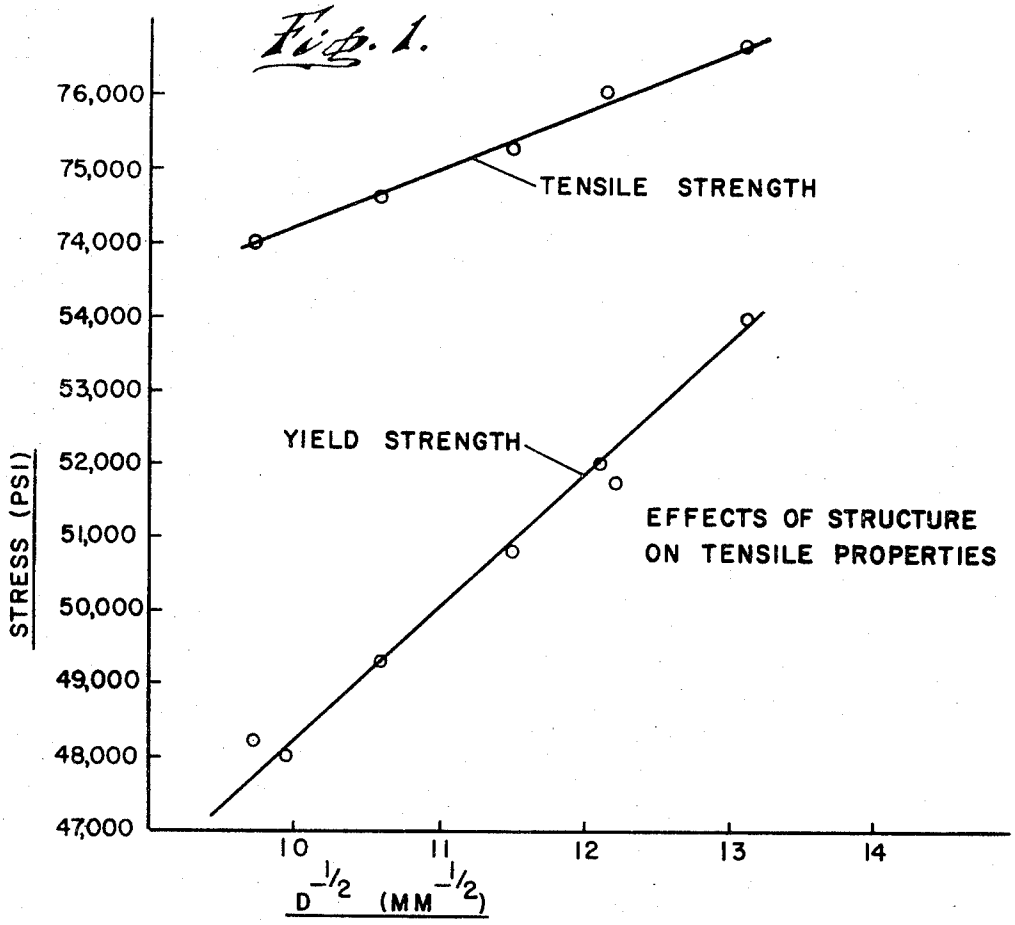
LOW TEMPERATURE STEEL PROCESS

Original Filed July 24, 1967 5 Sheets-Sheet 1

Fig. 1.



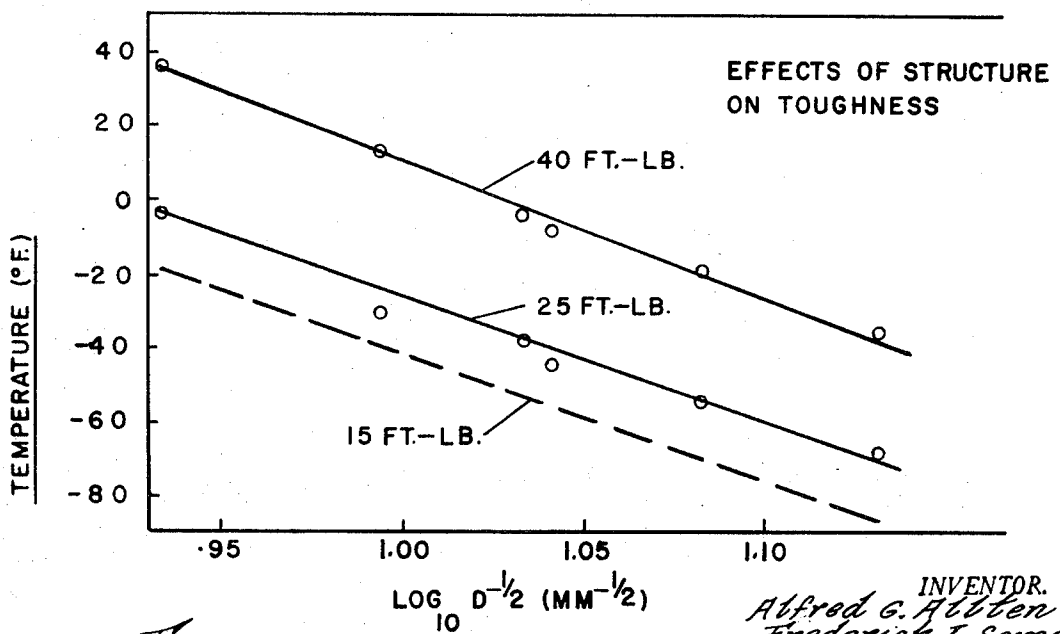


Fig. 2.

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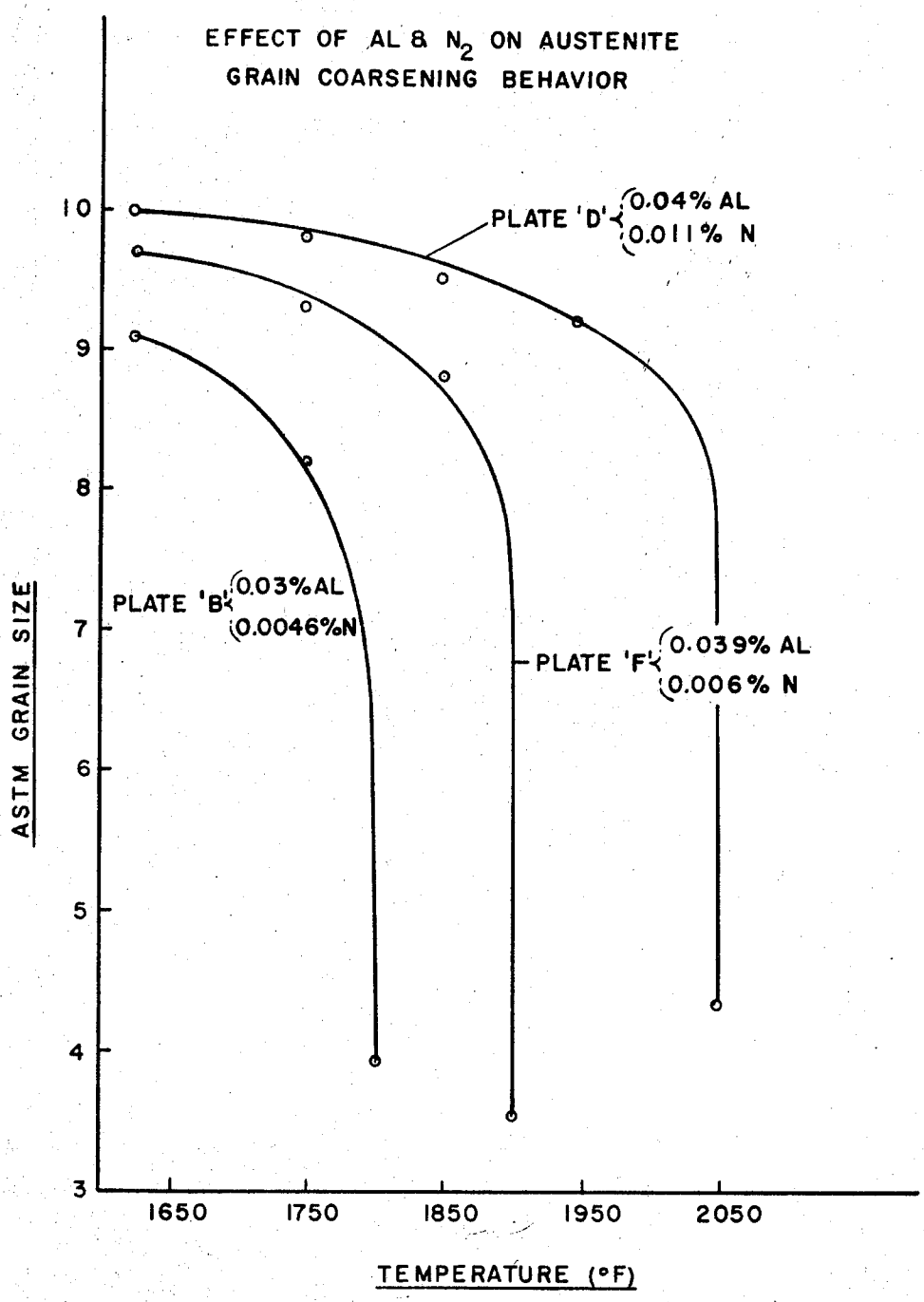


Fig. 3.

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LOW TEMPERATURE STEEL PROCESS

Original Filed July 24, 1967 5 Sheets-Sheet 3

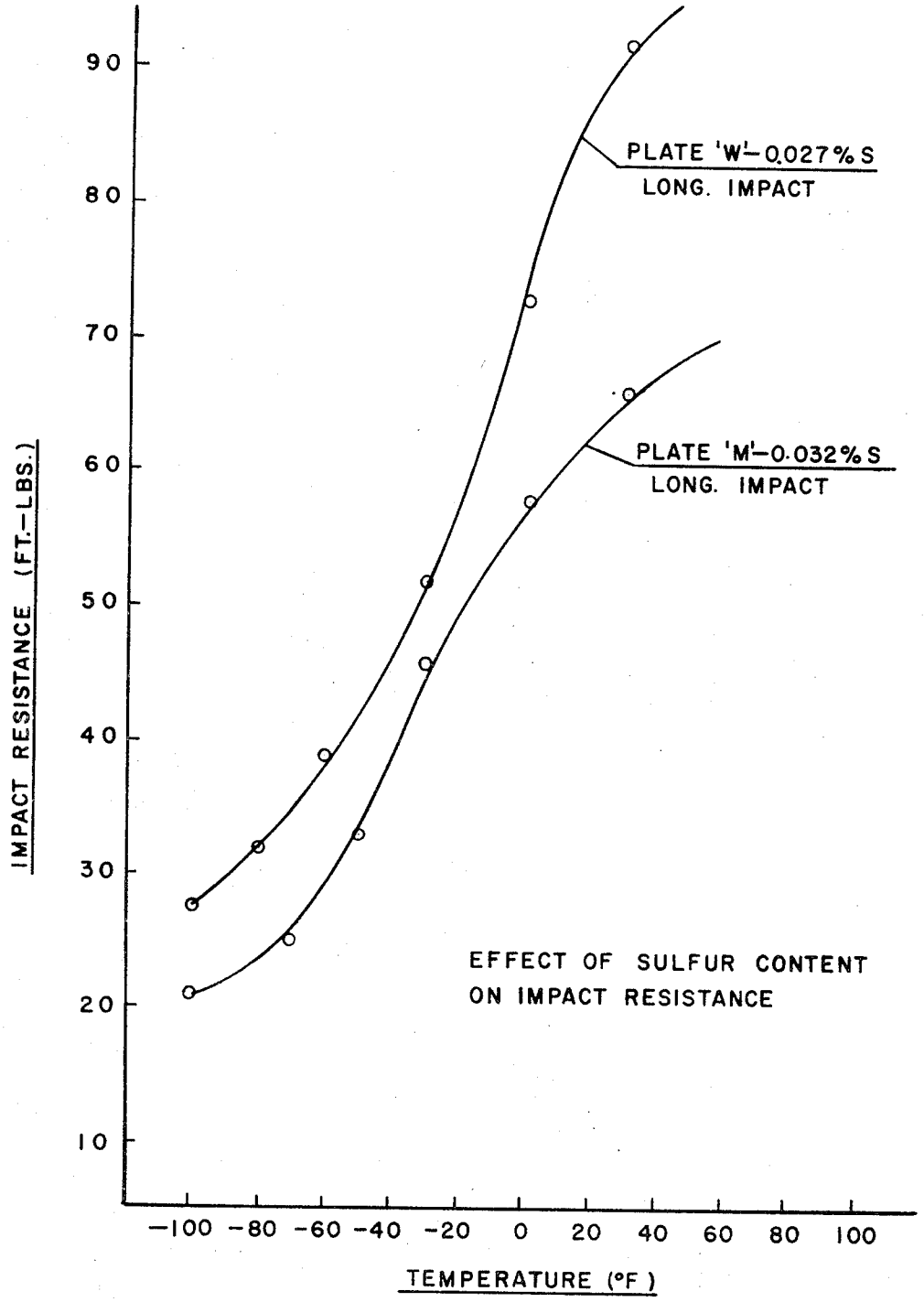


Fig. 4.

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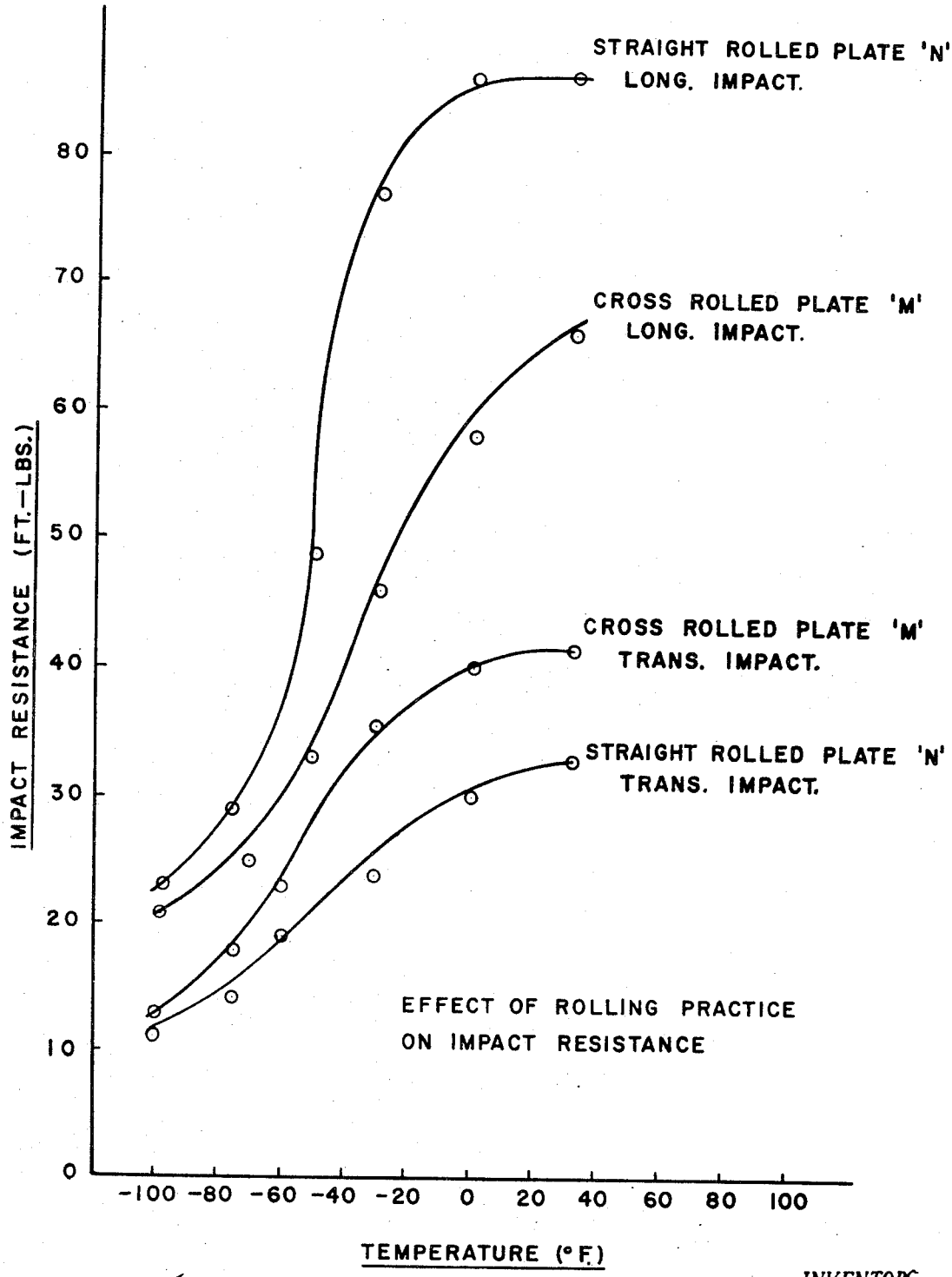


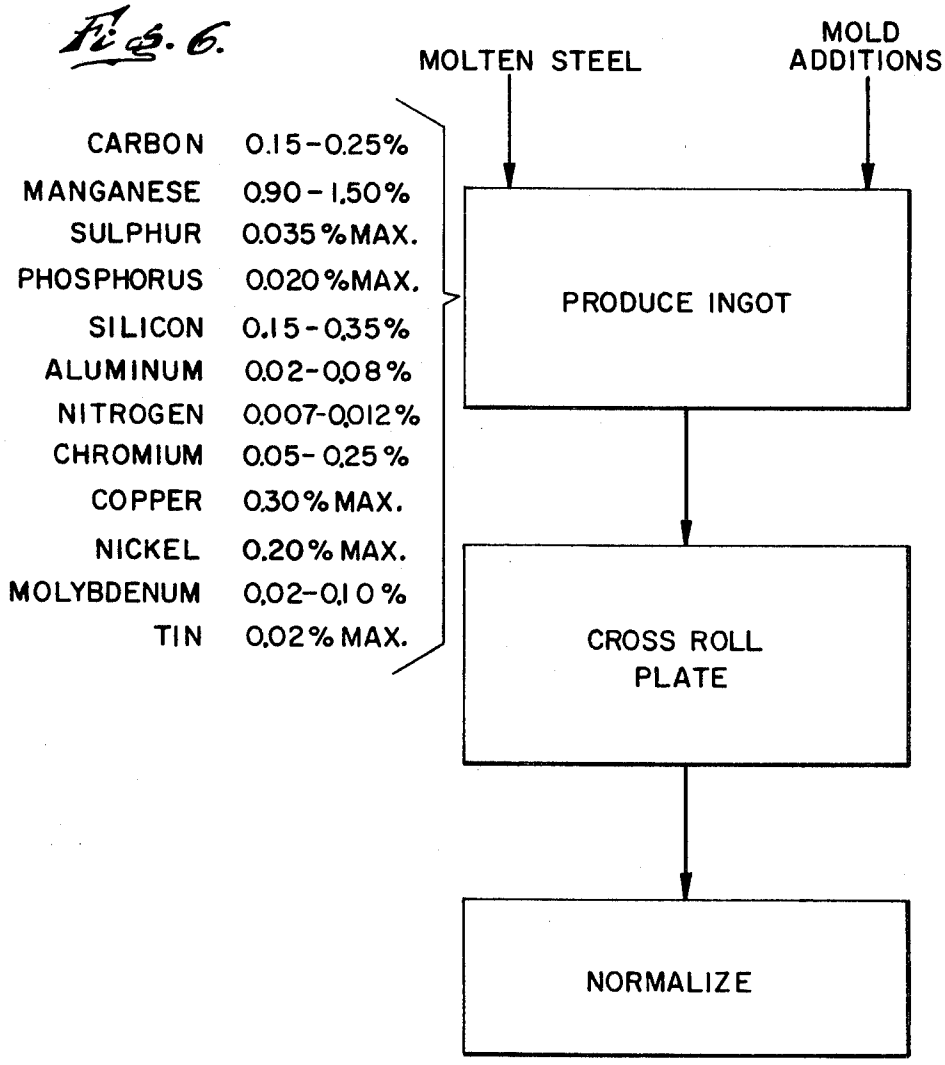
Fig. 5.

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LOW TEMPERATURE STEEL PROCESS

Original Filed July 24, 1967 5 Sheets-Sheet 5

Fig. 6.



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United States Patent Office 3,738,874
Patented June 12, 1973

3,738,874

LOW TEMPERATURE STEEL PROCESS

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Original application July 24, 1967, Ser. No. 655,465, now abandoned, and a continuation-in-part of application Ser. No. 883,490, Dec. 9, 1969. Divided and this application May 26, 1971, Ser. No. 147,030
Int. Cl. C21d 1/28, 7/14
U.S. Cl. 148—12 3 Claims

ABSTRACT OF THE DISCLOSURE

The process of making a low temperature weldable steel plate of plain carbon grade and unusually high impact resistance and yield strength in normalized condition. The steel contains carefully controlled amounts of carbon, manganese, sulfur, phosphorus, silicon, aluminum and nitrogen, plus alloying elements which may include chromium, copper, and nickel, certain of which components can be achieved as residual elements in scrap. The alloy will be used especially as plate.

DESCRIPTION OF INVENTION

The present application is a division of application Ser. No. 655,465, filed July 24, 1967 for Low Temperature Steel, now abandoned, and it is a continuation-in-part of Ser. No. 883,490 filed Dec. 9, 1969 for Low Temperature Steel Process, now abandoned. The product subject matter is claimed in our application Ser. No. 45,392, filed June 11, 1970 for Low Temperature Steel, now abandoned.

The present invention is concerned with a process of making a cross rolled normalized steel of plain carbon weldable grade with small alloying additions, which has favorable properties for low temperature service.

A purpose of the invention is to produce a weldable steel for use particularly in plate form in low temperature applications such as tanks and pressure vessels, at very moderate cost.

A further purpose is to produce steel plate for low temperature service without expensive alloying additions by control of the relative quantities of carbon, manganese, silicon, chromium, copper, nickel, aluminum and nitrogen, without other significant alloying additions.

A further purpose is to obtain superior impact resistance combined with unusually high yield strength in carbon steel plate with minor and inexpensive alloying additions while permitting welding, the steel merely being normalized.

A further purpose is to produce weldable steel plate for low temperature service in normalized condition by introducing controlled amounts of aluminum and nitrogen in essentially a plain carbon steel, and adjusting other alloying elements to compensate.

Further purposes appear in the specification and in the claims.

The drawings are curves useful in explaining the invention.

FIG. 1 shows the effect of structure on tensile properties, plotting stress in pounds per square inch as ordinate against the inverse square root of the mean ferritic grain diameter.

FIG. 2 shows the effect of structure on toughness, plotting the transition temperature in degrees Fahrenheit as ordinate against the logarithm to the base 10 of the inverse square root of the mean ferritic grain diameter as abscissa.

FIG. 3 shows the effect of additions of aluminum and nitrogen in the steel on the austenitic grain coarsening behavior, plotting ASTM austenitic grain size as ordinate against temperature in degrees Fahrenheit as abscissa.

FIG. 4 shows the effect of sulfur content on impact resistance, plotting impact resistance in foot-pounds against transition temperature in degrees Fahrenheit.

FIG. 5 shows the effect of rolling practice on impact resistance, plotting impact resistance in foot-pounds as ordinate against transition temperature in degrees Fahrenheit as abscissa.

FIG. 6 is a block diagram showing steps in the process of the invention.

Before considering the description in detail, it may be well to present in summary certain highlights in respect to the present invention:

(1) Carbon steels without special processing and special compositions do not have favorable properties in low temperature service (that is, do not have Charpy impact values of at least 15 ft./lbs. at −75° F.) even at moderate strength levels, of the order of 45,000 p.s.i. yield strength, in plate thicknesses.

(2) It has been asserted that special finishing at low temperatures from hot rolling of carbon steel plate can produce the low temperature properties desired. As explained below, this was tried without success using steels made by open hearth practice.

(3) It has been found that normalizing of carbon steels is far more effective in producing desired low temperature properties than mill processing techniques. However, starting with ordinary open hearth steel, the desired low temperature properties were not obtained by normalizing or normalizing combined with controlled mill processing as later explained.

(4) We find that we want as part of our invention, and can get, in steel in the normalized condition, a fine ferritic grain size in excess of ASTM 10.5, preferably at least 11.0, and most desirably higher than that, which would be especially desirable where the carbon content is from 0.20% to 0.25%, inclusive. Generally, the higher the carbon content, the finer should be the ferritic grain size. Controlled rolling or normalized carbon steel without control of the carbon, manganese, aluminum and nitrogen will not produce the desired grain size, especially when the aluminum and/or nitrogen is low. The grain refinement increases impact resistance, and also increases tensile properties, especially yield strength.

(5) It has been determined that aluminum and nitrogen are both necessary to provide aluminum nitride which in turn keeps the austenitic grain size small during normalizing treatment. Generally, the finer the austenitic grain size, the finer will be the resulting ferritic grain size.

(6) Ordinary open hearth practice and basic oxygen steel-making practice produce steels which are of low nitrogen content.

(7) By the conjoint addition of aluminum and nitrogen to an open hearth steel, it was possible to produce low temperature properties with some improvement in tensile properties in carbon steel. An important aspect of the invention, therefore, is the controlled addition of aluminum and particularly of nitrogen.

(8) In order to get the highest tensile properties in carbon steels it is also necessary to control the addition of manganese and the carbon level. However, there are definite upper limits to these additions because of the need to maintain weldability. It is possible, however, as shown by our data to increase the contents of carbon and manganese so as to obtain a yield strength of 45,000 to 55,000 p.s.i. in view of the presence of aluminum and nitrogen in a normalized steel. The ultimate tensile strength, however, is largely controlled by the level of manganese and carbon. Limitations in existing specifications and accepted control of steel making make it difficult to obtain a tensile

strength much in excess of 85,000 p.s.i. and a yield strength much in excess of 45,000 p.s.i. in the heavier gages of normalized steel plate (up to about 2 inches inclusive).

There is a considerable need for a steel plate for low temperature vessels which can contain liquified gases at temperatures in the range between zero and −60° F. Such a steel must be of low cost and therefore cannot have high contents of any expensive alloying ingredient. It must be weldable since welding is an essential method of fabrication. It must be unusually tough, having a high impact resistance at low temperature. It must also be of unusually high tensile properties considering the other characteristics.

Table 1 below shows the required mechanical properties:

TABLE 1.—MECHANICAL PROPERTY SPECIFICATIONS

Gauge, inches	Up to 2" inc.
Yield strength, p.s.i.	45/55,000.
Tensile strength, p.s.i.	65/85,000.
Transverse Charpy-V-Notch at −75° (ft.-lbs.)	15.

To meet the above requirements, it is necessary that the steel be of what would normally be considered a carbon grade, in order that it may be of low cost and of high weldability without preheat.

It has been difficult to find a commercial carbon steel which has the desired low temperature impact properties, since the transition temperature from ductile to brittle in most carbon steels is well above −75° F., and which also has the required tensile properties. Faced with the problem, it did not seem to be practical to make a simple modification in a carbon steel grade to meet these unusual requirements. It should be remembered that the well known "scissors function" indicates that where tensile properties are increased, ductility is correspondingly decreased. Accordingly, it has been found that carbon steels which will meet the tensile properties fall short of the impact requirements, often by a rather wide margin. This is true even though the steels have been normalized.

In an effort to solve the problem, silicon killed steel meeting ASTM specification A36, having 0.20% carbon and 0.90 to 1.1% manganese was teemed into various ingots, and alloying additions were made in the mold. The ingots were of 26 x 59 inches size, hot topped, full weight. Alloying additions were made in the mold of 6% nitrogen containing nitrided electrolytic manganese, regular electrolytic manganese, and high purity aluminum to produce the compositions listed in Table 2. The maximum addition in any case was 0.35% by weight.

rolling temperature of approximately 2350° F. Initially controlled rolling procedures were used, involving low finishing temperatures. The low finishing temperatures were achieved by holding the plate prior to the last pass until the temperature had dropped to the desired value. In subsequent rolling low finishing temperatures were given up and rolling was carried out according to usual steel rolling mill procedures, finishing at a temperature of about 1800° F. (½ inch) or 1950° F. (1 inch). Except for a limited study of the effect of straight-away rolling, all of the slabs were turned after the scale-breaking pass and cross rolled completely. A total of 25 plates were made and data for 18 of these is given in Table 2. Other plates will be discussed later.

The heat treating practices used to normalize the plates are indicated in Table 3.

TABLE 3.—HEAT TREATING PRACTICES

Gauge, inches	Furnace temperature, ° F.	Minimum total time, hours
To (inclusive):		
½	1,625	¾–1
¾	1,625	1¼
1	1,625	1½
1¼	1,625	2
1½	1,625	2¼
1¾	1,625	2½
2	1,625	2¾

A minimum soaking time of ½ hour at 1600° F. ±10° F. was provided. In some cases the plates were held in the furnace for of the order of ¼ hour beyond the time mentioned. The plates after heating were air cooled in still air.

CONTROLLED ROLLING

An attempt was made to obtain the properties required by controlled rolling. It appeared from the literature, particularly Phoenix Steel Corporation, The Low Temperature Steel Story, and R. W. Vanderbeck, Welding Research Supplement (March 1953) 114S, that it might be possible to obtain required properties by using low finishing temperatures and relatively large final reduction to obtain a very fine grain size.

Plates A, B and C in Table 2 were rolled to 1 inch gauge from stocked slabs of ASTM–A36 steel made by aluminum fine grain practice. The various plates were finished at successively lower temperatures, plate A at 1900° F., plate B at 1550° F. and plate C at 1450° F., and each was subjected to increasing amounts of deformation in the final pass. The maximum final reduction was 50%. The effect of normalizing after rolling was also determined.

The microstructures in plates A, B and C in the as-rolled and normalized conditions were observed. It was found that low finishing temperature and increase in final reduction produced a slight improvement in grain size in

TABLE 2.—CHEMICAL COMPOSITION AND DETAILS OF MANUFACTURE

	Chemical composition percent by weight												Rolling practice		
	C	Mn	P	S	Si	Ni	Cr	Cu	Sn	Al	N	Mn/C	Procedure	Finishing temp., ° F.	Plate size, inches
A	.20	1.10	.014	.035	.27	.09	.06	.17	.018	.032	.0045	5.5	Normal cross rolling	1,900	1 x 84 x 420
B	.20	1.07	.014	.035	.26	.09	.06	.16	.018	.030	.0046	5.3	Controlled cross rolling	1,550	1 x 84 x 360
C	.18	1.05	.016	.032	.26	.09	.06	.18	.018	.032	.0043	5.8	do	1,450	1 x 84 x 340
D	.20	1.19	.011	.025	.26	.03	.03	.08	.007	.040	.011	5.9	Normal cross rolling	1,680	1 x 96 x 324
E	.20	1.19	.012	.024	.26	.03	.03	.07	.007	.039	.011	5.9	do	1,800	1 x 96 x 324
F	.21	1.24	.013	.024	.26	.03	.03	.09	.007	.039	.006	5.9	do	1,780	1 x 96 x 324
G	.21	1.21	.012	.024	.26	.03	.03	.08	.007	.037	.006	5.8	do	1,825	1 x 96 x 324
H	.19	.94	.012	.034	.18	.09	.06	.18	.007	.046	.010	5.0	Normal cross rolling	1,870	1 x 96 x 330
I	.19	1.10	.013	.032	.20	.09	.06	.20	.009	.050	.005	5.8	do	1,860	1 x 96 x 315
J	.19	1.05	.012	.034	.19	.09	.06	.19	.008	.050	.005	5.5	do	1,890	1 x 96 x 315
K	.15	.85	.006	.027	.26	.07	.04	.16	.007	.057	.010	5.6	Normal cross rolling	1,830	¾ x 96 x 450
L	.16	.81	.004	.026	.24	.06	.03	.16	.011	.053	.007	5.1	do	1,675	⅜ x 96 x 910
M	.21	1.37	.013	.031	.27	.09	.05	.16	.011	.036	.0090	6.2	Normal cross rolling	1,770	1 x 96 x 320
N	.21	1.44	.013	.031	.27	.09	.05	.16	.010	.040	.0093	6.5	Normal straight away rolling	1,720	1 x 72 x 430
O	.18	1.19	.008	.031	.19	.06	.03	.13	.009	.058	.010	6.6	Normal cross rolling	1,860	1¼ x 96 x 240
P	.18	1.19	.008	.031	.19	.06	.03	.13	.009	.058	.010	6.6	do	1,890	1 x 96 x 320
Q	.18	1.12	.009	.031	.20	.06	.02	.13	.007	.037	.014	6.2	do	1,840	¾ x 96 x 430
R	.18	1.12	.009	.031	.20	.06	.02	.13	.007	.037	.014	6.2	do	1,830	½ x 96 x 360

Two slabs 7 x 96 inches were obtained from each ingot. The slabs were heated uniformly in the furnace to a

the as-rolled condition. Lowering the finishing temperature and increasing the final reduction tended to reduce the occurrence of Widmanstätten side plates and refine the regular ferritic and pearlitic constituents. Banding was evident in all three steels. The microstructure also showed that normalizing had a pronounced effect upon the structure. After normalizing, each of these steels was a uniformly fine grain mixture of ferrite and pearlite, but banding was still evident. In the normalized condition, each of the steels had a considerably finer grain size than in the controlled rolled condition. Comparison of the microstructures of the normalized steels, using quantitative metallography, also showed that the structural differences initially introduced by controlled rolling were removed by normalizing. From this it was concluded that, from the standpoint of structure, controlled rolling would not be of value in producing the desired result if normalizing were to be used.

The longitudinal tensile and impact properties of plates A, B and C in both the as-rolled and normalized conditions are shown on Table 4. The transverse as-rolled properties were not determined. The transverse normalized properties were found to be the same as those shown in the table.

TABLE 4.—LONGITUDINAL TENSILE AND IMPACT PROPERTIES OF PLATES A, B AND C

Condition	Plate	Yield strength, p.s.i.	Tensile strength, p.s.i.	Elongation percent in 2 in.	15 t. lb. transition temp. ° F.
As-rolled	A	48,000	75,000	32	0
	B	47,500	76,500	32	−9
	C	50,000	75,000	32	−20
Normalized	A	47,500	77,000	32	−59
	B	49,000	75,000	33	−65
	C	47,500	77,500	33	−62

Notwithstanding that considerable changes in microstructure were accomplished by processing, comparison of results shown in Table 4 with the desired properties listed in Table 1 shows that the desired properties were not obtained in either the as-rolled or the normalized conditions. While the tensile and yield strengths of all of the steels were adequate, the transition temperatures of the impact resistance values were about 15% too high in the normalized condition and rather higher in the as-rolled condition.

The analysis of the data in Table 4 suggests the possibility that the steel is behaving anomalously. It is evident that neither controlled rolling nor normalizing was very effective in altering the tensile properties. These results were not expected in view of the microstructures obtained. Usually with carbon steels, the yield strength and to a lesser extent the tensile strength will increase as the grain size decreases, but for a reason which is not apparent, this did not occur in the steels under investigation.

Processing had a more pronounced effect on impact resistance than it did on yield strength. The greatest improvement appeared to be due to normalizing. It was also noted that the transition temperatures in the normalized specimens are grouped fairly closely together. These findings suggest that the differences introduced by controlled rolling were eliminated to a large extent by normalizing. This agrees with the observations based on microstructure.

VARIATIONS IN ALLOYING ELEMENTS

Experiments were initiated to obtain more effective properties in the steel under investigation by normalizing. As a first step, the influence of ferrite grain size on mechanical properties was investigated quantitatively. It was necessary to obtain samples which were otherwise similar and which had the correct analysis, but which differed in grain size. Samples of as-rolled plate B were heat treated under various conditions of time and temperature. Care was taken to maintain a fairly constant pearlite content in all of the specimens. The average grain size for each specimen was determined using the linear intercepts method, ASTM Standards (1961, Part 3) Metals Test Methods 647, but corrections were not made for pearlite content. The mechanical properties were determined as in previous experiments.

The semi-empirical theory of Petch, Journal Iron and Steel Institute (May 1953) 25; N. J. Petch, Fracture (Wiley 1959) 54–64, was employed. The mechanical properties were correlated with the inverse square root of the mean grain diameter, $D^{-1/2}$ for each specimen. The results are shown in FIGS. 1 and 2.

The plot of transition temperature in FIG. 2 involved approximating the position of the curve for 15 foot-pounds, since the scatter of the experimental results was too great to permit exact plotting from the data. The other curves on FIG. 2 were determined directly from the data, and they support the approximation of the curve relating toughness to grain size for 15 foot-pounds.

FIGS. 1 and 2 show several interesting features. The yield strength and the impact resistance increase as grain size decreases. This seems to indicate that the Petch theory holds for steels having carbon contents as high as 0.20% since previous work suggested that it had only been explored for steels of considerably lower carbon contents. R. J. Irvine and F. B. Pickering, Journal Iron and Steel Institute (November 1963) 944; W. B. Morrison and J. H. Woodhead, Journal Iron and Steel Institute (January 1963) 43; J. Heslop and N. J. Petch, Philosophical Magazine (September 1956) 866; A. Cracknell and N. J. Petch, Acta. Met. (March 1955) 186 and R. Phillips, W. E. Duckworth and F. E. L. Copley, Journal Iron and Steel Institute (July 1954) 593.

The results of FIGS. 1 and 2 are encouraging in that they suggest that it should be possible to achieve the properties desired using the steel in question. However, the data suggest also that the alloying composition must be changed. It would seem that allowing a suitable tolerance, an ASTM ferritic grain size of about 11.3 must be secured. From the controlled rolling experiments it seems that the optimum attainable ferritic grain size from the steel without alloy change cannot reliably exceed ASTM 10.5.

From the intercept values of the yield strength in FIG. 1 (depending on the slope) the so called "friction stress" or the component of strength due to solution hardening was found to be 29,000 p.s.i. This appears to be substantially higher than would be expected from a steel of the same content of manganese and silicon. This suggests that minor alloying elements present as residuals in the carbon steel add to the friction stress and thus to the mechanical properties in this steel. Examination of the chemical analysis in Table 2 tends to support this. Since the residual alloy content cannot be depended upon, it is necessary to consider that low residuals may be present in a particular steel. It would seem, therefore, that in the case of low residuals alloying additions would have to be made. It was thought that the combined grain refining and solution hardening effects of small further additions of either silicon or manganese can offset the effect of low residuals.

The slope of the yield strength curve in FIG. 1, which is usually referred to as k_y, is also significant. This measures the increase in yield strength due to an increase in the inverse square root of the mean grain diameter. The greater the value of k_y, the greater the corresponding increase in yield strength of given decrease in grain size. In this particular case the value of k_y (1900 p.s.i. mm.$^{1/2}$) is at least 20% lower than the lowest value found in the literature for any carbon steel. N. J. Petch, Fracture (Wiley 1959) 54–64; R. J. Irvine and F. B. Pickering, Journal Iron and Steel Institute (November 1963) 944. This means that the steel under investigation responds in yield strength to structural changes less than most other steels. It is therefore urgently needed to increase the k_y

value. It appears evident from the literature that the value of k_y can be increased by decreasing the carbon content.

The results in FIG. 1 show that the ultimate tensile strength varies with grain diameter.

An intensive study was made of the effects of grain refining additions and slight increases in manganese content. In these initial experiments the carbon content was kept at its original high level to simplify interpretations of the results.

Aluminum and nitrogen were added together as grain refining elements. Generally in steels which contain aluminum for grain refinement, residual nitrogen forms aluminum nitride. In the present tests additional nitrogen was also added. The purpose was first of all to further refine the grain size if possible. The second purpose was in the hope that nitrogen would contribute to solution hardening effects and thus raise the yield strength. R. J. Irvine and F. B. Pickering, Journal Iron and Steel Institute (November 1963) 944; L. A. Erasmus, Journal Iron and Steel Institute (January 1964) 32; R. Phillips, Carbon Steels (BISRA Special Report 81) 36; W. C. Leslie, Nitrogen in Ferritic Steels, American Iron and Steel Institute (January 1959) 57; J. A. Rinebolt and W. J. Harris, 43 Transactions American Society for Metals (1951) 1175; R. Phillips and J. A. Chapman (BISRA Special Report 81) 60; J. W. Halley, 167 Transactions American Institute Mining Metallurgical and Petroleum Engineers (1946) 224.

Two ingots were modified from a regular A36 steel heat, silicon killed and made to aluminum fine grain practice. The base composition was 0.20% carbon, 1.08% manganese and 0.26% silicon. Nitrogen and additional aluminum were added to one ingot with the aim to increase the nitrogen content to 0.01% and the aluminum content to 0.05%. Slight increases in manganese or silicon having been thought necssary to overcome the effect of possible low residuals, it was decided to add the nitrogen in the form of 6% nitrogen-containing nitrided electrolytic manganese. Assuming a residual nitrogen in the heat of 0.005% and 50% recovery of nitrogen, the nitrided electrolytic manganese was added in quantities of 3 pounds per ton. The anticipated increase in manganese content from this addition was roughly 0.15%. This was believed to be adequate to counteract the effect of low residuals. Aluminum was added in a quantity of ½ pound per ton. This addition was based upon an assumed aluminum residual of 0.03% and an expected aluminum recovery of 80%. Similar additions of aluminum and manganese were made to the second ingot except that the manganese used was regular electrolytic manganese so that no nitrogen was added with the manganese. After teeming the ingots were processed in accordance with normal mill procedure. Plates D through G in Table 2 are the products of these ingots.

The mechanical tests were performed according to the same procedure followed previously. In addition to the mechanical tests, austenitic grain coarsening experiments were conducted. The specimens were soaked for 2 hours at a series of temperatures above A3 followed by controlled cooling to outline the austenitic grain boundaries with proeutectoid ferrite. The various grain sizes produced were determined by the intercept method and the resulting values were converted to the equivalent ASTM numbers.

TABLE 5.—MECHANICAL PROPERTIES OF MODIFIED A36

Plate	Yield strength, p.s.i.	Tensile strength, p.s.i.	Elongation percent in 2"	15 ft.-lb. transition temp. ° F.		Ferritic grain size, ASTM
				Longitudinal	Transverse	
D	54,500	80,000	33	−80	−75	11.3
E	54,000	82,500	34	−75	−75	11.2
F	51,000	79,000	36	−75	−75	11.1
G	50,500	77,000	33	−80	−80	11.2

The longitudinal tensile properties and the longitudinal and transverse impact properties of the four plates in the mill normalized condition are shown in Table 5. The corresponding ASTM ferrite grain sizes are also given. The preliminary microstructural examinations had shown that the plates had relatively coarse grain structures in the as-rolled condition and it was expected would not exhibit the desired properties.

All of the normalized plates mentioned in Table 5 had the required properties. Major improvements were obtained in yield strength, impact resistance and ferritic grain size. Slight improvement had also been made in tensile strength and elongation. The highest yield strength achieved was 54,500 p.s.i. and the lowest transition temperature was −80° F. The average yield strength was 52,500 p.s.i. and the average transition temperature for impact resistance was −77° F. As is usual with cross-rolled steel, each of the plates was, at the 15 foot-pound impact response level, essentially isotropic with regard to toughness and hence the value of −77° F. for the transition temperature is applicable to both the longitudinal and transverse directions. The average tensile strength and elongation values achieved were 79,500 p.s.i. and 34% respectively. The ferritic grain sizes vary between ASTM 11.1 and 11.3, an average being 11.2. This represents a distinct improvement over the controlled rolled plates which had an average ferritic grain size of 10.1. The values also for the average ferritic grain size are close to the ones estimated on the basis of the Petch analysis.

The data show that the hoped for added improvements in ferritic grain size had not occurred to any appreciable extent from the additions of nitrogen but that there had been increases in yield strength. Accordingly steels D and E which contained the extra nitrogen had almost the same grain size values as steels F and G, but steels D and E had significantly higher tensile properties. The average difference in yield strength between the steels was 3500 p.s.i. This appears to be due to solution hardening effects. The data of FIGS. 1 and 2 on the effects of structure on properties when applied to the grain size values obtained with steels D through G only account for an increase in yield strength up to about 50,500 p.s.i. In other words, they only explain the yield strength values in steels F and G. Thus, the difference in yield strength between steels D and E and steels F and G must be attributed to solution hardening affected by a difference in composition. By examining Table 2 it is evident that the only significant difference in composition is the increase in nitrogen.

While an increase in yield strength of 3500 p.s.i. is not large by ordinary standards, it must be remembered that the increase in yield strength associated with grain refinement was only about 3000 p.s.i.

Austenitic grain coarsening studies were conducted in order to further establish the effect of the aluminum and nitrogen additions on grain size. Austenitic grain size was used rather than ferritic grain size so as to eliminate the error due to the transformation from austenite to ferrite in which some of the solid solution elements have an effect on grain size.

The technique used was to compare the coarsening behavior of the modified steels with that of the controlled rolled steels. FIG. 3 shows the findings for steels B, D and F where the ASTM austenitic grain sizes were plotted against the test temperatures. The corresponding aluminum and nitrogen contents are shown on FIG. 3. It will be noted that there are startling differences between the various curves on FIG. 3.

Steel D with the highest overall aluminum and nitrogen contents, had the finest austenitic grain sizes and the highest coarsening temperature. Steel F, with intermediate aluminum and nitrogen contents, had intermediate austenitic grain sizes and intermediate coarsening temperature. Steel B, which was produced by controlled roll-

ing, has the lowest aluminum and nitrogen contents, and with them the coarsest austenitic grain size and the lowest coarsening temperature. Thus, there appears to be a correlation between austenitic grain size, coarsening temperature and the amount of aluminum and nitrogen present. As far as the austenitic grain size is concerned, it was concluded that the additions of aluminum and nitrogen had the desired effect.

It was considered that essentially the same conclusion could be drawn with respect to the ferritic grain size. Ordinarily, such a conclusion would be untenable since the ferritic grain size comparisons upon which it is based are between steels which exhibit differences in alloy content other than those in aluminum and nitrogen and unlike the austenitic grain size which is almost entirely dependent upon the aluminum and nitrogen levels in so far as they affect the number and disposition of the aluminum nitride precipitates, the ferrite grain size is fairly sensitive to effects arising from the presence of other alloying ingredients as well. However, in the present case, a careful comparison of the compositions of steels A through C with those of D through G in Table 2 will show that outside of the differences in aluminum and nitrogen, the alloy differences which exist are differences of kind, rather than amount and, as will be appreciated by those experienced in the art, are of such a nature that while it is conceivable that they may have had some slight effect, it is highly unlikely that they could be responsible for the very substantial grain size improvements which were observed. Thus, the aluminum and nitrogen levels being the only other really significant differences present, it is, as indicated above, felt to be a reasonable conclusion that the aluminum and nitrogen additions had the desired effect with respect to the ferrite grain size as well as to the austenitic grain size.

It will be recalled that an earlier analysis of the findings indicated that the improvements in the tensile and impact properties which are achieved were attributable to the ferrite grain size improvements and to a small but significant solution hardening effect of the nitrogen. Thus, the ultimate conclusion to be drawn from the results of the present analysis is that the aluminum and nitrogen additions through their effects on grain size and solution hardening, were in essence responsible for the improved mechanical properties which were observed.

A series of experiments was now conducted to determine the effects of general variations in alloy content, of rolling practice and of plate thickness. Variations in alloy content were achieved by ingot mold additions and by use of heats with selected carbon, manganese and silicon contents.

Eventually a full heat of the steel was made. It was produced with a base manganese content of 1.10% and this was adjusted in the ingots required for the tests to approximately 1.35% using mold additions of regular electrolytic manganese. The important additions of aluminum and nitrogen were in this case made entirely in the ladle.

TABLE 6.—MECHANICAL PROPERTIES

Plate	Inch, gauge	C, percent	Mn, percent	Si, percent	Residual	Yield strength, p.s.i.	Tensile strength, p.s.i.	Elongation, percent in 2"	15 ft.-lb. transition temp., ° F.	
									Longitudinal	Transverse
H	1	.19	.94	.18	.33	50,000	74,500	34	−80	[1] −60 (12)
I	1	.19	1.10	.20	.35	48,400	73,500	36	−80	−70 (13)
J	1	.19	1.05	.19	.34	48,500	75,500	38	−80	−75
K	¾	.15	.85	.26	.27	44,600	69,500	[2] 30	−85	−60 (12)
L	⅜	.16	.81	.24	.25	47,100	66,650	[2] 28	−100	−60 (11)
M	1	.21	1.37	.27	.30	63,000	85,000	30	−100	−75
N	1	.21	1.44	.27	.30	57,000	83,000	34	−100	−75
O	1¼	.18	1.19	.19	.22	47,700	71,500	36	−80	−80
P	1	.18	1.19	.19	.22	48,700	71,000	36	−80	−75
Q	¾	.18	1.12	.20	.21	49,100	70,000	[2] 30	−80	−60 (11)
R	½	.18	1.12	.20	.21	51,500	70,500	[2] 29	−75	−75
S	2	.20	1.37	.26	.33	53,000	80,500	31	−80	−80
T	1¾	.19	1.38	.26	.32	51,000	80,000	34	−80	−80
U	1½	.21	1.37	.26	.33	53,500	80,500	32	−90	−80
V	1¼	.20	1.33	.26	.33	54,000	82,000	34	−100	−80
W	1	.20	1.32	.25	.31	55,000	84,000	31	−100	−85
X	¾	.20	1.33	.27	.34	55,000	83,000	[2] 27	−100	−100
Y	⅜	.19	1.31	.26	.33	56,000	88,000	[2] 25	−90	−80

[1] Values shown in parentheses are energies absorbed in ft.-lbs. at −80° F.
[2] Elongation in 8".

TABLE 7.—EFFECTS OF ALLOY CONTENT ON MECHANICAL PROPERTIES

C, percent	Mn, percent	Si and residuals, percent	Al, percent	N, percent	Yield strength, p.s.i.	Tensile strength, p.s.i.	15 ft.-lb. transition temp., ° F.		Ferritic grain size, ASTM
							Longitudinal	Transverse	
.15	.85	.53	.057	.010	44,600	69,500	−85	−60	10.2
.19	.94	.51	.046	.010	50,500	74,500	−80	−60	10.6
.18	1.19	.41	.058	.010	48,700	71,500	−80	−75	10.8
.20	1.21	.40	.037	.006	50,750	78,000	−80	−75	11.2
.20	1.32	.56	.050	.010	55,000	84,000	−100	−75	11.7
.21	1.37	.59	.036	.009	57,000	85,000	−100	−75	11.9

Table 6 shows the mechanical properties of plates H through Y. Steels H through R were made by mold additions, the specific analyses being listed in Table 2. Steels S through Y were made from the experimental heat and had an average analysis as follows:

	Percent
C	0.20
Mn	1.35
P	.014
S	.027
Si	.26
Ni	.08
Cr	0.5
Cu	.20
Sn	.014
Al	.050
N	.010

In addition to the mechanical properties, the table also gives the gauge and the carbon, maganese, silicon, and residual alloy contents for each of the steels listed. The residual alloy content was taken as the sum total of the nickel, chrome, and copper contents. By use of horizontal lines, the table also divides the plates according to heat. Thus plates H through J were from one heat, and plates K and L were from another heat, etc.

An analysis of the data in Table 6 showed that alloy content, plate thickness, and rolling practice each had significant effects on mechanical properties. The most important of these was considered to be alloy content. To illustrate more clearly its effects, data taken from Table 6 and additional data on ferrite grain size and on aluminum and nitrogen contents were listed in Table 7. To avoid confusion with the effects of the other variables mentioned, the steels in Table 7 were with one exception selected on the basis that they were all rolled using essentially the same practice and to the same thickness (i.e. the 1" gauge). The exception referred to is the first steel listed in the table. It was rolled to the ¾" gauge. The data on this steel were included in order to show the effects of relatively low alloy contents.

The general trend in the results in Table 7 is rather evident. As the alloy content was increased, the tensile and impact properties and the ferritic grain size were all improved. The improvements in impct resistance and the very substantial improvements in ferritic grain size were unexpected. Instead, it had been thought before the tests that the ferritic grain size would stay the same or at best improve only slightly and that as a consequence the impact resistance would decrease with increasing alloy content because of the associated solution hardening effects and increases in pearlite content. However, it appears that what actually happened was that in addition to the solution hardening effects and increases in pearlite content, the alloy increases also effected significant improvements in ferritic grain size and that these improvements were sufficient not only to maintain but in a number of cases to improve the impact resistance. Of special significance in this connection is the fact that the data in Table 7 clearly shows that the improvements in ferritic grain size correlate especially well with the increases in carbon and maganese contents and to a lesser degree with those in combined silicon and residual contents but bear no obvious relation to the aluminum and nitrogen contents. In view of earlier findings as to the effects of aluminum and nitrogen, this result was thought to be of paramount importance. In particular, it was considered to show that the presence of aluminum and nitrogen, although necessary, is not in itself sufficient to insure the ultra-fine ferritic grain sizes and other structural requirements needed to achieve optimum properties. Thus, the conclusion was drawn that the choice of a composition range, especially the carbon and manganese limits, is equally as important to the development of a steel with the desired properties as is the use of aluminum and nitrogen.

It will be recalled that in addition to alloy content, it was mentioned that plate thickness and rolling practice also had important effects on mechanical properties. Thus, it will be appreciated that prior to selecting a composition range, it is necessary to consider the magnitude of the effects of these variables.

Returning to Table 6, the effects of gauge on properties are indicated in the results on steels O through R and S through Y. Both series show essentially the same trend. With increasing gauge, the tensile and longitudinal impact properties decrease whereas the transverse impact properties either remain fairly constant or tend to increase slightly. For the most part, the magnitude of the changes in the various properties is not too great. However, in the case of the yield strength the changes are thought to be large enough that it may be necessary in certain instances to compensate for the effect of gauge by the use of increased alloy contents.

The variation in the transverse impact properties with gauge is of interest. Usually the effects of changes in gauge are attributed to the influence which attendant changes in cooling rate have on the austenite to ferrite transformation temperature. For example, increasing the gauge decreases the average cooling rate thus causing higher transformation temperatures and concomitant increases in grain size and decreases in pearlite content. These changes lead in turn to decreases in both tensile and impact properties. Since there is no reason to believe that the structural changes should be anisotropic, the associated decreases in mechanical properties would be expected to occur in both the longitudinal and the transverse directions. Thus, the fact that the transverse impact properties remained fairly constant or in some cases even increased slightly with increase in gauge was unexpected.

Microstructural examinations in this connection provided an explanation. These studies showed that the anticipated differences in grain size and pearlite content with changes in gauge were not the only differences present. There were in addition significant differences in inclusion morphology, and this was especially evident in the case of the sulfide inclusions. In the heavier gauges, the sulfides appeared to be elongated to about the same extent in both the longitudinal and transverse directions. In the lighter gauges, however, the sulfides were obviously longer in the longitudinal than in the transverse direction. Although all of the steels under consideration had been cross-rolled using essentially the same practice, these differences were undoubtedly an effect of rolling. Most important in this connection was the fact that they were with one exception very similar to the differences observed when comparing cross-rolled to fully straight rolled steels. The exception mentioned was that the differences arising with change in gauge were greatly attenuated by comparison with those seen between cross-rolled and straight rolled steels.

In any event, however, the similarity in the two cases was thought to be significant because, as is well known, cross-rolled steels exhibit significantly greater transverse impact properties than do straight rolled steels and it is generally agreed that this is primarily an effect of the differences between the two in inclusion morphology or, as it is more often called, mechanical fiber structure. Thus, in view of the similarities noted, it was considered that the unusual variation in transverse impact properties with gauge was explainable as an effect of varying degrees of cross-rolling which were manifested by noticeable differences in mechanical fiber structure and which arose entirely as a result of rolling to different gauges but with otherwise the same practice.

It often happens in applications involving the lighter gauges that the steel will be melted to the lean side of the composition range in order to take advantage of the increase in mechanical properties which normally occurs with decrease in gauge. The foregoing results are thought to be especially significant in this connection in that they strongly indicate that such a practice should not be applied in the event that transverse impact properties are an important part of the mechanical property requirements.

In order to show the importance of rolling practice on impact properties in general as well as to develop supporting evidence on behalf of the explanation of the variation in transverse impact resistance with gauge, plates M and N in Table 6 were rolled using different practices. Both plates were produced using slabs from the same ingot. Plate M was cross-rolled and except for a small amount of cross-rolling which was needed to make width, plate N was straight-rolled. The variation in impact resistance with temperature for each plate is shown graphically in FIG. 5. It is evident from these data that rolling practice had a pronounced effect on toughness. As indi-

cated earlier, the cross-rolled plate exhibited the higher transverse impact properties. The data also showed that the opposite was true in the case of the longitudinal direction. Accordingly, the straight-rolled plate exhibited the higher impact properties. Aside from its importance as general knowledge, this finding was of special interest because by analogy with the explanation of why the transverse impact resistance of the steels in Table 6 decreased with decreasing gauge, it suggested an additional reason why the longitudinal impact resistance of these steels was observed to decrease with increasing gauge.

In view of the effects which a change in the morphology of the sulfide inclusions was observed to have on impact resistance, an effort was made to establish the magnitude of the effect arising from sulfur content itself. Although extensive studies in this connection were beyond the scope of the investigation, a careful analysis of the data available from the various other studies were conducted provided some information. While far from conclusive, the indications of this analysis were, as might be anticipated, that the lower the sulful content the better. As an example, the temperature variation of impact resistance of plates M and W are presented graphically in FIG. 4. These data show that plate M with the higher sulfur content had the lower impact resistance. Aside from sulfur content, plates M and W were very similar to each other with respect to composition, processing, and microstructure.

Using the data in Tables 6 and 7 as well as the indications of the analyses of these data, a composition range for a steel exhibiting mechanical properties as indicated in Table 1 was established. In setting the upper limits of this range, consideration was given to the requirements that the steel be weldable without the need for preheat and that it be of reasonable cost. In seting the lower limits of the range, consideration was given to the importance of grain size and to the effects of alloy content in general as well as to those of aluminum and nitrogen in particular in achieving the ultra-fine ferritic grain sizes required.

The most important alloying ingredients were considered to be carbon, manganese, silicon, sulfur and, of course, aluminum and nitrogen. The limits set for these ingredients were as follows:

Carbon	0.007 to 0.10%.
Manganese	0.15 to 0.25%.
Sulfur	Over 1.00 to 1.50% and preferably 1.15 to 1.35%.
Silicon	0.35% max.
Aluminum	0.15 to 0.35%.
Nitrogen	0.04 to 0.10%.

It will be appreciated that other elements will occur in residual quantities within the steel as a consequence of the manufacturing process. With certain of these elements strict controls are an absolute necessity. For example, it is well known that both tin and pohsphorus have pronounced adverse effects on impact resistance. Thus, it is essential that these elements be held to the lowest practical levels. Copper, nickel, chrome, and molybdenum, on the other hand, can have beneficial effects, and it may in certain instances be useful to take advantage of these effects. For example, to met the varying requirements of different applications, it may be necessary in some cases to add copper to improve the steel's corrosion resistance. Or, in other applications, it may be necessary to melt to the lean side of the carbon range because of unusually stringent welding requirements and therefore to substitute either chrome or molybdenum which are not as detrimental to welding to build up sufficient alloy content to achieve the required mechanical properties. Or, as another example, it may be necessary to add nickel to develop the required transverse impact properties in an application where because of the sizes ordered, it is impossible to take full advantage of the effects of cross-rolling. Thus, in view of these considerations, the limits set on residual ingredients were as follows:

	Percent
Tin (max.)	0.20
Phosphorus (max.)	0.02
Copper	0.02–0.30
Nickel	0.02–0.25
Chromium	0.02–0.25
Molybdenum	0.02–0.10

The recognition of the significance of the ferrite grain size to mechanical properties and the incorporation into the design of the steel of the fact that the alloy contents in general and especially the carbon and manganese contents are equally as important as the presence of aluminum and nitrogen to the achievement of the required ultra fine grain sizes is throught to be major distinguishing characteristic of the invention. Other investigators who have worked on similar type steels have generally not taken advantage of the combined effects of both alloy content and aluminum and nitrogen. For example, in United States Patent 3,155,495 granted Nov. 3, 1964, Nakamura used aluminum and nitrogen to achieve fine grain sizes but owing to the fact that the steels he used in his examples had a low manganese content of decidedly less than 1%, and thus also much below 1.15%, and also because of their relatively low carbon content, he did not achieve any grain sizes substantially finer than ASTM 10 by normal processing (i.e. normalizing—air cooling from above the critical). Also, possibly because of the use of these low carbon and maganese contents Nakamura overestimated the minimum nitrogen content needed to effect fine grain sizes. For example, in his claims, Nakamura indicated that a minimum aluminum nitride content of 0.03% is necessary. It is easily shown that this corresponds to a minimum nitrogen content which is in excess of 0.010%, especially when the fact is considered that as a practical matter his steels actually always have nitrogen in excess of the amount which is combined in the aluminum nitride.

In summary, the test results show that the properties of an A36 carbon silicon killed steel are not adequate for the low temperature service contemplated both where controlled rolling is used and also where normalizing is employed. Controlled rolling is beneficial on properties and structure in the as-rolled condition but these effects were eliminated by the heat treatment. The most significant benefit on impact resistance was obtained by normalizing.

Experiments were made with modifications of alloy content. Utilizing the Petch analysis, it was found that both yield strength and impact resistance increased as the ferritic grain size decreased, and it appeared that with this steel a minimum ferrite grain size of ASTM 11.3 is required to achieve the required properties.

Since ferrite grain size values of this magnitude connot be obtained on a practical basis using A36 as produced with fine grain practice, efforts were made to obtain further grain refinement. It was also observed that high residual alloy content was beneficial in obtaining mechanical properties. Since high residual alloy content cannot be relied upon, it would appear to be necessary to compensate for this by alloy additions. It, therefore, is contemplated to increase the additions of manganese or silicon, or both.

Two levels of nitrogen content, one of which corresponded to a residual content and the other of which corresponded to a nitrogen addition, were investigated. The increased nitrogen content very markedly improved the structure and the mechanical properties. The average ferritic grain size achieved was 11.2, while both the tensile and impact properties were within the required range.

The test tensile properties occurred in steels with the increased nitrogen content. In other respects, the properties and structures of the steels were similar, and it is evident that with the exception of the effects of the increased nitrogen, the other improvements were due largely or entirely to the grain refinement. A series of austentic grain coarsening studies were conducted. Based on these

it appears that both the austentic and ferritic grain sizes and the mechanical property improvements are due to the aluminum and nitrogen additions.

Subsequently studies were carried out to determine the effects of general variations in alloy content, of rolling practice, and of plate thickness. Briefly, these studies showed that each of these variables had significant effects. With regard to alloy content it was determined that this variable, especially the carbon and manganese contents, was equally as important as the presence of aluminum and nitrogen to the achievement of the required ultrafine ferritic grain sizes. It was also shown that beneficial effects on impact resistance could be achieved by cross rolling as opposed to straight rolling. And finaly, evidence was presented which showed the usual effects of gauge and also indicated an unusual effect of gauge in that transverse impact resistance tended to increase with decrease in gauge.

It would appear that a cross-rolled steel plate which is normalized will have the properties sought if it has the following analysis:

	Percent
Carbon	0.15–0.25
Manganese	Over 1.00–1.50
Sulfur (max.)	0.035
Phosphorus (max.)	0.020
Silicon	0.15–0.35
Chromium	0.02–0.25
Copper (max.)	0.30
Nickel (max.)	0.25
Molybdenum	0.02–0.10
Tin (max.)	0.02
Aluminum	0.04–0.10
Nitrogen	0.007–0.010

Thus, it will be seen that aside from carbon, manganese, sulfur, phosphorus, silicon, aluminum and nitrogen, the steel of the invention contains between 0.08 and 0.94% of other alloying ingredients, the balance being iron.

FIG. 6 shows in the form of a block diagram steps which will be followed in carrying out the process of the invention according to usual mill practice.

In view of our invention and disclosure, variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art to obtain all or part of the benefits of our invention without copying the process shown, and we, therefore, claim all such insofar as they fall within the reasonable spirit and scope of our claims.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. Process of making a weldable steel plate having superior tensile and impact properties at low temperatures, which comprises making up a steel ingot having a composition as follows:

	Percent
Carbon	0.15–0.25
Manganese	Over 1.00–1.50
Sulfur (max.)	0.035
Phosphorus (max.)	0.020
Silicon	0.15–0.35
Aluminum	0.04–0.10
Nitrogen	0.007–0.010

a total remaining alloy content of between 0.11 and 0.87%, the balance being substantially iron, cross-rolling the ingot to produce a plate and normalizing the plate.

2. A process of claim 1, in which the remaining alloy content substantially consists of at least one of chromium, copper, nickel, molybdenum and tin.

3. A process of claim 1, in which the remaining alloy content substantially consists of:

	Percent
Tin (max.)	0.02
Phosphorus (max.)	0.02
Copper	0.02–0.30
Nickel	0.02–0.25
Chromium	0.02–0.25
Molybdenum	0.02–0.10

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,738,874 Dated June 12, 1973

Inventor(s) Alfred G. Allten and Frederick J. Semel

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 72, Cr is "0.5" and should be --.05--.

Column 11, line 27, "impct" should be --impact--.

Column 13, line 63, "met" should be --meet--.

Column 14, line 4, Tin is "0.20" and should be --0.02--.

Column 14, line 31, "maganese" should be --manganese--.

Column 14, line 69, "test" should be --best--.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,738,874 Dated June 12, 1973

Inventor(s) Alfred G. Allten et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 13, lines 44 to 51, should appear as shown below:

Carbon	0.15 to 0.25%
Manganese	Over 1.00 to 1.50%, and preferably 1.15 to 1.35%
Sulfur	0.035% Max.
Silicon	0.15 to 0.35%
Aluminum	0.04 to 0.10%
Nitrogen	0.007 to 0.010%,

Signed and sealed this 8th day of January 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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