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F. M. BECKET

ZIRCONIUM STEEL AND PROCESS OF MAKING SAME

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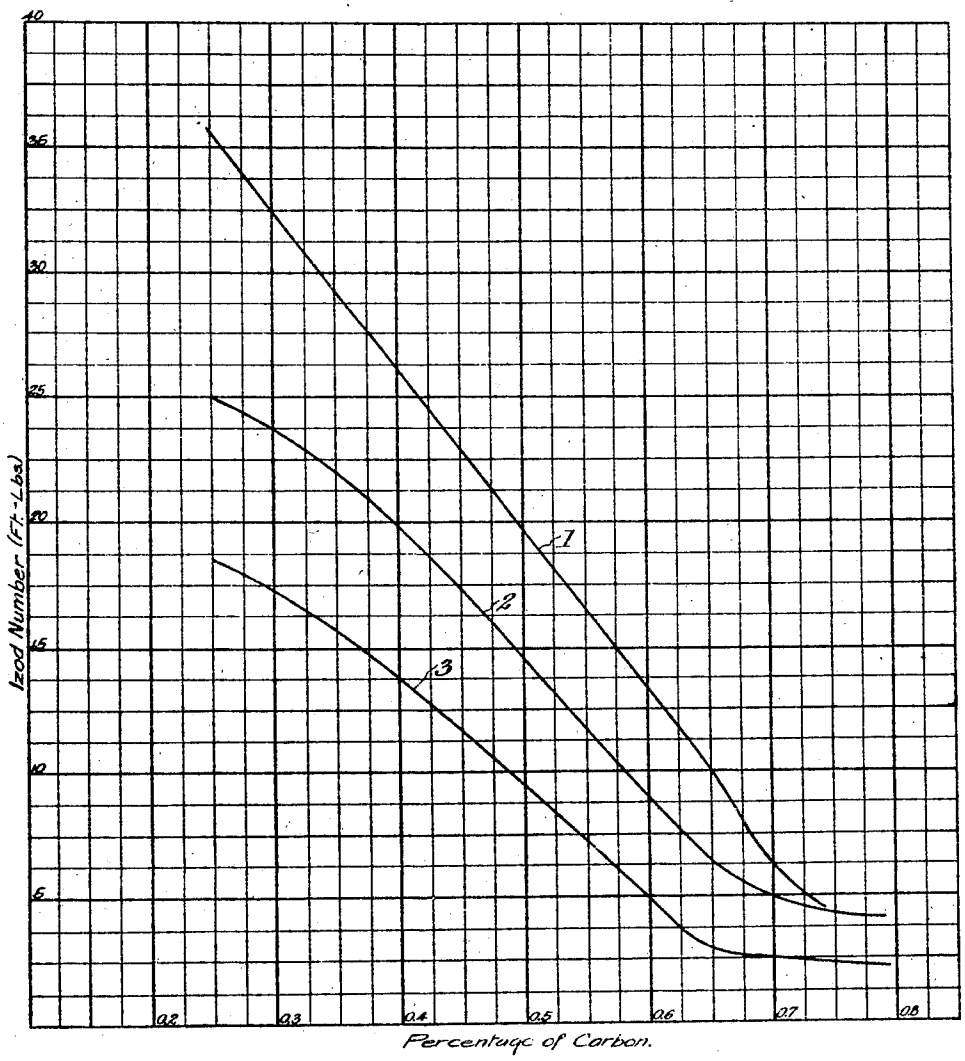

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UNITED STATES PATENT OFFICE.

FREDERICK M. BECKET, OF NEW YORK, N. Y., ASSIGNOR TO ELECTRO METALLURGICAL COMPANY, OF NEW YORK, N. Y., A CORPORATION OF WEST VIRGINIA.

ZIRCONIUM STEEL AND PROCESS OF MAKING SAME.

Application filed January 10, 1922. Serial No. 528,283.

To all whom it may concern:

Be it known that I, FREDERICK M. BECKET, a citizen of the United States, residing at 565 Park Avenue, New York, in the county of New York and State of New York, have invented certain new and useful Improvements in Zirconium Steel and Processes of Making Same, of which the following is a specification.

This invention relates to the art of steel manufacture, and comprises a process of treating high phosphorus steels whereby they may be rendered acceptable under the usual engineering specifications. The invention comprises also, as a novel product, a steel of high phosphorus content, said steel being nevertheless free from such brittleness as has heretofore been considered as a necessary characteristic of all such high phosphorus steels. These results are attained, in accordance with the present invention, by the addition of zirconium to the molten steel, optimum treating conditions being hereinafter set forth.

The use of zirconium as a deoxidizer, solidifier and scavenger of steel has often been proposed. Such uses of zirconium are to be clearly distinguished from that described herein, which contemplates the employment of this metal for the specific purpose of counteracting in greater or lesser degree the brittleness which has heretofore been regarded as an inherent characteristic of the high phosphorus steels. The present invention rests upon the discovery that zirconium, when added to high-phosphorus steels in the proper manner and in suitable proportions, will exert an heretofore unsuspected beneficial effect upon the mechanical and physical properties of such steels. This effect is best measured and determined by the so-called "notch-toughness", as measured by the Izod notched-bar impact test. This beneficial effect upon resistance to impact of notched bars is not obtained in the case of ordinary (low phosphorus) steels which have been treated with zirconium in similar manner, from which it is concluded that zirconium exerts a specific beneficial effect upon high-phosphorus steels.

Under the conditions employed in this investigation no appreciable diminution of the phosphorus content of the treated steels has been detected, from which it is concluded that the observed beneficial effects of zirconium upon high phosphorus steels are not attributable to the elimination of phosphorus. This suggests the possibility that zirconium may perhaps enter into combination with phosphorus in presence of or in association with some or all of the other components of the steel; but as yet no definitely recognizable compound of zirconium and phosphorus has been detected upon microscopic investigation of polished and etched sections of zirconium-treated high phosphorus steels. The percentage of zirconium which must be added to the molten steel to obtain the maximum beneficial effects is determined by a multiplicity of factors, including temperature and degree of oxidation of the steel bath; the composition of the steel; the composition of the alloy or aggregate containing zirconium which is used; the manner in which the addition is made; and the mechanical and heat treatment to which the steel is subjected before it is put into use in finished form. For example, in the manufacture of annealed carbon steels containing around 0.15% phosphorus, I now prefer to obtain the desired beneficial results by the addition of from 0.02 to 0.50% zirconium calculated on the weight of the steel.

The Izod impact number of notched bars, which customarily is considered as inversely proportional to the so-called "brittleness" of steel, is only one of a number of mechanical properties which guide the engineer in the selection of a steel for a given application. In order therefore to obtain data on these correlated properties, the effects of zirconium upon various other properties of steel were investigated in detail, including the yield point or elastic limit, ultimate strength, percentage elongation and reduction of area, and fatigue resistance of several series of steels of varying carbon and phosphorus content, both treated with zirconium and untreated.

Preliminary to the investigation into the effects of zirconium upon high and low phosphorus steels, an investigation on the efficacy of zirconium as a deoxidizer and solidifier of steel was undertaken. A large number of comparison ingots, treated with zirconium and untreated, were split longitudinally through their central axis and examined macroscopically and microscopically for blow holes, pipe, segregation, inclusions, etc.

Working along the lines formerly followed by Brinell in his classical work on the relative solidifying power of manganese, silicon and aluminum, it was established that zirconium has a solidifying power greater than that of silicon, but less than that of aluminum. By the term "solidifying power" is meant the capacity of the added element to eliminate blow holes from and promote soundness of structure in the ingot as cast. Careful microscopic examination failed to show the presence of harmful, characteristic slag inclusions such as are formed by the use of aluminum. In general, the zirconium-treated steels were cleaner, that is to say, more free from slag and oxid inclusions, than the ordinary steels. Chemical analysis of numerous heats indicated that the average recovery of zirconium in the steel, when added as silicon-zirconium in the amount of 0.15% added zirconium, is around 60%.

The investigation into the treatment of high phosphorus steels with zirconium has included the making of numerous heats of steel; the casting or ingots; the forging of ingots; the annealing of forged bars; and the machining and testing of the various test-pieces. Equal weights of molten steel were tapped from the furnace into three separate ladles in the case of each heat. The "A" ladle was in each case treated with zirconium-ferrosilicon; the "B" ladle with 50% ferrosilicon; and the "C" ladle with silicon-zirconium, each of the three additions being adjusted to correspond to the same amount of added silicon. The ladles of steel after treatment were teemed into tapered molds of the usual type and the three ingots from each heat were forged under the same conditions of temperature and working. The forged bars from each separate heat were then subjected to an annealing treatment at a suitable temperature and for a suitable period of time, after which they were cooled slowly. This operation was carried out at the same time on all the forged bars of any given heat in order to obtain uniformity of practice and certainty of comparison.

As typical examples, analyses are given below of a zirconium ferrosilicon and of a silicon-zirconium which were used in the course of this work:

	Zirconium ferrosilicon. Per cent.	*Silicon-zirconium.* Per cent.
Zirconium	9.97	36.65
Silicon	72.14	48.74
Iron	12.75	12.97
Titanium	0.39	0.43
Carbon	0.12	0.07

In the accompanying drawing the figure is a chart wherein the curves indicate graphically the effect of the addition of 0.15% by weight of zirconium in overcoming the brittleness due to phosphorus in the case of a particular series of annealed carbon steels of varying carbon content. The Izod impact number in foot pounds is plotted against carbon content. The curves are based on a large number of measurements carried out with great care. Curve No. 1 embodies the data obtained for low phosphorus (0.02% phosphorus) steels; curve No. 2 for high phosphorus (0.14% phosphorus) zirconium-treated steels; and curve No. 3 for high phosphorus (0.14% phosphorus) steels, not treated with zirconium. The percentages of silicon, manganese, and sulphur were kept substantially constant for all the steels, the actual values for this particular series being 0.20% silicon; 0.50% manganese; and 0.035% sulphur.

It will be evident from an examination of these curves that zirconium exerts a strongly marked specific beneficial action upon the embrittling effect of phosphorus. In fact, at around 0.80% carbon, in the particular series of steels illustrated, the Izod numbers of the untreated low phosphorus steel and of the zirconium-treated high phosphorus steel coincide. In other words, for this composition the added zirconium has completely counteracted the embrittling effect of phosphorus. In the other compositions of high phosphorus steels, this embrittling effect has been partially counteracted. It will also be apparent from the curves that where the carbon is above 0.5% the Izod number of the zirconium-treated steel exceeds that of the untreated high-phosphorus steel by more than 50% and by more than 75% when the carbon content is above 0.6%.

In the investigation above described, zirconium was used in the form of alloys containing silicon and iron as ingredients. Zirconium has been also used however in other forms, and this invention is not restricted to the treatment of high phosphorus steel with the particular type of alloys mentioned by way of example. It has been conclusively demonstrated that it is zirconium which is responsible for the beneficial effects under discussion, and this invention contemplates therefore its addition in any preferred or desirable form, including metallic zirconium, aggregates containing zirconium, or a wide variety of zirconium alloys. The preferred method of adding the zirconium to the molten steel is to make the addition to the ladle, although it may at times be more effectively or conveniently added in the furnace or in the mold.

It is found that in the particular series of steels mentioned above, zirconium, has increased the ultimate tensile strength by an amount which averages around 100 pounds per sq. in per 0.01% of carbon present; and that the percentage elongation and percentage reduction of area are either not appre-

ciably affected or else are favorably affected. While it is true that the yield point in this series has been somewhat lowered, this effect is counterbalanced by the fact that the endurance limit, as measured by the rotary alternating fatigue test, is much closer to the observed yield point of zirconium-treated steels than to that of ordinary steels. Moreover this invention contemplates raising the yield point, where desirable, by suitable modifications in the composition of the steel, for example by additions of carbon, manganese or silicon, or combinations of mixtures of these, as may be found to accomplish the desired result in any particular case.

The effects just mentioned upon the tensile properties and fatigue resistance appear to be characteristic of all zirconium-treated steels of the above series whether of high or low phosphorus content. On the other hand, the beneficial effects of zirconium in overcoming brittleness and in increasing the Izod impact number of notched bars appear to be confined to high phosphorus steels. For this reason the present invention is primarily concerned with the improvement of such high-phosphorus steels by zirconium additions thereto.

The term "high phosphorus steel" for the purpose of the present invention, and as used in the claims, is to be interpreted in view of the use for which the steel is intended, or for which it is generally understood to be suitable. If a steel contains more phosphorus than is generally agreed to be permissible for the use to which steel of that grade is ordinarily put, then the steel is "high phosphorus" in the sense of this application, even though the identical percentage of phosphorus may be normal or subnormal in steel of a different grade intended for another use.

The A. S. T. M. and other engineering societies has set upper phosphorus limits for steels for about one hundred different uses, including all the usual uses for steel where brittleness is of any consequence. The limit ranges from 0.115% for Bessemer bar steels and 0.10% for Bessemer rails to 0.06% for acid open-hearth steel for bridges, buildings and railway cars; to 0.05% for structural steel for locomotives, for steels for springs, axles, wheel and tires, and for forgings; to 0.04% for basic open-hearth structural steels; and to as low as 0.03% for certain alloy steels used in the automobile industry.

"High phosphorus steel" as used in the claims imports a steel having a phosphorus content so high as to disqualify the steel for the use for which it is intended or for which steel of the grade to which it belongs is ordinarily applied.

The above described process will, it is believed, greatly increase the applicability of the acid Bessemer process for the production of steel, by rendering available for this process enormous deposits of non-Bessemer grade ore in which the ratio of iron to phosphorus lies below one thousand. Since Bessemer grade ore is sold at a premium and is becoming increasingly scarce, the cost of treatment with zirconium will be largely, or more than off-set by the lower price of ore. At the same time the advantages peculiar to the acid Bessemer process will be retained. Similarly, in the case of the acid open hearth process it will be possible to utilize scrap steel, pig iron and iron ore higher in their phosphorus content than the limits which practice has heretofore established. Also in the manufacture of basic open hearth steel the use of zirconium in accordance with this invention will make it possible to finish the heat at a higher phosphorus content than is the present custom, a change of practice of which the benefits will be obvious to those familiar with this art. The production, by means of any of these or other standard processes, of high phosphorus steel, rendered acceptable to engineering specifications because of treatment with zirconium, is regarded as an integral part of the present invention.

Claims:

1. Process of treating high phosphorus steel to counteract the detrimental effects of the phosphorus and increase the Izod impact number which comprises adding zirconium to the steel.

2. The process of treating high phosphorus steel to counteract the detrimental effects of the phosphorus and increase the Izod impact number which comprises adding to the steel 0.02 to 0.50% of its weight of zirconium.

3. As a new composition of matter, high phosphorus steel containing zirconium.

4. As a new composition of matter, high phosphorus steel containing zirconium and upward of 0.5% carbon.

5. As a new composition of matter, high phosphorus steel containing zirconium and upward of 0.6% carbon.

6. As a new composition of matter, high phosphorus steel containing zirconium and characterized by a high Izod impact number as compared with a steel of like composition free from zirconium.

In testimony whereof, I affix my signature.

FREDERICK M. BECKET.