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The Role of Ferroboron and Ferrotitanium in Steels: Production Methods, Quality Aspects, and Addition Techniques

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This paper indicates some of the reasons why boron and titanium are added to steels, especially the stainless varieties. It mentions the addition techniques for introducing the elements into the steel, and highlights the production routes for the two ferroalloys.

An attempt is made to show how a ferroalloy producer can be of service to the steel industry, the key areas for both the alloy producer and the steelmaker being those of improving quality and developing new and better products.

Introduction

This paper highlights some details as to why boron and titanium are added to chromium-containing steels, particularly the stainless types, and gives information relative to the production of both ferroboron and ferrotitanium.

Boron

Certainly the best known and most widely used addition of boron to steel is to improve the hardenability of carbon and alloy steels. This effect has been known since the late 1930's but, as this Congress is specifically designed around chromium steels and alloys, this paper will concentrate on the other uses of boron.

Boron markedly affects the mechanical properties of stainless steels, specifically their

- hot shortness
- creep resistance
- intergranular corrosion resistance
- neutron-absorption capacity.

Hot Shortness

The low ductility of austenitic stainless steel and some superalloys at hot-working temperatures causes cracking or tearing in rolling and forging operations. The highly alloyed grades are particularly prone to this phenomenon, which is often referred to as hot shortness.

In the mid 1950's, it was established by Armco Steel Corporation[1] that small additions of boron eliminate hot-shortness problems by significantly increasing the hot ductility and workability of these steels (Figure 1). This, in turn, enables the steel producer to achieve the maximum yield of mill products by eliminating the necessity for expensive reheating cycles and costly grinding operations to remove surface defects.

The amount of boron required to produce a measurable increase in hot ductility is very small. The effect of boron levels on type 316L stainless steel is shown in Figure 2, and

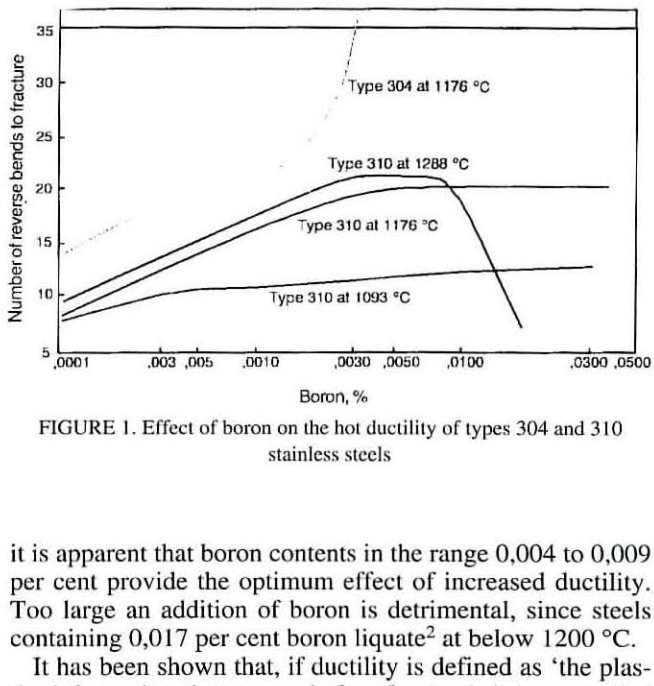

FIGURE 1. Effect of boron on the hot ductility of types 304 and 310 stainless steels

it is apparent that boron contents in the range 0,004 to 0,009 per cent provide the optimum effect of increased ductility. Too large an addition of boron is detrimental, since steels containing 0,017 per cent boron liquate[2] at below 1200 °C.

It has been shown that, if ductility is defined as 'the plastic deformation that occurs before fracture', it is controlled by the nucleation and propagation of cracks, together with the dislocation and grain-boundary processes that influence the deformation of the matrix[2]. Thus, alloying elements influence the hot ductility in one of two ways:

(a) by modifying the inclusions
(b) by affecting the dynamic recovery and recrystallization process.

It is believed that boron may influence the fracture process by its effect on non-metallic inclusions.

Creep

The beneficial effect of small additions of boron on the creep properties of stainless steels has been known for

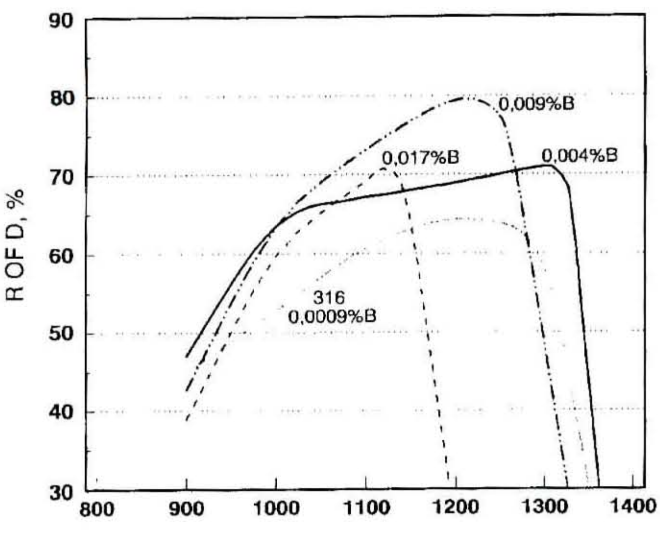

FIGURE 2. Effect of boron additions to type 316

many years, and is manifested[3] by a substantial increase in creep-rupture life that is usually accompanied by a simultaneous increase in creep ductility, as seen in Figure 3. It is believed that these improvements are associated with the reduction in grain-boundary cavitation attributable to the influence of boron in the size and distribution of borocarbides.

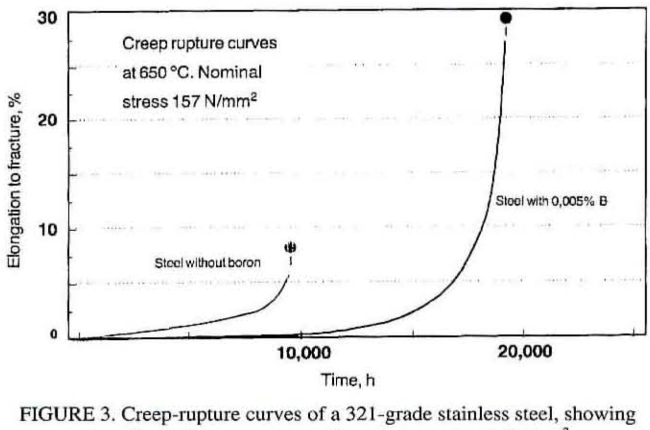

FIGURE 3. Creep-rupture curves of a 321-grade stainless steel, showing the effect of boron on creep lfe and elongation to failure[3]

An addition of 0,005 per cent boron (50 p.p.m.) to types 316, 321, and 347 stainless steels increases the main stress-rupture life by a factor of 3. There is evidence that the effect is related to the composition in that stabilized grades show marked improvements in stress-rupture properties while type 304 (with no molybdenum, titanium, or niobium) remains unaffected.

Intergranular Corrosion

Unstabilized stainless steels such as type 304 are susceptible to intergranular corrosion due to chromium depletion at grain boundaries when chromium carbides are precipitated during sensitization. There is evidence to show that, even in concentrations as low as 4 p.p.m., boron can retard the precipitation of chromium carbides with significant beneficial effects on the intergranular corrosion of sensitized stainless steels. This is illustrated in Figure 4.

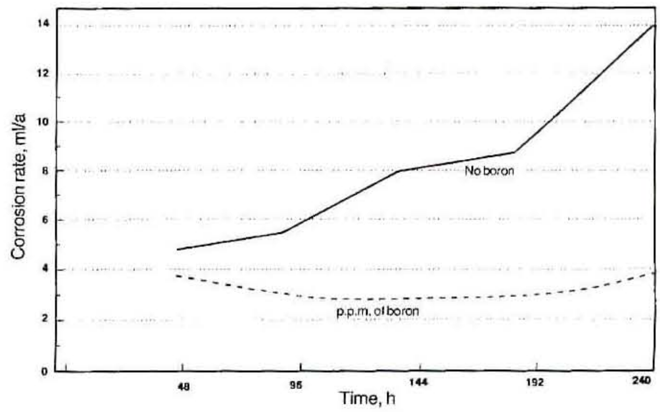

FIGURE 4. Effect of 4 p.p.m. of boron on the corrosion rate of type 304 stainless steel

Nuclear Applications

Boron has a high capacity for neutron absorption, and is added to highly alloyed stainless steels for use in the nuclear industry. The boron is added to the molten steel in the form of ferroboron, in which boron exists as a mixture of two isotopes, B^{10} and B^{11}. The B^{10} isotope, which is present as approximately 20 atomic per cent, is the one that provides the absorption effect[5].

Superalloys

While increased hardenability accounts for most of the metallurgical consumption of boron, other uses for the element have already been mentioned, and the improvements in creep resistance and hot workability of austenitic stainless steels extends to many nickel- and cobalt-based superalloys. Alloys such as Incoloy 713C, B 1900, MarM 200, and Waspalloy, used mainly in jet-aircraft turbines, contain significant levels of boron (0,006 to 0,015 per cent).

Methods of Addition of Boron to Steel

Boron is generally added to steel in the form of ferroboron. It combines aggressively with oxygen and nitrogen dissolved in steel, and it is thus necessary to exercise care in steelmaking to prevent such reactions; otherwise, the effectiveness of the boron will be irretrievably lost.

A standard practice is to reduce the oxygen levels to a minimum, probably with a calcium silicon treatment, and then to add ferroboron to the ladle between the time the ladle is 1/4 to 3/4 full, but certainly after all the other alloying additions have been made. Precautions against re-oxidation of the heat are recommended. Recoveries of 60 to 65 per cent are normal, and up to 80 per cent can be achieved with carefully controlled practice.

Production and Quality of Ferroboron

Until well into the 1970s, ferroboron was produced by the aluminothermic reduction of boric oxide. While producing a good product, the process used expensive aluminium powder and boric oxide – an expensive form of boron. Inherent in this process was a high residual aluminium content, well in excess of 1 per cent, thus making the alloy unsuitable for certain applications.

Today, most ferroboron is produced by the carbon reduction of boric acid in small electric-arc furnaces (Figure 5). Since the use of ferroboron in the Western World is still only around 8 kt per annum, large-scale ferroalloy furnaces are not required.

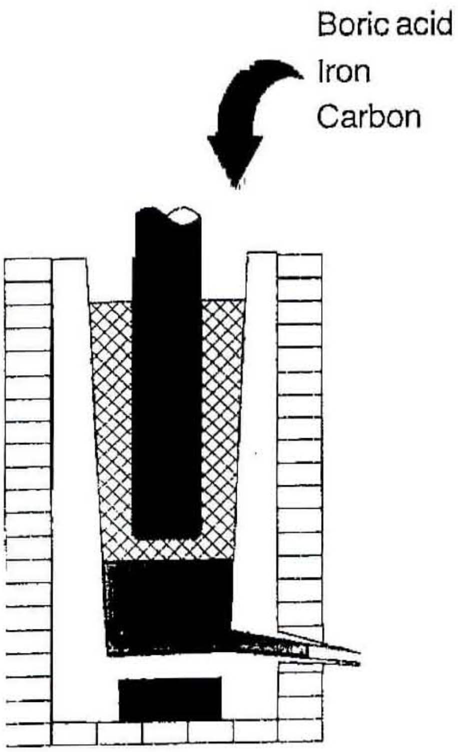

FIGURE 5. The single-phase arc furnace

Typical analyses of the material produced by the two production routes are given in Table I.

TABLE I
ANALYSES OF FERROBORON FOR THE TWO PRODUCTION ROUTES USED

Element	Aluminothermic %	Carbothermic %
Boron	17 to 20	17 to 20
Aluminium	4 max.	0,2 max.
Carbon	0,1 max.	0,5 max.
Silicon	1 max.	0,5 max.
Iron	Balance	Balance

The main differences in the two products are the carbon and aluminium contents, but the London & Scandinavian Metallurgical Co. Limited (LSM), by fully explaining its commitment to quality assurance, has been able to explain to the customer that raising of the carbon level from 0,1 per cent maximum to, say, 0,5 per cent maximum has no adverse effect on the steel quality when boron is added to the steel at the 25 to 50 p.p.m. level. (i.e. a carbon increase in the steel of 0,7 to 1,4 p.p.m.).

The quality requirements of ferroboron demanded by the steel industry continue to grow in respect of its chemical composition, sizing, and cleanliness. To upgrade the quality on a regular basis, improved procedures are required throughout the process. The words *quality control* are now deliberately avoided since the true requirement is quality assurance of the production from the purchase of the raw materials to a thorough understanding of the customer's requirements.

Titanium

Titanium is highly reactive in steelmaking processes with elements such as carbon, oxygen, nitrogen and sulphur. While this accounts for some of the desirable properties, it also leads to some of the difficulties.

Titanium additions can be made in the form of metal scrap, sponge or, more normally, as a ferrotitanium alloy. Originally, ferrotitanium was supplied as a 40 per cent titanium alloy made by the aluminothermic process. With the increasing use of titanium metal in the aerospace industry, large volumes of turnings and other forms of titanium scrap became available at relatively low prices. This led to the present production route, which converts the titanium scrap into a eutectic grade containing 70 per cent titanium.

From Figure 6 it can be seen that the 70 per cent alloy has the lowest melting point of all alloys.

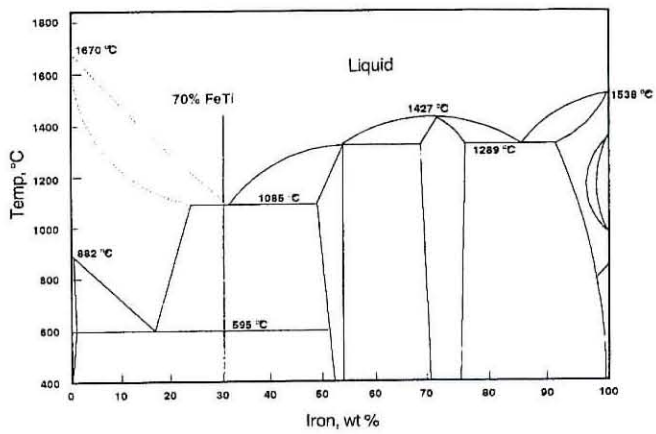

FIGURE 6. The ferrotitanium phase diagram

The 70 per cent ferrotitanium alloy has a number of advantages over the 40 per cent alloy.

(1) With a melting point of around 1100 °C compared with 1500 °C for steel, it goes into solution more rapidly.
(2) The lower melting point of the 70 per cent eutectic alloy enables it to be added to the ladle rather than to the furnace, thus increasing the recovery.
(3) With a higher titanium concentration, a smaller addition of the 70 per cent alloy is required, and thus the chilling effect is reduced.
(4) With a lower inherent aluminium content, the 70 per cent grades give a cleaner steel.

Stabilization of Stainless Steels

By far the major use of ferrotitanium is in the production of stainless steel (approximately 50 per cent). Unless austenitic steels are stabilized, reheating in the range 400 to 900 °C causes precipitation of chromium carbide, the amount of which depends on the time and temperature. Precipitation of chromium carbide may also occur on slow cooling from the annealing temperature.

Precipitation usually takes place preferentially along the austenitic-grain boundaries, and the regions immediately adjacent to the grain boundaries become denuded of chromium with a consequential loss in corrosion resistance and a tendency to disintegrate in certain corrosive media. This effect occurs when some types of stainless steel are welded, and the corrosion resistance of the material in the heat-affected zone is seriously impaired – a feature commonly known as weld decay.

The problem is readily overcome by the use of certain grades of stainless steel containing additions of titanium (5 times the carbon content). These so-called stabilized steels can be welded by normal methods.

The titanium forms a stable carbide that dissolves in the austenite only at very high temperatures. Consequently, the carbon in solution is low when the steel is annealed at normal temperatures, and the possibility of subsequent precipitation of chromium carbide as a continuous grain-boundary phase is thus prevented.

Production of Ferrotitanium

Raw materials for the manufacture of ferrotitanium are purchased from around the world from approved sources. They can be in many forms, such as turnings, sheets, heavy sections. Careful sampling is required; this is not easy in the case of mixed lots of turnings and small solids, but is relatively easy on large plate. The materials are subjected to crushing, degreasing for turnings, or cutting to size for solids. Blends are made up and charged into the coreless induction furnace with ferrous scrap. The reaction is extremely vigorous and aggressive on furnace linings. After alloying, the melt is poured into a large cast-iron pan and, after solidification, the material is crushed, sieved, blended, and packed.

Additions and Recovery

Prior to the addition of ferrotitanium, the steel should be thoroughly de-oxidized to avoid oxidation of the titanium and thus maximize the titanium recovery.

Many of the steelworks in the UK utilize secondary ladle steelmaking units, and in these cases the ferrotitanium is added during this cycle.

The recovery of titanium is affected by the steelmaking practice but, for ladle additions, is generally in the range 60 to 70 per cent. For cored wire, where the addition is made late and deep into the ladle, recoveries of around 90 per cent are the norm.

Ferrotitanium Specifications

The specifications for many ferroalloys, drawn up by the user, are based on his requirements, and there has generally been little consultation with the ferroalloy producer. This has led to a situation in which the specifications are unnecessarily tight and thus restrictive to the producer. For example, many customers in the UK, Continental Europe, and the USA stipulate a maximum aluminium content of 4,5 per cent, which cannot be produced from a 100 per cent charge of the 90–6–4 alloy (titanium–aluminium–vanadium), i.e. the most common scrap arisings. This, in turn, necessitates the use of a higher-priced commercially pure grade of scrap, thereby increasing the price of the alloy. In many cases, this 4,5 per cent restriction could readily be increased to between 5,0 and 5,5 per cent with no detrimental effect to the steelmaker.

This argument can, of course, be applied to many other elements such as lead, bismuth, tin. The levels of tolerable elements vary depending upon the application.

Low-nitrogen Ferrotitanium

Currently, one element that is causing a great deal of concern, especially in the stainless-steel field, is nitrogen.

Most commercial stainless steels are produced by ladle steelmaking processes, i.e. AOD, VOD, VAD, and the carbon levels are lower than ever. Austenitic and ferritic steels thus need less niobium or titanium for stabilization.

There has always been some controversy over the precipitate phases obtained in preventing the formation of intergranular chromium carbide, $Cr_{23}C_6$. In niobium steels, the phase is almost certainly a carbonitride, $Nb_4 [CN]_3$. In titanium steels, it is generally accepted that two phases, titanium carbide and titanium nitride, are formed, with some slight solubility of the other interstitial elements.

Since titanium nitride forms preferentially to titanium carbide according to thermodynamic considerations, it is essential *either*

(1) to add sufficient titanium to tie up the nitrogen first of all and then the carbon

or

(2) to reduce the nitrogen as low as possible by other techniques.

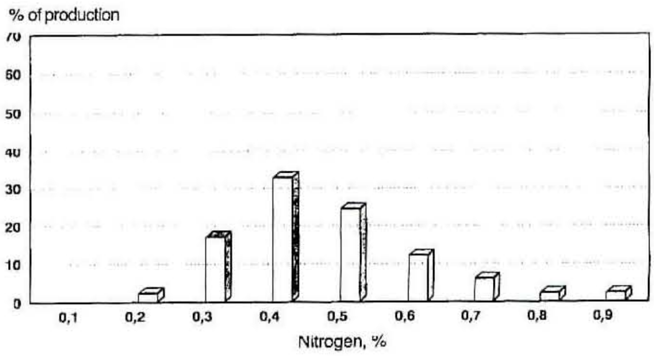

FIGURE 7. Nitrogen levels in standard-production ferrotitanium

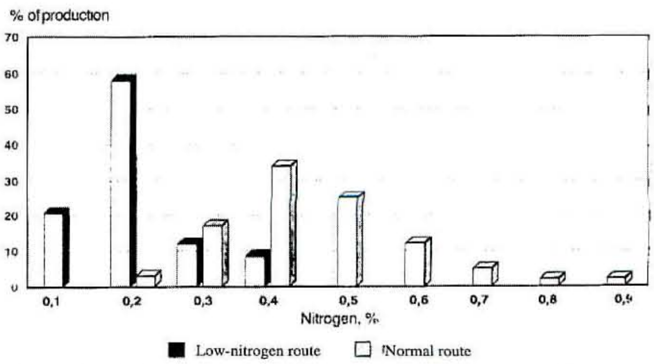

FIGURE 8. Comparison of low-nitrogen ferrotitanium-production route

One factor that can assist in this aim is, of course, the production of a low-nitrogen ferrotitanium.

The nitrogen levels in standard-production ferrotitanium are shown in Figure 7, and the reduction of these to the required 0,3 per cent maximum for the bulk of the production at LSM presented many problems. Nevertheless, based on the same sound quality-assurance techniques as apply to the production of ferroboron, this was achieved, as shown in Figure 8.

Conclusion

Experience at LSM has shown how a ferroalloy producer can be of service to the steel industry, the key areas for both the alloy producer and the steelmaker being those of improving the quality and developing new and better products. In line with these aims, it is felt that a greater dialogue between the customer and the producer can be of mutual benefit both commercially and technically.

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