

Small cause, large effect

F. Hanus, Dillinger Hütte, Germany, assesses the influence of trace elements on the properties and weldability of structural and pressure vessel steels.

Steel plant technology has undergone significant improvements in recent decades.¹ Between 1996 and 2002, Dillinger Hütte has spent more than US\$ 150 million on further improving the facilities in its steel plant. The investments were aimed at cost reduction and enhanced productivity, but also for improved process control and better steel quality.

Figure 1 outlines how harmful trace elements in the steel could be gradually reduced as a result of improved processes and facilities, (for example by ladle metallurgy and vacuum treatment). Other targets were homogeneous properties, achieved by replacing ingot with sophisticated continuous casting, and the very specific achievement of an aimed chemical composition.

However, fabricators and users are less concerned with the details of steelmaking, taking more interest in the advantages of modern steels, and in what risks may result from using cheap material of inferior quality.

Status of modern steelmaking

Today, the LD process can achieve sulfur contents below 0.001% (10 ppm), and contents of nitrogen below 0.005% and phosphorous below 0.01% are also attainable. Even contents of less than 0.005% can be assured in special cases. However, in the case of structural and pressure vessel steels such as EN10025, EN10028, EN10113, ASME and ASTM, modern steelmaking permits significantly lower limits than those specified in corresponding national and international material standards. Some examples of Euronorms are given in Figure 2.

The permissible sulfur and phosphorus content limits decrease as demand for strength, toughness, formability and safety in structural steels increases (Figure 2). The purchase of steels that merely fulfil the standard requirements may result in considerable difficulties when processing and in service.

The effects of sulfur

Due to the high affinity between sulfur and the manganese alloyed to structural steels, little dissolved sulfur exists in a metal's solid state. Instead, sulfur is essentially present in the form of sulfide inclusions. As sulfur content increases, so too does the amount and size of these sulfides. Moreover, they are becoming ever more harmful to the metal's material properties.

Taking normalised structural steel with a yield strength of 355 MPa as an example, Figure 3 shows how impact energy has been improved in recent decades, thanks to the removal of sulfur to the minimum level technically achievable. The upper shelf of impact energy has almost been increased by a factor of 10.

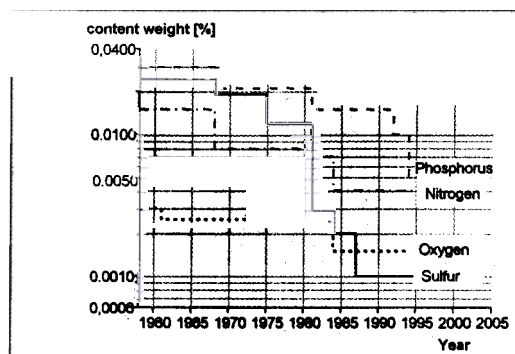


Figure 1. Limits of some trace elements achieved in production at the Dillinger Hütte steel plant.²

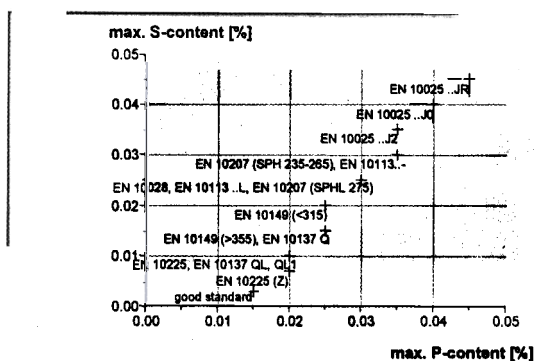


Figure 2. Permissible phosphorus and sulfur contents for selected grades of steel; figures in brackets indicate yield strength class.

Lamellar tearing

Lamellar tearing is a defect that occurs in susceptible plates or beams when shrinkage stresses result in excessively high loads in the through thickness direction. Such cracks are located parallel to the plate surface, and are caused by non metallic inclusions (sulfides, silicates and oxides) aligned parallel to the surface by the rolling process. It is easy to perceive that high sulfur and oxide contents promote the risk of lamellar tearing.

Figure 4 indicates that low sulfur contents have a favourable effect on striction in the through thickness tensile test, particularly when combined with sulfide shape control (which prevents elongation of the sulfides during hot rolling).

Sour gas resistant steels

Non alloyed and low alloy steels are susceptible to cracking if exposed to fluids containing hydrogen sulfide. Such

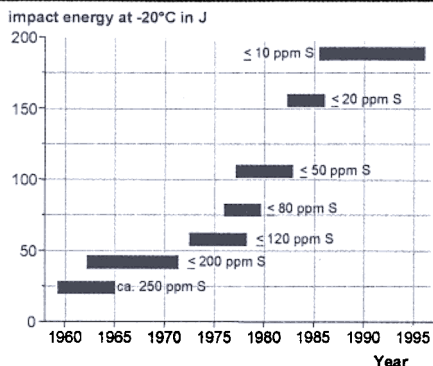


Figure 3. Notched impact energy achievable in the parent material as a result of improvements in steel making and the corresponding sulfur contents.

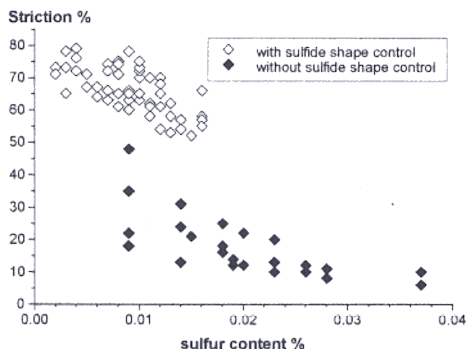


Figure 4. The influence of sulfur content and sulfide shape control on striction in the through tensile test as a measure of susceptibility to lamellar tearing.

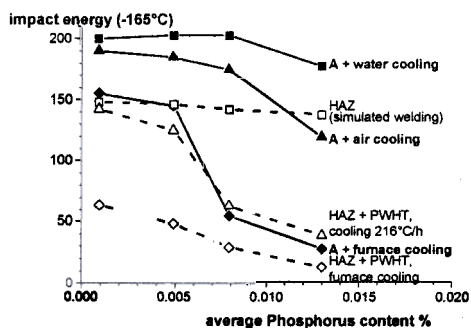


Figure 5. Low temperature steel containing 9% nickel, the effects of phosphorus content and the cooling rate after tempering the impact energy of the parent material and HAZ microstructure.⁴

conditions may occur in certain areas of oil and gas production, in pipelines, and in petrochemical (particularly desulfurisation) plants. Practical experience was reported at the 3rd Dillingen 'pressure vessel and boilermaking' colloquium.³ A sulfur content below 0.001% results in a high level of resistance to sour media, provided the material shows homogeneous microstructure and little segregation.

The influence of phosphorus on steel properties

It has long been known that phosphorus effectively increases the tensile properties in ferrite, but has an adverse effect on the toughness of steel. This chemical element causes severe segregation, first during solidification of the steel, and secondly in the solid state to grain boundaries. Consequently, even a moderate bulk concentration can lead to a significant embrittlement under critical conditions.

The removal of phosphorus in steelmaking is more difficult than is the case with sulfur, as it can only be extracted by selective oxidation during oxygen blowing in the converter process. Removal by secondary metallurgy is not feasible. As it is not fixed in stable inclusions, at least some phosphorus is dissolved in the steel matrix in a solid state, and at a sufficiently high temperature. Solubility decreases at lower temperatures, and phosphorus atoms tend to segregate and precipitate primarily at grain boundaries. Grain cohesion is thereby weakened, under unfavorable conditions embrittlement is obtained, and even intercrystalline fracture can occur. Phosphorus segregation is most effective at 450 - 500 °C, during heat treatment, slow cooling or when at a high service temperature.

Figure 5 shows how the impact energy was affected by intergranular embrittlement for a steel containing 9% nickel, intended to be used at cryogenic temperature.⁴ In this investigation, phosphorus concentrations at the grain boundaries encompassed different bulk compositions of 0.001 - 0.013% and different cooling rates. Due to its coarser microstructure, the HAZ specimen proved to be more susceptible than the fine grained parent material. A similar effect has also been caused by, amongst others, tin and antimony.⁵

Embrittlement during high temperature service

Embrittlement at high service temperatures is often simulated and studied by applying a special heat treatment ('step cooling'). The temperature shift in impact testing, from brittle to ductile fracture, is examined before and after such treatment. Watanabe related the shift of the impact transition curve to the concentrations of silicon, manganese, phosphorus and tin present in the steel.⁶ It was observed that steels with a J factor of less than 100 were not prone to embrittlement. As a sufficient amount of silicon and manganese are necessary to match the tensile properties, only low phosphorus and tin concentrations are able to satisfy this value. The formula for the J factor is:

$$J = [(Mn+Si)*(P+Sn)*10000]$$

Dillinger Hütte's test did not fully confirm Watanabe's formula, but it remains in many specifications for CrMo alloyed steels for use at high temperatures. However, it is important to note that this formula is not applicable to weld metals.

Effects of trace elements on weldability

Hydrogen induced cold cracking in the HAZ

Carbon equivalents (predominantly CE, P_{cm} and CET)⁷ are normally used to characterise the weldability of a steel (Table 1).

They do not entail the use of sulfur and phosphorus, as these elements are not relevant in this regard. Some years ago, it was argued that sulfides were trapping hydrogen introduced by welding, with the result that steels containing very little sulfur were suspected to be more susceptible to cold cracking. Hence, they should require higher preheat for safe welding. In order to clarify this matter, cold cracking tests⁸ were performed on various steel grades containing different levels of sulfur. As can be seen in Figure 6, the critical preheat temperatures were indeed independent of the sulfur content, since the experimental results were satisfactorily predicted by the formula.

In the context of preheat, another type of trace element should also be considered, including typical alloying elements such as Cr, Mo, copper or nickel, which are unintentionally added in this case. Depending on the scrap that is used for steel production, considerable amounts of such elements may be present in the finished steel. EN 10113 and 10028 permit 0.3% of Cu, Ni and Cr and 0.10% of Mo (DIN 10028, 0.08%), totalling less than 0.70%. When using CET,

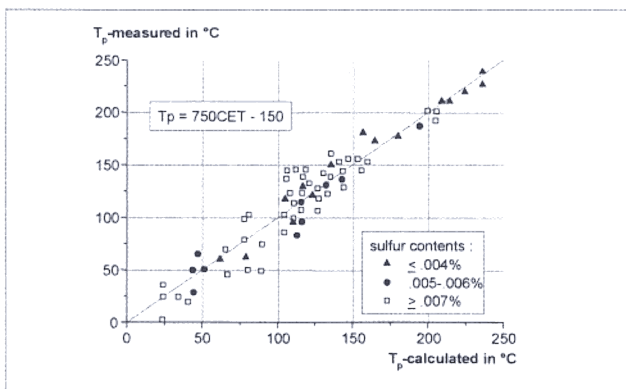


Figure 6. Influence of various sulfur contents on necessary preheat temperature (T_p) as determined in the Tekken test. Configuration: root pass of highly restrained butt weld.

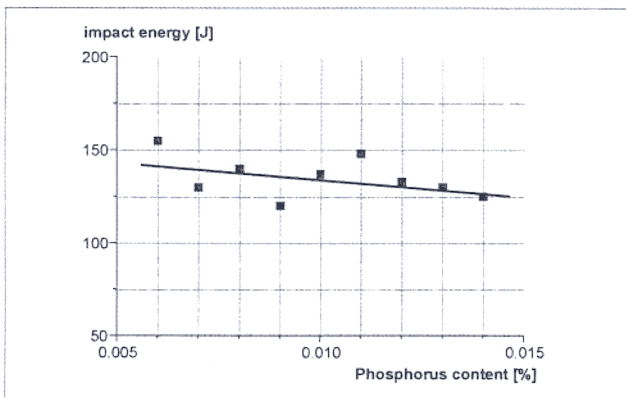


Figure 7. Impact energy for the HAZ of steel S355N; Offshore grouped according to their phosphorus contents. Tests in the 'as welded' condition at $-40\text{ }^\circ\text{C}$.

Table 1. Current carbon equivalent formulae characterising the influence of the chemical composition on (1) hardenability and (2/3) susceptibility to cold cracking within the heat affected zone
(1) $CE = C + Mn/6 + (Cr + Mo + V)/5 + (Cu + Ni)/15$
(2) $CET = C + (Mn + Mo)/10 + (Cr + Cu)/20 + Ni/40$
(3) $Pcm = C + Si/30 + (Mn + Cu + Cr)/20 + Ni/60 + Mo/15 + V/10 + 5B$

Table 2. Formulae for the quantification of the sensitivity of steels to solidification cracking as a function of the chemical composition (%)
Submerged arc welding: ¹³
$UCS = 230xC + 190xS + 75xP + 45xNb - 12.3xSi - 5.4xMn - 1$
$UCS < 10$ for unfavourable welding conditions
$UCS < 30$ for favourable welding conditions
TIG welding:
$42xC + 847xS + 265xP - 10xMo - 3042xO + 19 \leq 20$
Laser welding of shipbuilding steels: ¹⁴
$Fc = [S/Mn] + P \leq 0.020\%$

the preheat temperature has to be raised by $25\text{ }^\circ\text{C}$ if the most harmful elements (Mo, Cr and Cu) reach the upper tolerance limit. As the steelmaker is not obliged to mention in the certificates these contents if they were not added intentionally, the welding engineer will be unaware of any such 'traces', and may consequently prescribe unsafe welding conditions. In this respect, steels produced from 100% scrap by the electric arc process cause more concern than steel produced via the blastfurnace and converter process.

Hot cracking

A 'hot crack' is a discontinuity that occurs during welding, casting or hot forming at temperatures at which individual areas of the material are in the two phase 'liquid/solid' range, and at which tensile stresses occur simultaneously.⁹

Solidification cracking

A 'solidification crack' is a hot crack that occurs at the end of the solidification of (weld metal) melts that have been subjected to shrinkage induced tensile stresses. Therefore, in the context of welding, solidification cracking is primarily a problem of the weld metal and its composition.¹⁰ The chemical composition of the parent material only plays an important role in welding processes that produce a high level of mixing. TIG welding without filler wire, submerged arc welding with a deep penetration, electron beam welding, and laser welding should also be mentioned. It is apparent from Table 2 that all formulae to quantify susceptibility to cracking ascribe a particularly severe effect to sulfur and phosphorus. This is due to the fact that both elements accumulate in the residual melt during solidification, and form phases with low melting points. In order to minimise the risk, steels intended for laser welding should have particularly low sulfur and phosphorus contents.^{11,12}

HAZ hot cracking

An 'HAZ hot crack' is an intercrystalline hot crack that occurs as a result of the liquefaction of low melting point phases at grain boundaries under the influence of tensile stresses. The causes are primarily sulfides of iron and nickel. Steels with an adequate manganese content have no tendency to HAZ hot cracking unless their sulfur content is excessively high. The problem is solved if the sulfur is fixed in thermally stable inclusions by means of a calcium treatment.

Toughness in the HAZ

The influence of phosphorus

The results of 121 submerged arc welded joints produced with a heat input of 3.0 kJ/mm were available to assist in assessing the effect of phosphorus on the toughness in the HAZ. The welded plates were made of a normalised 355 MPa yield strength offshore steel, for which weldability had to be proven in the case of the thickest plate per heat of material delivered. The tests were performed in the as-welded condition. The target composition for the steel was kept constant, but heat to heat variations allowed assessment of the effect of individual chemical elements. The impact values with notch position at the weld fusion line of all heats with the same phosphorus content were averaged, and these values are shown in Figure 7. A slight trend towards lower HAZ impact energy with increased phosphorus is observable, but the effect is not pronounced. As all material was used in the as-welded condition, the effect of phosphorus after PWHT was not tested.

Embrittlement and cracking during post weld heat treatment

Not only does PWHT relieve residual stresses, but HAZ and deposited materials are also tempered, mostly by improving their properties. However, undesirable precipitation and segregation of tramp elements may occur simultaneously. The basic metallurgical processes have recently been summarised in a literature survey.¹⁵

As with phosphorus, some metallic impurities have proved to be harmful in grain boundary contamination; in particular arsenic, tin and antimony. Steels produced by an electric arc process generally contain significantly higher amounts of these elements than steels produced via a converter,¹⁶ and are therefore more prone to such embrittlement. If fabrication and service conditions become critical, this should be taken into account when ordering steel.

In the case of the HAZ, during PWHT an accumulation and reprecipitation of phases dissolved at high temperatures

close to the fusion line can occur. These include sulfides (particularly those at relatively low manganese contents),¹⁷ nitrides (Al and V) and carbides (Nb, Mo and Cr).

In the case of rapid cooling, renewed precipitation is suppressed, with the result that the atoms remain in a supersaturated solution in the matrix. During PWHT, or whilst already heating, dissolved atoms can diffuse and precipitate. The former austenite grain boundaries offer particularly favourable sites for thin layers of such precipitates. This can weaken grain cohesion and may, under unfavourable conditions, cause reheat cracking. Surprisingly high local concentrations, (almost completely covering the former austenite grain boundary surface) were reported, although the bulk concentrations of phosphorous were low.¹⁸

Conclusion

The contents of sulfur and phosphorus permitted by most standards are far in excess of the values that are currently easily achievable with modern steelmaking technology. Today, improved material properties and safer processing can justify the slightly higher price of properly desulfurised steels.

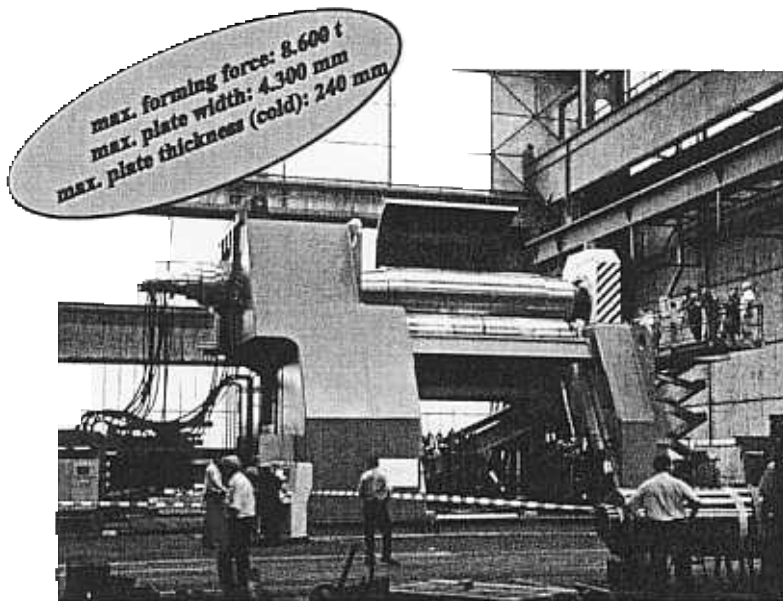
Reducing phosphorus to concentrations significantly below 0.015% necessitates considerable extra costs to the steel plant. A technical advantage is achieved only for particular applications. Steel merely fulfilling the requirements of the standards can cause serious problems and extra costs in fabrication and service.

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