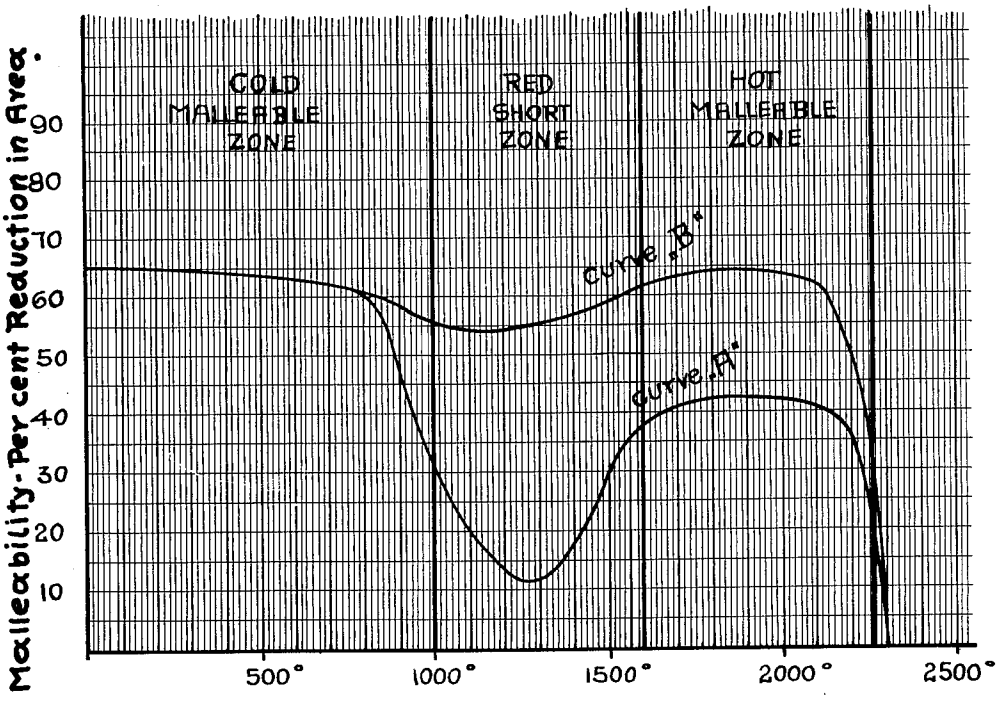
March 7, 1939. C. G. BIEBER 2,150,094

TREATMENT OF NICKEL AND NICKEL ALLOYS AND PRODUCTS RESULTING THEREFROM

Original Filed Feb. 21, 1935

CURVE "A" REPRESENTS A NICKEL-COPPER ALLOY DEOXIDIZED WITH 0.10% ALUMINUM 1.00% MANGANESE AND 0.08% MAGNESIUM.

CURVE "B" REPRESENTS A NICKEL-COPPER ALLOY PRODUCED WITH 0.20% TITANIUM PLUS 0.03% PHOSPHOROUS IN ADDITION TO 0.10% ALUMINUM, 0.05% MAGNESIUM AND 1.00% MANGANESE.



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TREATMENT OF NICKEL AND NICKEL ALLOYS AND PRODUCTS RESULTING THEREFROM

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9 Claims. (Cl. 75—82)

The present invention relates to an improved treatment of nickel and nickel alloys and to the improved products resulting therefrom.

It is well known that nickel and nickel alloys in their native state were non-malleable. In other words, those skilled in the art know that nickel and nickel alloys as customarily produced before Fleitmann from known ores by conventional industrial processes have been non-malleable. Fleitmann provided the art with a process of treating nickel and nickel alloys with magnesium which made the nickel and nickel alloys malleable in the broad sense. Various auxiliary scavengers and deoxidizers such as aluminum, manganese and the like have been used in conjunction with magnesium. Even when the Fleitmann and other treatments were applied to nickel and nickel alloys, certain shortcomings were involved, including a lack of malleability under certain conditions. Thus, an alloy of nickel and copper, particularly one containing about 65% to 75% of nickel and about 35% to 25% of copper, showed a tendency to "red shortness" or low ductility in a certain hot condition, especially within a temperature range from about 1200° F. up to about 1700° F. In this temperature range the nickel alloy had reduced ductility which had the tendency to cause certain difficulties in the hot working operations. In view of this situation care had to be exercised in the hot working of the foregoing nickel-copper alloys. Furthermore, nickel and other nickel alloys had a tendency to "red shortness" under certain conditions. Although various attempts and efforts have been made to eliminate the difficulties due to "red shortness" under all conditions, none as far as is known, has been proposed which is capable of being carried into practice wholly successfully on an industrial scale to give commercially acceptable products.

It has been discovered that certain constituents occurring as minute traces or in very small amounts in nickel and nickel alloys appear to be responsible for "red shortness" under certain conditions and that certain elements including some of which have heretofore been considered as harmful to nickel and nickel alloys have been found to be highly beneficial when present in proper quantities in eliminating "red shortness" in nickel and nickel alloys.

It has likewise been found that the elimination of "red shortness" from nickel and nickel alloys may be accomplished most effectively by utilizing a combination treatment of a plurality of malleableizing elements.

It is an object of the present invention to provide a simple, economical and practical treatment of nickel and nickel alloys which will substantially eliminate "red shortness" and which will produce nickel products with improved properties.

A further object of the invention is to provide an improved process which can be carried into practice conveniently on an industrial scale to produce commercially acceptable products.

It is also within the contemplation of the invention to provide a process of treating nickel and nickel alloys in which the treated nickel and nickel alloys have imparted to them a high degree of malleability throughout the range of hot working temperatures.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawing which illustrates two curves depicting the malleability of a prior alloy and of a new alloy treated in accordance with the present invention.

Broadly stated, the invention contemplates the elimination, neutralization or counter-action of the effects of detrimental constituents, particularly those occurring as traces or in small amount. It has been found that these detrimental constituents find their way into nickel and nickel alloys from the ore; the reagents utilized in the concentrating and the refining operations; the slags employed in smelting and refining; the refractories of furnaces, ladles, etc.; the atmosphere; and the various apparatus with which the ore, the concentrates, the matte, the intermediate products, and the metallic nickel and nickel alloys come in contact from the initial to the final operations. Among these harmful constituents may be mentioned sulphur, selenium and tellurium which are elements apparently carried over from the ore; calcium, strontium, barium, sodium, potassium and lithium, which are elements picked up from refractories, slags, scavengers, deoxidizers, etc.; and gases such as hydrogen and nitrogen. For the elimination of the harmful effects due to the detrimental constituents, a malleableizing agent or element or a combination of two or more agents or elements may be added to the nickel or nickel alloys under treatment. A malleableizing agent, such as phosphorus, is added to a melt to convert a harmful constituent, such as calcium, into a harmless product and a malleableizing element, such as titanium, is added to convert a harmful constituent, such as selenium, into a harmless product. By proceeding in accordance with the foregoing and in accordance with the principles set forth hereinafter, new and improved results may be obtained and malleable nickel and nickel alloys may be obtained which are completely malleable throughout the hot working range.

Nickel

When certain detrimental constituents such as lithium are present in nickel "red shortness" occurs in the final product. When lithium-con-

taining nickel is subjected to hot working within the range of about 1200° F. to about 1500° F., the product cracks, splits and disintegrates. Although lithium has heretofore been considered as a very effective scavenger and deoxidizer, nevertheless, the occurrence of "red shortness" makes the nickel product unacceptable. For the conversion of the harmful residual lithium into a harmless product an appropriate malleableizing element is added in proper amount. Thus, when lithium is present to the extent of 0.007%, it is preferred to introduce about 0.01% of boron for the purpose of eliminating the "red shortness" in the final product.

It is to be observed that heretofore boron has been considered harmful and very detrimental to the malleability of nickel and nickel alloys. Nevertheless, it has been discovered that when boron is used in proper amounts, it is highly beneficial in eliminating certain constituents which cause "red shortness" in nickel and nickel alloys. Under commercial conditions, it has been found that it is possible to use titanium, or phosphorus in the place of boron. Under certain conditions, it has been found that even arsenic may be used in the proper amount for the purpose of eliminating excesses of harmful basic constituents which cause "red shortness". Although lithium was specifically referred to, excess of calcium, sodium, potassium, magnesium, strontium and barium which may cause "red shortness" may be likewise counteracted in nickel and nickel alloys by the foregoing malleableizing elements.

It has been found by the use of the present method that splits which have given difficulty under certain circumstances may be eliminated in addition to the elimination of "red shortness". In this manner, it is possible to produce a substantially seam-free nickel without introducing "red shortness" into the metal.

In some instances, a combination treatment may be employed. Thus, a combination of boron and titanium may be used instead of boron alone. In practice, about 0.05% magnesium, about 0.05% titanium, and about 0.01% boron may be added to the melt to impart malleability to the product.

Nickel-copper alloys

In the treatment of nickel-copper alloys, particularly those containing more than 25% and up to about 85% of nickel, "red shortness" may be eliminated and a sound metal may be produced at the same time. Thus, a nickel-copper alloy having about 65% to about 75% of nickel and about 35% to about 25% of copper which are contaminated with detrimental constituents including such elements as selenium, tellurium, sodium, potassium and calcium, were treated with about 0.25% of titanium. With this addition of titanium, "red shortness" which usually occurs in a temperature range of about 1200° F. to about 1700° F. was eliminated.

For best results, it has been found that a combination treatment is to be preferred. For instance, improved results have been obtained by the use of about 0.05% of titanium in conjunction with about 0.015% of phosphorus or about 0.01% of boron.

In carrying the invention into practice on an industrial scale a melt of a nickel-copper alloy (70% nickel and 30% copper) containing about 0.10% carbon, about 1 to 3% iron, and about 1 to 2% manganese is treated with auxiliary scavengers and deoxidizers containing aluminum. For instance, such a scavenger and deoxidizer may contain about 0.10% of aluminum and about 0.05% of magnesium. In adding malleableizing elements according to the present invention, it is preferred to introduce them into the melt which has been given a preliminary deoxidizing treatment just prior to pouring into molds or other equipment for the production of a solid product. Thus, satisfactory results were obtained when a melt of a nickel-copper alloy was treated with the foregoing deoxidizer of aluminum and magnesium and then was treated in accordance with the present method with about 0.015% of phosphorus and about 0.025% of titanium. The thus treated bath is then tapped into a ladle and then teemed into molds. It is to be observed that the deoxidizers and the malleableizing agents may be added to the melt in any desired and appropriate order.

The ingot, for instance, is milled and overhauled in accordance with the customary procedure. Thereafter it may be subjected to hot and/or cold working or combinations thereof to produce sheet, strip, rod, etc. The nickel-copper alloy produced by the present process may be hot worked down to practically any temperature which the mills are capable of handling. In practice, the standard hot rolling mills are capable of handling metal having a temperature as low as 1000° to 1200° F. This is in distinct contrast to prior procedure wherein great care had to be exercised to maintain a finishing temperature within a safe zone above the "red shortness" range of about 1200 to 1700° F. Formerly when the hot work was carried into the "red short" range the finished product would develop seams, cracks, splits, fissures, etc., which tended to require extra expense in cleaning up the products or resulted in the rejection of the product.

Nickel-copper-aluminum alloys

Alloys containing about 60% to about 70% of nickel, about 35% to about 25% of copper, and about 1% to about 5% of aluminum may be treated by the present method to eliminate "red shortness" which has heretofore occurred in nickel-copper-aluminum alloys within a temperature range of about 1200° F. to about 1900° F. To these alloys a malleableizing element is added in appropriate amounts. Thus, a malleableizing element such as titanium may be added in controlled critical amounts and the final product has a wider range of workability. In this manner, the nickel-copper-aluminum alloys may be worked and rolled with the equipment available at a mill. For instance, an alloy containing about 66 or 67% of nickel, and about 28 or 29.5% of copper may have added to it up to about 2.75 or 3% of aluminum. In actual practice, it is preferred to prepare a melt of the nickel-copper alloy having a slag, preferably of an oxide-fluoride type on the surface thereof. Aluminum is then introduced into the melt in any customary way. After stirring the melt thoroughly, about 0.6% of titanium is incorporated in the body of the melt and thoroughly distributed. The treated melt may be then tapped and teemed in the usual manner.

It has been found that a nickel-copper-aluminum-titanium alloy containing about .01% to about .25% of carbon can be produced which has a wide range of hot workability. Thus, it has been found that the foregoing alloy treated in accordance with the present method has a working range of about 1500 or 1600° F. to about

2250° F. Experience has demonstrated that forging, rolling and other hot working operations may be conducted within this range to give wholly satisfactory results and to produce commercially acceptable products including sheets, bars, strip and rods without checking or cracking. These new results are surprising, particularly in view of the fact that a prior alloy containing about 66% nickel, about 28% copper, and about 3.75% aluminum can only be hot worked in the temperature range from about 1800—1900° F. up to about 2250° F.

Generally speaking, the present invention contemplates the treatment of nickel-copper-aluminum alloys having the following range of compositions:

	Per cent
Nickel	50.0 to 80.0
Copper	20.0 to 40.0
Aluminum	2.0 to 5.0
Manganese	.10 to 2.0
Silicon	.02 to 1.0
Iron	.10 to 2.5
Carbon	.01 to 0.3

The physical properties of the heat treated alloy are better than those heretofore obtainable. The following comparative schedule demonstrates the new results obtained by the present method with nickel-copper-aluminum alloys annealed at 1500° F. and then hardened by heat treating for twenty-four hours at 1100° F. The prior alloy contained 66.8% nickel, 30% copper, 3% aluminum and 0.15% carbon and is denoted as "Old alloy" where as the new alloy had substantially the same composition except that it contained about 0.50% titanium and is denoted as "New alloy".

Comparative schedule

Properties	Old alloy	New alloy
Proportional limit pounds per square inch	53,000	81,000
Yield point do	71,000	103,000
Breaking strength do	126,000	154,000
Reduction in area percent	54	44.3
Elongation in two inches do	43	32

The new and improved results of the invention can be observed from the data obtained from a series of comparative tests with a nickel alloy containing about 66% of nickel, about 28% of copper, about 2.75% of aluminum and about 0.15% of carbon and the present improved alloy containing about 66% of nickel, about 28% of copper, about 2.75% of aluminum, about 0.15% of carbon, and about 0.60% of titanium, the former alloy being designated in the following schedule as the "Old alloy" and the latter alloy as the "New alloy".

Comparative schedule

Properties	Old alloy	New alloy
Proportional limit pounds per square inch	40,000	82,000
Yield point do	49,500	105,000
Breaking strength do	94,000	149,000
Reduction in area percent	70.5	41.5
Elongation in two inches do	37.0	30.0

It is to be noted that there is an increase of over one hundred (100%) percent in the proportional limit and the yield point.

When nickel-copper-aluminum alloys are treated by the present method, the final product responds to heat treatment to give a product with higher hardnesses and strengths for a given aluminum content than heretofore obtainable without the addition of titanium or an equivalent element.

It appears that excess amounts of detrimental constituents including magnesium, calcium and sodium are counteracted by the addition of titanium or equivalent metal. In this manner the harmful effects apparently due to calcium, sodium, etc., which apparently are picked up from the slags may be counteracted. It is also to be observed that detrimental effects apparently due to selenium and tellurium are likewise eliminated by the titanium treatment.

For the treatment of nickel-copper-aluminum alloys, the present method involves the use of controlled, restricted amounts of titanium. Thus the following range of percentages of titanium may be used:

	General	Preferred
	Percent	*Percent*
Titanium	0.05 to 1.25	0.55 to 0.85

When titanium is used, certain restricted amounts are found in the treated alloys. Thus, titanium may be present in the final treated alloys as follows:

	General	Preferred
	Percent	*Percent*
Titanium	0.025 to 1.00	0.50 to 0.75

Nickel-iron-chromium alloys

An alloy containing about 55% to about 99% of nickel, about 0.25% to about 20% of iron, and about .5% to about 25% of chromium may be treated to eliminate "red shortness", splits, seams and blow holes. In addition, the present method improves the malleability over practically the entire high temperature range.

An alloy containing 80% of nickel, about 6% of iron, about 14% of chromium, and carbon preferably less than 0.15% is melted in the usual manner and is subjected to slagging and refining operations and finally to deoxidizing treatments with elements such as aluminum and/or magnesium. Just prior to tapping an addition is made of a malleableizing element or elements. Thus, about 0.25% of titanium and 0.01% of boron may be incorporated in the melt just prior to tapping. After thorough distribution of the malleableizing element or elements, the melt is quickly tapped and teemed. Of course, the addition of the malleableizing element or elements may be made in a ladle instead of in a furnace. Under certain conditions, it is preferred to make the addition in the ladle rather than in the furnace.

The alloy containing nickel-iron-chromium and titanium produced by the foregoing method is sound and free from blow-holes, is substantially free from seams or splits or cracks, and is substantially free from "red shortness". Heretofore nickel-chromium-iron alloys, particularly those made from scrap metal or containing scrap metal had a tendency to contain blow holes made from gases which were evolved during solidification. These gases were principally nitrogen, hydrogen and carbon monoxide. Of these gases, it appeared that nitrogen was the most troublesome. Furthermore, prior nickel-chromium-iron alloys

generally possessed "red shortness" and were not hot malleable within a range of about 1200° F. to about 1800° F. or 2000° F. Moreover, certain difficulties were heretofore encountered in the nature of seams, splits, cracks and the like which tended to increase the cost of production and finished products, particularly those requiring a high and bright surface finish and luster. These prior shortcomings and difficulties have been eliminated and counteracted by the present method and the final products have been found to be very satisfactory and were commercially free from the difficulties noted hereinabove.

Although the exact nature of the mechanism of the physico-chemical and/or metallurgical reactions or phenomena have not been definitely ascertained, nevertheless, it is believed that the following theory will be helpful in understanding the principles underlying the present invention. By referring to the drawing a clear-cut impression may be gained graphically of the comparison of the new method with the prior method. Thus, if reference is made to curve "A" which represents typical prior practice, it will be observed that percent reduction in area has been illustrated against temperatures in degrees Fahrenheit. The data for this curve were obtained from series of standard high temperature tensile tests. Generally speaking, the curve or graph may be divided into three parts or zones, namely; the cold working zone, the red short zone, and the hot malleable zone. In the drawing the cold malleable zone extends up to about 1000° F.; the red short zone from about 1000° F. to about 1600° F. to 1700° F.; and the hot malleable zone extends from about 1600° or 1700° F. to about 2250° F. In the red short range it will be observed that the percent reduction in area which is a measure of malleability, drops from about 60% to about 15 or 20%. Within this range it has been impractical heretofore to perform other than light hot working operations on the nickel containing material. From a commercial point of view this has been a serious handicap due to the fact that the hot malleable zone is a very limited one and that it is difficult to complete hot working operations with the standard mill equipment entirely within the hot malleable zone. Heretofore this shortcoming required the completion of the working in the cold malleable zone which, as is well known, is a very expensive procedure. In the event that hot working was carried into the red short zone, cracks and other imperfections developed in the surface and body of the material which necessitated expensive operations such as grinding, slitting, overhauling and the like. Under certain conditions, if hot working were continued into the most severe part of the red short range, it was necessary in many instances to completely scrap the material.

In contrast with prior practice, curve or graph "B" in the drawing shows the results of the present novel method. The data for this curve were obtained from the records of the physical tests under comparative conditions. It will be observed that the curve does not possess a U-shape loop at an intermediate portion thereof and is substantially free from a zone of "red shortness" or low malleability. The hot malleability resulting from the present process is superior to the malleability heretofore obtainable. In fact, even in the hot malleable zone, the malleability of the new alloys is considerable higher than the malleability of prior alloys as may be clearly seen from the drawing. Instead of the maleability falling off and developing "red shortness", the curve depicting the results of the new process is substantially horizontal. In the illustration in the drawing there is a slight curve between the cold malleable zone and the hot malleable zone. Of course, this transition from the cold zone to the hot zone is so slight as to be unimportant from a commercial point of view.

In general there are apparently two major effects contributing to the condition of "red shortness" in prior nickel alloys. One was due to the presence at the grain boundaries of embrittling products which lowered the inter-crystalline cohesion of the material while the other was due to colloidal or nearly colloidal refractory particles precipitated within the crystals which retarded the free movement of the metal along its normal planes of flow and prevented rapid recrystallization during hot working.

The degree of grain boundary embrittlement in nickel-copper alloys could be accounted for by the presence of 8 ounces of tellurium in 100,000 pounds of the nickel-copper alloy. In other words, as minute a quantity as 0.0005% of tellurium will cause distinct "red shortness" in a nickel-copper alloy. Likewise, a somewhat larger amount of selenium will produce the same detrimental effect. Heretofore the magnesium additions counteracted the embrittling effect of sulfur but did not remedy nor counteract the "red shortness" which was apparently due to other causes including those due to the presence of tellurium or selenium. In distinct contrast thereto, additions of titanium or the like according to the present method completely cared for or counteracted or eliminated "red shortness" caused by tellurium, selenium, etc.

The second component of red shortness referred to above is due to the presence of refractory particles within the grains. These refractory particles are principally the oxides and silicates of the aluminum and magnesium deoxidizers. A portion of these oxides remains practically colloidally or nearly colloidally dispersed throughout the charge. Additions of elements such as boron or phosphorus convert these refractory abrasive particles into constituents which are fluid at the melting temperature of the metal. These molten compounds can collect into larger particles which are much less harmful to hot malleability.

For the purpose of controlling the addition of a malleableizing element to a melt under treatment and determining the sufficiency of such addition, use is made of the "hammer and anvil" test. In conducting this test, a spoonful (about 3 to 5 lbs.) of melted metal is removed from the furnace and a test bar (about ⅞" x 1½" x 6" and about 1 lb.) is poured. The solidified test bar is hammered with a sledge hammer (about 10 lbs.). In the event cracks develop, the metal is judged to be "red short". A further controlled addition of malleableizing element is made to the melt and another test bar is made and tested. This procedure is repeated until the test bar withstands the hand forging operation without cracking. The melt is then treated properly and is poured into the mould.

In industrial practice, it is to be noted that a series of high temperature bend tests are conducted on material from each melt after the melt has been cast into ingots and before it is further processed. These tests provide a means of measuring the hot ductility and thus predicting the rolling quality of the material. In con-

ducting bend tests, a forged bar ½" thick x 1" wide x 6" long is heated in an electrically controlled furnace to a predetermined temperature. It is then withdrawn from the furnace and bent 180 degrees with a single blow of a steam hammer. If the test piece withstands this deformation without cracking it is designated as good; if not, it is called bad. This test is repeated at intervals of 100° F. over the range from 1200° F. to 2300° F.–2500° F. The dimensions of the bend test specimens have been so chosen that a good bend at any temperature indicates that the material is capable of being hot worked at that temperature without cracking.

I claim:

1. The improved process of treating a nickel mass of the group of materials consisting of malleable nickel and malleable nickel alloys having red shortness to render the same substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness which comprises subjecting a nickel mass of the aforesaid character to a preliminary deoxidizing and malleableizing treatment to produce a deoxidized and malleableized nickel mass possessing red shortness; then adding to said deoxidized and malleableized nickel mass, while molten, a controlled, restricted, and critical amount of a counteracting agent of titanium and of a counteracting agent of the group consisting of boron and phosphorus to render said mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart to said nickel mass, when solidified, malleability permitting working with standard mill equipment from the hot malleable zone to and into the cold malleable zone; determining the sufficiency of the controlled, restricted and critical amount of the aforesaid agents on test samples by the "hammer and anvil" test while the mass is maintained molten; and repeating the aforesaid adding operation until the "hammer and anvil" test determines the sufficiency of the controlled, restricted and critical amount of the agents added to render the nickel mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart malleability to said nickel mass, when solidified, from the hot malleable zone to and into the cold malleable zone, whereby the treated nickel mass can be worked with standard mill equipment from about 2000° F. in the hot malleable zone through the red short zone extending from about 1500° F. to about 1000° F. and into the cold malleable zone below about 1000° F.

2. The improved process of treating a nickel mass of the group of materials consisting of malleable nickel and malleable nickel alloys having red shortness to render the same substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness which comprises subjecting a nickel mass of the aforesaid character to a preliminary and conventional deoxidizing and malleableizing treatment to produce a deoxidized and malleableized nickel mass possessing red shortness; then adding to said deoxidized and malleableized nickel mass, while molten, a controlled, restricted, and critical amount of a counteracting agent of titanium and of a counteracting agent of the group consisting of boron and phosphorus to render said mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart to said nickel mass, when solidified, malleability permitting working with standard mill equipment from the hot malleable zone to and into the cold malleable zone; determining the sufficiency of the controlled, restricted and critical amount of the aforesaid agents on test samples while the mass is maintained molten; and repeating the aforesaid adding operation until the test determines the sufficiency of the controlled, restricted and critical amount of the agents added to render the nickel mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart malleability to said nickel mass, when solidified, from the hot malleable zone to and into the cold malleable zone, whereby the treated nickel mass can be worked with standard mill equipment from about 2000° F. in the hot malleable zone through the red short zone extending from about 1500° F. to about 1000° F. and into the cold malleable zone below about 1000° F.

3. The improved process of treating a nickel mass of the group of materials consisting of malleable nickel and malleable nickel alloys having red shortness to render the same substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness which comprises subjecting a nickel mass of the aforesaid character to a preliminary deoxidizing and malleableizing treatment to produce a deoxidized and malleableized nickel mass possessing red shortness; then adding to said deoxidized and malleableized nickel mass, while molten, a controlled, restricted, and critical amount of a counteracting agent of the group consisting of titanium, boron and phosphorus to render said mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart to said nickel mass, when solidified, malleability permitting working with standard mill equipment from the hot malleable zone to and into the cold malleable zone; determining the sufficiency of the controlled, restricted and critical amount of the aforesaid agent on test samples by a physical test while the mass is maintained molten; and repeating the aforesaid adding operation until the physical test determines the sufficiency of the controlled, restricted and critical amount of the agent added to render the nickel mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart malleability to said nickel mass, when solidified, from the hot malleable zone to and into the cold malleable zone, whereby the treated nickel mass can be worked with standard mill equipment from about 2000° F. in the hot malleable zone through the red short zone extending from about 1500° F. to about 1000° F. and into the cold malleable zone below about 1000° F.

4. The improved process of treating a nickel mass of the group of materials consisting of malleable nickel and malleable nickel alloys having red shortness to render the same substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness which com-

prises subjecting a nickel mass of the aforesaid character to a preliminary deoxidizing and malleableizing treatment to produce a deoxidized and malleableized nickel mass possessing red shortness; then adding to said deoxidized and malleableized nickel mass, while molten, a controlled, restricted, and critical amount of a counteracting agent of the group consisting of titanium, boron and phosphorus to render said mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart to said nickel mass, when solidified, malleability permitting working with standard mill equipment from the hot malleable zone to and into the cold malleable zone, the said titanium, boron and phosphorus being used within a range of about 0.025% to about 0.60%, about 0.005% to about 0.015%, and about 0.01% to about 0.05%, respectively; determining the sufficiency of the controlled, restricted and critical amount of the aforesaid agent on test samples by a physical test while the mass is maintained molten; and repeating the aforesaid adding operation until the physical test determines the sufficiency of the controlled, restricted and critical amount of the agent added to render the nickel mass, when solidified, substantially free from defects including seams, splits, cracks and the like and to render the same substantially free from red shortness and to impart malleability to said nickel mass, when solidified, from the hot malleable zone to and into the cold malleable zone, whereby the treated nickel mass can be worked with standard mill equipment from about 2000° F. in the hot malleable zone through the red short zone extending from about 1500° F. to about 1000° F. and into the cold malleable zone below about 1000° F.

5. As an article of manufacture, an improved nickel mass of the group consisting of malleable nickel and malleable nickel alloys containing at least 50% nickel having a structure substantially free from defects including seams, splits, cracks and the like and having a constitution resulting from deoxidizing and malleableizing operations and from a subsequent treatment with a controlled, restricted and critical amount of at least two counteracting agents of the group consisting of titanium, boron, and phosphorus, the said nickel mass being substantially free from red shortness and possessing malleability from the hot malleable zone to and into the cold malleable zone and having been worked through the red short zone extending from about 1500° F. to about 1000° F.

6. As an article of manufacture, an improved nickel mass of the group consisting of malleable nickel and malleable nickel alloys containing at least 50% nickel having a structure substantially free from defects including seams, splits, cracks and the like and having a constitution resulting from deoxidizing and malleableizing operations and from a subsequent treatment with a controlled, restricted and critical amount of at least one counteracting agent of the group consisting of titanium, boron and phosphorus, the said neckel mass being substantially free from red shortness and possessing malleability from the hot malleable zone to and into the cold malleable zone and having been worked through the red short zone extending from about 1500° F. to about 1000° F.

7. An article of manufacture as set forth in claim 6 in which the malleable nickel mass consists principally of nickel.

8. An article of manufacture set forth in claim 6 in which the malleable nickel mass consists of a nickel-copper alloy containing at least 50% of nickel.

9. An article of manufacture as set forth in claim 6 in which the malleable nickel mass consists of a nickel-chromium alloy containing at least 50% of nickel.

CLARENCE GEORGE BIEBER.