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METHOD FOR PRODUCING NITRIDE-BEARING LOW-CARBON DUCTILE STEEL

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4 Claims. (Cl. 75—129)

This application is a divisional application of my earlier filed application Serial No. 88,411, filed February 10, 1961, which is more particularly directed to the composition of nitride bearing steel.

This invention relates to processes for production of nitride-bearing low carbon ductile steel.

This invention is concerned with obtaining a new nitride-bearing low carbon ductile steel containing from 0.015% to 0.090% by weight of a stable nitride selected from the group consisting of beryllium nitride, columbium nitride, a combination of aluminium nitride and beryllium nitride, a combination of aluminium nitride and columbium nitride, a combination of beryllium nitride and columbium nitride and a combination of said three nitrides which possess certain degree of solubility into the solid state steel at an elevated temperature and/or from 0.01% to 0.10% by weight of another kind of nitride selected from the group consisting of titanium nitride, zirconium nitride and a mixture of both nitrides which has practically no solubility in the steel either in the solid or molten state and further less than 0.35% by weight by carbon and if desired, less than 1% by weight of alloying element selected from the group consisting of nickel, chromium, molybdenum, vanadium, manganese, silicon and like.

I discovered that a steel containing a nitride or a plurality of nitrides, a part of which is dissolved in the matrix thereof and another part of which exists as free nitride therein, is capable of precipitating out dispersedly its nitride at its grain boundaries and within its grain during the plastic working performed at an elevated temperature, and that such steel with the structure as described above possesses mechanical properties far superior to a steel with the same composition, particularly as regards its low temperature toughness which is remarkably improved and the transition temperature which is markedly shifted towards a lower temperature.

Nitride-bearing low carbon steels of this invention are produced by one of the following two processes. According to these processes nitride-bearing low carbon steels may be obtained by blowing into molten steel nitrogen gas or a mixed gas compound of nitrogen and an inert gas thereto or by blowing calcium cyanamide into the melt with nitrogen or an inert gas or a mixture gas thereof during the reduction period of the steel-making process to render the molten steel nitrogen-bearing. Subsequent to the nitrogen enrichment there is added one or more of such metal elements as aluminium, beryllium, and columbium which combine with the nitrogen to form metallic nitride that possesses a certain degree of solubility in the solid state steel, to be thereby nitridized by the said nitrogen within

the aforementioned molten steel. Thereafter there is added zirconium or titanium or both, to yield even more stable nitrides, and thereby convert the excessive nitrogen into a further nitride or nitrides. Thereafter, if desired, the steel thus produced may be heat treated to precipitate out a part of the nitride, whereafter the steel is subjected to a plastic deformation at an elevated temperature by such rolling or forging or the like.

The steels utilized in this process are pure iron, low carbon steels with approximately 0.35% carbon or less, or low carbon low alloy steels containing alloying elements other than carbon in less than 1.0% each.

I have found that when from 0.010% to 0.10% of nitride or nitrides of metal or metals such as aluminum, beryllium, or columbium are present in a steel, the said steel possesses superior mechanical properties at atmospheric and elevated temperatures, particularly as regards its impact strength at a low temperature while the transition temperature is remarkably shifted to a lower temperature, as compared to the properties expected of a steel with the same components except the nitride.

The nitride-bearing steel may be successfully produced using any one of an over-blowing converter, an open-hearth furnace, an electric arc furnace, or a high-frequency electric furnace, and the production method can be placed into two categories, as now will be described more fully in the following.

The first category consists in blowing into molten steel nitrogen gas or a mixed gas composed of nitrogen and a gas or gasses that is inert thereto (for example, a mixed gas constituted of nitrogen and argon or helium or the like), subsequently adding thereto one or more than one kind of metal that reacts with nitrogen to form a hard nitride having a certain degree of solubility to solid state steel, such metal being selected from the group consisting of aluminum, beryllium, or columbium, to form a nitride-bearing ductile steel. One practical example of producing ductile steel in an electric arc furnace by the process mentioned above is now described in detail.

EXAMPLE 1

Firstly, scrap steel was melted in an electric arc furnace and refined under oxidizing conditions, then 0.35% of ferro-silicon and 0.70% of ferromanganese were added for deoxidation, then nitrogen gas was blown into the molten steel through a conduit pipe for about 6 minutes at a pressure of 5 kg./cm.^{2}, following which stage and finally, 0.20% of aluminium in one case or 0.10% beryllium in the other was added prior to casting of the steel into ingots. The Table 1 shows the chemical composition of two (2) representative steels produced by the aforementioned process.

Table 1

Steel	C	Si	Mn	P	S	N_2	Al	AlN	Al_2O_3	Be	Be_3N_2
B	0.07	0.25	0.61	0.015	0.022	0.035	0.15	0.088	0.020	------	------
D	0.07	0.31	0.65	0.015	0.022	0.015	0.006	------	------	0.120	0.024

As may be seen, a part of the aluminum which is added is combined with the oxygen that was present at the molten steel to become aluminium oxide, while the rest of the aluminum is retained as aluminium nitride. Also, the beryllium nitride, Be_3N_2, was clearly shown by the chemical analysis.

Nextly, ingots thus produced were brought to a temperature between 1150° C. and 1250° C., which corresponds to a state where the nitride exists partially in a dissolved and partially in a solid phase, and the steel was then forged thereat and finished at a temperature 850° C. The steel was then left to cool to atmospheric temperature, subsequent to which process, the said steel was heated again at 950° C. for one (1) hour, then cooled in air. Table 2 compares the mechanical properties of steels produced by the above method with a commercially available high killed mild steel with a comparable chemical composition.

Table 2

Steel	Tensile strength, kg./sq. mm.	Yield point, kg./sq. mm.	Elongation, percent	Reduction of area, percent	Impact value,[2] kg.-m./sq. cm.	Tr15, ° C.	Trs, ° C.
B	42.0	32.0	40.0	79.0	35.5	−105	−85
D	46.7	38.0	39.0	71.0	31.0	−100	−70
Mild steel [1]	44	30	28	57	8.0	−47	−30

[1] 0.13% C. killed.
[2] At 0 ° C.

From the table it can be stated that the present method is fully capable of producing a nitrogen-bearing ductile steel. The present method can be applied to, other than an electric arc furnace as described above, such as for example to an over-blowing converter, an open hearth furnace, a high frequency electric furnace, or the like with the same result.

Furthermore, this process of nitrogen blowing has an additional effect of obtaining cleaner steel by virtue of the stirring action the nitrogen gas induces within the molten metal, thus stimulating the coagulation of various deoxidization products that are present therein.

If a nitride bearing steel is to be produced by the aforementioned process and the ingot is not stabilized, or killed, it becomes similar to a so-called rimmed ingot containing blow holes therein since an amount of nitrogen gas that is left uncombined tries to escape therefrom as the metal solidifies. However, even this kind of ingot is of no disadvantage when offered for sale on the market, as far as the quality of the steel is concerned, since the aforementioned blow holes can readily be welded together during forging or rolling.

However, killed steels are often more desirable when higher quality ingots are wanted. In order to achieve this purpose, it generally requires in heretofore known processes a quantity of aluminium, if used alone of about 1%.

I have succeded in stabilizing, or killing, the nitride-bearing ductile steel by fixing the excessive nitrogen gas that would escape therefrom upon its solidification by means of a metal or metals that form even more stable nitride or nitrides than those of aluminium or beryllium and which do not dissociate at a solidification temperature of the steel. Of metals with aforementioned property, titanium and zirconium were found to be most suitable, and an addition of about 0.03% to 0.3% thereof was seen to be sufficient to achieve the purpose. The titanium nitride and zirconium nitride resulting therein are all insoluble in the molten steel, one part of which is eliminated therefrom, while the rest is floating therein and becomes finely and dispersedly suspended therein as the steel solidifies. The particles of said metallic nitride in a form as described above, have no adverse effects whatsoever on the steel, and even have a favorable influence on the steel.

In Table 3 are shown the chemical composition and mechanical properties of a steel produced by the process described above.

Table 3

Steel	C	Si	Mn	P	S	N_2	Al	Zr	AlN	Al_2O_3	ZrN
B [1]	0.08	0.23	0.57	0.016	0.021	0.032	0.085	0.06	0.084	0.021	0.02

Tensile strength, kg./sq. mm.	Yield strength, kg./sq. mm.	Elongation, percent	Reduction of area, percent	Impact value,[2] kg.-m./sq. cm.	Tr15, ° C.	Tra, ° C.
41.0–42.2	31.5–33.5	39.2–40.7	77.4–78.4	36.0	−100	−80

[1] Ductile steel.
[2] At 0° C.

It may be seen that the fixation of free nitrogen by means of adding such metallic element selected from the group consisting of zirconium and titanium is evidently effective for producing killed steel.

The second method involves adding calcium cyanamide to the steel at the reduction period of steel-making process, so that nitrogen is introduced into the molten steel as a result of decomposition of said agent. The calcium cyanamide is added by blowing the calcium cyanamide into the molten steel together with an inert gas for example, argon or nitrogen or a mixed gas consisting of nitrogen and an inert gas, so that nitrogen is introduced into the steel as a result of decomposition of said agent or of a direct reaction of gaseous nitrogen or both, and subsequent to the above, an amount of a metallic element or elements that yield the desired nitride is introduced as before, thus rendering the steel nitride-bearing and ductile.

I therefore particularly point out and distinctly claim as my invention:

1. A method of manufacturing nitride-containing ductile steel, the nitride being selected from the group consisting of aluminum nitride, beryllium nitride, columbium nitride and mixtures thereof, comprising impregnating molten steel with nitrogen to a content of at least 0.010% nitrogen by blowing into said molten steel a gas selected from the group consisting of nitrogen gas and mixtures of nitrogen gas with gases which are inert to molten steel, said gas being blown into said molten steel at a pressure of substantially 5 kg./cm.^{2} and then adding to the thusly nitrogen-impregnated steel a material selected from the group consisting of aluminum, beryllium, columbium and combinations thereof.

2. A method as claimed in claim 1 comprising adding to the nitrogen-impregnated molten steel a further material selected from the group consisting of zirconium, titanium, and combinations thereof.

3. A method as claimed in claim 1 comprising blowing calcium cyanamide into the molten steel, along with said gas, under a pressure of substantially 5 kg./cm.^{2}.

4. A method as claimed in claim 1 comprising solidifying the molten steel, heating the solidified steel to a temperature sufficient to cause a portion of the nitrides formed with said material to exist in the free solid phase and the remaining portion to be dissolved in the matrix and then working the heated solidified steel.

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