MICRO-METALLURGY OF ALLOY STEELS

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Abstract

Whilst extensive literature exists on the effects on the properties of steels of alloying elements present in relatively large amounts, data are scanty and dispersed on the role of minute additions which exercise relatively far larger physical and metallurgical effects. The elements involved may be added in traces or present in residual amounts. It has been endeavoured to highlight the highly beneficial effects of minute additions in many respects, such as those of rare earths to cast plain carbon and boron-treated steels, to wrought steels, to high-alloy stainless steels, etc. The subject is of recent development, but is of great importance in view of the immense resources in India of the rare earths group of minerals.

The extraordinary effects of minute additions of boron to heat-treatable and carburizing grades of steels in promoting hardenability have also been brought out. In this paper, the value of boron in replacing a sizeable quantity of nickel, chromium, molybdenum and other critical elements has been emphasized. Boron is most effective in steels of low carbon content. The relative position of boron steels in the U.K. and the U.S.A. has been reviewed and mention made of grades of boron steels in production, both of the plain carbon and alloy types. Attention is also drawn to applications for which boron-containing steels have special merits and warrant consideration other than as substitute materials.

The subject of stabilization of carbides by minute additions of carbide-stabilizing elements has been touched upon in relation to inter-granular brittleness and weld decay in austenitic stainless steels.

Introduction

IN the present context, micro-metallurgy means the metallurgy of minute additions. In the past many connected with the science and practice of metallurgy have been fully aware of instances of highly damaging effects of minor amounts of impurities, including gases, tramp elements and metalloids. The study of these damaging impurities has perhaps constituted a major proportion of research carried out on steels, but it is only recently that it was realized that minute additions may confer extraordinary beneficial effects. The general subject was brought to the fore recently by several striking instances — (i) the case of semiconductors, which have led to the development of transistors, now effecting revolutionary changes in the communications industry, and (ii) the highly beneficial effects of minute additions of rare earths to plain carbon cast and wrought steels, high-alloy steels and stainless steels; (iii) the effects of minute additions of boron in promoting hardenability in heat-treatable and carburizing grades of steels. The value of 0·003 per cent boron in replacing sizeable quantities of nickel, chromium, molybdenum and other critical elements is now established and utilized in many steel-producing countries, particularly in the United States; (iv) the stabilization of carbides by small additions of carbide-stabilizing elements in suppressing intergranular brittleness and weld decay in austenitic stainless steels.

Of these perhaps the most striking cases are those of boron in acting on hardenability of steel when added to the extent of 10-30 parts in a million and the role of cerium in amounts ranging to 20 parts in a million in lowering the tough to brittle transition of mild steel — a change which caused many failures in welded liberty ships during World War II. The highly beneficial role of minute additions of aluminium introduced to the extent of 200-500 parts to a million has also been well established in improving impact toughness and in suppressing temper-brittleness through the lowering of ductile to brittle fracture temperature ranges. Valuable research has been done in India on this important subject.

Cerium has also been shown greatly to improve the oxidation characteristics of nickel-chromium alloys such as the 80-20 wires and grids used for electrical heating elements. The preferred additions consist of a few hundredths per cent alkaline earth metals, preferably calcium, along with 0·15-0·2 per cent of rare earth metals, preferably cerium. Similar results are achieved by the introduction of calcium 0·03 per cent residual, thorium (say, 0·07 per cent) and a few hundredths parts per cent of phosphorus, arsenic or antimony.

Addition of vanadium to the extent of 0·02-0·05 per cent in carbon and low-alloy steels contributes temperature stability and small particle size to the carbide phase. Similar additions of vanadium are made to heavy forgings to insure adequate yield strength with maintenance of the highest ductility in transverse and radial directions. These small vanadium percentages are also added to low-carbon medium-manganese plate along with minute amounts of titanium and in a number of constructional low-alloy steels where 0·04 per cent vanadium contributes to maximum hardenability. At slightly higher levels, vanadium is useful in steel castings.

Austenitic Stainless Steels

It is established that austenitic steels of the nickel-chromium type with a maximum carbon content of 0·03 per cent serve adequately without damage or deterioration due to intergranular brittleness through what is known as weld decay. However, in the steels of 0·06-0·08 per cent carbon contents, carbides are liable to form which are mainly chromium carbide (Cr_4C), every 0·1 per cent carbon being combined with 15-18 times its amount of chromium, and these impoverish the steel locally in chromium which is the basis of the corrosion resistance. When these steels are heated in the critical temperature range, the carbon being a small interstitial atom diffuses fairly quickly from the interior of the crystal to reach the grain boundaries, at which carbide precipitation occurs; the chromium atom diffuses at these temperatures relatively far more sluggishly and the chromium entering the precipitate is thus derived mainly from contiguous regions. These areas thereby suffer a severe loss of chromium resistance in service. Austenitic stainless steel, whilst in this condition, if subjected to corrosive conditions, suffers rapid attack at grain boundaries and even disintegrates in time. In very recent work it has been shown that austenitic stainless steels are heated for very long periods in the sensitizing range of temperature, they show susceptibility in the standard boiling 65 per cent nitric acid test even though their carbon content may be as low as 0·017 per cent. The phenomenon can be counteracted by introducing elements in minute amounts which have greater affinity for carbon than chromium. The most commonly used additions introduced in micro amounts to prevent intergranular corrosion of stainless steel are of titanium — niobium and tantalum are also effective.

The improvement in oxidation resistance to steels caused by additions of aluminium, silicon and chromium are well known; the latest to enter the field is beryllium. The effect of zirconium in inhibiting hairline cracking due to the presence of hydrogen in inconel castings, has also been lately demonstrated. All these topics are of interest to India owing to the abundant resources of the relevant raw materials.

Rare Earths — Not so Rare Now

'Rare' earths may no longer be the proper terminology for the oxides of elements

57-47-71. Current interest in thorium has caused an increase in its production, and since monazite sand, the principal ore for both thorium and rare earths, contains roughly 5 per cent thorium oxide and 50 per cent mixed rare earth oxides, each pound of thorium produced carried with it production of about 10 pounds of rare earth metals. These are:

Atomic No.
57 Lanthanum
58 Cerium
59 Praseodymium
60 Neodymium
61 Promethium
62 Samarium
63 Europium
64 Gadolinium

Atomic No.
56 Terbium
66 Dysprosium
67 Holmium
68 Erbium
69 Thulium
70 Ytterbium
71 Luterium

39 Yttrium
90 Thorium } Not rare earths, but always occur with them

Rare Earth Additions to Stainless Steels — The martensitic and ferritic steels hot-roll easily and no special additions are required to promote workability; austenitic steels are more difficult to hot-roll, being characterized by two types of hot-shortness, one due to a duplex austenite-ferrite structure, the other inherent in the higher-alloyed steels of this type; hot-shortness due to duplex structure can be prevented by correct balance of the constituent elements, by judicious selection of the hot-rolling temperature, and by soaking for adequate periods at suitable temperatures prior to hot-rolling; inherent hot-shortness in higher alloy austenitic stailness steels increases with the size of the ingot, and is considered to be related to coarseness of grain. Addition of a deoxidizing ferro-alloy, containing substantial proportions of titanium and aluminium, effects some improvement, but hot-shortness is best counteracted by the addition of rare earth metals or oxides. Experiments with rare earth metals done by Herke and Lula[1] showed that best results are obtained by the use of 4-5 lb. per ton of steel. Such additions tend, however, to impair the cleanliness of the steel: impurities resulting from them segregate close to the surface of the ingot, giving rise in the finished sheet material to a defect designated as 'hairs'. These 'hairs' are associated with cracking during upsetting of the bar.

In view of these findings, and in the interests of economic production, experiments were made with rare earth oxides. When used in amounts of about 3 lb. per ton in steels already treated with deoxidizing ferro-alloy, or to the extent of 5 lb. per ton in steel not previously treated with a special deoxidizer, highly successful results were obtained. Cerium appeared to be the most potent constituent in the rare earth oxide addition, and the optimum amount of rare earth oxide addition was 0·036-0·400 per cent express as cerium.

Work carried out by the Allegheny-Ludlum Steel Corporation has proved the use of rare earth oxide additions to be so advantageous that it has been adopted as standard in their plant, and ingots for which a two-stage conversion was previously necessary can now be hot-rolled in a single stage. Ingot yield has also markedly improved.

Evans[2] has summarized the effects of rare earth metal additions on austenitic and ferritic steels as follows:

'During the past four or five years other important effects have been attributed to the rare-earth metals, for example, increased ductility, at forging and rolling temperatures of austenitic steels and improved mechanical properties of ferritic steels, resulting from the addition of mischmetal or lanceramp. In the U.S.A., from where most of the published information on this subject has emanated, these developments have been acclaimed as two of the most important in the ferrous field during the last half-century. With regard to the stainless steel field, treatment of the molten steel by mischmetal is reported to effect considerable improvement in the hot-workability of the austenitic types. In other grades, such as 19-10 chromium-nickel, 22-12 chromium-nickel and 16-10-2 chromium-nickel-molybdenum, which are not considered exceptionally difficult to work, the addition of mischmetal has increased the ingot-to-slab yield by a value of 6-12 per cent, an improvement which amply compensates for the cost of the rare earth metal addition. Furthermore, the appearance of the edges and the surfaces of the hot-finished strip are more satisfactory and required less grinding. It has been found that for this purpose residual contents of the order of 0·02-0·05 per cent of rare earths are required in the steel. The more outstanding effect of the rare earths is evident in the more highly alloyed stainless steels. Although steels such as those containing 20 per cent chromium, 26 per cent nickel, 3 per cent molybdenum and 3 per cent copper, required for exposure to severely corrosive conditions, have been available in the form of castings, only small quantities have been produced in wrought form, due to the poor hot-workability of this steel. Treatment of such steels with mischmetal, to give a residual content of about 0·20 per cent rare earths, has made possible rolling to plate and strip with a reasonably good yield. There is a critical range of cerium and lanthanum contents required to obtain the best hot-working properties, and that the maximum amount of rare earth metals essential for maintenance of hot-workability decreases as the nickel content increases.'

As an alternative to mischmetal, austenitic steels have been successfully treated with rare earth metal oxides in the form of 'T' compound, added together with suitable reducing agents, such as calcium boride and sodium nitrate. Although the hot-workability of the lower alloy austenitic steels has been improved by such treatment, there is some doubt whether this mixture is effective in the more highly alloyed steels. Additions of cerium fluoride have also been found to improve hot-workability, but only in the lower alloy austenitic steels containing titanium. In contrast to the residual amounts of cerium and lanthanum in the finished steels treated with mischmetal, no rare earth elements were found in the steels after treatment with the oxide or the fluoride which probably accounts for the relative ineffectiveness of the alternative addition agents.

The mechanism for the improvement or promotion of hot-workability of austenitic steels by treatment with mischmetal is also not clearly understood. It is thought that such additions more completely deoxidize the melt, a condition which could contribute to improved hot-workability. Further, it is known that rare earth metals, when present in sufficient amounts, can prevent the hot-shortness developed by sulphur, but it is also possible that, as in cast iron, the rare earth metals act as 'scavengers' and counteract the harmful effects of subversive elements such as lead, tin and silver, which are known to impair the working properties of stainless steels.

Similar treatment with rare earth metals has been found to have a beneficial effect on the ductility and toughness, at ordinary and sub-zero temperatures, of cast carbon and low-alloy steels[3]. Reports of the work carried out in this field indicate that mischmetal and lanceramp are employed; either is added after deoxidation of the steel with aluminium. Lanceramp, containing 30 per cent or more of lanthanum, has been claimed to be more potent than mischmetal in its beneficial effects on carbon and low-alloy steels. The influence of this treatment for a cast 0·24 per cent carbon steel in which it will be noted that, by adding 4 lb. of mischmetal per ton of steel, the elongation, reduction of area and impact values are increased, and, further, that the higher level of impact properties is maintained at sub-zero temperatures. Similar improvements in these properties are obtained also in cast low-alloy steels after quenching and tempering to any hardness level. In addition to the beneficial influence of rare earths on the mechanical properties of cast steels, it has been reported that the fluidity of the treated steels is increased, while the susceptibility to hot tearing is reduced. Published work shows that the hardenability and susceptibility to temper-brittleness are not affected by rare earth treatment.

Aluminium-killed steels required for green sand mould castings are very susceptible to the formation of intergranular films of sulphide, which must obviously have an adverse effect on the ductility and toughness of the steel. The addition of rare earth metals, as also of tellurium and selenium (which are not in the rare earth group), raises the freezing temperature of the sulphide phase and consequently enables the sulphide to precipitate earlier in the solidification process, in the globular form instead of as intergranular films. This is undoubtedly one of the reasons for the improved mechanical properties of rare earth-treated cast steels. Further, due to the desulphurizing effect of the rare earth metals, steels treated in this way show a lower sulphur content than an untreated steel, which must be recognized as a factor contributing to the improvement in properties. The ability of the rare earths to deoxidize and to remove nitrogen and hydrogen from steels is probably an additional contributory factor, which has to be taken into account.

Rare Earth Addition to Cast Boron Steel — Cerium[4] rare earths have been found to increase the impact strength of quenched and drawn-cast boron basic electric steel of the composition:

	Per cent
C	0·28-3·40
Mn	10·1-1·70

Usual Si, S and P.

The beneficial effect appears to decrease with decreasing temperature. Apparently rare earths do not directly increase hardenability. Half of each heat-treated with rare earths has a hardenability greater than the half not treated with rare earths. A 35-45 per cent increase has been obtained in 3-6 heats containing 0·009-0·016 per cent N. It is known that this level of N inhibits the boron effect in improving hardenability.

In case of a normalized high-tensile, low-carbon, low-alloy steel of the composition: C, 0·1-0·18 per cent; Mo, 0·4-0·6 per cent, by adding boron to it, U.T.S. increases from 45,000 to 65,000 p.s.i. with good impact strength except at low temperatures. This drawback can be overcome if further tests substantiate the results of one heat to which 0·10 per cent rare earths were added. The cerium rare earths increased the impact from 8 to 18 ft.-lb. at −40°. Mischmetals have been used in boron steels with interesting results. For example, 3-5 lb. of mischmetal added to a ton of 8640 steel increased the impact strength from about 30 ft.-lb. up to between 40 and 50 ft.-lb.[5]

Bucknall and Mayer[6] have studied some aspects of boron-treated steels with the following results:

The hardenability of boron-free and boron-treated tripe-alloy steels containing 0·15-0·53 per cent carbon was investigated by means of Jominy tests on specimens from 4-in. billets. The boron-treated steels showed marked hardenability variations, but were on average much improved in hardenability, whatever their carbon content. The mechanical properties of the boron-treated steels were in general consistent with their hardenability, ruling section and hardening treatment, but two advantages were found in boron-treated steels, namely good impact values at high tensile levels after full hardening and an attractive combination of hardenability and weldability.

Plain Carbon and Alloy Steels Based on Boron Additions for Maximum Hardenability With or Without Molybdenum Additions

In India cobalt, columbium, tungsten, nickel and molybdenum are practically non-existent. Some of these elements find extensive alloying applications in different grades of alloy steels, such as heat-treatable constructional grades for the purpose of imparting hardenability.

In most applications of constructional alloy steels, boron can replace a sizeable quantity of nickel, chromium, molybdenum and other critical elements. In addition to conserving alloy elements, however, boron has other advantages. It improves the hot and cold-working properties of the steel, gives a shorter annealing cycle, and imparts better machinability. When boron is used as an alloy replacement in carburizing steels, the treatment is simplified by the shorter annealing cycle, and the retained austenite and undissolved carbides in the carburized case are minimized.

In some applications which require medium or high-carbon steels, too, a boron steel can replace a richer alloy with considerable savings, not only in steel cost, but also in fabrication. In the last part of World War II, thousands of tons of boron steels were used in foreign countries for military equipment. Since 1945, large production applications for boron steels have been found in diesel locomotive crankshafts, heavy-duty tractor axles, cold-headed parts, etc.

Boron Effect

In the past the difficulty in understanding why so small an addition of boron can adequately be substituted for by relatively far larger amounts of strategic alloys has interfered with their general acceptance in some countries. Battelle Memorial Institute (U.S.A.) have postulated that boron improves hardenability by lowering the nucleation rate of ferrite and bainite. The necessary energy for nucleus formation is provided by the concentration of lattice imperfection at the grain boundaries. Boron, because of its atomic diameter, concentrates at lattice imperfections which will provide suitable sites for the purpose. By thus occupying these sites, boron decreases the energy of these local areas, thus reducing their potential as nucleating sites for ferrite and bainite transformation. The loss in hardenability and the boron precipitation that takes place when holding steels at about 1100°C. are accounted for on the basis of increased boron concentration at grain boundaries with increasing temperatures to exceed a critical value and cause establishment of more favourable sites for nucleation and hence transformation of the steel to ferrite and bainite. This explanation emphasizes the probable importance of distribution as well as overall amount on the effect of such powerful micro-additions.

For boron to exercise its characteristic beneficial effects on hardenability, it was absolutely necessary that the nitrogen must be held as nitride by pre-treatment with efficient deoxidizers such as vanadium, titanium, aluminium, etc. This would, of course, exclude deoxidation with silicon. Of these three deoxidizers, aluminium was the most effective as nitride-former. It was not the intention to state that without pre-treatment with aluminium, no boron steel could be made possessing requisite hardenability characteristics. The well-known boron additions such as silcaz, grainal, etc., are known to contain optimum combination of these deoxidizers in order to fix the nitrogen as nitride such as aluminium nitride, etc., so that subsequent boron additions will exercise the maximum beneficial effect in promoting improved hardenability and will not be fritted away in forming boron nitrides. This aspect has been well established by various workers in the field such as Imai and Imai [*Science Reports of the Research Institutes, Tohoku University*, **2**(2) (1950), 260-269] who have stated that boron only improved the hardenability of carbon when nitrogen was less than 0·008 per cent or when the steel was heavily killed with aluminium or titanium but not silicon, since aluminium and titanium form more stable nitrides than silicon. They suggested that a high nitrogen content

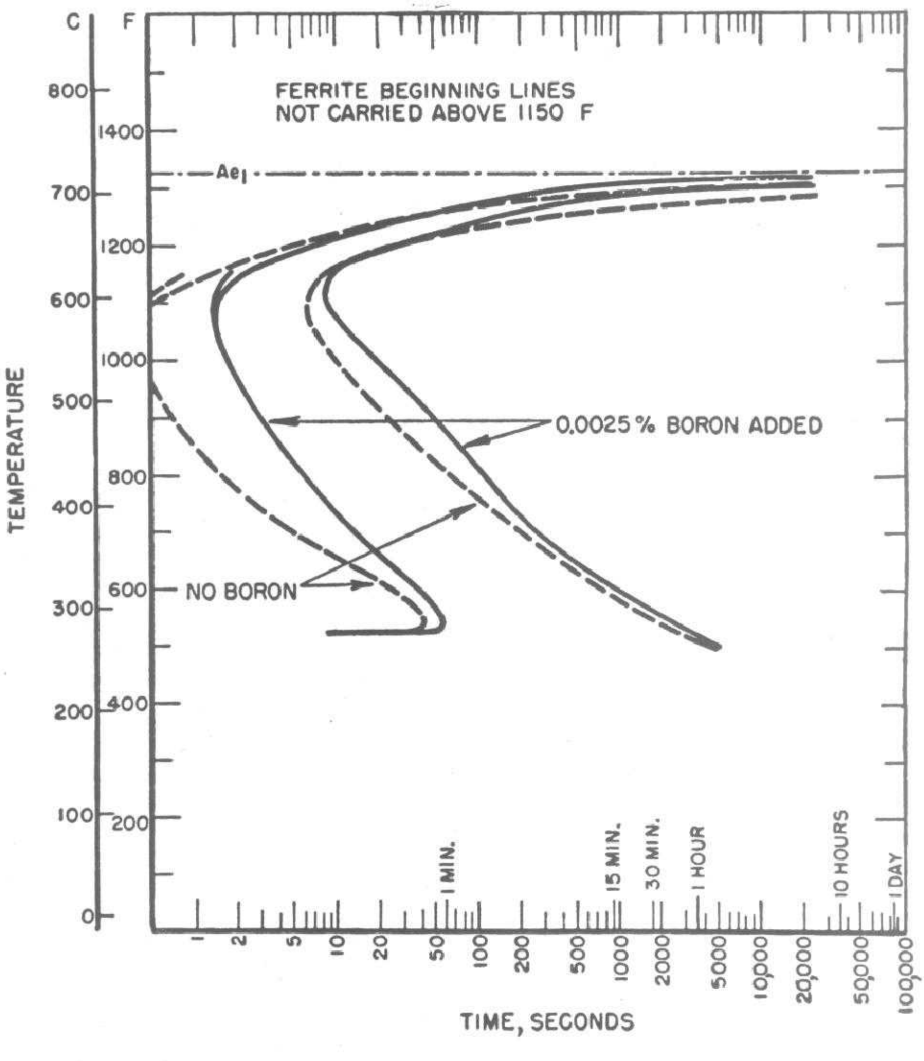

FIG. 1 — COMPARISON OF ISOTHEMAL TRANSFORMATION CURVES FOR 0·63 C, 0·87 Mn STEEL WITH AND WITHOUT BORON (BOTH AUSTENITIZED AT 1500°F., GRAIN SIZE 5-6)

fixed the boron as boron nitride and rendered it inactive. Similar conclusions have been arrived at by Digges and Reinhart [*Trans. A.S.M.*, **40** (1948), 1124-1146].

The effect of boron on the isothermal transformation diagram of hypoeutectoid steels to which it is added is well established[7-10], is similar on all such diagrams so far studied, and is unique compared with effects of other alloying agents. A typical example is shown in Fig. 1, which shows curves for a 0·63 per cent C, 0·87 per cent Mn steel taken from the *Atlas of Isothermal Transformation Digrams* published by the United States Steel Company. Boron suppresses the nucleation of pearlite and ferrite, thus increasing the time before transformation starts. This is responsible for the increased hardenability. At the same time, the curve indicating the finish of transformation is not greatly shifted, indicating that rates of pearlite formation are not decreased but possibly even increased. This is the reason why annealing characteristics of a boron steel are similar to those of steels of the base composition, rather than to those of steels of similar hardenability obtained with other alloys.

The temperature at which ferrite and pearlite are formed is not decreased by boron — a fact of importance because the ordinary elements added to improve hardenability shift the start-of-transformation curves both to lower temperatures and longer time. This explains boron's lack of power to produce the finer pearlite and higher yield strength in a normalized steel that came from the addition of the other elements.

Boron, likewise, does not affect the temperature range at which martensite is formed in steels to which it is added. Thus, on the premise that tendency toward quench-cracking in steel is not a function of hardenability, but rather of the relative shifting of the martensite transformation temperature by the elements added to improve hardenability, boron should not change the quench-cracking tendency of the base steel to which it is added and boron steels should have less quench-cracking tendencies than steels of equivalent hardenability which they can replace. This effect of boron on quench-cracking tendencies has been confirmed[8,11]. It should be a factor favouring use of boron-treated steels.

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