, the niobium concentration and the amount of reduction in the rolling passes. This temperature can be readily determined for each steel composition either by experiment or by model calculation.

Linepipe is formed from plate by the well known U-O-E process in which plate is formed into a U shape, then formed into an O shape, and the O shape is expanded 1-3%. The forming and expansion with their concomitant work hardening effects leads to the highest strength for the linepipe.

The following examples illustrate the invention described herein.

A 500 lb. heat of the alloy represented by the following chemistry was vacuum induction melted, cast into ingots, forged into 4 inch thick slabs, heated at 1240°C for two hours and hot rolled according to the schedule in Table 2.

TABLE 1
Chemical Composition (wt%)

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>Mo</u>	<u>Cr</u>	<u>Nb</u>	
0.090	1.84	0.12	0.40	0.61	0.083	
<u>V</u>	<u>Ti</u>	<u>Al</u>	<u>S</u>	<u>P</u>	<u>N(ppm)</u>	<u>P_{cm}</u>
0.081	0.023	0.025	0.004	0.005	40	0.24

The alloy and the thermomechanical processing were designed to produce the following balance with regard to the strong carbonitride formers, particularly niobium and vanadium:

- about one third of these compounds precipitate in austenite prior to quenching; these precipitates provide recrystallization resistance as well as austenite grain pinning resulting in fine austenite grains before it transforms;
- about one third of these compounds precipitate during austenite to ferrite transformation through the intercritical and subcritical region; these precipitates help strengthen the ferrite phase;
- about one third of these compounds are retained in solid solution for precipitation in the HAZ and ameliorateing or eliminating the normal softening seen with other steels.

The thermomechanical rolling schedule for the 100 mm square initial forged slab is shown below:

TABLE 2

Starting Thickness: 100 mm
 Reheat Temperature: 1240°C
 Reheating Time: 2 hours

<u>Pass</u>	<u>Thickness After Pass, mm</u>	<u>Temperature °C</u>
0	100	1240
1	85	1104
2	70	1082
3	57	1060
----- Delay (turn piece on edge) (1) -----		
4	47	899
5	38	866
6	32	852
7	25	829
----- Delay (turn piece on edge) -----		
8	20	750

(1) Delay amounted to air cooling, typically at about 1°C/second.

To vary the amounts of ferrite and the other austenite decomposition products, quenching from various finish temperatures was conducted as described in Table 3.

TABLE 3**Finish Rolling and Cooling Parameters**

Designation	Finish Roll Temp °C	Thickness After Finish Rolling, mm	Start Quench Temp °C	% Ferrite	% Martensite
A1	830	25	560 *	50	50
A2	800	25	660 *	35	65
A3	800	25	600 *	50	50

* Ambient air cooled to these temperatures after finish rolling.

The ferrite phase includes both the proeutectoidal (or "retained ferrite") and the eutectoidal (or "transformed" ferrite) and signifies the total ferrite volume fraction.

Quantitative metallographic analyses were used to track the amount of austenite transformed as a function of finish temperature from which quenching was carried out and this data is plotted in Figure 1 and summarized in Table 3.

Quenching rate from finish temperature should be in the range 20 to 100°C/second and more preferably, in the range 30 to 40°C/second to induce the desired dual phase microstructure in thick sections exceeding 20 mm in thickness.

As seen from Figure 1, the finding is that the austenite is transformed anywhere between 35 to 50% when the quench start temperature is lowered from 660°C to 560°C. Furthermore, the steel does not undergo any additional transformation when the quench start temperature is further lowered, the total staying at about 50%.

Because steels having a high volume percentage of the second or martensite/bainite phase are usually characterized by poor ductility and toughness, the steels of this invention are remarkable in maintaining sufficient ductility to allow forming and expansion in the UOE process. Ductility is retained by maintaining the effective dimensions of microstructural units such as the martensite packet below 10 microns and the individual features within this packet below 1 micron. Figure 2, the scanning electron microscope (SEM) micrograph, shows the dual phase microstructure containing ferrite and martensite for processing condition A1. Remarkable uniformity of microstructure throughout the thickness of the plate was observed in all dual phase steels.

Figure 3 shows a transmission electron micrograph revealing a very fine dispersion of interphase precipitates in the ferrite region of A1 steel. The eutectoidal ferrite is generally observed close to the interface at the second phase, dispersed uniformly throughout the sample and its volume fraction increases with lowering of the temperature from which the steel is quenched.

A major discovery of the present invention is the finding that the austenite phase is remarkably stable to further transformation after about 50% transformation. This is attributed to a combination of austenite stabilization mechanisms and ausaging effects:

(a) Austenite Stabilization: There are at least three mechanisms of stabilization that operate in the steels of the present invention helping to explain the arrest of its further transformation to ferritic phases:

(1) Thermal Stabilization: The strong driving force for partitioning of carbon from the transformed ferrite phase to the untransformed austenite during austenite transformation leads to several effects, all commonly grouped as thermal stabilization. This mechanism can lead to some general enrichment in C in austenite and more specifically a C concentration spike at the austenite/ferrite interface discouraging the further transformation locally. Furthermore, the C can also segregate in an enhanced fashion to

the dislocations at the transformation front immobilizing this front and freezing the transformation in place.

(2) Concentration Spike: C and the other strong austenite stabilizers such as Mn are driven to the remaining austenite during its transformation. However, due to the slow diffusion and lack of sufficient time, no significant homogenization of this partitioning can occur, resulting in local concentration spikes in C and Mn at the austenite transformation front. This enhances the hardenability of the steel locally, leading to stabilization. A general depression in the transformation range will help this process by eliminating the possibility for homogenization.

(3) Chemical Stabilization: Due to the appreciable Mn in the steel and the presence of Mn banding, the austenite regions that remain untransformed are the one which also have higher Mn, thereby enhancing the hardenability of this region well beyond that of the overall alloy. For the cooling rates used and thermomechanical processing used, this can result in stabilization of austenite to ferrite transformation.

- (b) Ausaging: This is believed to be a major factor in the steels of the present invention. If austenite phase has high amounts of Nb and V dissolved in solid solution in a supersaturated state as is the case with the steels of the present invention, and if the austenite transformation temperature is low enough, then the excess Nb and V can lead to fine precipitation/pre-precipitation phenomena. The pre-precipitation can include dislocation atmospheres both in the general austenite and at the transformation in particular, which can immobilize this transformation front, stabilizing the austenite to further transformation.

Table 4 shows ambient tensile data of alloys processed by conditions A1, A2 and A3.

TABLE 4

Designation	% Ferrite/ % Martensite (1)	Orientation	Tensile Strength (ksi) (2)	0.2% Yield Strength (ksi)	Yield Strength After 2% Deformation (ksi)	% Total Elong.
A1	50 / 50	Trans.	139	110	130	15
A2	35 / 65	Long. Trans.	142 141	86 91	132 132	20 15
A3	50 / 50	Long. Trans.	140 136	86 84	131 130	20 16

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(1) Including small quantity of bainite and retained austenite

(2) ASTM specification E8

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Yield strength after 2% elongation in pipe forming will meet the minimum desired strength of at least 100 ksi, preferably at least 130 ksi, due to the excellent work hardening characteristics of these microstructures.

Table 5 shows the Charpy-V-Notch impact toughness (ASTM specification E-23) at -40°C performed on longitudinal (L-T) and transverse (T) samples of alloys processed by A1 and A2 conditions.

TABLE 5

<u>Designation</u>	<u>Orientation</u>	<u>Energy (Joules)</u>
A1	L - T	145
	T	50
A2	L - T	148
	T	50

The impact energy values captured in the above table indicate excellent toughness for the steels of this invention.

A key aspect of the present invention is a high strength steel with good weldability and one that has excellent HAZ softening resistance. Laboratory single bead weld tests were performed to observe the cold cracking susceptibility and the HAZ softening. Figure 4 presents an example of the data for the steel of this invention. This plot dramatically illustrates that in contrast to the steels of the state of the art, for example commercial X100 linepipe steel, the dual phase steel of the present invention, does not suffer from any significant or measurable softening in the HAZ. In contrast X100 shows a 15% softening as compared to the base metal. By following this invention the HAZ has at least about 95% of the strength of the base metal, preferably at least about 98% of the strength of the base metal. These strengths are obtained when the welding heat input ranges from about 1-5 kilo joules/mm.

CLAIMS:

1. A method for preparing a dual phase steel comprising ferrite and martensite/bainite phases and of at least 100 ksi yield strength after 1-3% deformation which comprises:

- (a) heating a steel billet to a temperature sufficient to dissolve substantially all vanadium carbonitrides and niobium carbonitrides;
- (b) rolling the billet, and forming plate, in one or more passes to a first reduction in a temperature range in which austenite recrystallizes;
- (c) rolling the plate in one or more passes to a second reduction in a temperature range below the austenite recrystallization temperature and above the A_{r3} transformation point;
- (d) cooling the further reduced plate to a temperature between the A_{r3} transformation point and about 500°C.
- (e) water cooling the finished rolled plate to a temperature $\leq 400^\circ\text{C}$.

2. The method of claim 1 wherein the temperature of step (a) is about 1150-1250°C.

3. The method of claim 1 wherein the first rolling reduction is about 30-70%; the second rolling reduction is about 30-70%.

4. The method of claim 1 wherein the cooling of step (d) is air cooling.

5. The method of claim 1 wherein the cooling of step (d) is carried out until 20-60 vol% of the steel has transformed to a ferrite phase.

6. The method of claim 1 wherein the cooling of step (e) is carried out at a rate of at least 25°C/second.

7. The method of claim 1 wherein the plate is formed into a circular or linepipe material.

8. The method of claim 7 wherein the circular or linepipe material is expanded 1-3%.

9. The method of claim 1 wherein the steel chemistry in wt% is:

0.05 - 0.12 C
0.01 - 0.50 Si
0.40 - 2.0 Mn
0.03 - 0.12 Nb
0.05 - 0.15 V
0.2 - 0.8 Mo
0.015 - 0.03 Ti
0.01 - 0.03 Al
 $P_{cm} \leq 0.24$

the balance being Fe.

10. The method of claim 9 wherein the sum of the vanadium and niobium concentrations ≥ 0.1 wt%.

11. The method of claim 10 wherein the concentrations of each of vanadium and niobium are $\geq 0.04\%$.

12. The method of claim 9 wherein the steel contains 0.3-1.0% Cr.

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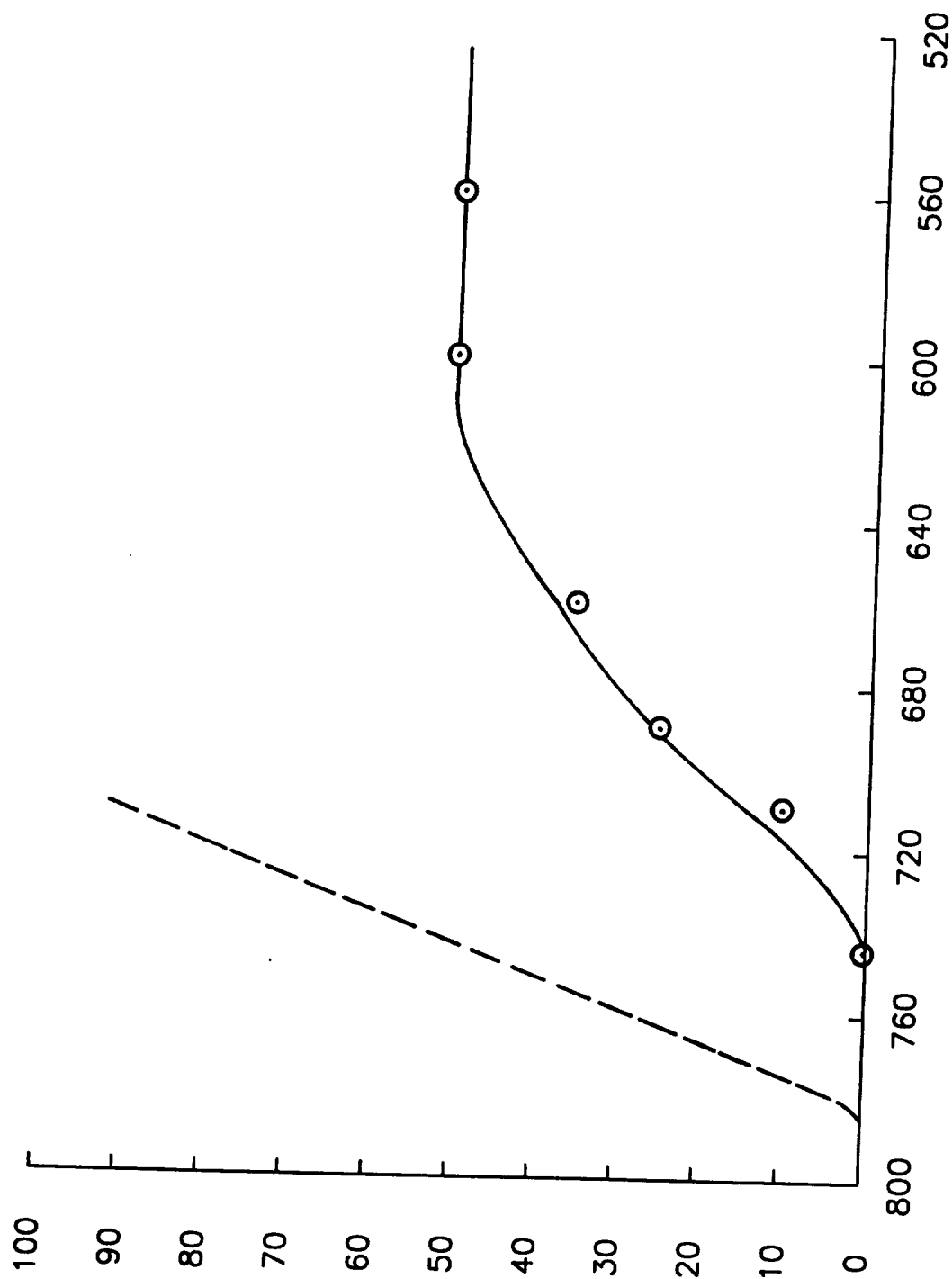


FIG. 1

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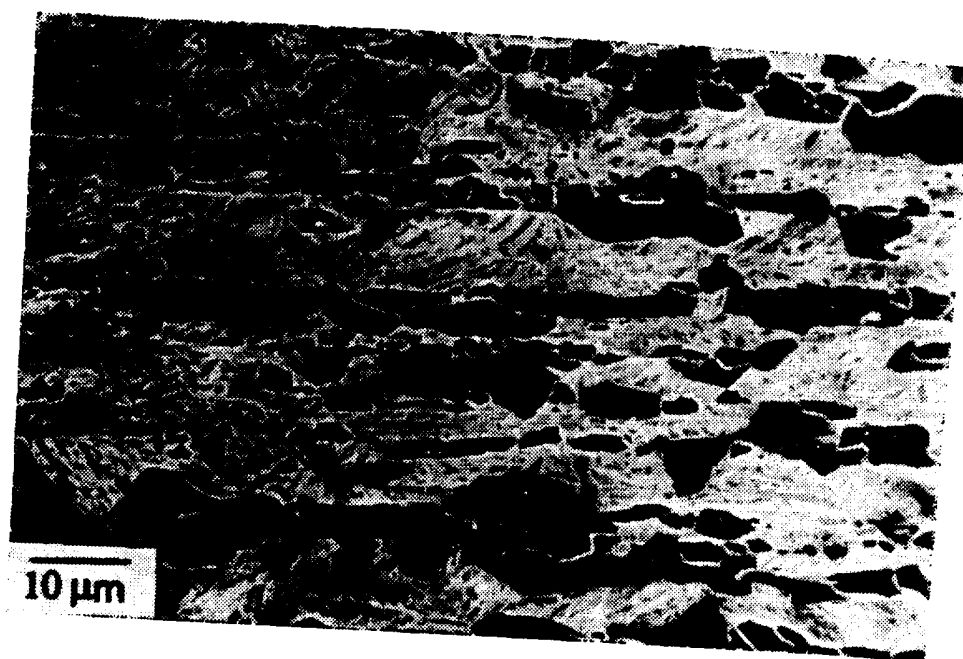


FIG. (2a)

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FIG.(2b)

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FIG. 3

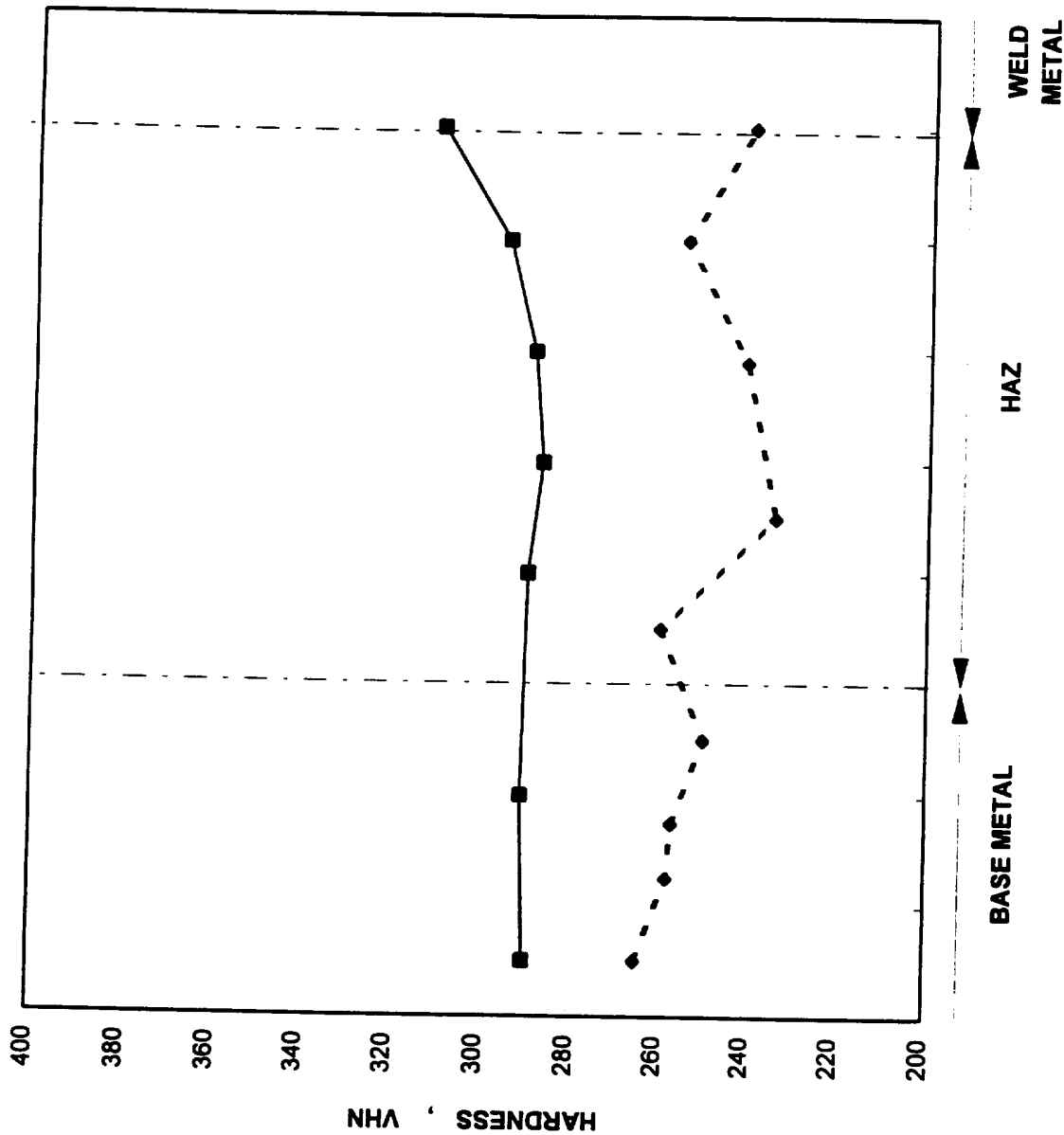


FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15725

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C21D 8/02

US CL :148/653, 654

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/653, 654

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 58-34131 (Kawasaki Steel KK) 28 February 1983 (02.02.83), english abstract and page 164.	1 to 12
A	JP, A, 60-0177128 (Nippon Kokar KK) 11, September 1985 (11.09.85), english abstract.	1 to 12
A	JP, A, 57-134518 (Kawasaki Steel KK) 19, August 1982 (19.08.82), english abstract.	1 to 12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

20 FEBRUARY 1996

Date of mailing of the international search report

25 MAR 1996

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