What Antimony May Do for You in Gray and Ductile Iron

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ABSTRACT

Antimony (Sb) in small amounts under 0.1% is used in Europe both in gray and ductile iron and in at least one ductile iron foundry in the US. It readily dissolves in iron and iron can hold about 5% Sb in solid solution at ambient temperatures.

In gray iron it is a powerful pearlitic stabilizer: twice as strong as tin (Sn). It eliminates ferrite skin, increases wear resistance and stabilizes pearlite toward heat, so that the useful life of gray iron thermally cycled up to 1300°F (704°C) is doubled.

In ductile iron, an addition of 0.005% Sb with the inoculant can make the graphite fully nodular even at the center of 8-in. cube castings so they can meet SAE design specifications for D4018, D4512 and D7083. Initial recovery of Sb is about 70% in cupolas and more in induction furnaces. In using recycled iron, the recovery of Sb is about 80%, so new Sb additions can be reduced.

Excess Sb beyond 0.1 to 0.2% tends to promote chill through carbide formation and thereby may reduce notch toughness. Since purchased scrap, as well as ladle refractories, can contain uncertain amounts of Sb, lead (Pb) and bismuth (Bi), a small addition of cerium (Ce) will avoid the need for tight composition controls and insure spherical graphite even in thick ductile iron castings.

Introduction

Since Sb is used as an additive in a considerable number of iron foundries abroad, but very rarely in US foundries, it seems appropriate to describe its use in some detail, to stimulate its wider adoption.

Sources and Production

Antimony either as a metal or in chemical compound form is one of the oldest known elements. Thus natural antimony sulfide was used as medicine and an eyebrow cosmetic in Biblical times. Currently, the principal uses of the metal are with lead in storage battery grids and type metal and with tin in antiflashing pastes, whereas antimony oxide is used increasingly to enhance the fire resistance of flammable materials.

Antimony occurs mainly in ores as the mineral stibnite (Sb₂S₃) and is also present in some lead and copper ores from which it is recovered as a byproduct. Secondary antimony derived from processing lead storage battery scrap provides a large fraction of the total amount of Sb consumed in both metal and compound form, which in a normal year, such as 1969, was estimated at about 40,000 tons in America.

Available Forms of Antimony

Primary antimony is normally available as 60-lb ingots or slabs. As consumption exceeds production in the US, about half the total demand has been met by imports in recent years, largely from Yugoslavia, China, Mexico, Japan, United Kingdom and Belgium-Luxembourg. However, it is expected that a new domestic source of supply will become available before 1977 and this will probably offer Sb in small fragments well adapted to foundry usage. In the meantime, the 99.5% Sb ingots or slabs, being brittle, can be reduced to fines by fracture.

Chemical and Physical Properties in Relation to Iron

Antimony, with a density of 6.6 at ambient temperature, is slightly lighter than cast iron. It melts at 1167°F (630°C) and boils at 2889°F (1587°C). Liquid iron and Sb are mutually soluble in all proportions, which insures quick solution of the customary amount used, which is under 0.1%. The maximum solubility of Sb in solid iron is 11% at 1832°F (1000°C) and slightly under 5% at room temperature.

Antimony in Gray Iron

Basic Effects

Solidification Process — Antimony induces some liquid undercooling which lowers the temperature of eutectic freezing so that the eutectic cell size becomes smaller and promotes type D graphite. Sufficient undercooling promotes free carbide which may occur if Sb is much above 0.1% and in sufficient amount free carbide induces chilling.

Austenite Transformation Process — Antimony strongly retards austenite from transforming to ferrite after freezing until the eutectoid temperature is reached, at which it transforms largely to pearlite, even in thick slowly cooled castings.

Practical Results

Antimony is a powerful pearlitic stabilizer, 100 times stronger than copper (Cu) and twice as strong as Sn. 0.05% antimony is sufficient to change a 4-in. green-sand casting from all ferrite + graphite to all pearlite + graphite.

This same characteristic can eliminate the ferrite skin of castings, which reduces the hardness and machinability of gray iron. Antimony makes it practical to pearlitize a wide range of casting thicknesses.

Less than 0.1% Sb stabilizes pearlite toward heat. During repeated thermal cycling to 1300°F (704°C), the antimonial iron showed 200% longer life in minimizing growth from graphitization of pearlite. Antimony was the most effective additive found and the repetition in heating reached 2700 times vs 1300 times for the base iron before growth and oxidation failure as shown in Table 2.

If wear resistance is a controlling factor, Sb increases it by pearlite being harder than ferrite and by a chill factor forming free iron carbide if Sb is much over 0.1%. These means offer two to three times increased wear resistance.

If ease of cutting is the controlling factor, Sb up to 1.8% improves cutability (machinability) by transforming the customary silver chips into powder chips.

Table 1 lists the mechanical properties of antimonial gray iron under a variety of processing conditions. It shows that the first small addition of Sb generally raises the tensile strength as well as hardness, due to its intense pearlitzing effect. When the matrix is fully pearlitic, any more Sb induces the formation of free iron carbide, which reduces tensile strength and ductility but continues to raise the hardness. Antimony would not be expected to improve toughness because any pearlitzing has the opposite effect. However when Sb is added with an inoculant, such as calcium silicide, that treatment decreases the eutectic cell size and almost restores the original toughness.

Incorporating Antimony into Gray Iron

The Sb addition, crushed rather fine, may be made in the ladle before or during the filling. If before the filling, it is placed in the ladle bottom. From there it rises through the liquid iron as it dissolves and is stirred by the turbulence of the ladle filling. To eliminate ferrite skin, a 0.001-in. mold coating will suffice. For some purposes such as higher mechanical properties, its addition can be made with the inoculant.
Table 1. Effect of Antimony on Mechanical Properties of Gray Cast Iron

<table>
<thead>
<tr>
<th>Sb</th>
<th>Castr Section</th>
<th>Hardness</th>
<th>Tensile Strength</th>
<th>Hostile</th>
<th>% Possible</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Note 0</td>
<td>1.52</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.05</td>
<td>1.2</td>
<td>2.05</td>
<td>34</td>
<td>G3000</td>
<td>~100</td>
</tr>
<tr>
<td>0.05</td>
<td>4.0</td>
<td>2.05</td>
<td>34</td>
<td>G2500</td>
<td>100</td>
</tr>
<tr>
<td>0.01</td>
<td>1.0</td>
<td>2.05</td>
<td>34</td>
<td>G3000</td>
<td>90</td>
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<td>6.0</td>
<td>2.05</td>
<td>34</td>
<td>G2500</td>
<td>90</td>
</tr>
</tbody>
</table>

Note 1: No effect on graphite size, shape, distribution or the chill depth detected.
Note 2: Inoculation with 0.2% SiC (100%) increased eutectic cell size and eliminated chill effect of excess Sb, 10% improved impact toughness.
Note 3: Sb represents amount added in all except last two rolls, which represent Sb recovered.

Table 2. Thermal Cycling of Gray Cast Iron

<table>
<thead>
<tr>
<th>Optimum Additive</th>
<th>No. Cycles to Failure</th>
<th>Relative Length Increase</th>
<th>Growth Area</th>
<th>After Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1200</td>
<td>-</td>
<td>4.0</td>
<td>370.100</td>
</tr>
<tr>
<td>0.02% Sb</td>
<td>2130</td>
<td>-</td>
<td>4.0</td>
<td>377.111</td>
</tr>
<tr>
<td>0.02% Al</td>
<td>2400</td>
<td>-</td>
<td>4.0</td>
<td>377.128</td>
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<tr>
<td>0.02% B1</td>
<td>3654</td>
<td>-</td>
<td>4.0</td>
<td>365.125</td>
</tr>
<tr>
<td>Control</td>
<td>2850</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.02% Sb</td>
<td>2910</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

SOURCES OF ANTIMONY IN SCRAP CHARGES

Enamelled cast iron may contain 10-15% Sb in the enamel. Galvanised steel may contain 0.1% Sb in the coating. Non-magnetic pieces should be eliminated by magnetic separation, as these may contain damaging elements, such as lead (Pb). The Sb content of 13 European pig irons ranged from 0.094 to 0.010%.

RECOVERY IN GRAY IRON

Reported recoveries in production range from 50 to 70%, depending on the amount added and the process of getting it into solution in the liquid iron.

RECYCLING GRAY IRON RETURNS

Once in, Sb tends to remain in recycled cast iron and one investigator reported no burnout in remelting.

MODE OF OCCURRENCE AND DISTRIBUTION IN GRAY IRON

Antimony and carbon (C) appear relatively incompatible, so Sb tends to concentrate in the ferritic regions of pearlite, where it remains dissolved. When iron-antimony alloys up to 50% Sb are used (splat), cooled from the liquid, they show two phases (Ferrich and Sb-rich) because the solidification range is very broad (2800-1840°F) (1538-1010°C).

When 0.05% Sb is added to malleable iron, microhardness traverses across ferrite show lowest hardness at the interface with graphite. So it appears that there is an Sb gradient in ferrite, maximum at the center and minimum at the graphite interface. As this is on a micro scale, it has no practical effect on the customary mechanical properties.

When Sb dissolves in iron, it increases its hardness, tensile and yield strengths, because it has a 17% larger atomic diameter and so must considerably expand the iron crystal structure.

The concentration of Sb in ferrite is reported to cause part of the silicon (Si) to segregate to ferrite boundaries which retards oxygen diffusion, thereby improving resistance to thermal failure by oxide crack penetration along graphite flakes. Growth results from this oxide penetration and iron graphitization of the iron-carbide constituent of pearlite. The combination of grain growth resistance and oxidation resistance makes antimonial iron five times more resistant to growth and twice as resistant to failure by oxidation cracking under thermal cycling as shown in Table 2. This quality should lead to its consideration in brake drums, cylinder heads and liners and permanent molds for casting metals and glass.

Antimony increases wear resistance both by pearlitizing and by reducing the eutectic cell size, which promotes stubbier type D graphite.

ADVANTAGES AND LIMITATIONS OF ANTIMONIAL GRAY CAST IRON

The power of Sb to completely pearlitize a ferrite or partially ferritic iron in thicknesses up to 4 in. with less than 0.1% Sb addition is undoubtedly its greatest asset.

The effect is to decrease wear by a factor of 1.5 to 2.5 and increase strength sharply. The impact resistance can be partially maintained, despite the pearlitic matrix, if the addition is accompanied by an inoculation of calcium silicide. Without such inoculation, impact strength falls with increasing Sb content and tensile strength also falls beyond 0.1% addition. The drop in toughness is inherent in pearlitizing gray iron by any means.

When resistance to thermal cycling is desired, a very stable pearlite is needed, namely, resistance to growth from graphitization and oxidation and for that Sb is the preferred additive as Table 2 shows. Thermal cycling must be limited to about 1300°F (704°C), because the solids, beginning of melting, occurs at 1345°F (728°C) for alloys atom-rich in iron.

Ferritic skin which makes the rim zone soft and gummy is detrimental to machining, but can be prevented by 0.05% Sb. For this the Sb can be added to the ladle or applied as a mold coating.

Antimony in excess of about 0.1% induces free carbidite and thus increases the depth of chill.

ANTIMONY IN DUCELITE IRON

Basic Effects in DuCELITE Iron

SOLIDIFICATION PROCESS — Antimony is reported to decrease the solubility of carbon in iron-carbon liquid, thereby inducing some spheroidal graphite formation above the eutectic temperature.

Antimony also induces some liquid undercooling which lowers the temperature of eutectic freezing so that the eutectic cell size becomes smaller. In extremely small amounts it can prevent the formation of degenerate graphite even at the center of thick castings.

Larger amounts of Sb, possibly beyond its kinetic solubility in gamma iron, appear to react with magnesium (Mg) forming intermetallic compounds and therefore require the concurrent presence of Ce to avoid degenerate graphite.

AUSTENITE TRANSFORMATION PROCESS — As in gray iron, Sb retards transformation of austenite to ferrite in the region 1300 - 1000°F (704 - 538°C) where pearlite forms first, so it promotes some pearlite even in thick castings.
Practical Effects in Ductile Iron

When 20-50 ppm (0.002-0.005%) Sb is added alone in the absence of Ce, and if tramp elements are extremely low, Sb has the profound effect of making the graphite fully spheroidal even at the center of an 8-in. cube casting, as shown in Fig. 1, so that even the center can meet SAE specifications D4018 and D4512.22 Without this Sb, shown in Fig. 2, the center could not meet any SAE design specification. To obtain these enhanced properties it must be added with the inoculant when the iron has cooled to below 2500°F (1371°C).23

Since Sb tends to remain in recycled iron, its total amount from unknown scrap and additions may easily exceed 50 ppm, so the recommendation is made to include from 0.01 - 0.05% Ce to insure against the unexpected invasion of excessive Sb and tramp elements and maintain fully nodular structures even in thick castings. The action of Ce is still unexplained but it seems without question the ductile iron foundryman’s best medicine for ailing thick castings, aside from a controlled trace of Sb or small amount of arsenic (As).24 A controlled amount of Ce can prevent the damaging effects of tramp elements such as Pb and Bi, as well as permitting more Sb without risk of reversion to degenerate graphite.25

At least one foundry is making ductile iron successfully with Sb and Ce supplementing Mg. They find that a little Sb refines the graphite and makes it rounder in thick castings, where graphite ordinarily tends to be coarse and irregular-shaped.

Table 3 shows how Sb changes the mechanical properties of ductile iron particularly with increasing thickness and how Ce modifies these properties.

The work of Campomanes has been outstanding in demonstrating that as little as 20 ppm (0.002%) Sb raises the nodular count with no deterioration of graphite.26 Still more striking is its effect on an 8-in. cube casting, illustrated in Fig. 1 and 2. With no Sb, the center zone failed to meet any of the current SAE standard grades because of degenerate graphite, but with 50 ppm (0.005%) Sb added with the inoculant, even the center zone was practically 100% spheroidal and met two SAE grades D4018 and D451228 along with almost a doubled nodular count. Since, as noted in Table 2, 20 ppm Ce was present in both heats represented by Fig. 1 and 2, it should be evident that the improvement in Fig. 1 is primarily due to Sb.

The balance of Table 3 shows that overdosing with Sb requires Ce or mischmetal of the composition of rare-earth metals, particularly Ce) to eliminate the degenerative effects most noticeable in low elongation. Also since the Sb, Pb and B1 contents of unanalyzed scrap and ladle or furnace refractories are generally unknown, it is wise to add some Ce with the Sb, unless tramp elements are tightly controlled.

Incorporation in Ductile Iron

Particularly for thick castings, the Sb addition should coincide with the inoculant when the iron has cooled to 2500°F (1371°C) or
somewhat lower. It can be made as primary antimony or master iron-antimony alloy granules. In practice, because of the recovery of recycled Sb, only the balance needs adding in late ladle additions with the inoculant, because the tolerance for Sb is greater even in excess Mg above 0.06%.  

Recovery in Ductile Iron  
In recent work, recovery of Sb is reported to be 80-85%, in contrast to a reported recovery of 30-50% in work done almost a quarter century ago.  

Recycling in Ductile Iron  
Antimony is largely recovered in recycling ductile iron returns, particularly in the newer induction melting processes involving less oxidation. Antimony, as well as Pb and Bi, are absorbed in hot refractories such as furnace or ladle linings and thereby can be gradually transferred to molten metal. This characteristic and the uncertainty of contaminants in scrap provide two good reasons for using a bit of Ce.  

Safe Practices  
Antimony is classed by a leading nutritionist as a nonessential trace element like aluminum. In the 1973 Edition of "Toxic Substances," the US Department of Health, Education and Welfare has set the maximum allowable concentration of Sb in any 8-hr day at 0.5 mg/m² of air, which is five times more than that for tellurium (Te). An exhaust ventilation system will be required to handle Sb fume. With proper ventilation the lower Te limit should not be considered a detriment.  

In industrial practice the Sb additive is kept dry and handled with gloves or pre-bagged mechanically. Since OSHA now requires effective ventilation in fume zones, the control of Sb fume, possibly with the aid of a baghouse, should be relatively easy.  

Summary  
Figure 3 summarizes the range of Sb additions usually made to cast irons. When Sb is added alone to ductile iron to the amount of 50 ppm it can make graphite fully nodular to the center of very thick castings. If it is added to the amount of 50 ppm with the inoculant when the iron has cooled to 2500°F (1371°C), the ductile iron product will meet two SAE design specifications even at the center of very thick castings in contrast to none without the addition. However since the Sb, Pb and Bi contents of unannealed scrap and ladle refractories are uncertain, it is preferable to include a bit of Ce with the Sb addition to insure that the graphite will be spheroidal throughout even thick castings.

In gray iron, Sb is possibly the most powerful pearlitizing agent known and if added with the inoculant can maintain the resultant strengthening effect with no more detrimental to ductility than is normal for pearlite. The pearlitic structure together with a trend to type D graphite improves wear resistance and is so stabilized that the product can withstand up to double the number of thermal heating cycles of the untreated iron.  

In concluding, the author suggests that if you have never tried Sb, it deserves your evaluation.

References  
5. S. I. Karsav, Private Communication.  