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Some Examples of Industrial Applications of Ultra-High Purity Steels

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Abstract : In the last decade, the evolution and control of steelmaking practice have enabled drastic reductions to be made in the impurity content of low alloy steels (mainly S, P, O, N and H) and the resulting superclean steel products have seen their in-service behaviour greatly improved. The following examples concerning CLI products are presented : 1 - The reduction of S content by a factor of more than ten and the control of O content have considerably reduced the Hydrogen Induced Cracking (HIC) sensitivity of the C-Mn steel grades for the storage of oil and gas in sour environments. 2 - Superclean Ni Cr Mo V steel grades for turbine rotors shafts have a very low sensitivity to lower nose temper embrittlement. 3 - Thick (> 100 mm) plates or forgings in Mn Ni Mo steel grade used for nuclear pressure vessels welded by the electron beam process offer high toughness in fused areas when S + P are reduced to less than 30 ppm. 4 - Steel grades very close to pure iron have been developed to improve the performance of magnetic circuits in large accelerators.

1. INTRODUCTION

The evolution and control of steelmaking practice has enabled drastic reductions to be made in the main impurity contents of low alloy steels used for the manufacture of heavy components. The main development concerns Sulphur and Phosphorus individually, and in addition, the sum S+P which has been reduced from about 0.030% to 0.003% in thirty years. Other significant reductions have been made in so-called "gas" impurities (O, N and H) whose content in steel was reduced overall by 50% in the same period. So now, "superclean" steels are today available at CLI, as heavy plates and components (forgings and castings), for use in power plants and the nuclear and petrochemical industries.

This paper will present four examples of these applications where the reduction of impurities is the key to success :

- C-Mn vessel steels exposed, in oil and gas fields, to high levels of H₂S and CO₂, liable to develop Hydrogen Induced Cracking ;
- Superclean NiCrMoV steel grades for turbine rotor shafts operating at temperatures where lower nose temper embrittlement may occur ;
- Mn Ni Mo steel grade for nuclear pressure vessel weldability by the electron beam process ;
- Special steels developed for improving the magnetic performance of large accelerators.

2. INDUSTRIAL SOLUTIONS TO THE PROBLEMS RELATED TO H₂S ENVIRONMENTS

2.1 Description of the problems

When they are used in H₂S environments, carbon and low alloy steels can be severely embrittled. The damage results from hydrogen embrittlement phenomena due to production of atomic hydrogen at the surface, by a corrosion reaction, and the diffusion of hydrogen into the steel. Several kinds of damage have been recognized for low alloy steels : Hydrogen Induced Cracking (HIC), Sulphide Stress Cracking (SCC) and Stress Oriented Hydrogen Induced Cracking (SOHIC).

Hydrogen Induced Cracking manifests itself in "soft" steels in the form of surface blisters and/or internal cracks in the absence of an applied stress. Hydrogen absorbed into the steel diffuses and can be trapped in defects in the steel. At such "discontinuities" the hydrogen atoms combine to form molecular hydrogen gas. High hydrogen pressures can be developed and cracks can initiate and propagate.

Sulphide Stress Cracking occurs in the presence of external or residual stresses. Generally cracks initiate at the corroding surface and propagate into the material perpendicular to the principal stress. It is generally recognized that the higher the strength, the poorer the resistance of the steel. As a consequence, NACE standard MR01-75 restricts maximum hardness to Rc22 in the case of carbon and low alloy steels for sour service. In fact strength is not the absolute parameter, the microstructure is the governing parameter. It is generally admitted that tempered microstructures are more resistant than untempered ones.

Stress Oriented Hydrogen Induced Cracking can be considered as a combination of these two phenomena. SOHC can occur in steels which can suffer HIC. When a stress is applied, the steel exhibits cracks parallel to the surface of the material but aligned or stacked in the through-thickness direction. Linking of these cracks by SCC can then occur.

In this paper we will focus on low alloy steel for pressure vessels. This consists of normalized steel with relatively low mechanical characteristics (UTS < 600 MPa). The thickness of the plates concerned lies in the range 10 to 150 mm. Typically of the relatively low mechanical characteristics, the main problem encountered with the base materials is Hydrogen Induced Cracking. Sulphide Stress Cracking may affect welded areas where a hard microstructure may be created due to the thermal cycles performed (particularly in the HAZ).

2.2 Improvement of HIC resistance of the base material

HIC cracks can initiate at "discontinuities" in the steels where high hydrogen pressure can develop. Then the nature and extent of the damage is determined by the size, location and distribution of the discontinuities. It has long been recognized that non-metallic inclusions are the main crack initiation sites. Large, elongated and aligned inclusions are more dangerous than small, globular and randomly dispersed inclusions.

Among these inclusions, elongated manganese sulphide inclusions have been found to be the worst. It has been shown that the reduction of sulphur content is very effective in reducing the number and the size of sulphide inclusions. Figure 1 shows that as the sulphur content decreases, the sulphides become more globular. Another way to achieve globularization of sulphide inclusions is to perform a calcium treatment. The influence of calcium treatment on sulphide shape parameters is shown in Figure 1. It can be seen that calcium treatment is effective when the S content is greater than 0.002%. On the other hand, for a very low sulphur content, sulphides are already globular and a Ca treatment is not necessary. A correlation between HIC behaviour and the sulphur content is shown in Figure 2. This figure gives the envelop of 50 HIC tests results obtained in the BP solution. It is clear from this figure that a decrease in S content is effective in improving HIC behaviour. While for S content > 0.002% the calcium treatment is effective in reducing HIC sensitivity, this is not so clear for very low sulphur levels (< 0.001%). In fact, in very low sulphur steel, in the absence of segregation, the HIC behaviour is very good. The worst results found in low sulphur steel are generally associated with a high oxide content. Thus calcium treatment for very low sulphur steels can be harmful, because of the strong tendency of calcium to form oxides. Oxide inclusions are generally less dangerous than sulphide inclusions. However small cracks can be found initiating at oxides. To limit the occurrence of small cracks associated with oxides, it is necessary to decrease the amount of oxygen in the steel.

It has been observed that very good cleanliness can be achieved by limiting the sulphur content (<0.001%) and the oxygen content (<0.002%).

However HIC behaviour does not depend only on the cleanliness of the steel. The extent of crack propagation depends on the microstructure. In plates, the microstructure is not perfectly homogeneous. Segregated areas enriched in alloying elements can be found at mid-thickness of rolled products. Due to the higher hardenability of segregated areas, bainitic or martensitic microstructure can be found in these areas. The intensity of segregation depends on the chemical composition, but also on the casting process. It is well known that for plates made from continuous castings, the segregation is located at mid-thickness of the product, whereas for ingot casting, segregation is mainly found at the top of the ingot. In ingot casting, the intensity of segregation depends on the weight and shape of the ingot. In order to avoid top segregation, cropping of the top of the plate is necessary. As the percentage of cropping increases, the homogeneity through the thickness of the plate becomes better.

Figure 1 : Influence of S content on sulphide shape

Figure 2 : Influence of S on HIC test result (CLR) - Influence of Ca treatment

Quantitative electron microanalysis was performed through segregated areas of different plates. Profiles of several elements have been obtained through cracked areas or uncracked ones. In Table 1 the rate of segregation in P, Si, Mn is shown for 4 plates with different carbon contents. While the rates of segregation for Mn and Si are not different for cracked or uncracked areas, it appears that in cracked areas there are always very high rates of phosphorus segregation. In Figure 3 a comparison is made between the rates of segregation in cracked and uncracked areas as a function of C content. Rates of segregation between 235 and 670% are found in cracked areas, against segregation of between 100 and 230% in uncracked ones.

Moreover, an increase in the rate of phosphorus segregation is found when the carbon content increases. Our results do not show a high rate of manganese segregation, though the manganese content in the steels investigated was quite high. It seems that in segregated areas, it is phosphorus segregation which controls HIC behaviour. One way to limit segregation is to decrease the proportion of hardenable elements (i.e. decrease C_{eq}). However this is not always compatible with the mechanical properties required.

	C	P	Si	Mn
Analysis	114	7,7	290	1340
Seg. (%)	Cracked	350	14	21
	Uncracked	100	13	23,5
Analysis	142	11,4	365	1360
Seg. (%)	Cracked	488	20	29
	Uncracked	233	23	23
Analysis	165	8,8	268	1340
Seg. (%)	Cracked	670	51	53
	Uncracked	115	37	37
Analysis	80	8	320	1450
Seg. (%)	Cracked	235	17	18
	(2 zones)	402	18	21
	Uncracked	135	16	16

$$\text{Seg (\%)} = \frac{\text{Average content in segregated area - heat analysis}}{\text{heat analysis}} \times 100$$

Table 1 : Comparison of segregation rates in P and Mn in cracked and uncracked areas for different carbon contents

Finally it must be pointed out that a tempering treatment decreases the sensitivity of segregated areas. The effect of the tempering treatment is to soften the segregated hard zones. The final PWHT which is performed in pressure vessel is then also favourable for the HIC resistance of the base material.

2.3 Conclusions

Ways to improve the behaviour of low alloy steel for pressure vessels in H_2S environments were investigated.

- Concerning the base material, it has been shown that an improved HIC resistance can be obtained by :
- The use of very clean steel : this means very low sulphur and oxygen contents ($S < 0,001\%$; $O \leq 0,002\%$).
 - The use of steel with homogeneous microstructures.

Figure 3 : Comparison of S segregation rates between cracked and uncracked areas for 4 plates with different C contents

3. SUPERCLEAN STEEL FOR TURBINE ROTOR SHAFTS

3.1 Objectives of superclean steel forgings

Low pressure (LP) turbine rotor shafts are generally made from NiCrMoV steel grades with a Ni content range of 2.8 to 3.7%, depending on the size of the turbine rotor. For the largest ($\varnothing$ from 1,700 to 1,900 mm) forgings, the typical Ni content is 3.5%. This steel grade has a high temper embrittlement (lower nose) susceptibility and the operating temperature is limited to 350°C maximum. The mechanisms of embrittlement of 3.5 Ni Cr Mo V steel grade were described several years ago [1, 2, 3]. Temper embrittlement susceptibility is increased by the alloying elements Si, Mn and by impurities such as P, Sb, Sn, As, etc. To increase the operating temperature above 350°C in power plants, it is necessary to use materials with reduced susceptibility to temper embrittlement. These steel grades are named "superclean".

3.2 Properties of typical superclean steel forgings

As mentioned above, the chemistry of the steel is the major key to reducing its susceptibility to temper embrittlement. Different indexes or formulae are proposed to evaluate this susceptibility, for example :

- the Bruscato index : $\bar{X} = (10P + 5Sb + 4Sn + As) / 100$ with contents in ppm

- the J factor : $J = (Si + Mn) (P + Sn) \cdot 10^4$ with contents in %.

That control of impurities by modern steelmaking practice is effective is shown in Figure 4, which displays statistical data on heavy rotor forgings manufactured by CLI in recent years.

A typical chemical analysis of a superclean LP rotor forging, with simultaneous reduction content of Si and Mn and of impurities, is given in Table 2.

C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu	Sn	Al	As	Sb	$\bar{X}$	J
0,240	0,0003	0,0023	0,013	0,029	3,53	1,76	0,425	0,097	0,016	<0,001	<0,002	<0,002	<0,001	≤3.4	1.4

Table 2 : Chemical analysis (in wt%) of superclean LP rotor forgings

$\bar{X}$ is lower than 3.4 ppm and the J factor is 1.4 (%)². These extra-low values conduce to a very low embrittlement effect, as suggested from curves resulting from very long term (up to 100,000 hours) ageing tests performed in Japan [4].

Figure 4 : Statistical results of S, P, Sn, As, Sb contents (LP rotor forgings from 1986 to 1990)

Figure 5 : Relationship between increase of $\Delta FATT$ and $\bar{X}$

3.3 Advantages in the use of superclean steel turbine rotor forgings

An evaluation of worldwide data [5] on superclean 3.5 Ni Cr Mo V steels concluded as follows :

- This steel can be used for service applications at temperatures up to 480°C or 500°C.
- There is no temper embrittlement and long term embrittlement is negligible for bainitic microstructure : so, good initial toughness values can be achieved, even in the case of slow cooling rates after tempering.
- Other advantages concern their creep resistance and yield strength, which are better than those of conventional materials.

The improved characteristics due to these steel developments, and thus the resulting higher loads and temperatures that can be withstood by the components, represent a possible way of improving the thermal efficiency of the turbines. So the increased cost of the components (+20%) is largely compensated for by the savings in operating costs.

4. IMPROVING ELECTRON BEAM WELDS OF Mn Ni Mo STEEL

4.1 Metallurgical factors acting on the toughness of fused zones by E.B.W.

For the welding of thick products in Mn Ni Mo steel for nuclear pressure vessels, EB Welding is an attractive process due to its high efficiency. However, industrial feasibility requires, for welding thicknesses around 100 mm, a width of fused zone of about 4 to 5 mm and, for thicknesses around 200 mm, a width of fused zone of about 6 to 7 mm.

The width of the fused zone is the main parameter controlling the cooling rate, and in consequence, the microstructure of the fused zone (FZ) and heat affected zone (HAZ). The effect of microstructure on toughness has been shown in a previous paper [6].

These results have been confirmed by Japanese work [7, 8] with in addition the demonstration of another effect due to the segregation of impurities in the weld area.

4.2 Reduction of impurity content (S, P) and the effect on EBW toughness

Table 3 shows the evolution of S, P and S+P content in the materials for nuclear pressure vessels manufactured by CLI. In twenty years maximum S+P content has been reduced by a factor of more than 4.

4.3 Modern steelmaking and electron beam welding

In addition to the benefits of the reduction of S and P content, modern steelmaking, conducing to a significant decrease of elements likely to produce gaseous reactions during welding (O, N, H), reduces the risk of porosities in the weld.

5. CONTROL OF MAGNETIC PROPERTIES IN VERY LARGE STEEL PIECES

5.1 Required properties of steel

In large accelerators, magnetic circuits are big steel structures performing two functions simultaneously :

- They have to carry the induction flux at minimal expense of ferromagnetic material and of magnetic excitation field.
- They are also mechanical structures.

The steel producer has to answer two kinds of requirements :

- Magnetic requirements which may be :
 - minimum values of induction at different values of the magnetic field
 - high saturation induction
 - low value of coercivity
 - minimal magnetic ageing with time and/or temperature.
- Mechanical requirements : they generally rely on yield and tensile strengths and sometimes toughness requirements.

But the designer first wants homogeneous characteristics at different locations in a given part as well as in different parts of a batch.

5.2 Some solutions

5.2.1. Principles

To obtain good magnetic properties, the following guidelines are generally accepted.

The chemical analysis has to be very close to pure iron (% Fe ~ 99.99) and a very low carbon content is mandatory.

This is sufficient to achieve high saturation induction (which is a structure insensitive property), but for permeability, coercive force, residual induction, it is also necessary to achieve a metallurgical structure with large ferritic grain, without internal stresses and precipitates. However, a few relatively coarse precipitates in the grain boundaries are less detrimental than many fine precipitates in the matrix.

5.2.2. Steel melting

Selected scrap is melted in an arc furnace. Refining and degassing are achieved in the ladle by vacuum processing.

The main difficulties are :

- The control of non-oxidizable elements (Cu, Sn, ...) : the only practical way is the selection of scrap.
 - Decarburization without oxidation of the melt with vacuum processing.
 - Necessity of a very low Sulphur content if low Mn is required (Prevention of hot shortness).
 - Phosphorus is said not to be detrimental to the magnetic properties and it strengthens the ferrite.
- However, the segregation factor of P being very high, for large pieces, P is limited to very low values (generally < 50 ppm).

5.2.3. Heat treatment

The final aim being a very coarse ferritic grain, it is necessary first to obtain a coarse austenitic grain by austenitization at high temperatures.

YEAR	S max.	P max.	S+P max.
	ppm	ppm	ppm
1972	160	150	310
1982	90	120	210
1992	20	50	70

Table 3 : Maximum impurity content of heats of 18MND5 steel grade manufactured for nuclear pressure vessels in France

For testing the possibility of improving the toughness of EBW, some industrial heats of 18MND5 steel grade were made at CLI with the objective of guaranteeing a total $S+P \leq 30$ ppm (as required by customers interested in this welding process).

EBW was performed on a heat containing $S = 12$ ppm and $P = 18$ ppm, at the limit of the acceptable maximum. The results of Charpy V notch tests are presented in fig.6 in comparison with some literature data and with an "old" material.

The effects of microstructure (related to the width of FZ), of impurity content and of Post-Weld Heat Treatment conditions are clear.

Due to the two impossibilities :

- a significant increase in the PWHT temperature to keep good strength in the base material,
 - a high modification of the hardenability of steel within the limits of alloying elements,
- the only way to improve the toughness of FZ is severely to reduce the impurity content.

Figure 6 : Toughness of electron beam weld fused zone for different conditions

5.3 Examples of applications

5.3.1 Steel castings for a cryogenic accelerator

In the magnetic circuit of a cryogenic accelerator, castings are preferred as this technique needs fewer parts.

The larger pieces weigh up to 90 tons and are 950 mm in thickness.

The most stringent magnetic requirements are for pole pieces :

Intrinsic Induction ($B - \mu_0 H$) at $H > 200$ kA/m (approaching saturation) :

$$A > 2.14 \text{ T}$$

and Coercive force

$$H_c < 70 \text{ A/m.}$$

For other parts, the specification is less severe for H_c but demands better mechanical characteristics :

$$A > 2.14 \text{ T} \quad - \quad H_c < 100 \text{ A/m.}$$

Preliminary tests have indicated that a 1% Nickel addition improves both magnetic and mechanical properties.

Consequently, parts with the higher mechanical specification were cast with about 1% Ni and the other parts without voluntary additions of this element (% Ni < 0.15%). For both cases, very low content of C, S, P and Si were achieved. All parts were annealed at 840°C for 8 hours.

The Ni addition is specially efficient for the Yield Strength (+30%) and it decreases the coercive force but without noticeable effects on induction at low fields or on intrinsic induction (Table 4).

	Induction			Intrinsic Induction	Hc (A/m)
Heats	H = 200	H = 300	H = 500		
Low Nickel					
A	0,864	1,140	1,413	2,159	66
B	0,874	1,128	1,406	2,156	61
C	0,860	1,119	1,396	2,166	64
D	0,885	1,165	1,449	2,158	69
E	0,845	1,103	1,386	2,155	63
F	0,873	1,121	1,386	2,154	60
High Nickel					
G	0,913	1,147	1,372	2,154	43
H	0,828	1,074	1,343	2,169	57
I	0,842	1,090	1,349	2,166	61
J	0,858	1,111	1,373	2,153	57
K	0,859	1,107	1,354	2,158	62
L	0,825	1,074	1,332	2,155	65

Table 4 : Magnetic properties of large castings (Induction in Tesla ; field in A/m)

5.3.2 Heavy plates for two deflecting magnets

Good results were achieved for heavy plates by the following process. After hot rolling, the hot plates are very slowly cooled under a cover of volcanic ash : between 900 and 200°C, the cooling rate is 2°C/h. This process gives its best results with thick plates. Such plates have been used in two deflecting magnets of a large accelerator.

Figure 7 : Magnetic properties of heavy plates : Mean and extremal values for 19 heats

With the initial design, for each magnet, 400 tons of steel were necessary. But, after a discussion between the steel supplier and the designer, a completely new design was adopted. The delivery was no longer plates, but semi-finished parts very close to the final dimensions : an optimized oxycutting process (called "Flame cutting machining") gives, on 700 mm-thick parts, 10 mm guaranteed dimensional accuracy and better than 20 μm RA roughness. With such performance, only the functional surfaces need further machining and the total mass, for each apparatus, is reduced to 320 tons.

For this order, 19 heats were poured. The mean analysis was C $\sim$ 0.010%, Mn $\sim$ 0.280%, Si $\sim$ 0.130% and with a very low level of impurities (S < 0.010% and P < 0.006%). The thickness of the plates was up to 740 mm and for each plate, four specimens from different locations were tested. The magnetization curves are very homogeneous specially for low field values (Figure 7).

Finally, the new design of the magnets gave not only very good magnetic performance, but also considerable savings on machining costs.

6. CONCLUSIONS

These four examples show the benefits of the reduction of impurities in traditional materials such as special steels, using modern steelmaking processes.

These processes are now probably near their limits for the reduction of the impurities, but before going ahead on new processes, able to advance closer to ultra-high purity material, we need to answer a series of questions, typically :

- What are the properties of the materials which may be improved by a further reduction of impurities (S < 2 ppm, P < 10 ppm, O < 10 ppm) ?
- What methods can we develop for measuring with accuracy such levels of residual elements ?

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