

# The role of selenium and tellurium in ferrous metals

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**H**OW can you get a hard, wear resistant surface on cast iron, and still maintain a tough underlying body to meet severe operating service requirements?

How can you overcome the "gumminess" of stainless steels, so that they can be out or shaved to form them into the complex shapes often required for machine assemblies?

Selenium (Se) and Tellurium (Te) are providing quite unique answers to these and other basic problems in the ever increasing demands placed upon iron and steel products.

The properties they confer stem from their surface-active nature, and to this we will return later after a closer look at the variety of things that they do.

## Cutability

The annual cost of cutting or "shaving" metals to form them into the complex shapes required for myriad applications now runs into billions of dollars! The response of the metal to the cutting tool is a very important factor in this cost, so anything which favourably influences cutability is economically significant. Se and Te do just that.

Stainless steels, particularly the non-magnetic variety, first seize the cutting tool and then acquire a glazed surface. Both actions hinder efficient cutting. A quarter of a per cent of Se incorporated in the steel when liquid forms mainly selenide compounds with some of the metallic elements. Appearing as inclusions in the steel matrix they reduce seizing and glazing and the energy necessary to separate the chip from the work piece, thereby improving the "cutability" (a British term) or "machinability", the corresponding USA term. This improvement over the untreated steel, evident in greater productivity measured by longer cutting tool life or faster cutting rate or both, may amount to 50% or more. The addition of sulfur makes a similar improvement but at the expense of poorer hot workability, transverse ductility, corrosion resistance and surface finish. Se in even smaller amounts also enhances the

machinability of low alloy and plain carbon steels. Several USA steel makers add Se to low carbon steel carrying 1/4% sulfur and lead, with reported gains in performance up to 1/3 over the same steel without Se.

Te appears somewhat more efficient than Se *per unit weight* in improving machinability of carbon and low alloy steels because somewhat less is commonly found. Production of these Te steels, usually with 1/4% sulfur and lead, provides the largest use of Te in the iron and steel industry. However, even in the smaller amount, Te induces a tendency to surface cracking during the successive hot-working steps from steel ingot to bar in contrast to the relatively crack-free, hot-working of Se steel. This tendency of Te steels to hot brittleness seems to be enhanced by nickel, so that for improved machinability, Se is the preferred additive to nickel steels and is necessary for nickel-rich steels, such as invar, because either sulfur or Te induces serious cracking during hot working of those steels.

Selenium, tellurium and bismuth constitute the group of special additives which enhance the cutability of steel, each additive having its own advantages emphasized by its proponents.

Such steels, however, are still only a small fraction of the total volume of "free-machining" steels made without the benefit of these special additives, because most metal processing equipment and personnel are not as yet adapted to take economic advantage of the improved performance.

## Other benefits

The benefits of Se and Te have been demonstrated in a number of other ways, most of which are in the patent record stage, but are mentioned here:

Commencing with liquid steel, Se and Te sharply reduce the rate of absorption of nitrogen, so that Bessemer steel can be made with as little N as open-hearth steel, and the new basic oxygen process could possibly use lower purity oxygen.

When the steel freezes, Se and Te refine the grain structure, and as both are weak deoxidizers, it is thereby possible to produce a partially deoxidized fine-grained steel: a unique combination of higher product yield with better mechanical properties.

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In high alloy steel castings Se minimizes pinhole porosity associated with green sand molds.

When stainless steels freeze they are particularly inclined to develop a coarse dendritic structure; however, recent tests in Europe indicate that a small addition of Se to the ladle may promote the formation of a finer, more chunky, (equi-axed) structure with less directional differences in properties and better adapted to hot working if desired.

Both Se and Te counteract the embrittling effect of sulfur in fully deoxidized steels by changing the inclusion shape and distribution from a network of chains to a more random array of globules.

By refining the size of the grains as noted earlier, these elements also reduce hardenability, sensitivity to overheating and tendency to quench cracking of steels. These characteristics suggest improved steels for carburizing and for using directly as hot rolled without further treatment.

Turning now from their metallurgical and mechanical effects to their electrical effects in steel, recent Japanese work indicates that either element added to the standard silicon electrical steels aids the formation of a grain oriented structure with superior magnetic permeability. In such a structure the cube edge of the crystals tends to be aligned parallel to the rolling direction.

### Whitening iron

Returning now to the first question raised in this brief survey, we note the use of Te to induce a hard, wear resistant surface on cast iron. This use was probably the earliest application of either element to a cast ferrous product and is still the principal use of Te in cast iron. For example, chilled iron car wheels normally are made with an addition of 1 ounce of Te to 7 tons of liquid iron or slightly more than 1 part of Te in 1 million parts of iron, a beautiful example of the immense power of a surface active element. Again a hard, wear-resistant surface is needed on rolling mill rolls and Te can be a valuable additive as it shrinks the size of the weaker transition zone underlying the hard surface zone.

Malleable iron castings must freeze as 'white' iron, the hardest form of cast iron, prior to the softening malleabilizing treatment. This would severely limit flexibility in composition and thickness, were it not for Te, which, even in minute amount, acts as a powerful 'whitener' by suppressing the formation of graphite during freezing. More recently, bismuth, less potent than Te per unit, has largely replaced Te in this one application because it is more easily controlled.

Se functions in cast irons like Te but is less effective per unit, so it is generally not used in such applications when Te is available.

Normally hydrogen is an undesirable element in steel, but if anyone is looking for ways to increase the absorption of hydrogen in iron electrolytically, the addition of Se or Te will do it!

### Methods of addition vs. recovery

Every good cook knows there is an optimum sequence

in making any delectable product, depending on the characteristics of the additive. So the method of addition of these elements are varied to suit the conditions encountered in each particular type of application.

First, it should be noted that the lowest temperature of a liquid iron or steel bath is several hundred degrees above the *boiling point* of either Se or Te. Thus if added in the elemental state of atmospheric pressure, the element rapidly transforms to the vapour state.

Second, the density of solid or liquid Se or Te is considerably less than that of liquid iron or steel, so elemental Se or Te tends to rise towards the top of the liquid bath and float.

Third, both Se and Te react with oxygen to some extent to form oxides.

Fourth, Se and Te dissolve slowly and probably to a very limited extent in liquid iron or steel, and are nearly insoluble in solid iron or steel.

Consequently, the use of elemental forms of Se and Te require considerable ingenuity to ensure a satisfactory distribution and degree of recovery, measured by analysis of the element in the finished product. Various devices are used, ranging from injecting the element in powder or pelletized form into the pouring stream of liquid iron or steel, to a steel 'shoe' box containing the entire addition for a batch or heat, placed in the bottom of a ladle before filling.

About 2/3 of the addition is generally recovered by these methods and the remaining third, lost by fume, slag, etc. requires effective venting or exhaust systems.

The elemental forms are generally preferred for incorporating Se or Te in individual ingots or castings because they melt more rapidly.

The ferro-alloy form is generally preferred when the addition can be made to the entire batch or heat in the furnace as in electric melting of stainless steel. The ferro-alloy has a higher density, higher melting point and is less volatile, so the recovery is generally greater, with reported values up to 90% or more.

### Mechanism of action: what makes them tick?

Although there is no generally accepted explanation of the remarkable effectiveness of these elements in minute amounts in iron and steel, their surface-active nature appears the most probable cause. Briefly, the solubility of Se and Te in iron is very small, and they are believed to concentrate in extremely thin internal interface films, which can modify the normal characteristics of iron to a marked degree.

In closing these remarks it may be noted that the surface-active nature of Se and Te makes them promising elements to change the shape of graphite particles in cast iron from tiny flakes to balls or nodules. Since the demand for nodular graphitic iron is rising rapidly because it is much more ductile than conventional flake graphitic iron, the importance of the nodular particle shape can scarcely be overestimated. The particular conditions under which Se or Te can favourably influence the shape are under intensive study but not yet well understood.