

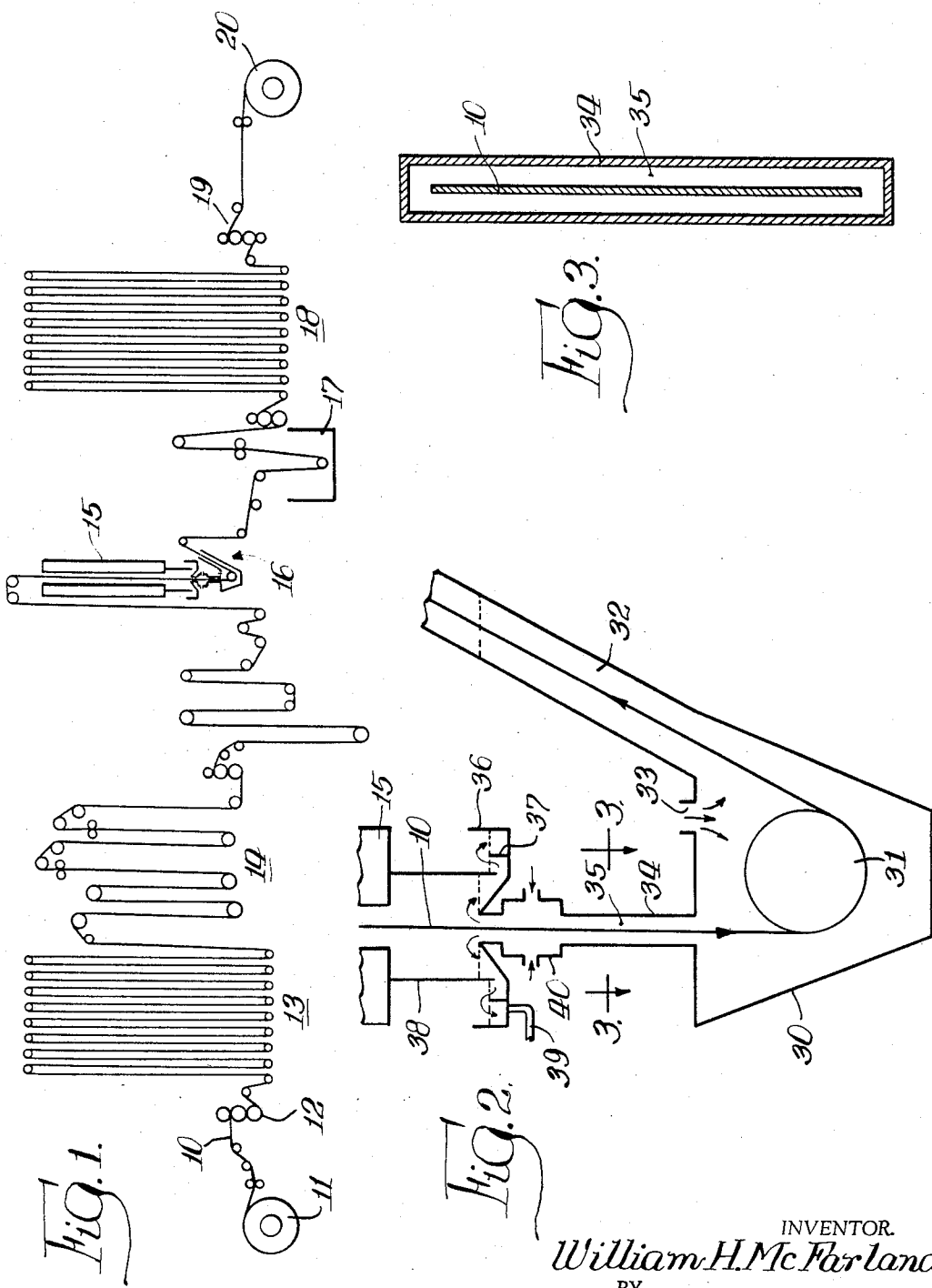
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MARTENSITIC STEEL

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MARTENSITIC STEEL

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This invention relates to novel martensitic steel sheet and strip products and to a novel continuous process for making the same. The invention also relates to novel coated products of the aforementioned character, especially martensitic tin plate.

High strength thin gauge steel strip is widely used for steel strapping. Coated steel products, such as tin plate, galvanized steel, and aluminum coated steel, in thin gauges with high strength are also highly desirable. It has been customary to obtain the desired strength in such materials, particularly tin plate, by cold reduction or cold rolling.

For example, in the manufacture of conventional black plate a low carbon steel strip is hot rolled to intermediate gauge, pickled, and then cold rolled to desired gauge which is on the order of .007 to .015 inch. However, the extent of cold rolling required impairs the ductility of the steel strip so that an annealing step is necessary to soften the steel before it is temper rolled and tin plated. The annealing step improves the ductility but reduces the tensile strength and yield strength. Conventional tin plate has a tensile strength of about 45,000 to 65,000 p.s.i. with an elongation in two inches of about 15 to 25%. To meet the requirements for the higher temper grades of conventional tin plate, it is usually necessary to resort to the use of rephosphorized or nitrogenized steel.

More recently, higher strength tin plate known as double reduced tin plate has been developed. In the manufacture of this product, the steel strip after annealing is given a second cold reduction either before or after the tin plating step. Usually the extent of reduction in the second cold reduction step is on the order of 30 to 35%. Double reduced tin plate may have a thickness on the order of .005 to .015 inch with a tensile strength of from about 80,000 to about 110,000 p.s.i. which is appreciably higher than the strength level of conventional tin plate, but the ductility of the product is poor, e.g., less than about 1% elongation in two inches. To obtain optimum properties in double reduced tin plate, it is considered necessary to nitrogenize the steel. Much thinner grades of double reduced tin plate with a thickness as low as .002 inch have also been manufactured commercially with generally the same properties as the heavier gauges.

The reliance on work hardening by cold reduction to obtain the desired strength in thin gauge steel sheet and strip products has serious disadvantages which are particularly acute in the case of double reduced tin plate. In addition to having poor ductility or formability, as mentioned above, double reduced tin plate is also characterized by a high degree of directionality or anisotropy, i.e., it has significantly different mechanical properties in the transverse and longitudinal directions with respect to the direction of rolling. Moreover, this product frequently has inadequate corrosion resistance.

The present invention avoids the aforementioned disadvantages of cold reduction and relies on the production of a high-strength microstructure, namely, a tempered martensite structure, to obtain thin gauge steel products having the desired properties.

Accordingly, the primary object of the present invention is to provide novel means for obtaining high strength in thin gauge steel sheet and strip products.

A further object of the invention is to provide novel products of the aforementioned character which have greater ductility and less anisotropy than thin gauge steel

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products in which high strength is obtained by cold reduction.

Another object of the invention is to provide novel coated steel products of the aforementioned character, particularly tin plate, galvanized steel, and aluminum coated steel.

An additional object of the invention is to provide a novel process for making thin gauge low carbon steel strip, and particularly coated strip such as tin plate, wherein the steel consists essentially of tempered martensite.

Other objects and advantages of the invention will become apparent from the subsequent detailed description taken in conjunction with the accompanying drawing, wherein:

FIG. 1 is a schematic diagram of a continuous heat treating and quenching line for the production of martensitic steel strip;

FIG. 2 is an enlarged schematic view of the quenching apparatus of the line shown in FIG. 1; and

FIG. 3 is an enlarged cross-sectional view taken along the line 3—3 of FIG. 2.

The principal constituents of steel which determine its properties are ferrite and cementite. At a relatively high temperature, which is dependent upon the carbon content, steel exists in the form known as austenite which is a solid solution of carbon or cementite in ferrite. When steel is cooled slowly from a high temperature at which austenite is stable, the ferrite and cementite precipitate together in a characteristic lamellar structure known as pearlite. However, dependent upon the rate of quenching and other factors, the transformation from austenite to pearlite proceeds through a series of different microstructures. The low temperature decomposition product in the transformation of austenite upon cooling is martensite which is a body-centered tetragonal structure in which the carbon atoms are thoroughly dispersed. Martensitic steels are characterized by high tensile and yield strengths.

In accordance with the present invention, thin gauge work hardened steel strip of low carbon content is subjected to suitable heat treatment and quenching so as to obtain a microstructure consisting essentially of tempered martensite. Thus, an exceptionally high tensile strength is obtained because of the microstructure and without the development of poor ductility and a high degree of anisotropy which are characteristic of severely cold worked products. As is well known, very rapid quenching of the austenite phase is required to obtain a fully martensitic product. Plain carbon steels of relatively high carbon content and certain alloy steels, particularly those containing hardenability agents such as boron, are more easily quenched to a fully martensitic structure, but the plain carbon steels of relatively low carbon content (such as .25 wt. percent max. C) are considerably more difficult to quench to martensite.

However, I have discovered that low carbon work hardened steel strip in thin gauges and commercial widths can be heat treated and quenched on a continuous line to obtain a tempered martensite microstructure. Moreover, by appropriate choice of quench techniques the resultant product may have acceptable flatness or can easily be rolled to the desired flatness. Quite unexpectedly, I have found that even though the tensile strength of the product is in excess of about 130,000 p.s.i. (typically, from about 150,000 to about 250,000 p.s.i.) and increases with increasing carbon content, nevertheless, within a carbon range of from about .03 wt. percent to about .25 wt. percent the ductility of the product is uniformly good, i.e., an elongation in two inches of at least about 1.5% and generally from about 1.5% to about 10%.

The steel employed as the starting material is plain

carbon steel having the following composition range (wt. percent: carbon .03-.25, manganese .20-.60, phosphorus .05 max., sulfur .03 max., and the balance iron with residual elements in the usual amounts. A significant feature of the invention is that the steel strip starting material which is to be heated and quenched to form tempered martensite is in "work hardened" condition. The term "work hardened," as used herein, refers to a steel strip which has been relatively severely cold reduced and is still in its as-cold reduced condition (sometimes referred to as "full hard"), i.e., without any subsequent annealing or tempering treatment. The extent of cold reduction should be at least about 40% and preferably at least about 60%. More specifically, a hot rolled strip of intermediate gauge is pickled and then cold rolled in one or more stages to effect a reduction of at least about 40% and preferably at least about 60%. The cold rolled strip in work hardened condition may have any desired commercial width, e.g., from about 18 to about 72 inches, and will have a tensile strength in the neighborhood of about 100,000 p.s.i. with very poor ductility, e.g., less than 1% elongation in two inches.

Although the final cold rolled gauge of the work hardened strip will usually and preferably be within the range of from about .002 to about .050 inch, the invention in its broadest aspect is also applicable to work hardened steel strip having a thickness as low as about .0002 inch and as high as about .100 inch. It should be understood, however, that for the very thin or foil gauges ranging from about .0002 to about .002 inch and for the heavier gauges ranging from about .050 to about .100 inch, it may be necessary to employ different quench media or to modify the heating, tension control, or quench systems as compared with the corresponding process system employed for the preferred thickness range of .002 to .050 inch.

As seen in FIG. 1, the work hardened or as-cold reduced strip 10 is fed from a payoff reel 11 through a bridle 12 and a looper 13 to a conventional cleaning and rinsing step 14 in which the residual rolling oil is removed. For example, an alkaline cleaning medium may be used either with or without electrolytic means. The cleaned strip then passes through the usual roll system and downwardly through a furnace 15 where the strip is heated to a uniform temperature above the A_3 critical point so that the steel is fully austenitized. This temperature may range from about 1525° F. to as high as about 2100° F., dependent upon the carbon content, but from a practical standpoint effective results may be obtained within the range of from about 1525° F. to about 1750° F. Immediately upon leaving the furnace 15 the heated strip passes into a quench system 16 (more fully described below) where the strip is rapidly quenched to ambient or room temperature at a rate in excess of the critical cooling rate required to obtain a substantially fully martensitic microstructure. The oxide scale formed during quenching is removed from the surface of the strip by pickling in an acid dip 17, and after passage through another looper 18 and bridle 19 the martensitic steel strip is recoiled on a take-up reel 20.

As will be understood from the customary isothermal transformation diagrams, plain carbon steels of low carbon content (.03-.25 wt. percent) require extremely rapid quenching in order to achieve a substantially fully martensitic structure. In general, it may be stated that the steel strip must be quenched from the austenitizing temperature to below the temperature for martensite formation in from about .1 to about .4 seconds. In addition, the quenching must be accomplished uniformly so as to obtain a uniform microstructure and so as to avoid excessive warpage or distortion of the strip.

Although the invention contemplates the use of any suitable quench system which will provide the necessary severity or rapidity and the desired uniformity of quenching, the quench system 16 (illustrated in more detail in

FIGS. 2 and 3) has been found to be particularly effective. The method and apparatus aspects of the quench system per se are more fully described and claimed in the copending application of Harold L. Taylor, Ser. No. 426,277, filed Jan. 18, 1965.

As shown in FIGS. 2 and 3, the quench system 16 comprises a tank 30 containing a sinker roll 31 and having a strip exit chute 32. Water, or other quenching liquid is supplied continuously to the tank 30 through an inlet 33. Extending upwardly from the tank 30 is an elongated conduit section 34 of rectangular cross-section which provides a restricted quench channel 35. Quenching water flows upwardly through the conduit 34 and spills over the upper edge into a trough 36 having an upright weir 37. Extending downwardly from the outlet end of the furnace 15 is a tubular connecting section 38 the lower end of which is disposed in the trough 36 below the upper edge of the weir 37. Effluent water is discharged from the trough 36 through a drain line 39. Since the water level in the trough 36 is determined by the height of the weir 37, it will be recognized that the lower end of the connecting section 38 is sealed by the water in the trough 36 so as to prevent infiltration of air into the furnace 15. If desired, a reducing or other non-oxidizing gas may be supplied to the connecting section 38 (by means not shown) for passage upwardly through the furnace 15, thereby preventing oxidation of the strip.

As the strip 10 heated to austenitizing temperature moves downwardly from the furnace 15 it passes quickly through the section 38 and enters the upper end of the quench channel 35 where it is immediately immersed in the upwardly flowing stream of water. Preferably, the quench section 34 is also provided just below its upper end with a plurality of submerged spray units designated schematically at 40 and having elongated slit orifices (not shown) for directing high velocity streams of water against opposite sides of the strip 10. As the strip 10 leaves the lower end of the quench section 34 it enters the tank 30, passes beneath the roll 31, and emerges from the exit chute 32.

As previously mentioned, uniformity of quenching is essential not only for the sake of obtaining a uniform microstructure with uniform physical properties but also to avoid warpage and distortion of the strip. Irregular vaporization of the water or other quenching medium in contact with the strip can result in substantial differentials in heat transfer rates between portions of the strip surface in contact with liquid water and other portions in contact with water vapor. These differentials cause different rates of contraction in the steel strip and result in quenching stresses and deformation. However, in the illustrated quench system the necessary high cooling rate and the desired uniformity of quenching are realized as a result of the high degree of turbulence and the high volume rate of flow of the water through the restricted quench channel 35 and as a result of the action of the submerged sprays 40. Consequently, a quenched strip of fully martensitic structure is obtained which is either flat enough for its intended use or can easily be rolled to flatness.

Although water is the preferred quenching medium, other media may be used including brine or other aqueous salt solutions, oil, liquid nitrogen, etc. Regardless of the quenching liquid used, however, the volume rate of flow of the quench liquid must be high enough to provide a cooling rate in excess of the critical rate required for complete transformation to martensite, and the turbulence of the quench liquid relative to the strip must be great enough to prevent the accumulation of vapor film which would lead to non-uniformity of quenching and consequent distortion of the strip.

Typical line speeds may range from about 100 ft./min. to about 2000 ft./min. dependent upon the gauge of the strip and the carbon content. The water introduced to the quench system may be at the ordinary available tem-

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perature, e.g., from about 35° F. to about 65° F., and the strip will normally be cooled to approximately the water temperature before leaving the quench tank. If desired, the water or other quench medium may be recirculated through a heat exchanger for temperature control.

Neither aging nor tempering treatments are required to improve the mechanical properties of the product. In the usual case, in situ tempering or self-tempering will take place during the quenching step because the martensite transformation temperature is quite high for plain carbon steels at the relatively low carbon levels contemplated by the present invention. For example, for plain carbon steel containing .03 wt. percent carbon and .40 wt. percent manganese, the martensite start temperature is estimated to be about 990° F. and the martensite finish temperature is estimated as about 610° F. For plain carbon steel of .25 wt. percent carbon and .40 wt. percent manganese the respective martensite start and finish temperatures are estimated as about 805° F. and about 470° F. Consequently, sufficient tempering of the strip will take place during the short time required to cool from the martensite transformation temperature range down to the ambient temperature or water temperature. Moreover, in those instances where the martensitic strip is subsequently hot dip coated, as in galvanizing or aluminum coating, further tempering will take place during the coating step.

However, the invention does not preclude the use of a subsequent tempering treatment where such is required for any reason. For example, the quenched martensitic steel product may sometimes have greater tensile strength and hardness than are desirable for a given end use, but by reheating the steel to a temperature of from about 400° F. to about 1100° F. for an appropriate time the tensile strength and hardness of the steel are decreased to the desired extent while the ductility of the steel is increased.

As discussed above, the invention is broadly applicable to work hardened steel strip having a low carbon content ranging from about .03 wt. percent to about .25 wt. percent in gauges ranging from as low as about .0002 inch to as high as about .100 inch. However, it will be well understood by those skilled in the art that the strip thickness, carbon content, and severity of quench are correlative factors and must be coordinated within the aforementioned broad ranges. In particular, for the thicker gauges of strip it will be necessary to use a higher carbon content or a more drastic quench system.

Assuming that the quenching operation has been carried out under optimum conditions, as discussed above, so as to achieve uniformity of quenching across the full width of the strip, the final quenched product will have acceptable flatness for many end uses, as mentioned above. However, it is an important feature of the invention that the quenched strip can readily be rolled, as on a temper mill, to provide adequate commercial flatness for any desired end use. For example, successful flattening is usually obtained by a single pass through a twin stand four high temper mill, each stand having two work rolls and two back-up rolls. Because of the unusual hardness of the fully martensitic strip, the work rolls may have a high degree of roughness without impairing the surface of the strip, thereby providing adequate flattening in a single pass. This is a particularly advantageous feature in the case where the steel strip is to be tin plated since the conventional black plate practice requires smooth or only slightly roughened work rolls. Although wet rolling may be used, dry rolling is entirely adequate and is preferred because it effects less reduction of the strip and therefore has a less detrimental effect on ductility. In general, the extent of reduction in the temper rolling step should not exceed about 5% and preferably should not exceed about ½ percent.

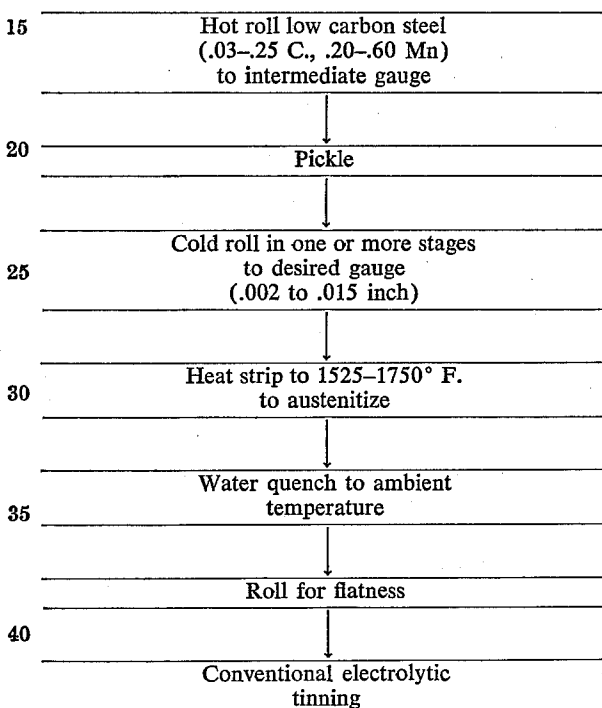
Following the step of rolling for flatness the strip may then be tin plated in a conventional electrolytic tinning operation, the details of which are well known to those

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skilled in the art. Alternatively, the martensitic strip may be galvanized or aluminum coated.

For illustrative purposes, the invention is hereafter described specifically in connection with the production of martensitic tin plate. However, it is to be understood that the invention also embraces other coated products such as galvanized martensitic steel and aluminum coated martensitic steel as well as the martensitic steel per se which is useful, for example, in the manufacture of steel strapping.

The steps involved in the production of martensitic tin plate may be summarized briefly in the following block diagram:



The resultant martensitic tin plate possesses an unusual combination of properties not previously available by any known process. For example, martensitic tin plate made in accordance with the present invention exhibits a tensile strength in excess of 130,000 p.s.i., e.g., from about 150,000 to about 250,000 p.s.i., dependent upon carbon content. Moreover, as previously mentioned, the ductility as measured by percent elongation in two inches remains essentially uniform, e.g., from about 1.5% to about 10%, for all carbon contents within the .03-.25 wt. percent range. Thus, at higher carbon contents within this range it is possible to obtain a product having maximum tensile strength without any excessive loss of ductility.

Prior to the present invention the most acceptable high strength tin plate used for beer can ends was double reduced nitrogenized tin plate which has a maximum tensile strength of about 110,000 p.s.i. and an elongation in two inches of less than 1%. The martensitic tin plate of the present invention is far superior to the double reduced nitrogenized product with respect to tensile strength and ductility, as discussed above. The martensitic tin plate also has the advantage of being isotropic or non-directional which is a particularly desirable property for can ends and bodies. In addition, the martensitic tin plate has better corrosion resistance as measured by the usual test and it also exhibits better buckle strength, rock strength, and dent resistance which are highly desirable properties for can making. As will appear more fully in the specific example below, the present invention makes it possible to achieve high strength with good ductility which was not possible heretofore in the known tin plate

processes. Moreover, the invention does not require the use of rephosphorized or nitrogenized steel.

For purposes of further illustration, but not by way of limitation, the following specific examples are presented.

A series of continuous runs were made on commercial scale equipment of the type illustrated in FIGS. 1-3 using lake water at ambient temperature as the quench medium. The starting material in each instance was cold rolled full hard strip of 32 $\frac{3}{4}$ inch width having a tensile strength of about 100,000 p.s.i. and an elongation in two inches of less than 1%. The chemical analyses and gauges of the test coils are shown in the following table:

TABLE I

Run No.	Gauge (in.)	Chemical Analysis (wt. percent)						
		C	Mn	P	S	Si	Cu	As
1-----	.0057	.09	.45	.011	.022	.001	.03	.018
2-----	.0084	.09	.45	.012	.022	.010	.02	.016
3-----	.0080	.11	.34	.012	.021	.004	.03	.013
4-----	.0083	.19	.42	.016	.022	.011	.03	.014

The processing data for the four runs are shown in Table II, as follows:

TABLE II

Run No.	Line Speed (ft./min.)	Steel Quench Temp.* (° F.)	Water Temp. (° F.)		Water Flow (gal./min.)	
			Entry	Exit	Inlet 33	Sprays 40
1-----	625-750	1,630-1,720	60-65	66-74	725	700
2-----	450-475	1,730-1,750	60-65	66-74	725	700
3-----	475-510	1,670-1,760	60-65	66-74	725	700
4-----	490-520	1,700	60-65	66-74	725	700

*Temperature of heated strip just before contact with the quench water.

Photomicrographs of test specimens from the quenched strips showed that the microstructure in each case was entirely tempered martensite.

The coils from each run were dry rolled for flatness on a twin stand four high temper mill. The work rolls had .010 inch crowns and were blazed with No. 14 grit to provide a rough surface. Because of the high hardness of the quenched material adequate flattening of the strip was obtained on a single pass with less than $\frac{1}{2}$ % reduction and without undue roughening of the strip surface. The coils from these runs were then tin plated in a conventional acid electrolytic tinning line. The average properties of the final tin plate product are shown in Table III below, the carbon contents and gauges being repeated for convenience.

TABLE III

Run No.-----	1	2	3	4
Carbon, wt. percent.-----	.09	.09	.11	.19
Gauge, in.-----	.0057	.0084	.0080	.0083
Tensile strength, p.s.i.-----	174,000	172,000	189,000	222,000
Elongation, percent in 2"-----	1.5-2.0	2.5-3.0	2.0-2.5	2.0-2.5
Olsen ductility, in.-----	.154	.158	.151	.151
Rockwell hardness, 30-N-----	53	53	58	63
Pickle lag*-----	5	6	4	3
ATC*-----	.02	.04	.03	.03

*Pickle lag test and ATC (alloy tin couple) test are described in "Tin plate Testing" (May 1960) by Tin Research Institute, Appendix XI and Appendix XIV, respectively.

From the foregoing data it will be seen that the product had exceptionally high strength even in very thin gauges. Moreover, the ductility of the product was uniformly good even at the highest carbon content in Run No. 4. Corrosion resistance, as measured by the pickle lag and ATC tests, was excellent. Although not shown in Table III, the difference between longitudinal and transverse measurements of tensile strength was slight so that the product was essentially isotropic.

In addition, Rockwell (30-N) hardness traverses were made at one inch intervals across the width of each strip with the following results:

Run No.:	Median value plus deviation
1-----	53 $\pm$ 3
2-----	54.5 $\pm$ 2.5
3-----	58 $\pm$ 1
4-----	63 $\pm$ 1

Thus, it will be evident from the uniform hardness of the strips that uniform quenching was carried out and that a very uniform martensitic microstructure was obtained.

The test results show that by the heating and quenching process of the present invention a full hard cold rolled strip having a tensile strength of about 100,000 p.s.i. and very poor ductility (less than 1% elongation in two inches) is transformed into a material having vastly improved tensile strength and ductility. In conventional tin plate processing sequences, which rely upon cold reduction to provide strength, it is impossible to obtain this desirable combination of properties. For example, when annealing is employed after cold reduction, ductility is improved at the expense of tensile strength. When double cold reduction is employed, the ductility is poor and even then the strength levels achieved are much less than can be obtained by the present invention. Moreover, the martensitic steel and the martensitic tin plate of the present invention are substantially isotropic. For example, the difference between longitudinal and transverse measurements of tensile strength will generally be on the order of 2-3% or less, whereas in a typical double reduced tin plate product such difference is 10% or more.

A further important advantage of martensitic steel strip made in accordance with the present invention is its marked resistance to breakage as compared with steel strip materials heretofore used in continuous processes. For example, double reduced tin plate has a relatively high transition temperature and is highly susceptible to fracture or tearing if edge cracks develop in the strip. This undesirable property is especially noticeable in nitrogenized double reduced tin plate. The martensitic steel strip herein described is much less sensitive in this respect since edge cracks do not tend to propagate as readily and less breakage of the strip is encountered. As will be appreciated, the foregoing advantage becomes increasingly important as the thickness of the strip decreases.

I claim:

1. A continuous process for making thin gauge high tensile strength steel sheet or strip which comprises passing through a heating zone a continuous sheet or strip of plain carbon thin gauge steel in work hardened state and having a carbon content of from about .03 wt. percent to about .25 wt. percent, a manganese content of from about .20 wt. percent to about .60 wt. percent, and a thickness of from about .0002 to about .100 inch, and therein heating the sheet or strip to a temperature above the A_3 critical point so as to austenitize the steel, said work hardened sheet or strip being obtained by cold reduction by at least about 40% of an intermediate gauge material and said work hardened sheet or strip being characterized by a tensile strength on the order of about 100,000 p.s.i. and an elongation in two inches of less than about 1%, and immediately thereafter passing the sheet of strip through a quench zone and therein uniformly quenching the austenitized steel sheet or strip to obtain a product having a microstructure consisting essentially of tempered martensite, a tensile strength of at least about 130,000 p.s.i., and an elongation in two inches of at least about 1.5%.

2. The process of claim 1 further characterized in that said temperature is from about 1525° F. to about 2100° F., dependent upon the carbon content.

3. The process of claim 1 further characterized in that said work hardened sheet or strip has a thickness of from about .002 to about .050 inch.

4. The process of claim 1 further characterized in that said intermediate gauge material is cold reduced by at least about 60%.

5. The process of claim 1 further characterized in that the quenched strip is thereafter rolled to flatten the same.

6. The process of claim 1 further characterized in that said product has a tensile strength of from about 150,000 to about 250,000 p.s.i. and an elongation in two inches of from about 1.5% to about 10%.

7. The process of claim 1 further characterized in that

said product is thereafter coated with another metal.

8. The process of claim 1 further characterized in that said product is thereafter coated with a metal selected from the group consisting of tin, zinc, and aluminum.

9. The process of claim 1 further characterized in that said steel sheet or strip has a thickness of from about .002 to about .015 inch and said product is thereafter tin plated.

10. The process of claim 1 further characterized in that said tensile strength and said elongation of said product are obtained without aging or tempering following the quenching step.

11. A product made in accordance with the process of claim 1.

12. Tin plate made in accordance with the process of claim 9.

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