Patented Aug. 4, 1942

2,291,842

UNITED STATES PATENT OFFICE

2,291,842

PRODUCTION OF STEEL

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No Drawing. Application July 18, 1940, Serial No. 346,141

18 Claims. (Cl. 75—58)

This application is a continuation in part of my co-pending applications, Serial No. 192,325, filed February 24, 1938, and Serial No. 296,422, filed September 25, 1939.

This invention relates to the production of steels having properties not residing in the steels known to and made by the methods of the prior art which possess the same essential or nominal chemical composition, as ordinarily understood, as the steels described in this specification. It provides for a novel treatment whereby a combination of properties not hitherto associated with carbon and very low alloy steels may be assured, thus producing in these steels an ability to satisfy uses from which they individually have heretofore been excluded. The properties and the steels in which they may be produced as well as the sphere of utility of these steels will be apparent to those acquainted with the art, from the description and explanation following.

In the manufacture and use of carbon and alloy steels and the adjustment or control of their compositions and methods of manufacture, with the objective of properly fitting the mechanical and other properties of the finished articles to the service that they are intended to render, it is recognized that the behavior of any steel when cooling it from some elevated temperature at a rate tending to produce hardening affords most valuable indications of its numerous mechanical and metallurgical characteristics. This behavior is influenced by many factors. Important among them is the carbon or carbide content and the size and number of the carbide particles prior to heating for hardening; equally important is the rate of solution of these carbides in the iron matrix at any temperature from which some hardening can be effected and, after solution, the rate and manner of their separation from the matrix on cooling at various rates; this functioning of the carbide is closely associated with the remainder of the steel composition and with the steel-making practice. In respect to the influence of the steel-making process, important effects are caused by the nature of the raw materials used, the type of slag covering employed for the purpose of effecting the refining operations performed on the molten metal, the changes in the composition and temperature of the slag during the course of the steel refining and during the adjustment of the steel composition, and principally by the final conditioning of the molten metal as, for example, the control of the content of oxygen or oxides and the materials and technique employed for this purpose. In respect to steel composition, not only are the elements added to carbon steels to produce alloy steels important, but also those elements added to both types of steels to at least in part effect control over the residual oxygen content. Theoretically, carbon steels are alloys of iron and carbon; practically, they contain in addition manganese or silicon or manganese and silicon to secure desired fabricating qualities, and sulphur, phosphorus, oxygen, nitrogen, non-metallic particles, and other impurities incident to the raw materials and manufacturing processes employed. Alloy steels contain in addition one or more other elements such as nickel, chromium, vanadium, molybdenum, copper, cobalt, etc., and/or increased quantities of manganese or silicon or of some of the elements regarded as impurities.

Other factors exert their influence, as will be referred to later, such as mechanical-thermal history of the steel, and the grain size of the matrix after partial or complete carbide solution; the latter in turn is the result of the conditions of heating for hardening combined with all of the phases of the steel-making and subsequent treatment. When hardening these carbon or alloy steels by heating and then cooling at a suitable rate, it is observed that the extent to which they harden is affected greatly by the mass of the article being hardened and further that the hardening characteristics as influenced by composition and manufacturing method, as noted above, determine whether a heated and quenched steel article of a given size or mass will harden throughout or only at and near the surface or not even harden fully at the surface. In many machine parts deep hardening is important from the standpoint of having uniform strength throughout the section. To measure the performance of steels in hardening, it is customary to use one of two methods. The older practice is to heat bars of any steel, of suitable length and of different diameters (as for example 1, 2, 3 and 4 inches) to the temperatures employed for hardening, cool them in the desired quenching medium and, either when they have cooled to room temperature from this operation or after mild tempering, cut them transverse to their length, measure the hardness along radii and plot the change of hardness against distance from the surface. The newer method, referred to as the Jominy method, is to heat a bar approximately 1 inch diameter and 3 inches long, to a suitable temperature and then transfer

it to a simple fixture in which it is rapidly cooled by a stream of quenching fluid (usually water) at one end only, while the remainder is exposed only to the atmosphere. A longitudinal flat surface is obtained by grinding away just a small amount of the cylindrical surface and the measured hardness along this strip is plotted against the distance from the quenched end.

As the temperature of carbon and low alloy steels is increased, for the purpose of hardening them, above a certain temperature range characteristic of each steel, the carbon (or carbides) present enters into solution in the iron or iron-alloy matrix to form the phase designated as austenite. On cooling the steel from this condition, at a rate tending to produce hardening, it may according to its mass, the composition and characteristics of the steel and the characteristics of the cooling medium, be retained in the austenitic form or in whole or in part be transformed to one or more of the products of decomposition of the austenite. The hardest of these is known as martensite and the others in the order of decreasing hardness troostite, sorbite, and pearlite. For the purpose of this presentation it is not necessary to define these constituents by their microscopic or other characteristics or to refer to the different variations in which they occur. It is sufficient to point out that for any selected carbon or low alloy steel, retention on quenching (from a state of partial or complete solution of carbon) of some austenite with martensite results in somewhat less than the maximum hardness of which the particular steel is capable, whereas all martensite retained on cooling gives the maximum of hardness; the occurrence of some or all troostite also means less than maximum hardness. The result in any instance depends on the actual cooling rate in the quenching operation. It has been observed that the time at constant temperature required for initiation of the decomposition of the austenite is at a minimum at about 900 to 1000° F. and that transformation is completed in minimum time at this temperature. Actually time and rate vary little over the range of about 1100 to 850° F. and experimental rates are measured over this approximate range. Hence for full hardening the cooling rate must be sufficient to prevent transformation in (or above) this temperature range (with the formation of troostite or softer constituents), and thereby enforce transformation of the cooled austenite at a lower temperature (probably not over 800° F.) resulting in a predominantly martensitic structure. The minimum rate necessary to attain this end is known as the "critical cooling rate." This critical rate is fixed by the composition and by the physical-metallurgical character of the steel as influenced by its mode of manufacture; for a given chemical composition as ordinarily determined it may vary widely according to its production history. Two major manufacturing factors are involved—one the conditions imposed up to the completion of solidification and the other the thermal-mechanical treatment in the solid state; of these the former is of primary importance, although the end results depend also on the latter.

Each melt of steel, therefore, reacts in accordance with its molten-state history and solidification conditions, quite independent of its ordinary chemical composition, which behavior is expressed in part in carbon-diffusion characteristics, etc., but primarily in the austenite grain size in relation to temperature and time at temperature. Its critical cooling speed is quite closely associated with the actual grain size existing at the temperature from which cooling for hardening takes place. Fine grain size (such as A. S. T. M. standard of 7 or smaller) has been observed to be accompanied by rapid transformation of the austenite on cooling and coarse grain size (such as A. S. T. M. standard of 4 or larger) by slower transformation. Thus for full hardening throughout of a fine-grained steel of some given composition and section, the actual cooling rate must be high to equal or exceed the critical rate (since the critical rate is high), whereas for a coarse-grained steel of the same composition and section the actual rate for full hardening need not be so high since the critical rate is lower. Or, in the case of a fixed cooling rate, the fine-grained steel will fully harden to a lesser depth than will the coarse-grained steel in the same section size.

It has also been observed that for the same ordinary chemical composition fine-grained steels possess to a much greater extent than do coarse-grained steels those attributes so much in demand in many structural and machine parts; namely, ductility, toughness, and resistance to impact stresses. It has further been observed that certain elements added to steels, influence the grain size. For example, small amounts of vanadium (such as 0.15%) or aluminum (such as 0.05%), or titanium, (such as 0.05%) added, in the form of high carbon ferro-titanium for example, to a carefully made 0.40% carbon steel tend to produce fine grain size and hence shallow hardening. On the other hand, relatively large amounts of nickel or molybdenum or chromium, for example, by their effect upon the rate of carbide diffusion and not any relatively great influence on grain size, so vastly alter the critical cooling rate that they produce deeper hardening steels. These latter elements greatly improve the properties of the steels since they produce deep hardening by a means other than promoting coarse grain size; however, they do not enhance the toughness and impact strength of the steels to nearly so great a degree as if they were accompanied by fine grain size obtained in the manner previously noted. If toughness and impact strength combined with full hardening in medium to large sections is required, it has been necessary to combine the two groups of elements and to use rather large amounts of the last-mentioned group as, for example, 5% of nickel, or 2% nickel with 1% chromium and 0.3% molybdenum, or 3% chromium, ½% molybdenum and ¼% vanadium. Manganese and silicon in practicable amounts greater than those present in commercial carbon steels also contribute to deep hardening (although not to the extent of the nickel or nickel-chromium-molybdenum or chromium - molybdenum - vanadium steels just noted). Manganese and silicon, however, tend to produce coarse grain size and hence require the grain refining elements to secure some degree of toughness and impact strength. But whenever the combination of deep hardening, toughness and impact strength has been required in high degree in manganese or silicon steels, these two elements alone plus the grain refining elements were not quite adequate so that other elements have had to be added as well—nickel, for example.

To summarize; fine grain is accompanied by toughness but shallow hardening, coarse grain is accompanied by deep hardening but low tough-

ness, so that in the prior art to secure full-hardened-throughout, impact-resistant medium to large sections it has been necessary to use the grain refining elements plus large total amounts of usually more than one element of the deep-hardening type. The higher the actual hardness required in any specified machine part the more necessary has been this combination of elements; moreover, to secure this high hardness along with very high toughness, especially in medium to large sections has demanded large amounts of these elements with their attendant cost, along with exceptionally careful manufacturing control, also costly.

I have now discovered that the hitherto diametrically opposed fine grain size (with its accompanying high toughness and impact strength) and deep hardening capacity may be secured simultaneously, without the use of large and costly amounts of the elements heretofore recognized as contributing to deep hardening, by the addition to steel in a late stage of its manufacture of very small amounts of an element heretofore regarded as contributing to fine grain size only and because of, or along with this contribution, to shallow hardening. This unexpected result is achieved by the addition of titanium provided that the element is in a certain state of restricted association with other elements.

I have further discovered that the addition of vanadium achieves certain advantages which are not imparted by the use of titanium alone. Still further advantages result from the incorporation of aluminum along with the vanadium and titanium under certain operating conditions so that the preferred addition is one comprising titanium, vanadium and aluminum.

It has long been known to deoxidize molten steels by the addition to them of titaninm alloys. Titanium for this purpose has been available in several forms, each developed for a particular class of uses and applied to certain groups of steels to attain results of definite nature. Uses outside the fields have been restrained by unfitness of alloys due to composition, by cost considerations, etc.

As will be shown hereinafter, there has been limited use of titanium as an alloy addition to stainless steel and special alloys; the quantity added in such instances is quite large, often 1.00 or 2.00% or more, but when not used for such purposes the addition has been made in small amounts for the mere purpose of deoxidation, scavenging or other purification.

High carbon ferro-titanium, containing about 7.5% carbon and 15 to 20% titanium has supplied the greatest tonnage of titanium for the metallurgical industry. In the deoxidation of killed steels of both carbon and low alloy types, it is in use in steel castings and also in ingot steels for railroad tires and wheels, rails, springs, heavy and light forgings and numerous other classes of articles. In the partial deoxidation of rimming steels for sheets subjected in fabrication to drawing and forming operations and for reinforcing bars, piling and other products in this category, it has been used in considerable quantity. For sheets, however, a lower carbon grade described as medium-carbon ferro-titanium has been recently preferred. With its 4% carbon and 15 to 20% titanium, it presents advantages due to the growing use of very low carbon steels for this purpose, namely 0.06% carbon and less, and the necessity for restricting the addition of carbon to the steel bath from all possible sources; this is important in controlling the uniformity of the product at minimum cost. Additions to these rimming steels are usually not over about three pounds of alloy per ton of steel or 0.006% carbon added but this is important and is preferably not exceeded. Lower carbon alloys would offer further advantage in this respect but their cost or the presence of other elements in them is highly objectionable in these rimmed sheet steels. In the killed steels previously mentioned, grain size is often an important specification requirement. This is usually secured by aluminum additions; high-carbon and medium-carbon ferro-titanium have been tried to simultaneously deoxidize and produce fine grain but even with amounts up to about 20 pounds per ton (about 0.18% titanium) they have not been successful and required simultaneuos use of some aluminum. Fine grain size produced by these practices has always been accompanied by shallow hardening unless, of course, large amounts of alloying metals such as nickel, molybdenum or chromium are present. If the additions are small and the steel coarse grained, it hardens somewhat more deeply but is then of lower toughness, especially when quenched and tempered to high hardness.

Numerous low-carbon titanium alloys have been available but their cost, due to necessarily costly production methods such as reduction by aluminum, has restricted their application to products of high value such as tool and electric furnace steels. They have been of no interest to the producer of tonnage steels of the carbon or low alloy class purely on the grounds of economy and there was, therefore, no stimulus to try to apply them or study them. Aside from a small tonnage entering into the production of non-ferrous alloys, the ferro-titaniums of less than 0.20% carbon and 20 to 45% titanium have found four major uses. Additions of ½ to 1% of titanium in the form of these alloys are made to austenitic nickel-chromium steels, in order to improve their resistance to corrosive attack under certain conditions of fabrication and use. The titanium combines with the carbon of the steel, removing it from solution in the austenitic matrix, thus preventing precipitation of intergranular carbides (detrimental to corrosion resistance) on heating within certain ranges of elevated temperature. For this purpose, it should be noted, a very low aluminum grade of low-carbon ferro-titanium is required, as aluminum is not desired in these austenitic corrosion-resisting steels; the aluminum content preferably does not exceed 15% of the titanium content. Another application of low-carbon ferro-titanium depends on this same association of titanium and carbon, namely, the use in medium to high chromium steels of from about 2½ to about 10 times as much titanium as there is carbon present in the steel in order to combine with this carbon, remove it from the steel matrix and thus prevent hardening on rapid cooling from heat treatment temperatures. This use, it will be observed, is directly opposed to that of the present invention. In both of the uses just mentioned the stated proportions of titanium to carbon are those in the finished steel; actual additions are higher, due to the losses sustained on adding, this loss usually being about 40%. For some time, these low-carbon ferro-titaniums were used in the manufacture of non-aging sheet steels; the use was confined to steels of low sili-

con and manganese content as well as low carbon content (not over about 0.06% and usually 0.01 to 0.03%) which obviously have very low hardness, of the order of 100 Brinell. In this instance also restraint of hardening is sought; this refers to hardening by means other than quenching from above the A3 transformation (for example, quenching from below A1 followed by aging) since the steel compositions are such that they are beyond the limits of appreciable martensitization by rapid cooling from above A3. This use has been discontinued, due to cost considerations. Another limited application of low carbon ferro-titanium is for deoxidation only (as contrasted with carbon-fixation of the first two uses) of special highly alloyed steels, especially castings, such as those used for heat resistance and corrosion resistance. Thus these low-carbon titanium alloys, in which the titanium content costs three to four times that of the medium and high-carbon alloys, have been used entirely in non-hardening steels or steels of high value such as those containing five per cent or more of alloying elements.

Other commercial ferro-titanium alloys have also been available. For example, an alloy containing about 13% titanium, 20% aluminum, 3% silicon, 4% carbon, balance principally iron has been suggested for carbon steels to deoxidize and produce fine grain. Another group of titanium alloys comprises ferro-titanium of about 20% titanium, 20% silicon, 0.3% carbon, and 0.3% aluminum, remainder principally iron, and silico-titaniums of about 35% silicon, 0.3% carbon, 0.3% aluminum, 35 to 55% titanium, balance principally iron; these alloys have been restricted in their commercial use to the addition of titanium to cast iron, since they are easily dissolved in iron alloys but add considerable silicon to the molten metal. Another class of alloys have been made containing manganese in large proportions; with about 30% titanium, 8% aluminum, 3% silicon and 35 or 55% manganese, balance principally iron and low carbon content, they have because of cost been restricted in use to non-ferrous alloys and to highly-alloyed steels of high value.

To summarize the foregoing, low-carbon titanium alloys have found their sphere of usefulness in non-ferrous alloys, special steels of restricted hardening capacity and highly alloyed steels of relatively high value. In the tonnage carbon and low-alloy steels such as automotive and other repetitive-manufacturing uses, titanium has been employed in the form of alloys of relatively high carbon content; in such use, when either small or large amounts have been added, the steels produced have either not shown a tendency toward fine grain or, if fine grained, due to the use of other grain-refining practices, have tended strongly toward shallow hardening on quenching. To get deep-hardening steels of fine grain size using the titanium-treated carbon and low-alloy steels of the prior art, substantial increase in the alloy-metal content of the steels has been required, such for example as adding or increasing the percentages of nickel, molybdenum, chromium, etc., in addition to the conditioning by titanium and aluminum. I have discovered that these results are obtainable, namely deep-hardening in the presence of fine grain size with the known high toughness due to the latter, without the addition of elements heretofore known to contribute greatly to deep hardening on quenching if, to the carbon or low-alloy steel, titanium is added in sufficient but not excessive amount and in the form of compounds or alloys in which it is present in certain restricted combination. To titanium in this form or condition I have applied the designation "reactive."

Titanium which has been combined with carbon or nitrogen or oxygen in sufficient proportion to form completely or even in large part the known stable compounds with these non-metallic elements, is not reactive and is not suited to the present purpose. For example, high-carbon or medium-carbon ferro-titanium, both suited for deoxidation of steels, as previously explained, will not produce deep-hardening of fine-grained carbon or low alloy steels; in these titanium alloys there is from almost-sufficient up to more-than-sufficient carbon to satisfy the formation of the chemical compound TiC. Likewise titanium nitride or cyanonitride or dioxide or mixtures or solid solutions rich in these compounds do not produce the novel effects. On the other hand low-carbon, low-nitrogen, low-oxygen alloys with iron, manganese, nickel, copper, cobalt or chromium, alone or together, do produce this result. Silicon may be present in the alloy but should be less than the titanium content; when equal to or more than the titanium the desirable effects are secured in considerably reduced degree and the properties of the steels are greatly inferior to those herein described. Effects in the direction indicated are obtained by the introduction of titanium only when in combination with carbon, nitrogen or oxygen in minor proportions. In other words, the metal titanium, or its alloys with, for example, the metals just enumerated may contain limited amounts of carbon, nitrogen or oxygen to function in this desired manner, but they must not contain sufficient to completely or in large measure satisfy the combining power of the titanium for these elements; to some degree, the amount of metal or alloy added to the steel bath may be increased when carbon, nitrogen or oxygen are present, over that required when they are virtually absent, to produce a given effect upon a given steel, whereby there would be added to the steel a sufficient quantity of reactive titanium, but of course not to such an extent as to chill the steel and/or prevent effective solution of the added alloy. However, in any case the titanium content should exceed about 8 times the carbon content plus about 15 times the nitrogen content plus about 10 times the oxygen content.

In the alloy as added to the steel bath, there may also be present elements which protect the titanium from loss during the process of addition (as for example by combination with oxygen or oxides) such as aluminum, zirconium and magnesium. In general, it is not necessary that they be present to an extent of more than 50% of the titanium content and in no case is it desirable that they total more than three times the titanium content. Further, in the case of aluminum, the addition via this alloy plus any aluminum added separately to the steel bath should not in most instances exceed about 0.15%.

Other elements may be present in the alloy, provided that they are not subversive of the characteristics herein described as imparted by the alloy to steels. While this statement applies to all elements, it may be specifically mentioned, by way of example, that vanadium, columbium, tantalum, molybdenum or tungsten may be present in the alloy in amounts up to about 5% each

without detracting from the properties imparted by the alloy to steels; in fact, there is in some cases a contribution by these elements in the desired direction of deep-hardening in the presence of fine grain size in spite of the very small amounts of the elements added to the steel by the alloy.

Thus an alloy of titanium with a carrier metal or metals with which the heat of combination, if positive, is not high, such as iron, manganese, nickel, copper, cobalt or chromium, contains "reactive titanium" if the titanium content of the alloy exceeds about 8 times the carbon present plus about 15 times the nitrogen present plus about 10 times the oxygen present and in which the titanium content also exceeds individually the aluminum content and the silicon content; alkali or alkaline earth elements may be present in appreciable quantities and up to twice the titanium content and if in total they exceed about 10% of the titanium content, the silicon need not be restricted and may be regarded as one of the carrier metals; zirconium or magnesium may be present up to about equal the titanium content; elements not subversive of the properties imparted by the titanium to carbon and low-alloy steels may also be present. In the appended claims the term "reactive titanium" is used with these limitations.

Obviously this invention relates to steels of the ferritic type in which hardness is raised by martensitization on rapid cooling from an elevated temperature and not to austenitic steels which are hardenable only by cold working or by precipitation of highly dispersed micro-constituents. In the former it is known, as heretofore mentioned, to add titanium in sufficient amount to combine with and remove the carbon from the steel matrix and thus largely prevent hardening. The amount required for this purpose is 2½ or more times, usually 6 times, the carbon content (exclusive of the usual 40% loss in making the addition). The present invention, however, consists in the discovery of an approximately opposite effect, not heretofore recognized, resulting from the addition of much smaller amounts of titanium, approximately 1/20 to ½ of the carbon content and in no case greater than twice the carbon content. In some cases, an effective amount may be exceedingly small. I have discovered that the large amounts of the prior art are not required and are actually detrimental to the objective sought, and on the other hand, the small deoxidizing additions of high-carbon alloys are equally ineffective. These statements are made due to the fact that the mechanism by which the titanium produces the observed effects described herein, is not fully understood. These effects may or may not, for example, bear some relation to the content of, and changes in, those elements present in small amounts in steels which are not determined by the conventional methods of chemical analysis. The effects may equally as well result from the removal of, or prevention on solidification of the formation of, intergranular films of non-metallic material or inclusions of particular nature or size, that when present serve as precipitation nuclei during rapid cooling of the steel from above the transformation range. Or it may be that reactive titanium in restricted amounts when present in austenite is extremely effective in restraining decomposition of the solid solution on cooling and that above these restricted amounts it forms easily precipitated carbide that by removing carbon from solid solution reacts in the opposite manner and decreases hardenability.

As illustrative of the effects produced, there are given in Table I the properties of a .40% carbon medium-manganese steel as influenced by adding various amounts of a low-carbon ferro-titanium alloy containing a small amount of aluminum. These steels were made in an electric induction furnace, cast into 3¼ inch square ingots, forged to 1 inch round bars, normalized, oil quenched and then tempered at 450° F. Hardenability was determined by the Jominy method on previously normalized bars and recorded as the distance from the hardened end of the quenched bar to the last point at which a hardness of 50 Rockwell "C" or higher was obtained; this measures fairly closely the depth of martensitization.

Steel No. 1 with no grain-refining addition is moderately deep-hardening but has low impact resistance and only moderately good reduction of area in tension. Steel No. 2, rendered fine grained by the customary aluminum addition made for this purpose, has far greater impact strength along with comparable reduction of area but very low hardenability. Steel No. 3 with only a very small amount of reactive titanium added shows very little change in properties except for a small increase in hardenability. The next larger addition of reactive titanium (steel No. 4) causes a further increase in hardenability and a large increase in impact resistance. With 0.10% reactive titanium (steel No. 5) there is an increase simultaneously in elongation, reduction of area, impact strength and hardenability. Further increase in the addition of titanium results in a slow decrease in these several properties although even with the largest addition made (steel No. 7) the impact strength and hardenability are substantially greater than those of the coarse grained or fine grained steels to which no low-carbon ferro-titanium has been added (steels Nos. 1 and 2).

TABLE I

Effect of titanium on medium manganese steels

Heat No.	Composition of steel				Titanium added	Composition of alloy			
	C	Si	Mn	Ti		C	Si	Al	Ti
1	.42	.24	1.80	.....	None (a)	.....	.....	.....	.....
2	.39	.24	1.81	.....	None (b)	.....	.....	.....	.....
3	.41	.26	1.77	.016	.025	.06	1.68	4.13	19.04
4	.40	.20	1.74	.033	.05	.06	1.68	4.13	19.04
5	.40	.20	1.79	.076	.10	.06	1.68	4.13	19.04
6	.41	.23	1.80	.120	.20	.06	1.68	4.13	19.04
7	.41	.27	1.82	.270	.40	.06	1.68	4.13	19.04

(a) Coarse grained. (b) Fine grained (Al added).

Heat No.	Mechanical properties					Hardenability max. distance to 50 Rockwell "C"	McQuaid-Ehn grain size
	Yield point	Tensile strength	Elong. in 2"	Reduction of area	Izod impact		
1	212,800	267,000	9.0	27.2	3.3	0.35	2 to 4
2	198,050	246,750	9.5	28.8	8.8	0.07	7 to 8
3	210,300	249,500	8.0	24.4	6.8	0.20	7 to 8
4	225,300	254,750	8.0	27.9	12.0	0.38	7 to 8
5	203,750	256,200	10.5	41.9	19.5	0.77	8
6	194,800	261,300	10.0	36.4	17.3	0.65	8
7	222,300	252,500	8.0	30.8	13.8	0.56	8

In Table II are shown the properties of steels of similar composition to which have been added 0.10% titanium in the form of various other titanium alloys. The processing of the steels is the same as in the case of those of Table I.

Heats 10, 13, and 12 show that with low carbon alloys, silicon in moderate amount is not detrimental but in amount approximating the titanium content prevents the development of the desired properties in the steel to which it is added, unless an alkali or alkaline earth metal is also present in the alloy in significant amount. Heats 14 and 17, compared with 15, 16 and 18 show the striking effect in the alloy of high carbon as distinct from relatively low carbon in preventing the attainment of the desired steel properties; heat 10, of course, with very low carbon, functions better than any of the higher carbon alloys.

TABLE II

Effect of composition of titanium alloy

Heat No.	Composition of steel				Titanium added	Composition of alloy				
	C	Si	Mn	Ti		C	Si	Al	Ti	Ca
10	.43	.28	1.73	.048	.10	.08	7.31	1.91	15.74	-----
11	.40	.30	1.79	.057	.10	.54	3.69	6.58	21.30	-----
12	.41	.47	1.71	.052	.10	.58	39.82	2.89	10.92	13.14
13	.41	.28	1.79	.044	.10	.33	21.36	.13	20.01	-----
14	.41	.31	1.81	.035	.10	1.98	5.25	3.54	20.86	-----
15	.42	.25	1.79	.024	.10	(a) 6.32	3.08	9.81	16.20	-----
16	.44	.21	1.81	.028	.20	(a) 6.73	3.28	3.90	17.27	-----
17	.42	.26	1.78	.072	.10	2.60	3.80	6.01	19.78	-----
18	.40	.26	1.77	.074	.10	5.04	5.47	17.90	10.33	-----

(a) Briquet of aluminum plus high carbon ferro-titanium (average analysis quoted).

Heat No.	Mechanical properties					Hardenability, max. distance to 50 Rockwell "C"	McQuaid-Ehn grain size
	Yield point	Tensile strength	Elong. in 2"	Reduction of area	Izod impact		
10	228,350	265,000	12.0	43.6	16.5	0.85	8
11	220,050	259,150	11.5	46.6	13.3	0.42	8
12	215,900	269,900	10.5	40.0	11.8	0.41	7 to 8
13	212,800	263,000	9.5	33.1	5.5	0.24	7 to 8
14	222,800	265,500	10.5	42.2	11.8	0.48	7 to 8
15	206,300	249,250	7.0	26.1	6.3	0.23	8
16	191,800	256,250	5.5	14.8	6.5	0.26	7 to 8
17	226,250	266,000	8.0	34.7	10.5	0.43	8
18	191,800	244,500	4.0	17.7	8.8	0.22	8

As noted above, the optimum titanium addition to steels made in the described manner is about 0.10%. This optimum amount may vary with the steel type or composition, the steel-making, pouring and teeming methods and the conditions under which the additions are made. It may vary from about 0.01 to 0.20% titanium but in any case is an amount required to increase the hardenability over that secured from the same steel without the addition and an amount below that resulting in loss of hardenability to below that of the untreated steel caused by combination of the titanium with the carbon of the steel, preventing in part or in whole their engaging in the hardening reaction.

From the foregoing description, it will be clear that ferro-titanium in which the titanium is reactive, that is, either uncombined or only partly combined with elements with which it produces compounds of high heats of formation, specifically carbon, oxygen and nitrogen and to a lesser degree silicon, will produce in carbon and low-alloy steels, even in the presence of fine grain size, hardenability and toughness at high hardness so greatly above these properties in the untreated steels as to set them apart from the latter due to the possession of distinctive properties rendering them serviceable in uses and under stresses for which the untreated steels are unfitted. As indicated, these results are not secured with titanium alloys of all compositions. The titanium content of the added alloy should preferably be within the range of 5 to 50% and more particularly 10 to 35%. The carbon content of the added alloy should be low, preferably under 0.25%, although moderately good results are secured with the carbon up to about one-eighth of the titanium content. Nitrogen and oxygen in the alloy should be below about one-fifteenth and one-tenth of the titanium content, respectively. Silicon may be present in the alloy up to about the titanium content unless alkali or alkaline earth elements are present in amounts above about 10% of the titanium content, in which case the silicon may appreciably exceed the titanium content. Aluminum may be present up to an amount about equal to that of the titanium content. The remainder of the alloy may be iron or manganese or nickel or cobalt or copper or chromium or any combination of them or other element or combination of elements not subversive to the attainment of the desired properties in the treated steels. This is largely included in the above noted definition of "reactive titanium."

Additionally I have discovered that the simultaneous introduction into the steel of vanadium with the reactive titanium confers further benefits upon the steel. When vanadium is associated with the titanium the amount of the latter necessary to insure continuously under commercial conditions the properties heretofore described is materially reduced and the characteristics of the steel improved. The use of vanadium along with smaller titanium additions is productive of greater cleanliness, which is a desired property in the finished steels especially so when the articles to be made of the steel are subjected to stresses in the direction transverse to rolling or forging and ductility in this direction must approach as nearly as possible to the ductility in the longitudinal direction. Machining and hot working characteristics are also benefited. Vanadium also is desirable in maintaining a uniform and consistent fine grain size and when it is used with reduced amounts of titanium or reduced amounts of titanium and aluminum, this objective is attained simultaneously with the above-mentioned improvement in cleanliness. Furthermore, the yield ratio when vanadium is used is higher than when it is not present. Thus a means is afforded whereby through the use of very small amounts of vanadium there are obtained in the steel not only the properties that have heretofore resulted from the so-called full vanadium content but in addition the deep hardenability and toughness at high hardness referred to above. It should be observed that this dual benefit is secured with very low amounts of vanadium, which if used alone in the form of an addition of ferro-vanadium would not produce either of these desired groups of properties.

The preferred form of the addition containing vanadium with titanium is a ferro-alloy of these two elements or a ferro-alloy containing vanadium, titanium and aluminum with the customary accompanying impurities common to such ferro-alloys. In these alloys the iron serves as a carrier metal and may be replaced in whole or in part by other carrier metals which are not subversive of the properties of the alloy from the standpoint of its effective introduction into the steel or of the properties of the steel to which the ferro-alloy is added. Such other carrier metals may be, for example, manganese,

copper, cobalt, nickel, chromium, molybdenum, tungsten, etc. Preferably the silicon is low although it may be present to any extent that is necessary to an economic method of manufacture of the alloy, or may be intentionally added to replace part of one of the carrier metals. The silicon is usually less than 5% and preferably should not exceed 10 or 15%, although it may under some circumstances be as high as 20% of the alloy. The silicon is preferably less than 60% of the combined vanadium and titanium.

Alloys of the following ultimate compositions have been successfully used:

Alloy No.	V	Ti	Al	Si	Mn
1	12.73	18.25	14.30	2.19	1.40
2	13.05	22.60	7.17	1.21	1.73
3	25.12	18.31	9.27	2.80	.85
4	34.10	9.73	3.18	4.83	.36
5	18.50	15.61	19.10	0.73	1.05
6	24.00	7.12	14.20	2.44	.60
7	16.00	31.43	22.60	2.05	1.62
8	9.50	16.25	5.95	3.38	.25
9	17.65	10.63	.25	17.58	.30
10	19.05	12.54	8.65	4.20	1.12

Remainder in each case is iron plus impurities.

Although the above are illustrative of the preferred materials used in practicing this form of the invention, other variations also may be employed. Vanadium may be substituted in part or in whole by one or more of columbium, tantalum and uranium. Titanium may be substituted in part or in whole by one or more of beryllium, boron and thorium, which are "reactive" under the conditions which render the titanium reactive. As heretofore pointed out, protection against oxidation, which may be at least in part the function of the aluminum where used, may also be attained by substituting for all or part of the aluminum one or more of zirconium and magnesium. Other carrier metals may of course replace iron in this alloy in whole or in part, as heretofore indicated. For example, half or three-quarters of the iron may be replaced by nickel; or manganese may be introduced in place of like amounts of iron to the extent of about 5 to 15%, or may replace it entirely.

In the group comprising titanium, beryllium, boron and thorium, titanium is preferred because it is the most satisfactory from the combination of ease of addition, effectiveness, cost, and absence of any undesirable properties in the finished steel. Likewise vanadium is preferred in the group comprising vanadium, columbium, tantalum and uranium and for similar reasons. In the group of protective elements again as a matter of effectiveness and ease and economy of use the preferred element is aluminum.

Among the alloys containing these several elements which have been used to secure the desired results are:

Alloy	V	U	Cb	Ta	Mo	W	Ti	Zr	Al	Ca	Si	Mn
1	19.88				17.90		13.98		6.96		*	*
2	22.30					13.16	11.59		7.31		3.12	2.38
3	11.00		15.23				11.40		8.91		*	*
4	8.70			10.98			11.63		6.55		*	*
5	24.48						7.33	5.81	8.12		8.10	*
6	27.37						19.22		6.51	4.97	16.92	*
7	23.55	10.07					13.11		9.90		2.13	*
8	14.06		9.75				16.00		10.02		0.23	0.40
9			23.85				13.35		11.05		1.05	7.72
10		8.10		10.22			12.48		2.06		*	*

* Not determined.

The remainder in each case is iron plus impurities.

When vanadium and titanium or their substitutes are added with little or no aluminum or its substitutes, they must be added in intimate association, and when vanadium, titanium and aluminum are added, at least two of them, but preferably all three, should be added in intimate association; since when added in intimate association they produce the results herein described which are not obtained when the elements are added separately. By intimate association, I mean a very close association of the several metals or elements ranging between the atomic or molecular association of a single-phase alloy through the relatively uniform fine mechanical mixture in fixed position of a multiple-phase alloy, through the coarser mechanical mixture of a briquet of intermixed 20 mesh or finer particles of alloys of the several metals or of the metals themselves, to the mixture in a container or the like of somewhat coarser particles of the several metals or their (for example) ferro-alloys, as contrasted with adding lumps of the metals or ferro-alloys at succeeding short intervals during pouring of the steel or mixing on a shovel or other implement metals or alloys in some standard size such as 2 inches by down and adding them together. Likewise when the titanium is used without vanadium as described earlier in this specification, the titanium is preferably added to the steel in the form of a ferro-alloy which in addition to the iron contains the other alloying elements to be added to the steel with the titanium; and if not in the form of a ferro-alloy, then the several elements are preferably added in intimate association. The line of demarcation between successful and unsuccessful methods cannot be sharp, depending as it does upon the metals used and the steel-making procedure in a specific case; the desired result is obtained when the metals added are dissolved in the iron or steel bath in their entirety in sufficiently close proximity in respect to both space and time that they may begin to react simultaneously upon any minute volume of the steel at their respective natural rates and not one or more of them reach this minute volume after the other or others have completed their reaction at this point (and perhaps the products of the reaction coalesced alone or with other substances and become relatively unreactive).

Aluminum may be absent in some cases or, when present, may be in small or large amount. A highly successful composition, for addition to carbon and low alloy steels intended for use in the wrought condition, and added in such amounts as to introduce about 0.02 to 0.05% vanadium contains 25% vanadium, 15% titanium and 10% aluminum. For addition to cast steels, alloys containing 10 to 35% vanadium, 10 to 35% titanium, with either about 4% or less alumi-

num or about 20% aluminum have been very effective; these alloys have been added in amounts corresponding to 0.03 to 0.10% vanadium and titanium taken together. An alloy containing 20% vanadium, 10% titanium, 15% silicon, and not over 2% aluminum, also produces the desired properties when added to molten steels in amounts corresponding to approximately 0.02 to 0.10% vanadium; similar results obtain if this alloy composition also includes 10% manganese.

The range of composition of the alloys productive of these results is from 6 or 7 to 50% of an element or elements of the group comprising vanadium, columbium, tantalum and uranium and 6 or 7 to 50% of an element or elements of the group comprising titanium, beryllium, boron and thorium. To these may be added up to 35% of an element or elements of the group comprising aluminum, zirconium and magnesium and up to 20% silicon. The remainder of the composition is iron or other carrier metal containing the usual impurities resulting from raw materials used or the process of manufacture.

The preferred composition contains about 10 to 30% of an element or elements of the above vanadium group and about 8 to 30% of an element or elements of the above titanium group, and less than 10 or 15% silicon. When an element or elements of the aluminum group is added it may be present in one of several preferred ranges depending upon the type of steel to which the addition is made; these preferred ranges are not over 4%, 7 to 12%, and 18 to 25%. Manganese when used in substantial quantities is preferably in the range of 5 to 15%. When silicon is not intentionally added it is generally not over 3% and manganese similarly not over 1.5%.

Similar to the requirements when using the reactive titanium without vanadium, the addition alloy or mixture when employing vanadium with titanium must not contain such amounts of carbon as will prevent their proper functioning. In the case of the vanadium-titanium-aluminum alloy in the preferred ranges of composition it is preferable that the carbon content be under 1% and more particularly not over 0.25%. In no case should the carbon content exceed about one-tenth of the vanadium content plus about one-eighth of the titanium content. The nitrogen and oxygen contents also should be limited, the former not exceeding about one-fifteenth the titanium and the latter not exceeding about one-tenth the titanium content.

In adding the vanadium-titanium alloy a combined addition of as little as 0.02% vanadium and 0.01% titanium is productive of the desired result in a large degree, the extent depending, of course, on the composition and manufacturing history of the steel. In the treatment of carbon steels of 0.40% carbon and manganese steels of 0.40% carbon and 1.75% manganese, additions of 0.03% vanadium, 0.02% titanium and 0.01% aluminum, following (if required by the steel-making practice) a prior addition of 0.03 to 0.08% aluminum, has yielded steels possessing the desired qualities, as illustrated hereafter. In general the range of amounts added to the steel needed to secure these properties are about 0.01 to 0.15% of vanadium or its substitute, and about 0.01 to 0.15% of titanium or its substitute. If indicated by the requirements in any particular case, aluminum or its substitute may be present in the addition up to 0.15% of the weight of the steel, silicon up to 0.18%, and manganese up to 0.25%. The preferred amounts are in the following ranges:

	Per cent
Vanadium	0.01 to 0.10
Titanium	0.01 to 0.08
Aluminum	0.005 to 0.10
Silicon	Trace to 0.10
Manganese	Trace to 0.05

The vanadium usually is 0.01 to 0.06% and the titanium 0.01 to 0.06%. The amount of aluminum usually varies more widely depending upon the type of steel. Where aluminum is objectionable in certain restricted amounts, as in some cast steels, the amount added, if any, is under 0.01% or about 0.06 to 0.10%. In steels to be hot or cold rolled, the amount of aluminum is often about 0.01% but may be and is frequently 0.03 to 0.08%. In some steels, certain amounts of aluminum are objectionable; for example, in cast steels of about 0.035 to 0.050 sulphur content, it is preferred to add either less than 0.01% aluminum or about 0.06 to 0.10%.

On adding the alloy or intimate mixture of this invention to steels, a large part appears to be retained in the steel, the amount, in proportion to the addition, depending on the condition of the steel bath, the technique of adding the alloy or mixture, and other factors. It is possible that the amount retained is entirely in the form of metal or (on cooling) associated with carbon either alone or with iron, manganese, etc., as carbide, but this is not a known fact due to the extreme difficulty of precisely distinguishing by analytical methods between metal as such or as carbide and metal in the form of compounds with oxygen, nitrogen, etc. Analyses for total residual metals from the addition have been made, without positive determination of the form or forms in which the metals exist. While these residual amounts may completely account for the novel combination of properties found in the steels of the invention, this cannot be stated with certainty and the invention is, therefore, not limited in this manner. The results of these analyses have, however, been within the following limits:

	Per cent
Vanadium	0.01 to 0.15
Titanium	0.002 to 0.08
Aluminum	0.002 to 0.08

The vanadium appears to be substantially all recovered. The titanium and aluminum are only partially recovered, the content as indicated by analysis being usually one-half to three-quarters of the original metallic addition. When the preferred amounts of titanium, vanadium and aluminum are added as indicated above, the residual contents of these elements in the finished steel will be approximately 0.01 to 0.10% vanadium, 0.005 to 0.05% titanium, and 0.002 to 0.05% aluminum.

Silicon and manganese, not being essential to the invention and being in practically every instance, added in further amount other than through the medium of the alloy herein described, no effort has been made to evaluate the amounts remaining from this addition.

Example I

Two basic open hearth steels, made in the same plant by as nearly as possible identical procedure and of the composition described as S. A. E. T–1340 are compared after forging, annealing at 1600° F., quenching in oil from 1550° F. (after

machining to 0.525 inch diameter), then tempered at 450° F. and subsequently machined to 0.505 inch diameter. The test data follow:

Steel	C	Mn	Si	Austenite grain size (A. S. T. M. standard) at—		Hardenability (Jominy) Rockwell "C" hardness			
				1700° F.	1550° F.	Surface	1/2"	3/4"	1"
A	0.39	1.89	0.23	7 (few 6 & 8)	9 (few 8)	62	50	36	32
B	0.41	1.74	0.21	6 (few 5, 6, 8)	9 (few 8)	63	56	52	48

Steel	Yield point, p. s. i.	Tensile strength, p. s. i.	Elongation, per cent in 2"	Reduction of area, per cent	Izod impact, ft.-lb.	Rockwell "C" hardness
A	243,200	270,200	12.5	46.1	10.5	49
B	240,200	266,900	13.3	48.1	20.0	49

Steel B was made similarly to steel A except for a final addition of 3⅓ pounds per ton of steel of an alloy of 25% vanadium, 15% titanium, 10% aluminum, 2% silicon, .5% manganese, balance iron and impurities. Note the increase due to the alloy in impact strength and hardness penetration with other properties practically identical.

A number of other tests of steels of the T–1340 type have been made, especially to note the factor of hardenability. With approximately equal yield point and tensile strength, the hardenability of the untreated steel has been such that with a Rockwell "C" hardness at the quenched end of the Jominy type test bar, of 60 to 63, a hardness not less than 50 extended along the bar for only ½ to ⅝ inch; with steels of 0.40 to 0.41% carbon and about 1.70% manganese, application of the process of the invention yielded this value at 1 to 1¼ inch, whereas with steels of 0.43 to 0.44% carbon and about 1.85% manganese, this high hardness extended along the bar to 1¾ or 2 inches. These properties have long been sought in inexpensive steels wherewith to produce hardened parts in medium sections and of very high quality, capable of sustaining very severe service loads.

Example II

Two heats of basic open hearth steel, made in the same plant, but not the plant of Example I, with no difference in procedure except for the addition of 3 pounds per ton of steel of an alloy similar to that used in Example I. The composition is S. A. E. 1040 with manganese at the upper limit of the range. The steels are compared after rolling, normalizing at 1600° F., quenching in oil or water from 1550° F. as ⅝ inch rounds, tempering at 600° F. and machining to 0.505 inch standard bars.

Steel	C	Mn	Si	Grain size (McQuaid-Ehn)
A	0.38	0.91	0.24	6 to 8
B	0.38	0.91	0.24	6 to 8

Steel	Quenched in—	Yield point, p. s. i.	Tensile strength, p. s. i.	Elongation per cent in 2"	Reduction of area, per cent	Brinell hardness
A	Oil	87,830	116,000	25.0	69.2	217
B	Oil	205,300	238,500	11.5	44.0	444
A	Water	155,820	183,030	11.5	44.3	387
B	Water	186,800	223,500	14.5	58.2	430

Steel B is the one to which the alloy of this invention was added. Note that steel A scarcely hardens in oil, whereas steel B hardens as well as it does in water and that when both steels are hardened in water, steel B is superior in both strength and ductility.

Example III

Two heats of silico-manganese spring steel (S. A. E. 9255) were made in a small electric induction furnace using the same procedure in making both except for the addition to one of 0.30% vanadium in the form of a ferro-alloy of 23% vanadium, 17½% titanium, 13% aluminum, and 3½ silicon. The ingots were forged from 3½-inch square to 2¼-inch and 1 inch rounds and normalized at 1625° F. The 2¼-inch bars were machined to 2-inch diameter, oil quenched from 1575° F., and cut transversely for hardness measurement. The 1 inch rounds were oil quenched from 1575° F., a similar section cut for hardness penetration measurements, and the remainder tempered at 800° F., then machined for tension and impact testing.

Heat	C	Si	Mn	Grain size (McQuaid-Ehn)	Hardenability, Rockwell "C" hardness				
					1" rd.		2" rd.		
					Surf.	Cent.	Surf.	Mid.	Cent.
A	0.57	2.02	0.78	4 (few 3 & 5)	61.5	56	46.5	36	34
B	0.58	1.94	0.84	6 (few 4 & 7)	63.5	62	58.0	41.5	34

Heat	Yield point, p. s. i.	Tensile strength, p. s. i.	Elongation per cent in 2"	Reduction of area, per cent	Izod impact ft.-lb.	Brinell hardness
A	214,550	231,150	7.5	20.2	7.5	459
B	225,000	243,000	10.0	35.7	9.8	471

The improvement in all properties of steel B, the one to which the alloy was added, should be noted.

Example IV

Two heats of basic open hearth steel (S. A. E. 1040 with manganese at the low side) were made in the same plant, differing from that of Examples I and II, the procedure being the same in the two cases except for the addition in one of 0.03% vanadium in the form of a ferro-alloy of 25½% vanadium, 15% titanium, 11½% aluminum, and 1¼% silicon. In the form of 1 inch rolled rounds the steels were normalized from 1650° F., water quenched from 1525° F., and then tempered as indicated in the table below:

Heat	C	Mn	Si	Grain size (McQuaid-Ehn)	Hardenability (Jominy) Rockwell "C" hardness			
					Surface	1/16"	1/8"	3/16"
A	0.40	0.66	0.14	8 (few 5, 6, 7)	Not measured	54	40	26
B	0.42	0.62	0.22	7 & 8 (few 6)	do	56	55	41

Heat	Tempered, °F.	Yield point, p. s. i.	Tensile strength p. s. i.	Elongation per cent in 2"	Reduction of area, per cent	Izod impact, ft.-lb.	Brinell hardness
A	800	98,530	125,850	20.0	59.5	78.4	259
B	800	123,900	154,350	18.0	63.4	50.8	339
B	950	105,330	127,730	20.3	64.9	84.8	273

Heat B is the one to which the alloy of this invention was added. The hardening capacity is higher as shown not only by the hardenability tests but by the test bars tempered at 800° F., yet with the higher strength, toughness as measured in part by reduction of area, is also higher in steel B. When tempered to equal hardness and strength, steel B has higher yield point, higher reduction of area and higher impact strength.

The so-called full-vanadium steels, of 0.15 to 0.25% vanadium content, possess in a measure the desirable properties of the steels of my invention. Vanadium contributes to shallow hardening through its definite and uniform effect upon grain size (thus also providing toughness) but it further contributes to deep hardening through its direct alloying effect in decreasing the critical cooling speed. Thus full-vanadium steels have long been esteemed and widely used for this desirable combination of properties. When fine grained, tough and exceptionally deep hardening steel has been necessitated by engineering requirements, especially in moderate to very large sections, low-alloy full-vanadium steels have not, however, been entirely adequate; these needs have been met by nickel-vanadium, nickel-molybdenum-vanadium, nickel-chromium - molybdenum-vanadium and chromium-molybdenum-vanadium steels of high total alloy content. These are today the important steels of very large sections in the principal members of heavy machinery but they are too costly for common use in the manufacture of mass-production articles. Steels of 0.10% vanadium have been used but the combined grain-refining and deep hardening effects have been somewhat less and the needed content of other alloying elements correspondingly higher. To illustrate these properties of the full-vanadium steels, two examples may be cited. (1) Carbon-vanadium tool steel hardens to a medium depth and is highly uniform in this performance, the hardened zone after quenching from the usual quenching temperature range of 1450 to 1600° F. being on a 1 inch round bar about 0.15 to 0.20 inch. The core is uniformly of high toughness. Carbon tool steel rendered fine grained by the addition of aluminum hardens fully to a lesser depth and successive heats show a wide variation in this depth as well as variable toughness in the metal beneath the fully hardened outer layer. Increasing the vanadium content of carbon-vanadium tool steel to about 0.40 to 0.50% increases the depth of hardening somewhat, but increasing the hardening temperature to permit more vanadium to go into solution in the austenite makes possible the hardening of a 1 inch bar throughout the section. Full-hardening of the carbon-vanadium tool steel of about 0.20% vanadium can also be attained by addition, for example, of chromium or molybdenum. (2) Fine-grained chromium-vanadium steel hardens much more deeply than aluminum-treated fine-grained chromium steel as noted below:

Steel	C	Mn	Si	Cr	V
A	0.30	0.74	0.20	0.87	.....
B	0.33	0.70	0.23	1.10	0.22

Steel	Hardness after oil quenching*				
	Surface	½"	1"	Center	Grain size (McQuaid-Ehn)
A	53	33	26	24	6 to 8.
B	54	39	34	35	5 to 8.

* Bars 3 inches diameter quenched in oil flowing at 105 feet per minute.

The steels to which my alloy is added possess these desirable properties of the full-vanadium steels but to an enhanced degree (corresponding to the complex heavily-alloyed full-vanadium steels) and as a result of only a very small total addition of elements, as heretofore described.

Grain-refining additions may be made to the steel other than those added for the specific purposes described herein in a manner depending upon other features of the steel-making practice and upon the article to be produced from the steel. Thus wrought steels such as a 0.40% carbon steel may have a small or a large addition of aluminum (0.25 or 2.00 pounds per ton of steel) prior to the addition of my material. A zirconium-silicon alloy or aluminum-silicon-iron or aluminum-silicon-titanium-iron or ferro-vanadium, as examples, may be employed in customary amounts. Other additions common in existing methods of steelmaking and known to those familiar with the art, may be employed without departing from the spirit of this invention.

Reactive titanium or the alloys or mixtures forming this invention may be added to the molten steel in the furnace, or in the ladle to the bath of metal partly formed therein, or into the metal stream as it issues from the furnace, or it may be added in the ingot molds if the ingot weight and cross-section are not so small as to prevent the alloy from entering and reacting with the molten metal. Surprisingly by the application to a number of steels of this latter method, no visibly harmful inclusions have been introduced to detract from the salutary effects of the alloy addition.

As set forth in the several examples given above, the steels to which my alloy additions are made are killed steels. The alloy is, therefore, not added merely for purposes of deoxidation, degasification, scavenging or other purification, for which purposes additions of titanium or the like have customarily been made.

In the foregoing, there has been described the method of improving the hardenability of steels that consists in the addition to them in a late stage in their manufacture of a titanium alloy in which this metal is in a reactive condition. The description has been given with reference to fine-grained steels because in the prior art titanium additions have assisted in producing fine-grain size (although not alone capable of producing very fine grain such as 7 to 8 on the McQuaid-Ehn scale) but fine grain size has been accompanied by shallow hardening except in steels containing rather large amounts of alloying elements. Coarse grained steels of any composition are more deeply hardenable than fine-grained ones of like composition. However, my reactive titanium may be used to further increase the hardenability of these coarse grained steels. The resultant steels will obviously not be as tough, especially at high hardnesses, as steels of

similar composition and treatment but of fine grain size.

I desire to emphasize, however, that in using the limited amounts of the addition element or elements to secure deep hardening there is usually only a slight contribution toward fine grain size, not necessarily production of very fine grain (A. S. T. M. standard 7 or smaller). Sometimes no appreciable change is observed. The extent to which grain size is decreased, if any, over that size that would result in a given heat of steel without these additions, depends upon the condition of the molten bath of metal at the time the addition is made, upon the remainder of the steel composition, upon other grain-refining additions made, and upon the total amount and the protions of the constituent elements in the specific alloy or mixture of this invention, that is employed. Thus while the grain size will not be coarse (such as A. S. T. M. standard 2 or larger), it may not in every case be very fine but rather medium in size, usually not larger than A. S. T. M. 5. For example a steel which as ordinarily produced will show a grain size of 4, may by the addition of this alloy have its hardenability considerably increased and yet the average grain size may be decreased only to 5 or not altered at all. Steels which are ordinarily made to 7 to 8 grain size may after the addition of these elements still be 7 to 8 grain size but their hardenability will be considerably increased. As previously explained, a nickel steel may have a grain size of 6 and on the addition of this alloy will have its hardenability increased, while its toughness likewise will be increased; the average grain size may be unchanged or decreased only to 7. Increase in carbon also tends to decrease grain size under like conditions of manufacture and therefore to decrease the critical cooling speed; thus in carbon steels while increased hardenability will be conferred upon compositions of different carbon content, the likelihood of decrease in grain size due to the addition will be less when the carbon content is higher. It should be understood that the invention is applicable to steels of all grain sizes, but is of most interest in connection with medium and fine grained steels, since under these conditions the best combination of properties is imparted.

Another feature of the invention is the obtention of the desired properties of the steel without resort to effective large amounts of alloying elements such as vanadium, nickel, chromium, molybdenum, cobalt, copper, etc. and also the two usual elements in carbon steels—manganese and silicon—above the limits common to commercial carbon steels, namely, 1.05% and 0.35% respectively. Whenever the term "alloying elements" is used in the specification or claims, or where low alloy steels are referred to, it is the intention that manganese is to be considered as an alloying element only to the extent to which it exceeds this limit of 1.05%, and silicon is to be considered as an alloying element only to the extent to which it exceeds 0.35%. To secure the full benefits of this invention, namely, complete hardening or nearly complete hardening throughout medium and heavy sections along with medium to fine grain size, it is not necessary to exceed about 5% of alloying elements and in most cases not to exceed about 3% of alloying elements. It has been observed that the critical cooling rate is decreased and hence the hardening capacity of steels is increased not only by the addition of certain alloying elements but also, within certain limits, by increase in carbon content. This limit of 3% of alloying elements is, therefore, not absolute but varies somewhat with the carbon content of the steels. Therefore, to produce tough steels capable of hardening throughout in medium to large sections there will generally not be over about 3.5% of total alloying elements when the carbon content is less than 0.25%, not more than about 3% of these alloying elements when the carbon content is in the range of 0.25% to 0.50% and not more than about 2.5% of these alloying elements when the carbon content exceeds 0.50%. It has been shown in the prior art that tough deep-hardening steels can be produced by large amounts of alloying elements but in the practice of this invention, these large additions are not usually required. Typical low alloy steels to which the invention is applicable have the following amounts of these alloying elements:

Ni	Cr	Mo	Mn	Si	V
------	------	0.50	Normal	Normal	------
------	1.00	------	Normal	Normal	0.18
------	------	------	1.65	Normal	0.18
3.00	------	------	Normal	Normal	------
1.50	0.60	------	Normal	Normal	------
0.50	1.00	------	Normal	Normal	------
------	1.00	0.25	Normal	Normal	------
------	------	------	Normal	2.00	------
------	------	------	1.75	Normal	------
1.75	------	0.25	Normal	Normal	------
1.00	1.00	0.25	Normal	Normal	------
------	0.60	------	1.00	------	------

Low alloy steels are those intermediate between the plain carbon steels and the so-called high alloy steels, such for example, the stainless steels and high speed steels. Low alloy steels have a limited alloy content of usually not more than 5 or 6%. The alloying elements that are included up to this limit of 5 or 6% are manganese and silicon above the limits common to ordinary carbon steels, nickel, cobalt, copper, chromium, tungsten, molybdenum, vanadium, and at times small amounts usually not over one-half percent of some other rare metal.

The carbon content of such low alloy steels may range from 0.10 to 0.75 or 1.0% or even higher, but is preferably from 0.20 to 0.65%.

The invention is equally applicable to plain carbon steels and has been successfully applied to steels containing from 0.10 to 1.00% carbon with manganese and silicon contents normal for the particular steels and their applications. In general, the invention shows greatest utility when applied to steels of 0.10 to 0.75% carbon and more particularly in the range of 0.20 to 0.65% carbon.

The iron is at least about 98% in the case of plain carbon steels and at least 94 to 95% in the case of the low alloy steels to which the invention is applicable.

Although great benefits are conferred upon steels that are quenched to a very hard state and subsequently tempered, and although the maximum benefits are conferred upon steel articles tempered at relatively low temperatures so that their hardness is above 250 Brinell and preferably 350 Brinell or higher, steel processed in accordance with this invention may be advantageously used for parts tempered at higher temperatures or as rolled, or as normalized or normalized and tempered. In some cases the hardening phenomena will be such that it is best to lower the carbon or alloy content or both, so that the steel articles will have strength equal

to that procurable with the original composition if the alloy of the invention were not used but will, with equal strength, possess greatly enhanced toughness.

Hot rolled or forged bars or billets made from steel ingots produced in accordance with this invention may be converted into various finished or semi-finished parts by the usual forging, machining and heat treating practices. Gears, for example, may be drop forged or upset, then subjected to either normalizing and tempering or annealing by the practices common to secure the desired machining qualities, then heated for quenching in a temperature range characteristic of the steel and the size of the gear made from it, namely, 1400 to 1700° F., and after cooling in the quenching medium to a temperature suitable to effect hardening of the steel, reheated to a proper temperature in the range of 350 to 600° F., followed either by slow or rapid cooling. The proper temperature for this reheating or tempering operation may be confined to the lower side of this range. In steels of the prior art, tempering in this lower part of the range often produced such high hardness that the gears or other similar parts made from the steel did not possess adequate toughness, and tempering in the higher part of the range caused the small amount of austenite retained on quenching to be converted to martensite with consequent embrittlement. Steels made in accordance with my invention may be tempered safely in the lower part of the range and the benefits obtained thereby of the higher hardness and wear resistance, because of the added toughness resulting from the practice of the invention. In the range of tempering temperatures used for springs, spline shafts and other similar parts, namely, 800 to 1000° F., the practice of this invention is also beneficial and an improved combination of average hardness throughout the section and of toughness is secured. The hardness of such parts (for both tempering ranges) is usually from about 350 to 500 Brinell or somewhat higher. In the case of articles such as drill pipe and sucker rods used in the oil producing industry and which are usually marketed in the normalized or normalized and tempered condition, the invention is practiced to best advantage by not adding the elements to a steel of the composition heretofore used but to one having a somewhat smaller content of those elements that produce hardening. For example, a steel of 0.35 to 0.40% carbon and 1.60 to 1.90% manganese would be replaced when practicing this invention by a steel of 0.30 to 0.35% carbon with 1.40 to 1.75% manganese, plus the additions as described herein. In certain plate steels used because of their ready weldability and ductility after welding without being subjected to heat treatment (at least in sections not over 1 inch in thickness), substitution of a steel of 0.15% carbon, 1.25% manganese and 0.10% vanandium would be made by lowering the manganese to 1.00% and adding the vanadium either in whole or in part as a vanadium-titanium or vanadium-titanium-aluminum alloy, or by adding reactive titanium in necessary amount, all as previously described.

Steels made in accordance with this invention are not limited to those heat treated by the methods outlined above, but may also be steels to be subjected to the more specialized methods of heat treatment such as carburizing, nitriding, austempering, etc. The use of the alloys and processes described herein greatly enhances the applicability of the austempering process in that larger sizes of a given composition may be effectively treated; or in a given size, smaller amounts of alloying elements are necessitated.

In the above examples and elsewhere in this specification, it has been pointed out that the practice of this invention results in steels of greatly improved toughness and possessing the hitherto unrealized combination of properties, namely, fine grain size and its accompanying toughness, along with deep hardenability, in carbon steels or steels containing small amounts of alloying elements. However, the practice of this invention results in additional advantages. The steels made appear to be freer from detrimental non-metallic inclusions than are steels not treated in accordance with this invention, and the mechanical properties as well as the machining characteristics, as noted below, are improved thereby. With, for example, the customary pre-machining heat treatments applied to gears of a given composition, they exhibit improved freedom from surface imperfections (raggedness, ridges, etc.) under given machining conditions, when compared with steels of otherwise similar chemical composition and grain size but not produced in accordance with these teachings. It is significant that increased hardenability is secured without increased tool wear in machining. The addition to the steel in the usual amounts of substances which improve machinability such as sulphur, phosphorus, lead, selenium, etc., and compounds containing them do not detract from the properties imparted to the steel by the addition alloy herein described. The substances may be added separately or may be included in the composition of the alloy.

As previously indicated, I do not know whether the element or elements described herein, when added to molten steel, are obtained in the solidified steel in the metallic form or whether they are present in simple or complex carbides or in the form of other compounds, such as oxides, nitrides, etc. Some part of the added elements remain and are determinable by chemical analysis but the form or combination in which they exist is not precisely determinable with assurance of correctness. The history of the steel melt and its condition at the time the alloy or mixture is added probably are determinative and these will vary and may necessitate variation in the amount or composition added, or both. The important facts are the results secured even though they be due only to the residue from the addition in whatever form it may exist, or to the removal of unrecognized substances normally interfering with the development of the very highest properties.

My addition alloy may contain the impurities usual in ferro-alloys and also may contain minor amounts of alloying metals or metalloids which it may be desired to introduce into the steel, and therefore when I speak of the ferro-alloy as being substantially all iron I do not mean to exclude such minor amounts of other substances.

While I have specifically described the preferred embodiment of my invention and the best modes now known to me for practicing it, it is to be understood that the invention is not so limited but may be otherwise embodied and practiced within the scope of the following claims.

I claim:

1. The process of treating steel containing from 0.20 to 0.65% carbon and of the class consisting of plain carbon steel and low alloy steels contain-

ing less than 5% alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from 0.01 to 0.20% of reactive titanium and in an amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without said titanium addition, and in the form of a ferro-alloy in which carbon is less than about one-eighth of the titanium, nitrogen less than about one-fifteenth of the titanium and oxygen less than about one-tenth of the titanium, the remainder being substantially iron and metal which is not subversive of the action of the titanium in imparting to the steel deep hardenability concomitant with great toughness.

2. The process of treating a steel containing from 0.20 to 0.65% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than 5% alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.20% of reactive titanium and in an amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without said titanium addition, and in the form of a ferro-alloy in which carbon is less than about one-eighth of the titanium, nitrogen less than about one-fifteenth of the titanium, oxygen less than about one-tenth of the titanium and silicon less than the titanium, the remainder being substantially iron, an amount of aluminum as a protective agent for the titanium but not more than three times the titanium and metal which is not subversive of the action of the titanium in imparting to the steel deep hardenability concomitant with great toughness.

3. The process of treating a steel containing from 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.20% of reactive titanium and in an amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without said titanium addition, said titanium being added to the steel in the form of an alloy containing carbon not over one-eighth of the titanium, the remainder being metal which is not subversive of the action of the titanium in imparting to the steel deep hardenability concomitant with great toughness.

4. The process of treating a steel containing from 0.10 to 1.00% carbon and of the class consisting of a plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.20% of reactive metal of the class consisting of titanium, beryllium, boron and thorium and in an amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without said reactive metal addition, said reactive metal being added to the steel in alloy form containing carbon not over one-eighth of the reactive metal, the remainder being metal which is not subversive of the action of the reactive metal in imparting to the steel deep hardenability concomitant with great toughness.

5. The process of treating a steel containing from 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.20% of reactive metal of the class consisting of titanium, beryllium, boron and thorium and in an amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without said reactive metal addition, said reactive metal being added to the steel in alloy form containing carbon not over one-eighth of the reactive metal, and also containing a substantial amount but not more than three times the reactive metal of protective metal of the class consisting of aluminum, zirconium and magnesium, the remainder of the alloy being metal which is not subversive of the action of the reactive metal in imparting to the steel deep hardenability concomitant with great toughness.

6. A deep hardenable ferritic steel containing from 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents together with titanium in the amount and form which results from adding to a killed steel while in a molten state 0.01 to 0.20% of reactive titanium and in an amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without said titanium addition, said titanium being added to the steel in the form of an alloy containing carbon not over one-eighth of the titanium, the remainder being metal which is not subversive of the action of the titanium in imparting to the steel deep hardenability concomitant with great toughness, said steel being characterized by a deeper hardenability and greater toughness after heating and quenching than that of a steel of otherwise identical composition but to which such reactive titanium has not been added.

7. A deep hardening ferritic steel containing 0.10 to 1.00% carbon and containing titanium in the amount and form resulting from adding to the steel after it is killed and while it is in a molten state from 0.01 to 0.20% of reactive titanium and in an amount sufficient to increase the depth hardening capacity of the steel over that of steel of identical composition but without the titanium addition, said titanium being added to the steel in the form of a ferro-alloy containing carbon not over one-eighth of the titanium, the remainder of said ferro-alloy being substantially iron and metal which is not subversive of the action of the titanium in imparting to the steel deep hardenability concomitant with great toughness, the remainder of the steel being iron with not more than 3.5% of alloying elements when the carbon is below 0.25%, not more than three percent of alloying elements when the carbon is between 0.25 and 0.50%, and not more than 2.5% of alloying elements when the carbon is above 0.50%, said steel being characterized by a deeper hardenability and greater toughness after heating and quenching than that of a steel of otherwise identical composition but to which such reactive titanium has not been added.

8. The process of treating a steel containing 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.20% of vanadium, about 0.01 to 0.15% of titanium, and silicon less than sixty percent of the vanadium and titanium, in the form of a ferro-alloy in which the carbon is less than about one-tenth of the vanadium plus one-eighth of the titanium, the remainder being substantially iron and metal which is not subversive of the action of the vanadium and titanium in imparting to the steel deep hardenability concomitant with great toughness, and in amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without the vanadium and titanium additions.

9. The process of treating a steel containing 0.10% to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.010 to 0.15% of vanadium, about 0.01 to 0.15% of titanium, about 0.005 to 0.15% aluminum, and silicon less than sixty percent of the combined metals of the first two groups, in the form of a ferro-alloy in which the carbon is less than about one-tenth of the vanadium plus about one-eighth of the titanium, the remainder being substantially iron and metal which is not subversive of the action of the vanadium and titanium in imparting to the steel deep hardenability concomitant with great toughness, and in amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without the vanadium, titanium and aluminum additions.

10. The process of treating a steel containing from 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.20% of a metal or metals of the group consisting of vanadium, columbium, tantalum and uranium, about 0.01 to 0.15% of a metal or metals of the group consisting of titanium, beryllium, boron and thorium, and silicon less than sixty percent of the combined metals of said groups, in the form of an intimate association and containing carbon not over about one-tenth of vanadium group metal plus about one-eighth of titanium group metal, the remainder being metal which is not subversive of the action of the metals of the vanadium and titanium groups in imparting to the steel deep hardenability concomitant with great toughness, and in amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without the vanadium and titanium group metal additions.

11. The process of treating a steel containing 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents to impart deep hardenability combined with great toughness, which comprises adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.15% of a metal or metals of the group consisting of vanadium, columbium, tantalum and uranium, about 0.01 to 0.15% of a metal or metals of the group consisting of titanium, beryllium, boron and thorium, about 0.005 to 0.15% of a metal or metals of the group consisting of aluminum, zirconium and magnesium, and silicon less than sixty percent of the combined metals of the first two groups, in the form of an intimate association and containing carbon less than about one-tenth the vanadium group metal plus about one-eighth the titanium group metal, the remainder being metal which is not subversive of the action of said intimate association in imparting to the steel deep hardenability concomitant with great toughness, and in amount sufficient to increase the depth hardening capacity of the steel over that of a steel of identical composition but without the vanadium, titanium, and aluminum group metal additions.

12. A deep hardenable ferritic steel containing from 0.10 to 1.00% carbon and of the class consisting of plain carbon steels and low alloy steels containing less than five percent alloying constituents together with vanadium and titanium in the amount and form which results from adding to the steel after it has been killed and while in a molten state from 0.01 to 0.20% vanadium, 0.01 to 0.15% titanium and silicon less than sixty percent of the vanadium and titanium, in the form of an alloy in which the carbon is less than about one-tenth of the vanadium plus about one-eighth the titanium, the remainder being metal which is not subversive of the action of the vanadium and titanium in imparting to the steel deep hardenability concomitant with great toughness, said steel being characterized by a deeper hardenability and greater toughness after heating and quenching than that of a steel otherwise identical in composition but to which such alloy has not been added.

13. A deep hardenable ferritic steel containing 0.10 to 1.00% carbon and of the class consisting of plain carbon steel and low alloy steels containing less than five percent alloying constituents together with vanadium and titanium in the amount and form which results from adding to the steel after it has been killed and while it is in a molten state from about 0.01 to 0.15% vanadium, 0.01 to 0.15% titanium, 0.005 to 0.15% aluminum, and silicon less than sixty percent of the vanadium and titanium, in the form of a ferro-alloy in which the carbon is less than about one-tenth the vanadium plus about one-eighth the titanium, the remainder being substantially iron and metal which is not subversive of the action of the alloy in imparting to the steel deep hardenability concomitant with great toughness, said steel being characterized by a deeper hardenability and greater toughness after heating and quenching than that of a steel of otherwise identical composition but to which such alloy has not been added.

14. A ferro-alloy for the treatment of steel containing about 10 to 30% vanadium, about 8 to 30% titanium, and less than 15% silicon, and capable of imparting deep hardenability conmitant with great toughness to steels of the class consisting of plain carbon steel and low alloy steels containing less than 5% of alloying constituents.

15. A ferro-alloy for the treatment of steel

containing about 10 to 30% vanadium, about 8 to 30% titanium, about 2 to 25% aluminum, and less than 20% silicon, and capable of imparting deep hardenability concomitant with great toughness to steels of the class consisting of plain carbon steel and low alloy steels containing less than 5% of alloying constituents.

16. A ferro-alloy for the treatment of steel containing about 7 to 50% vanadium, about 7 to 50% titanium, and 7 to 25% aluminum, and less than 20% silicon, and capable of imparting deep hardenability concomitant with great toughness to steels of the class consisting of plain carbon steel and low alloy steels containing less than 5% of alloying constituents.

17. A ferro-alloy for the treatment of steel containing 5 to 50% titanium together with aluminum and zirconium in amount to serve as effective protective elements for the titanium but not more than three times the titanium, and silicon less than 20%, said ferro-alloy being capable of imparting deep hardenability concomitant with great toughness to steels of the class consisting of plain carbon steel and low alloy steels containing less than 5% of alloying constituents.

18. A ferro-alloy for the treatment of steel containing 5 to 50% of reactive metal of the class consisting of titanium, beryllium, boron and thorium together with aluminum and zirconium in amount to serve as effective protective elements for said reactive metal but not more than three times said reactive metal, and silicon less than 20%, the remainder being metal which is not subversive of the reaction of said reactive metal in imparting to the steel deep hardenability concomitant with great toughness, said ferro-alloy being capable of imparting deep hardenability concomitant with great toughness to steels of the class consisting of plain carbon steel and low alloy steels containing less than 5% of alloying constituents.

JEROME STRAUSS.