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Examination of defects and long term crack growth in rolled bars during long term storage

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Abstract

This work has had the purpose to examine defects and the cause of crack growth during long term storage in rolled bars. The bars in question are rolled and stored at Ovako in Hofors. The problem is approached by theoretically examining the possibilities of hydrogen damage, room temperature creep and naturally occurring porosity.

Seven bars of three steel type groups and with different rolling dates were selected and examined for defects with ultrasonic testing. Four of the bars show defects. Specimens containing the defects are cut out and grinded so that the defects can be examined in the scanning electron microscope and analyzed with energy dispersive x-ray spectroscopy.

One of the specimens shows some form of cavity containing iron carbide. One of the others shows a surface with inclusions. The remaining two both shows inclusions and cracks that seem to originate from inclusions.

The theoretical studies show that there are two types of hydrogen damage that could be in effect in the studied case and also that room temperature creep could facilitate but not cause crack growth and that porosity could serve as crack initiation points. Steps should be taken to minimize the problems mentioned above when they are suspected causes. Further examination of inclusions in different steel types should be made if considered a problem.

Sammanfattning

Detta arbete har haft syftet att undersöka defekter och orsaken till spricktillväxt under långtidsförvaring av spårvalsade stänger. Stängerna i undersökningen är valsade och lagrade hos Ovako i Hofors. Problemet är angripet genom att teoretiskt undersöka risken för väteskador, kryp i rumstemperatur och naturligt förekommande porositet.

Sju stänger indelade i tre stålsortsgrupper och med olika valsningsdatum valdes ut och undersöktes med ultraljud. Fyra av stängerna visade på defekter. Prov innehållande dessa defekter blev utkapade och slipade så att defekterna kan bli undersökta i svepelektronmikroskop och analyserade med energidispersiv röntgenanalys.

Ett av proverna visar på ett hålrum innehållande en järnkarbid. Ett av de andra proverna visar på en yta med inneslutningar. De två återstående proverna visar på inneslutningar och sprickor som verkar utgå från inneslutningar.

De teoretiska studierna visar att det finns två typer av väteskador som är aktuella i det studerade fallet och även att kryp vid rumstemperatur kan underlätta spricktillväxt men inte orsaka den och att porositet kan tjäna som sprickinitieringsställen. Åtgärder för att minimera de nämnda problemen bör tas i fall där de är misstänkta orsaker. Ytterligare undersökningar av inneslutningsbilden bör göras om inneslutningar anses vara ett problem.

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1. Introduction

1.1. Background

The rolling mill division for Ovako in Hofors delivers different kind of steel bars in different dimensions to other Ovako divisions for further processing as well as to external customers. The full process from scrap to bar looks roughly as follows:

- The steel mill in Hofors melts scrap and processes the melt to the right composition and quality. There is no preheating of the scrap.
- The processed melt is then casted in molds.
- When the ingots have solidified they are sent to the rolling mill.
- The rolling mill soaks these ingots in soaking pits to minimize segregation.
- Then the 4.2 ton ingots are rolled in two or three set of rolls, depending on the final dimension, or forged. The rolling mill in Hofors produces bars with dimensions between 78 and 230 mm diameter and 147*147 mm bars. Bars with diameters between 240 and 350 are forged.
- The bars are cooled in room temperature after which they are checked for surface and internal defects. The latter is done with ultrasonic techniques.
- The bars are then transported to their destination. Either to an external customer, to Ovako in Hällefors for further rolling, to internal customers at Ovako in Hofors or to outdoor storage areas.

The microstructure of the steel after rolling is not always stable. Some of the steels are hardened and all the steels are cooled in air. Some steel manufacturers use heat treatment on their steels. At Ovako the time between rolling and processing into tubes or rings is generally so short that heat treatment is deemed not to be necessary.

Porosity is formed in the ingots during solidification. This porosity is reduced when the ingots are rolled. The reduction rate is dependent on the diameter of the finished bar. Larger diameters mean less reduction for the ingots. This increases the remaining porosity. Some steels are also more difficult to process which is considered to also increase the remaining porosity. Ovako also uses a small ingot size which decreases reduction.

An ultrasonic examination is done five days after rolling for steels which are aimed at more demanding products. During a testing period ultrasonic examination was also performed after one and three months. It is calibrated against a created defect with known size. This gives an indication of the defect sizes in the bars based on the level of the reflected ultrasonic signal which is proportional to the known defect size.

The bars are stored outdoors on two supports standing on gravel. Each pair of supports is used for storing several bars. Since not all of the bars are used up immediately there are bars that remain at the storage area for longer times. This time can be from a few days to more than a year. During this time the ultrasonic signal from the bars grows empirically which might mean that the existing defects are increasing in size.

Suspected mechanisms for this are flakes or possibly other hydrogen damage, residual stress from rolling, creep tension or any combination of these. A rough estimate puts the time from rolling until the bars is unusable to one year but this is depending on the steel type and the dimension of the bar. The bigger the diameter of the bar is the shorter is the time until it is unusable. This is assumed to be because there is more porosity in larger bars due to less reduction during rolling. Forging process the bars more in the center which is assumed to be the reason that forged bars shows fewer problems. There is a suspicion that growth of internal defects is the cause of certain customers complaints when the material used was stored during long times.

1.2. Purpose

The main purpose of this study is to examine theoretical possibilities of crack growth during long term storage in rolled bars and to examine defects in rolled bars stored for shorter and longer time. The purpose of the theoretical study is to evaluate if naturally occurring porosity can work as a crack initiation point, examine the effects of hydrogen damage and examine the effects of creep at room temperature. The purpose of the practical tests is to examine defects in the rolled bars with ultrasonic testing, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis. The data from both the theoretical studies as well as the practical examination are used to propose solutions for the problem.

1.3. Limitations

When examining steel specimens this work is limited to locating at least one defect for those specimens that showed defects with ultrasonic testing and to examine this surface. This means that the possibility of other defects within those specimens or in specimens without an ultrasonic signal will not be examined. To approach this work in a narrow enough way some theoretical possibilities, beyond what is suggested in the background, is not examined as thoroughly. Different forms of residual stresses is not examined due to the difficulties of practically measuring these and because this work is focused towards other areas. The selection of steel specimens is limited by available materials at Ovako in Hofors at the time of selection. Some other preferable steel specimens do not have specimens with different enough rolling dates since both older and newly rolled specimens get used up in production.

2. Steel casting

In this section the theoretical studies of this work will be presented.

2.1. Electric arc furnace

The production of steel by using scrap metal is done in an electric arc furnace which was invented in the beginning of the 20th century. Both direct current and alternating current is used but the latter is dominating. Three electrodes are lowered into the scrap and an electric arc is formed between them and the scrap. This produces heat which is used to melt the scrap. [1]

Except the metal scrap several other ingredients can be put into the furnace. Pig iron and direct reduced iron is used if available or economically favorable to produce. They generally contain lower amounts of cupper and tin than scrap which gives cleaner steel. A number of alloying elements are added to achieve the right composition. They can be added in their basic form, as oxides or as iron alloys. Reducing agents can be added in the form of carbon or silicon carriers to decrease metal loss to the slag. This is common when producing high alloy steels. Calcium oxides and magnesium oxides are added to give the slag the correct basicity to decrease lining wear. [1]

For the melting of the scrap to proceed optimally the scrap needs to be at a temperature of 2000° C. This means that in the initial stages the oven will work unevenly. To improve upon this it is possible to preheat the scrap metal. This also has a few other benefits which include removing moisture and oil from the scrap. [1]

2.2. Non-metallic inclusions in steel

Nonmetallic inclusions can originate from the slag or form during ladle treatment. If their size is bigger than 10-15 µm they can affect a number of properties like weldability, fatigue strength, roughness, machinability, corrosion properties and ductility. These inclusions have different mechanical properties depending on their composition. They are divided into four different groups depending on their deformation behavior. The groups are the following: [1]

a. Ductile: They follow the deformation of the steel and are elongated in the rolling direction. Examples are manganese sulfides and calcium and manganese silicates with a high SiO_2 level. [1]

b. Brittle: These inclusions break up into fragments during forming. Examples are deformed Al_2O_3 clusters, titanium carbonitride and MnO-Cr_2O_3. [1]

c. Brittle-ductile: Inclusions with a hard core surrounded by a deformable phase. An example is silicates with lower SiO_2 level than a. [1]

d. Hard inclusions: These deform very little or not at all during forming. Cavities are often detected in the rolling direction. Examples are calcium aluminates, MgO-Al_2O_3-spinels and small Al_2O_3 inclusions. [1]

A picture of the appearance of the four kinds of inclusion is shown in Figure 1.
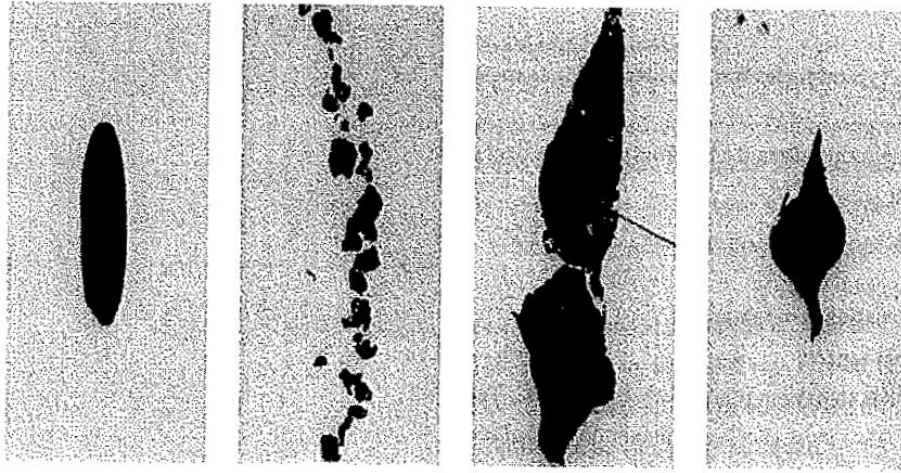
Figure 1: Picture of the appearance of inclusion types a-d.

2.3. The casting process

The aim of the casting process is to solidify the molten steel (or another metal) while keeping the percentages of different alloying elements from previous metallurgical processes constant. There are also several quality properties to consider. It is important to minimize segregation, pores, crack formation and to produce good surfaces. [2]

All the steel in one batch does not solidify at the same temperature. Since the steel contains alloying elements there is a temperature interval for solidification. The first one is the starting temperature. At this temperature the first part of the steel solidifies. This steel gets a slightly lower carbon content than the still molten steel. Higher carbon content in the melt means that it gets a lower solidification temperature. When the temperature drops further more and more steel solidifies and the remaining melt gets higher and higher carbon content. The last of the melt solidifies at 1340° C, in ideal circumstances, and has the highest carbon content. Because of this, different parts of the solid structure have different amounts of carbon. This phenomenon is called micro or macro segregation depending on which scale it is happening. [2]

2.3.1. Phenomena during casting

Steel have different densities depending on temperature. This is especially true when going from molten to solid forms. Because of this there is shrinkage during solidification. On the microscopic scale this means molten steel have to be sucked in between the forming dendrites. If the material transport is too slow pores might be formed. These pores are often easily sealed during hot working of the steel. On the macroscopic scale a pipe might form, which is a big cavity, see Figure 2. This is foremost a problem with ingot casting. [2]
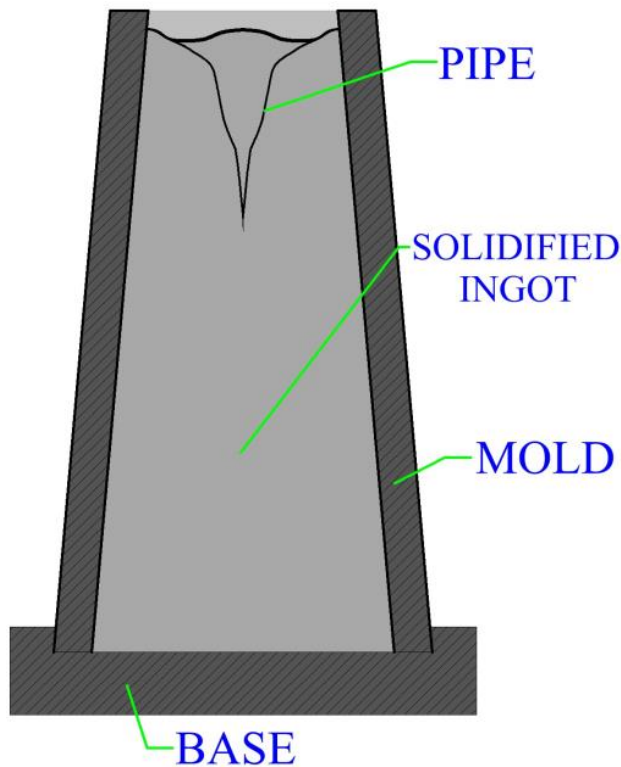
Macrosegregations is another problem when casting. This occurs when the molten steel move around in the mold because of differences in density arising from temperature differences. This leads to differences in composition in different parts of the molten steel. It influences the final positions of inclusions which is negative since it is desirable for those to end up with the mold powder on top of the melt. Macro segregation is more severe than micro segregation because it gives different properties in different parts of the material. [2]

For the steel to solidify there is some supercooling required. Depending on if the supercooling is high or low the steel forms different structures. In a mold the supercooling is highest along the walls of the container and lowers towards the center. Normally three zones are formed. The first one is a thin layer of equiaxed crystals followed by the second one which consists of column shaped crystals. The column shape arises when the heat travels through the first zone to reach the mold wall. The new crystals therefore form at the old ones and grow into the unaffected melt. In the center the temperature lowers below the melting temperature but above the final solidification temperature which means new crystals can form easier. This gives the third zone in the center consisting of larger equiaxed crystals. A picture of how this could look is shown in Figure 3. [2]
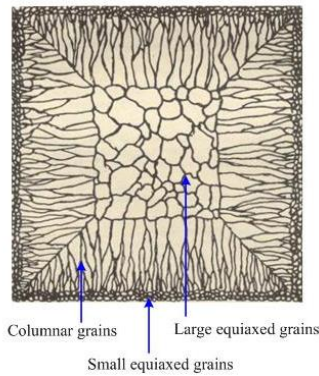
Figure 3: Picture of the crystal structure in a steel ingot [2].

Gas bubbles are another problem that needs to be considered when casting. These bubbles can either diffuse out to the surface or remain in the material. If the bubbles diffuse to the surface there could be problems with oxidation of the formed microscopic cavity when coming in contact with oxygen in the air. In that case they will not disappear during hot working. For bubbles that remain in the material there are two main kinds. Hydrogen and nitrogen that in most cases disappears into the material during hot working and argon that do not disappear since argon does not react with the steel at all. The last kind is rare but very negative. It is important to make that sure there is time between the last usage of argon and the casting so that the gas has time to diffuse to the surface. [2]

The position and size of inclusions after casting is important for the materials properties. The most dangerous inclusions are the primary inclusions. Primary inclusions are those who solidified before casting. The secondary ones, precipitated during solidification, rarely gets big enough to cause a problem. A big source for primary inclusions is the oxidation that occurs when pouring molten metal into the mold or tundish. Hence it is important to have an as good separation process as possible. For ingot casting heating the top of the mold improves separation while for continuous casting the form of the casting pipe and an electromagnetic break optimizes the separation. [2]

The formation of cracks is a big problem. Because of this it is important to design the casting process to minimize tension. It is also possible to design the steels high temperature properties in such a way that cracks need more tension to form. Alloying elements that accumulate in grain boundaries is especially dangerous. An example of this is sulfur that can form thin films in these boundaries. During continuous casting it is possible to create tension by choosing bad geometries or cooling speeds. [2]

2.3.2. Ingot Casting

Ingot casting is unusual today. Most steels casted by this method have a problem with segregation which hinders the use of continuous casting. But before this method was developed ingot casting was the norm dating back from the 19th century when liquid steel was started being used. [2]

The ingot is solidified in a form most often made of cast iron. When it has finished solidifying the mold is turned upside down to remove the ingot. The ingot is then either allowed to cool or transported to an oven to be kept warm before rolling. The cross section of a typical ingot can be seen in Figure 4. [2]
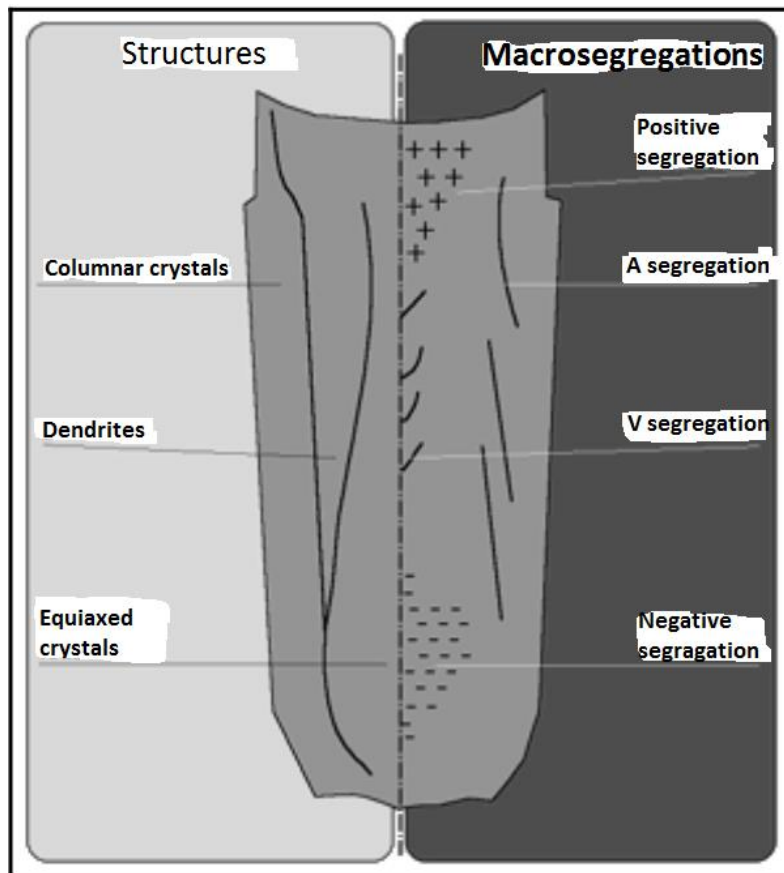
Figure 4: Structures in a solidified ingot [2]

This figure shows how the structure of the ingot goes from columnar dendrites to equiaxed crystals from the wall to the center. It also shows the different kinds of segregations found. To decrease the amount of air dragged down into the steel bottom casting is used. The steel then rise into the mold rather than being poured in from the top. [2]

A hot top is used in most molds which lowers the solidification rate at the top of the mold. This will decrease the pipe formation problem by making the top of the molten steel solidify more evenly in time. Casting powder is added to the top of the molten steel to protect it from the air and also insulate it, making it solidify more evenly. [2]

2.4. Porosity

There are two size classifications of pores, macroporosity and microporosity. Macroporosity refers to pores that are large enough to be seen with the unaided eye on a radiographic inspection while microporosity refers to pores that need magnification to be seen. Pores are a common kind of defect in castings. They can be connected to the surface or they can be internal. It is a combination of gas evolution and metal shrinking that form the pores during solidification. Though, their nucleation is difficult without the presence of some sort of substrate, like a nonmetallic inclusion, a grain refiner or a second phase particle. [3]

The effect on static and dynamic properties is dependent on the sizes of the pores. The static properties are reduced by at least the portion of the cross-sectional area that is taken up with the pores because there is no metal there to carry the load. Because the pores also cause a stress

concentration in the remaining material, static properties can be reduced by more than the percentage of cross-sectional area they take up. Micro pores do not affect static properties much because of their size. The dynamic properties are affected by pores longer than 0.2 mm. Even with bigger pores the effect is only slight. Though, because of the notch effect, the reduction in dynamic properties is great if the pores extend to the surface. For both static and dynamic properties the shape of the pores is important. Elongated pores have greater effect than round ones. [3]

The pores that exist after casting can be sealed during forging or rolling. Forging is effective at sealing pores due to that it works large portion of the material and subjects the material to high deformation. When rolling the material the percentage of pores sealed is dependent on the degree of deformation. This means that higher final diameter of the rolled bars gives less percentage of sealed pores. The size of the ingots casted affects it in the same way. A smaller ingots experiences less deformation when worked and therefore has more pores left after rolling. [4, 5]

The pores in the material are stress concentration points. The flatter the pores are the greater the stress concentration becomes. When subjected to stress microscopic cracks can form at the pore edges as a result of this. If the load is increased these cracks will grow. [6]

3. Hydrogen damage, creep at room temperature and ultrasonic testing

Hydrogen damage is often called hydrogen embrittlement. Since not all damage caused by hydrogen results in reduced load bearing capacity or fracture below yield stress, hydrogen damage is a better general term. The hydrogen helps defects form and propagate below stresses needed for mechanical fracture, create macroscopic damage and gives a general loss in ductility and/or tensile strength. This kind of damage easily occurs in high strength steel and many failures derive from it. It is a form of environmentally assisted failure caused most often by the combined effect of hydrogen and residual or applied tensile stress. [7, 8]

When producing steel there are several sources of hydrogen. The most common one is moisture from scrap metal. Other common ones are water from the slag or refractory materials in the furnace linings. To diffuse into the steel the hydrogen needs to be in atomic form rather than the more usual molecular form. There are certain other molecules containing hydrogen, especially hydrogen sulfide, where the bond is even looser and therefore these molecules is more dangerous than pure hydrogen gas. Hydrogen solubility is higher with higher temperature for many metals and when molten steel solidifies the hydrogen gets entrapped in the metal. The solubility is also higher for fcc than bcc which makes the entrapment worse when cooling from austenite to ferrite. Hydrogen can also enter the material during usage. When a high pressure hydrogen environment is present during high temperatures hydrogen can enter the metal. For high strength steel there are reports that hydrogen gas at a total pressure of only one atmosphere has caused cracking. [7]

There are several types of hydrogen damage. These are the following: [7, 8]

- Hydrogen embrittlement
- Hydrogen blistering
- Flakes, fish-eyes and shatter cracks
- Hydrogen attack
- Microperforation
- Degradation in flow properties

Properties of all these kinds of hydrogen damage are shown in Table 1, Table 2 and Table 3. More in depth description of them will follow in the following chapters.

Table 1: Properties of three kinds of hydrogen embrittlement [8]

	Hydrogen embrittlement		
	Hydrogen environment embrittlement	Hydrogen stress cracking	Loss in tensile ductility
Typical materials	Steels, nickel-base alloys, metastable stainless steel, titanium alloys	Carbon and low-alloy steels	Steels, nickel-base alloys, Be-Cu bronze, aluminum alloys
Usual source of hydrogen (not exclusive)	Gaseous H_2	Thermal processing, electrolysis, corrosion	Gaseous hydrogen, internal hydrogen from electrochemical charging
Typical conditions	10^{-12} to 10^2 MPa gas pressure	0.1 to 10 ppm total hydrogen content	0.1 to 10 ppm total hydrogen content range of gas pressure exposure
	Observed at -100 to 700 ° C; most severe near 20 ° C	Observed at -100 to 100 ° C ; most severe near 20 ° C	Observed at -100 to 700 ° C
	Strain rate important; embrittlement more severe at low strain rate; generally more severe in notched or pre cracked specimens	Strain rate important; embrittlement more severe at low strain rate; always more severe in notched or pre cracked specimens	Occurs without effect on yield stress; strain rate important
Failure initiation	Surface or internal initiation; incubation period not observed	Internal crack initiation	Surface and/or internal effect
Mechanisms	Surface or subsurface processes	Internal diffusion to stress concentration	Surface or subsurface processes

Table 2: Properties of hydrogen attack, hydrogen blistering and Shatter cracks, flakes and fisheyes [8]

	Hydrogen attack	Blistering	Shatter cracks, flakes, fisheyes
Typical materials	Carbon and low-alloy steels	Steels, copper, aluminum	Steels (forgings and castings)
Usual source of hydrogen (not exclusive)	Gaseous	Hydrogen sulfide corrosion, electrolytic charging, gaseous	Water vapor reacting with molten steel
Typical conditions	Up to 10^2 MPa at 200–595 °C	Hydrogen activity equivalent to 0.2 to 1×10^2 MPa at 0–150 °C	Precipitation of dissolved hydrogen during ingot cooling
Failure initiation	Surface (decarburization); internal carbide interfaces (methane bubble formation)	Internal defect	Internal defect
Mechanisms	Carbon diffusion (decarburization); hydrogen diffusion; nucleation and growth (bubble formation)	Hydrogen diffusion; nucleation and growth of bubble; steam formation	Hydrogen diffusion to voids

Table 3: Properties of micro-perforation, degradation in flow properties and metal hydride formation [8]

	Micro-perforation	Degradation in flow properties	Metal hydride formation
Typical materials	Steels (compressors)	Iron, steels, nickel-base alloys	V, Nb, Ta, Ti, Zr, U
Usual source of hydrogen (not exclusive)	Gaseous hydrogen	Gaseous or internal hydrogen	Internal hydrogen from melt; corrosion, electrolytic charging, welding
Typical conditions	2 to 8×10^6 MPa at 20–100 °C	1–10 ppm hydrogen content (iron at 20 °C) up to 10^2 MPa gaseous hydrogen	0.1 to 10^2 MPa gas pressure hydrogen activity must exceed solubility limit near 20 °C
Failure initiation	Unknown		Internal defect
Mechanisms	Unknown	Adsorption to dislocations; solid-solution effects	Hydride precipitation

3.1. Hydrogen embrittlement

Hydrogen embrittlement can be subdivided into three or four different categories. Here four types of hydrogen damage are put under hydrogen embrittlement: [7, 8]

- Loss in tensile ductility
- Hydrogen stress cracking
- Hydrogen environment embrittlement
- Embrittlement due to hydride formation

3.1.1. Loss in tensile ductility

Loss in tensile ductility occurs when distortions of the metal lattice caused by hydrogen atoms restricts dislocation movement. This phenomenon is only observed during slow strain rate testing and causes no visible defects, chemical products or cracking. It becomes more pronounced as the strain rate decreases. The extent of loss in area reduction as a function of hydrogen content is shown in Figure 5. This kind of damage is most often encountered in lower strength steel alloys and is fully reversible. By heating the metal it is possible to drive out the hydrogen and the rate of recovery is dependent on time and temperature. However, if heated to temperatures above 315° C, there is danger of high temperature hydrogen attack which will be explained in chapter 3.4. [7, 8]
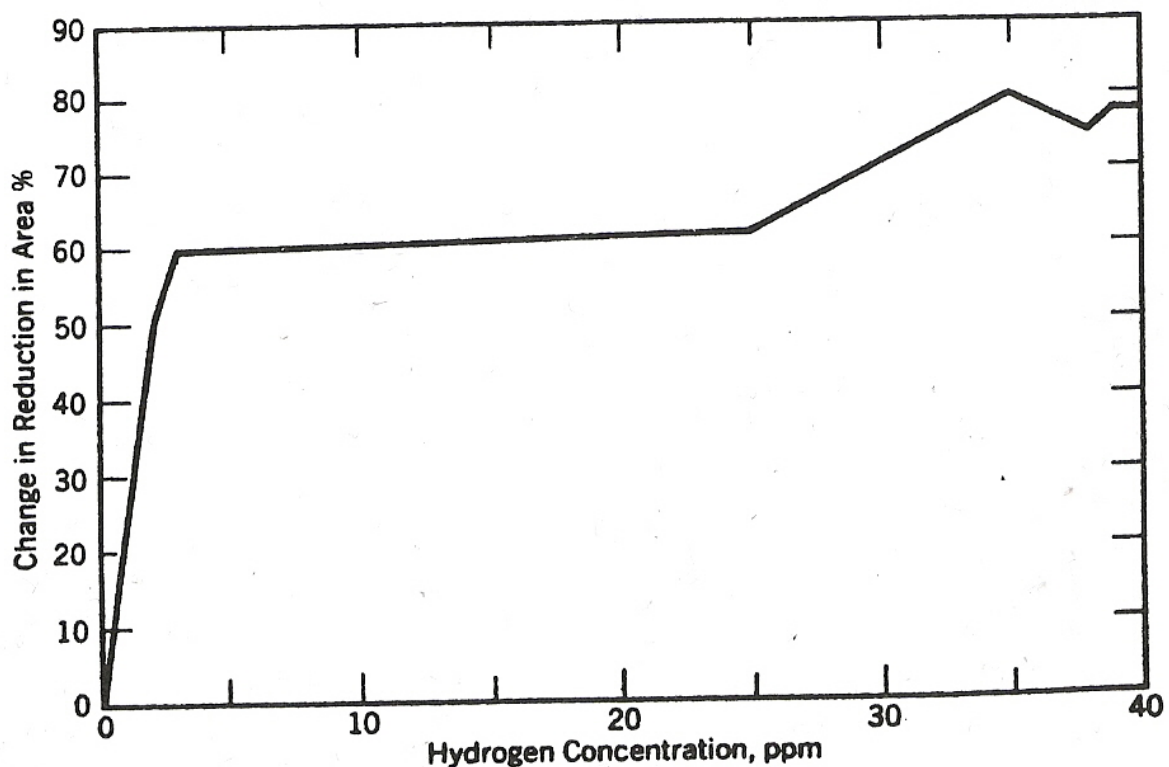
Figure 5: The change in reduction in area in percent as a function of hydrogen content in ppm [7]

3.1.2. Hydrogen stress cracking

Hydrogen stress cracking (HSC), which can also be referred to as hydrogen induced cracking (HIC), hydrogen assisted cracking (HAC), static fatigue or delayed failure, is a form of damage that affects normally ductile metal alloys. These alloys experiences crack growth and possibly brittle fractures during static load. These loads could be external, internal, caused by transformation, cold working or

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hardening. The total hydrogen concentration needed can be as low as 0.1 ppm even though local concentration values are substantially higher. Subsurface sites where the triaxial stresses are highest are good initiation sites for cracks if there are no cracks initiated in other manners available. The locally high hydrogen concentration ahead of the initiated crack tip then helps the subcritical crack to grow. [7]

The fracture time increases with decreasing load down to a steel strength and hydrogen environment dependent threshold level. Below this threshold there is no HSC. This threshold is higher for steel with lower yield- and tensile strength and this phenomenon usually does not affect steels below certain tensile strength levels. This means that the sensitivity to HSC increases with increasing ultimate tensile strength as can be seen in Figure 6. For ferrous alloys there is generally also a minimum hardness required at 22 HRC. [7]
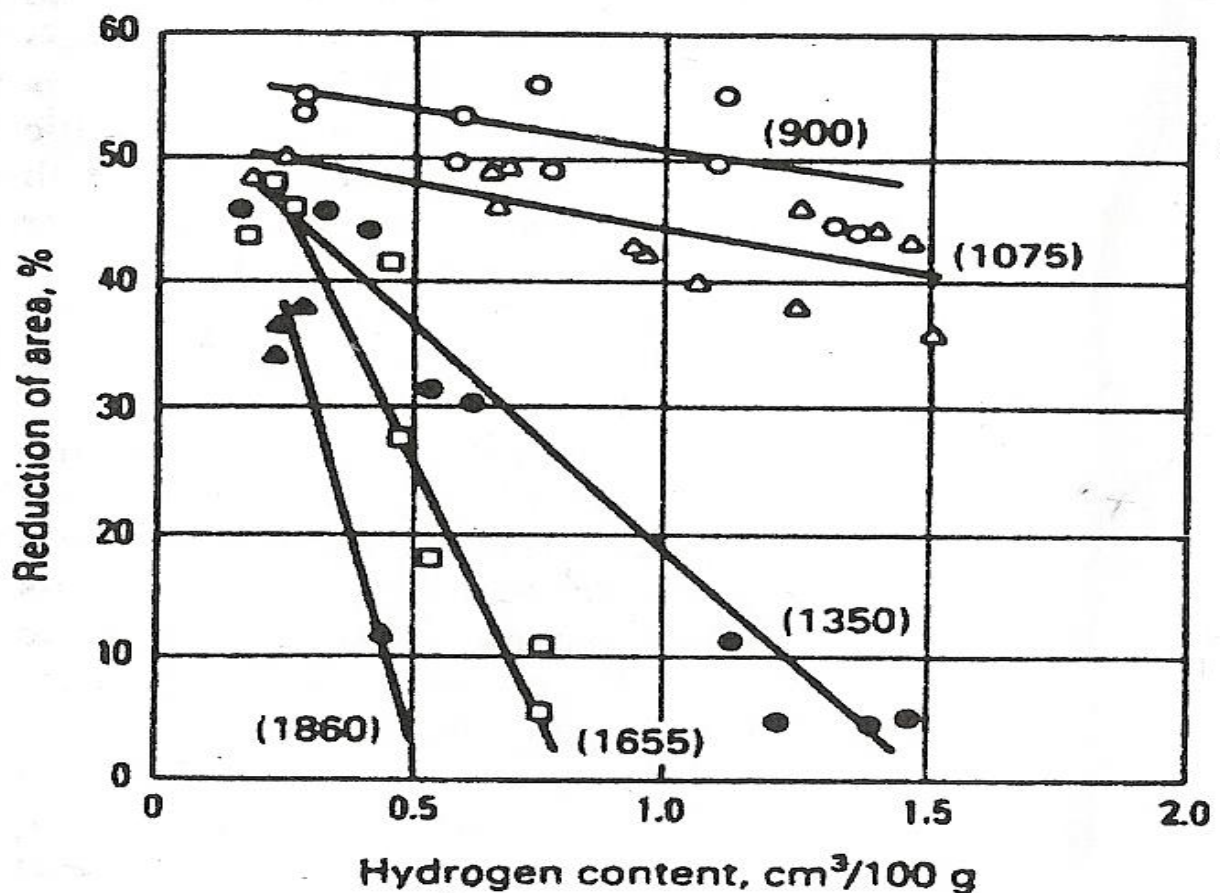

Figure 6: Ductility versus hydrogen content for various steels at various strength levels. The numbers in parentheses indicate the ultimate tensile strength in MPa [7].

Room temperature is the ultimate temperature for HSC. At this temperature the rate of hydrogen diffusion is such that there is a hydrogen buildup at crack nucleation sites and crack tips which is what creates this phenomenon. The need for diffusion of hydrogen makes this a delayed fracture mechanism dependent on hydrogen gas pressure and temperature. At temperatures well below room temperature the hydrogen diffusion is slow which makes the buildup slow. Therefore, HSC is not observed below -100° C. If the temperature reaches above 100° C the hydrogen tends to be homogeneously distributed in the metal lattice and the necessary buildup might not occur. [7, 8]

As can be seen in Figure 7 the HSC effect is reversible. If the hydrogen is removed by baking the steel at 150° C higher applied stress is needed for fracture after a certain time. Longer baking time increases the applied stress necessary. This work as long as the hydrogen has not formed any chemical bonding in the steel or if damage has already occurred before baking. [7, 8]
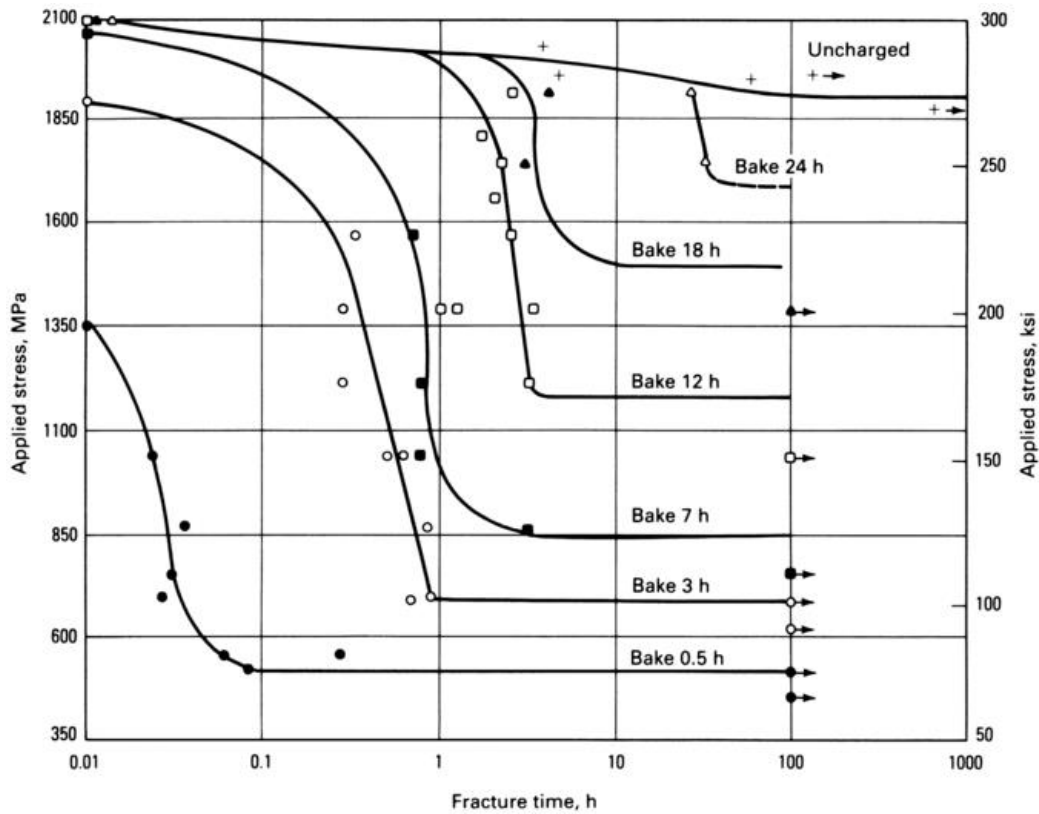
Figure 7: Static fatigue curves for various hydrogen concentrations obtained by different baking times at 150° C. Sharp notch strength steel specimens 1590 MPa; Normal notch strength: 2070 MPa [8]

Hydrogen can also induce cracking at slower strain rates. This hydrogen induced cracking has been observed during mechanical testing in hydrogen environments. As for delayed failure there is a minimum level of applied stress. This phenomenon is for the most part observed in higher strength steels and there is similar temperature dependence. This embrittlement of steel increases with decreasing strain rate because at higher strain rates the hydrogen does not diffuse fast enough for embrittlement to occur. This phenomenon can be seen in Figure 8. [7, 8]

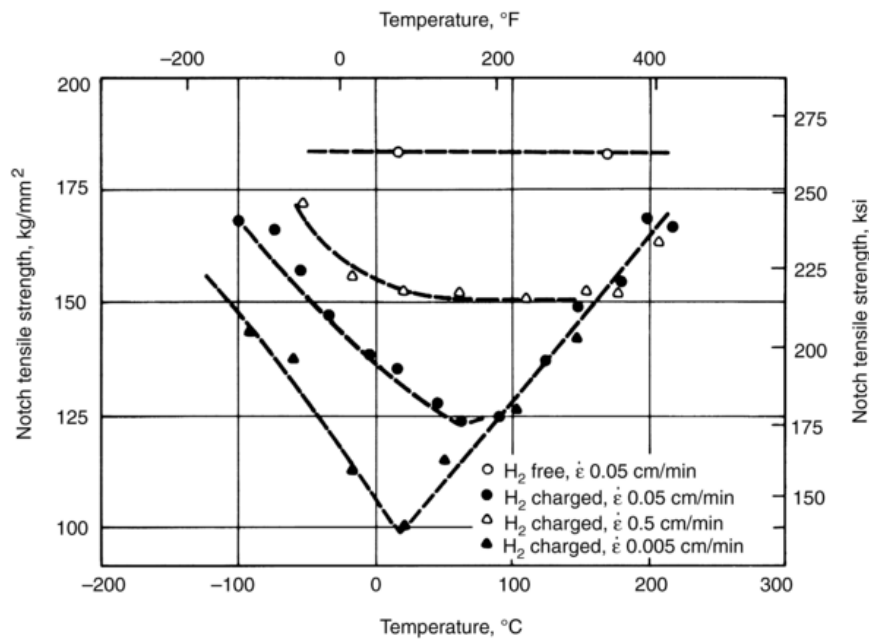Figure 8: Notch tensile strength of high strength steel plotted against testing temperature for three strain rates [7, 8]

The highest resistance to embrittlement in steels is found in highly tempered martensitic structure with equiaxed ferrite grains and spheroidized carbides evenly distributed throughout the matrix when comparing with normalized or bainitic steels at equivalent strength levels. The resistance also increases with decreasing prior austenitic grain size or if there is any retained austenite in the matrix. Individual alloying elements effect on crack susceptibility is associated with their effect on heat treatment, microstructure, and strength of the steel. Susceptibility increases with increasing strength. Generally, carbon, phosphorus, sulfur, manganese and chromium increases susceptibility while titanium decreases it because it decreases the amount of hydrogen available for cracking. [7, 8]

Fcc structure is relatively impermeable to diffusion of atomic hydrogen which makes the susceptibility if austenitic steels low. If heavily cold worked there is a risk for deformation induced martensite which increases the susceptibility of the steel. The martensitic steels are susceptible because of their high strength while ferritic steels are highly resistant because of their low hardness. In general, cold working and aging increases the susceptibility to cracking, the former due to the increase in strength and the latter because of segregation of sulfur and phosphorus to the grain boundaries. [7]

Intergranular cracks are generally observed in steels affected by hydrogen embrittlement. An example of an Intergranular crack can be observed in Figure 9. HSC usually produces sharp singular cracks like that one. The mode of fracture might be changed from the one normally observed into another. At higher stress intensities there have been reports of transgranular cracks in steel. The addition of silicon to an iron-carbon alloy also produced transgranular cracks. [7, 8]
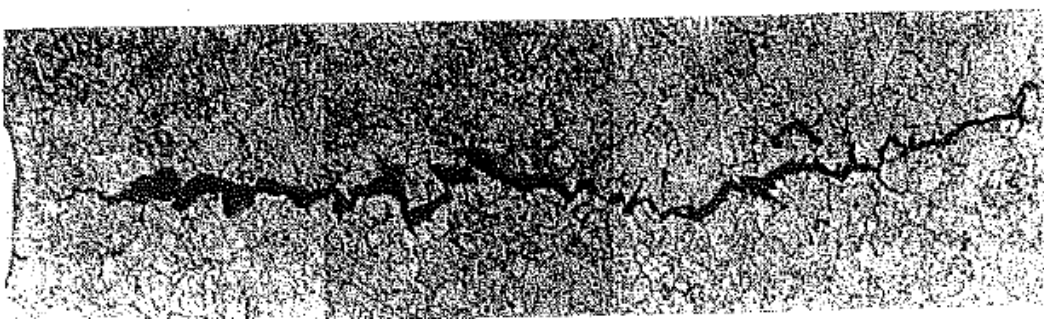
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Figure 9: Intergranular crack resulting from hydrogen embrittlement during chromium plating [7]

3.1.3. Hydrogen environment embrittlement

The characteristic for this kind of hydrogen embrittlement is comparable to HSC and there is therefore some debate if it is a phenomenon of its own or if it should be seen as HSC. It is encountered when performing plastic deformation of hydrogen free materials in hydrogen gas and it is strain rate dependent. The pressure of the hydrogen gas is between 35 and 70 MPa and it is most severe at room temperature just as for HSC. [7, 8]

3.1.4. Embrittlement due to hydride formation

This form of hydrogen embrittlement is found in a number of transition, rare earth and alkaline earth metals. The formation of hydride particles makes the former ductile metal become embrittled. It does not affect steel and is therefore not explained more thoroughly here. [7, 8]

3.2. Hydrogen blistering

The phenomenon of hydrogen blistering is caused by the pressure created when atomic hydrogen combines into molecular hydrogen. This can happen when a high enough concentration of atomic hydrogen accumulates at internal defects such as voids or inclusions in low strength unhardened steels. This could show as the formation of surface bulging, known as blisters, as can be seen in Figure 10 or delamination caused by internal blistering at grain boundaries as can be seen in Figure 11. It occurs predominantly in low strength alloys. [7, 8]
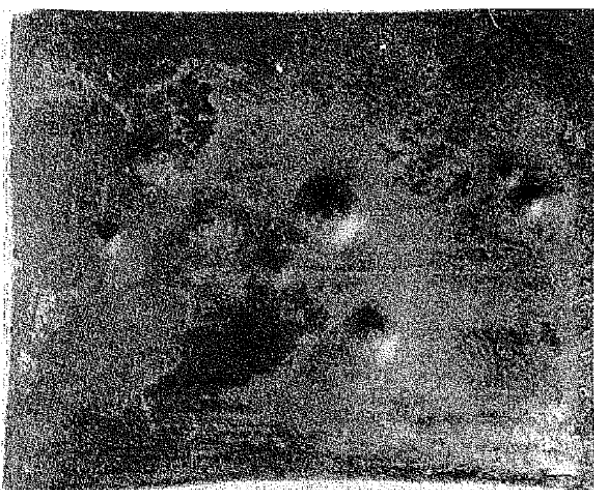

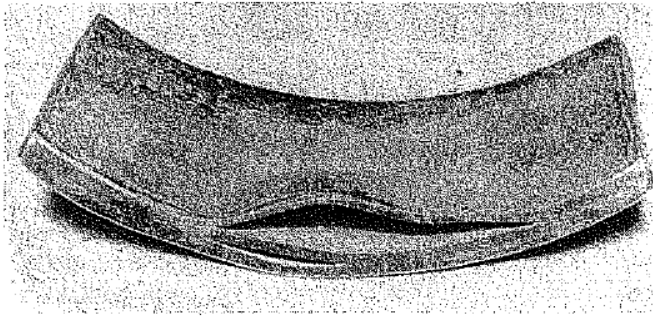Figure 10: Blisters in a carbon steel plate formed by hydrogen [7]

Figure 11: Delamination of a steel plate as a result of hydrogen blistering [7]

3.3. Flakes, fish-eyes and shatter cracks

Flaking refers to small internal fissures that occur in steel when cooled from temperatures in the order of 1100° C. They are also described by the terms fish-eyes and shatter cracks and are common features of hydrogen damage in forgings, weldments and castings. At higher temperatures of melting, welding or heat treatment in the austenitic range the solubility of hydrogen atoms is higher than in the solidified or lower temperature bcc state. The excess hydrogen accumulates at internal defects and the hydrogen atoms combine to form gaseous hydrogen. The mechanism for this as well as many features of it is similar to hydrogen blistering and it may therefore be considered a special case of hydrogen blistering. The extent of the damage is dependent on the time of exposure to a hydrogen containing environment. [7, 8]

3.4. Hydrogen attack

Absorbed hydrogen reacts with iron carbides or absorbed carbon to form hydrocarbon like methane. This takes place in carbon and low alloy steels exposed to high pressure hydrogen gas at high temperatures. The temperature has to be above 540° C for surface reaction and above 200° C for internal reaction. This phenomenon is called hydrogen attack and leads to weakening of the steel either by decarburization or by the defects and cracks generated by the hydrocarbon gas pressure. [7, 8]

The initial point of attack is often found at areas of high stress concentration since hydrogen diffuses to those areas. To prevent hydrogen attack from occurring it is a good idea to add carbide stabilizing elements such as vanadium, titanium, chromium or molybdenum. It does not occur in austenitic stainless steels which make them good choices for this kind of environments if they are suitable from other considerations. Operation limits of carbon steel and some alloy steels are shown in the Nelson curve in Figure 12. [7]
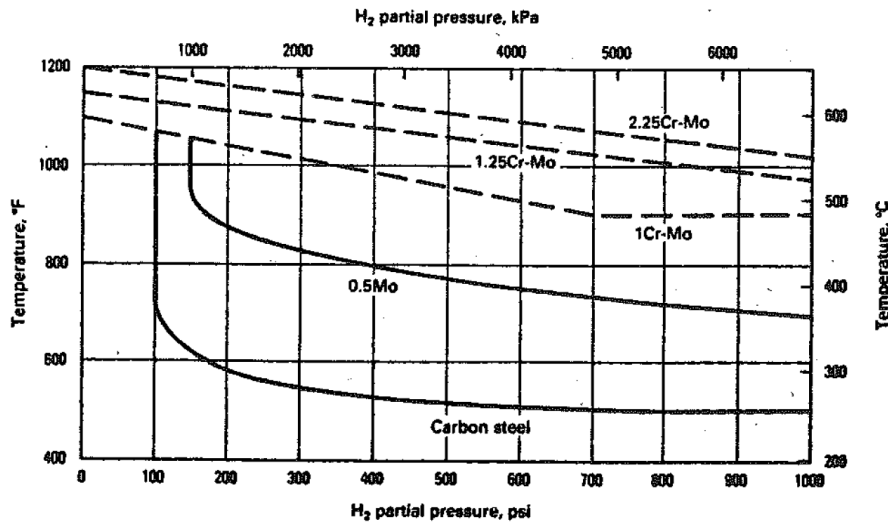
Figure 12: Nelson curves showing the operation limits of carbon and alloy steels in contact with hydrogen at high temperature and pressure [4]

3.5.Microperforation

In extremely high hydrogen pressure a network of small fissures can be formed. This occurs predominately in steels at room temperature and allows permeation of the alloy by gases and liquid. [8]

3.6.Degradation in flow properties

This is a form of hydrogen damage that occurs at ambient temperatures for iron and steel and at elevated temperatures for several other alloy systems. [8]

3.7.Preventive methods

For the different kinds of hydrogen damage there are different things that can be done to prevent the damage from occurring. Some of the things are similar between the types while some of the things only prevent one type of damage. [7]

3.7.1. Preventing hydrogen blistering or flaking

Blistering and flaking is similar which makes their prevention also similar and it is listed together. [6]

- Inclusions play a big role in blistering and flaking. Minimizing these is a good way of preventing blistering. Sulfur and sulfides have an especially poisonous effect on hydrogen evolution and the usage of low sulfur steels is recommended. The addition of rare earth elements can favor the formation of less detrimental globular sulfides. Hot rolled or annealed steel is preferred to cold rolled. [7]
- Material selection plays a big role in preventing blistering and flakes. It is good to avoid steels that contain a lot of voids like rimmed steels. Nickel containing steels are good since they generally have low hydrogen diffusion rates. [7]
- In finished products like tanks and containers, coatings can be used to prevent hydrogen penetration from the environment. [7]
- Removal of sulfides, arsenic compounds, cyanides and phosphorus containing ions greatly reduces hydrogen blistering. [7]

- When expecting hydrogen blistering design aspects has to be considered. For example, external support pads should not be continuously welded to the vessel itself to avoid hydrogen entrapment at the interface. [7]
- The decreased solubility of hydrogen in bcc structured steel compared to the fcc structure leads to flaking when cooling steel from high temperature. The faster the cooling is the more aggravated the damage gets because of hydrogen sensitive martensitic microstructure forming. At slower cooling rates the hydrogen will also have more time to be released from the steel and thereby eliminating the damage. [7]

3.7.2. Preventing hydrogen embrittlement
- In general, the susceptibility to hydrogen embrittlement increases with increasing tensile strength. For many steels a stress threshold exists. For non-acidic environments the threshold is considered to be around 1000 MPa. Choosing materials below this threshold and/or below 22 HRC is a good way to prevent this kind of damage. [7, 8]
- To remove hydrogen from a steel baking can be used. It is a heat treatment at low temperature (up to 200° C) for a longer period of time; se Figure 7.This can restore the mechanical properties almost to their normal levels as long as no irreversible damage has occurred. Heat treatment to improve the microstructure, especially untempered martensite which is the most susceptible phase, is a good way to prevent hydrogen embrittlement. Quenched and tempered microstructures fairs better than normalized and tempered ones. [7]
- Alloying the steel with hydride forming elements like titanium, molybdenum and vanadium reduces susceptibility. [7]
- Pickling is often the source for hydrogen pickup. The addition of inhibitors to reduce the corrosion of the base metal can largely decrease hydrogen pickup. [7]
- Proper cleaning and degreasing procedures and the use of dry electrodes and maintenance of dry conditions is important for avoiding hydrogen embrittlement when welding. Preheating and a postweld heat treatment are also recommended. [7]
- If the steel is in a gaseous environment the addition of 0.4-0.7 % oxygen is efficient at inhibiting the hydrogen embrittlement in the steel. This is though not effective in hydrogen sulfide gas environments. [7]

3.7.3. Preventing hydrogen attack
- Carbide forming elements like chromium and molybdenum increases the resistance to hydrogen attack. Low carbon content should be used as higher carbon content means decreased resistance. Austenitic stainless steels are immune to hydrogen attack but atomic hydrogen can still diffuse through thin sections and can affect nonresistant substrate materials. [7]
- The operation limit of any steel regarding hydrogen attack can be found in its Nelson curve, se Figure 12 for an example. The curves are based on long term refinery experience rather than laboratory studies and they are reviewed regularly. [7]

3.8.Room temperature creep

Time dependent plastic deformation is generally considered a high temperature phenomenon, above 0.4 times the melting point (about 440° C). But a form called room temperature creep (RTC) is common behavior in most steels and alloys such as stainless steels, pipeline steels and high strength steels. This deformation is the result of mobile dislocations and the creep rate gradually decreases and reduces to zero when the dislocation density is exhausted. Therefore, RTC alone may not cause serious failure in components. However it may affect stress corrosion cracking by causing local rupture of the surface passivation film or by enhancing hydrogen diffusion through dislocation movement. RTC is an important factor affecting crack propagation behavior even though no direct crack propagation is observed due to it even after hold times of several days. [9, 10]

3.9.Ultrasonic testing

Ultrasonic testing is more than 40 years old. It uses ultrasonic oscillations for detection of flaws in different materials. The principle is based on that solid materials are good conductors of sound waves. The sound waves are not just reflected on the interfaces but also on internal flaws. An ultrasonic pulse is transmitted into the material. Reflected parts of the ultrasonic pulse generate an electric signal that is displayed. Internal flaws as well as the edges of the material generate this signal. [11]

To determine the sizes of any internal flaws, a reference flaw, called a flat bottom hole, of known size is analyzed. The strength of the ultrasonic signal from the material tested is then compared to the value from the flaw of known size. The result size is presented as percentage of the known flaw size. [11]

4. Materials

Here there will be a brief description of the different steel types and their properties and possible application. In Table 4 a list of the different steel specimens with their steel types, diameter, rolling date, charge number and a brief description is shown. All of the steel specimens were round bars rolled with profile rolling.

Table 4: A list of Ovako steel type, diameter, rolling date, Ovako charge number and a brief description for the materials tested

Ovako steel type	Diameter (mm)	Rolling date (y-m-d)	Ovako charge number	Description of steel type
157C	190	2012-11-12	V9083	Ovako 157 is a high cleanliness case hardening steel used for bearing and transmission components.
157B	190	2012-06-03	V7817	
157B	190	2012-03-10	V6337	
826B	190	2013-03-13	D1103	Ovako 826B is a through hardening bearing steel that is mainly used for medium and large sized bainitic bearing rings, but it can also be used for machine components that require high tensile strength, hardness and toughness.
826B	190	2011-10-23	V5265	
281P	210	2013-03-06	D1051	Ovako 281 is an oil and water hardening microalloyed steel. Used for machine components etc. that require high tensile strength, good machinability and weldability
281T	210	2011-12-11	V5845	

In Table 5 the composition of the different steel types, their approximate hardness values (HB) and Tabular HRC and HV values derived from those are shown.

Table 5: Official composition of the steel types, their given HB values and tabular HRC and HV values [12-18]

Ovako steel type	Composition in weight%	C	Si	Mn	P	S	Cr	Ni	Mo	Approximate hardness after hot rolling (HB)	Tabular HRC	Tabular HV
157 B	min	0.17	0.20	0.55	-	-	0.50	1.65	0.90	250	25	250
	max	0.22	0.30	0.65	0.015	0.005	0.60	2.00	1.10	300	33	305
157 C	min	0.17	0.20	0.55	-	-	0.50	1.65	0.23	250	25	250
	max	0.22	0.30	0.65	0.015	0.005	0.60	2.00	0.28	300	33	305
826B	min	0.92	0.25	0.60	-	-	1.65	-	0.40	400	43	423
	max	1.05	0.40	0.80	0.025	0.015	1.95	0.25	0.50	500	52	565
281P	min	0.17	0.25	1.45	-	-	0.15	-	-	200	16	199
	max	0.22	0.40	1.75	-	-	0.25	<0.30	<0.10	250	25	250
281T	min	0.17	0.40	1.45	-	-	0.15	-	-	200	16	199
	max	0.22	0.60	1.75	-	-	0.25	<0.30	<0.10	250	25	250

For every charge at Ovako the hydrogen amount is measured and registered. The registered values for the charges used in this work are given in Table 6.

Charge number	H (ppm)
V9083	1.1
V7817	1.1
V6337	1.1
D1103	1.0
V5265	0.7
D1051	1.7
V5845	0.7

Figure 13, Figure 14 and Figure 15 shows CCT diagrams for the different steel types. Since Ovako in Hofors do not produce a finished product they are cooled in air and the exact cooling speed is not known and therefore neither is the exact structure they end up with. [12]
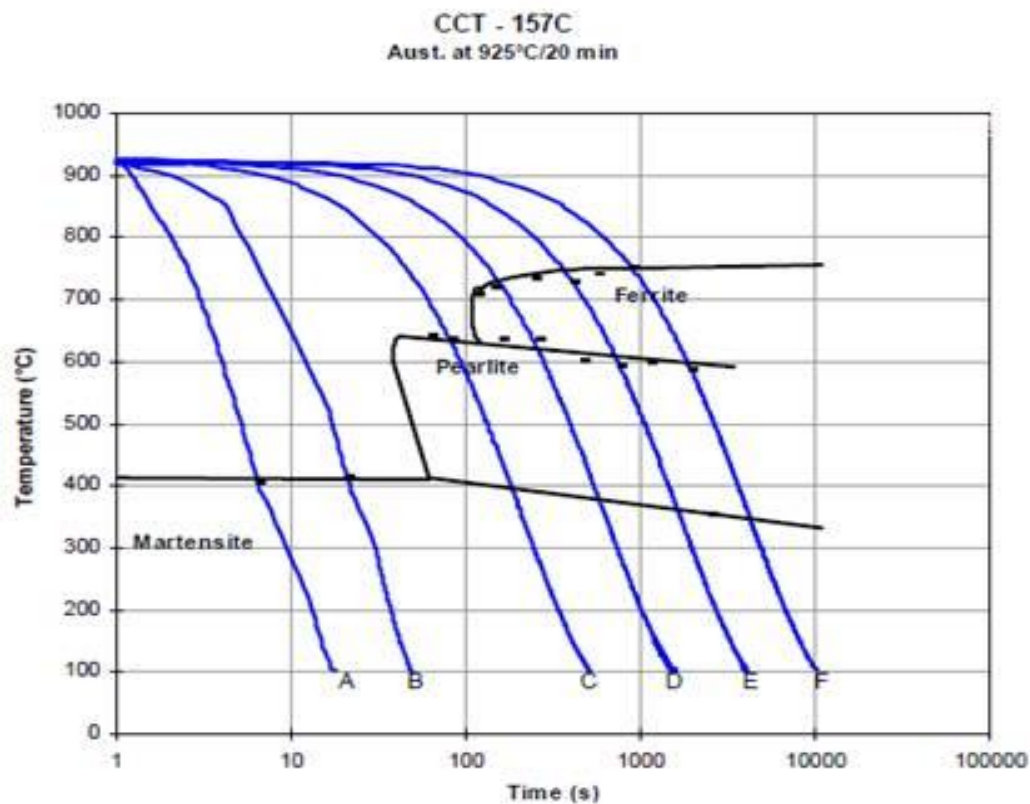

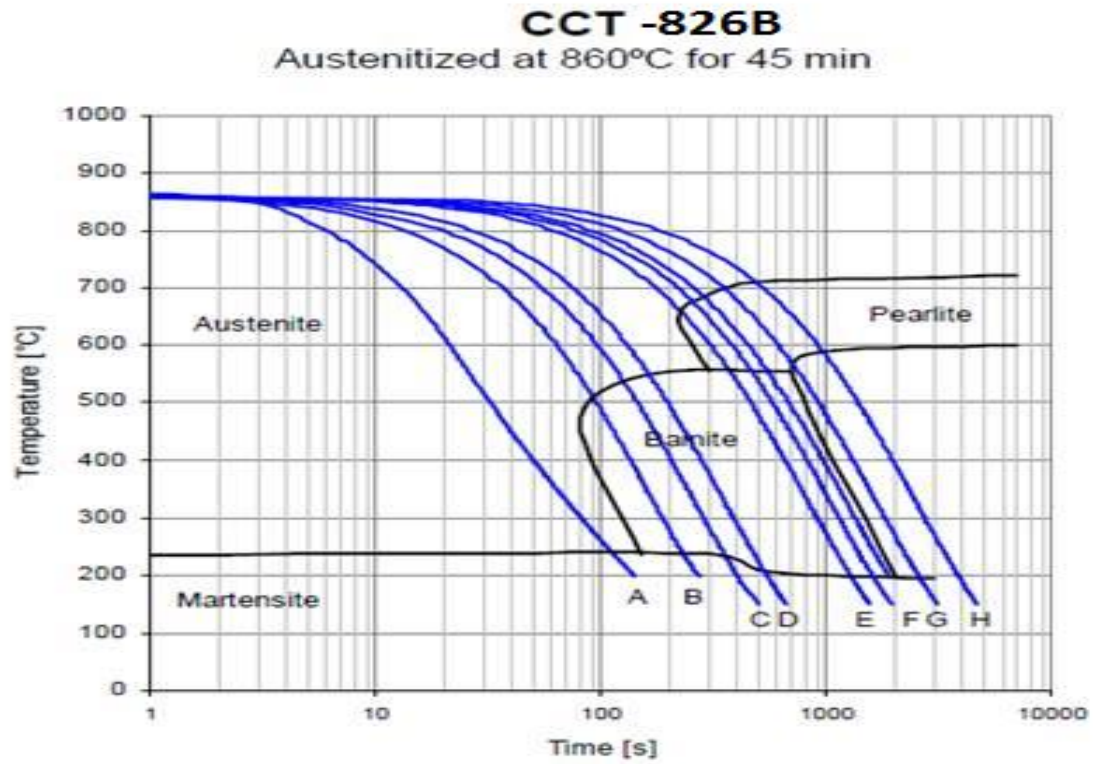Figure 13: CCT diagram for Ovako steel type 157C [12]

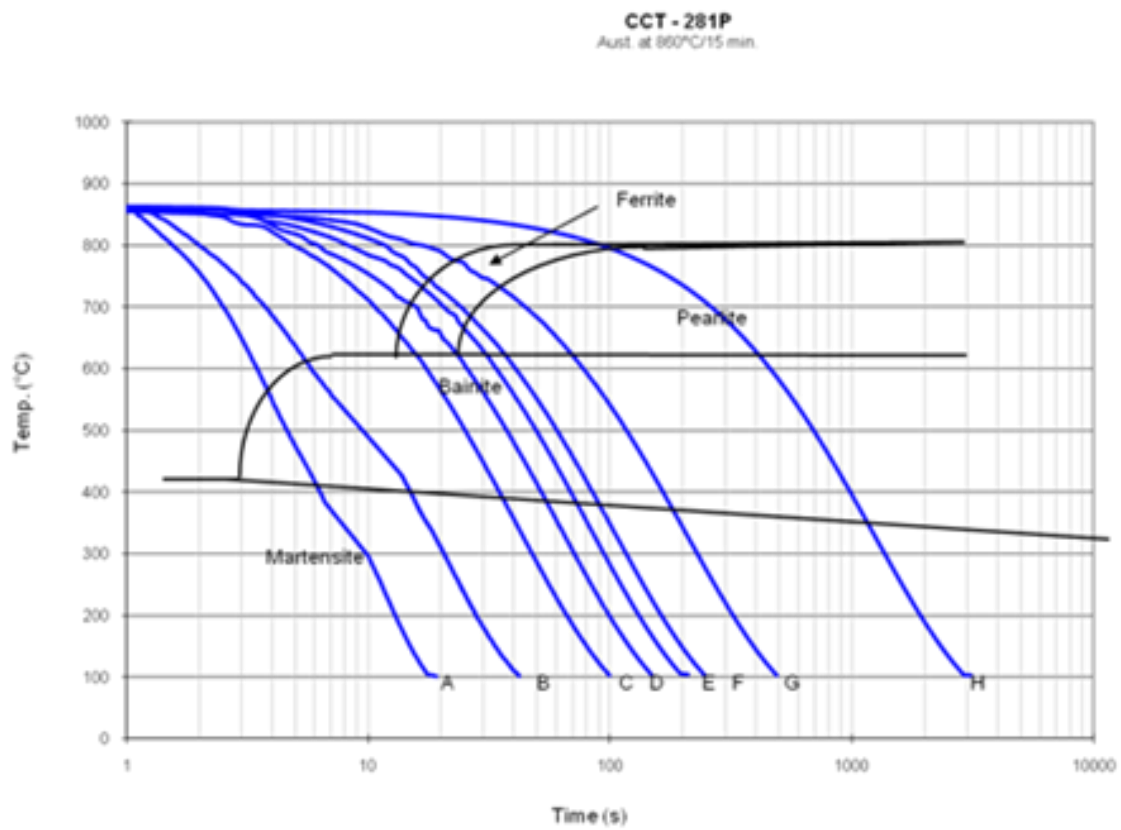**Figure 14: CCT diagram for Ovako steel type 826B [12]**

Figure 15: CCT diagram for Ovako steel type 281P [12]

5. Methods and equipment

Several sources of information was found and used to formulate an initial approach to the task. Then the steel type to be studied was selected. Here consideration had to be taken to what material was available. Three different steel types were selected where both materials newly rolled and material with older rolling dates was available.

5.1. Ultrasonic testing

The selected bars were examined with portable ultrasonic testing to find a part with an available defect to study. Two pieces were cut out from each bar, se Figure 16. One of the two was between 2 and 3 dm long and the other was between 1 and 2 dm long. The smaller one was cut out to include defects if any were found. The longer were cut out next to it.

Figure 16: Picture of the cut out pieces from three bars of steel type 157B and 157C.

The longer one was send to Ovako's lab where they were annealed and cut into a rectangular shapes around its center and analyzed in their ultrasonic testing machine calibrated against a 0.2mm FBH. The shorter ones were sent to Högskolan Dalarna. At Högskolan Dalarna an ultrasonic examination were made to try and localize the defects. The ultrasonic testing equipment used was Karl Deutsch D-5600 Wuppertal 1 type: 1013.0511 F-Nr 3033. With the nozzle: Karl Deutsch s12 HB4 art.nr 1411.0031 F-Nr 3105.

5.2. XRF analysis

The specimens that defects were found in were cut, during water cooling, into smaller pieces. The pieces where the defects were located were examined with the same ultrasonic testing equipment again to get a better estimation of the defect location. Then they were cut so that the pieces containing defects only needed to be cut once or twice more to be of appropriate size for grinding. At this stage the pieces containing defects were by mistake mixed with a few pieces without defects.

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Two or three pieces of each steel type were present in this mix. A few was possible to identify by visual cue. To identify all of them X-ray fluorescence (XRF) analysis were used. The equipment used was Thermo Scientific Nitron XL3t XRF Analyser.

To have something to compare with pieces from all of the involved material was used as a reference. From comparing the composition of these pieces with the result of the XRF analysis it was possible to sort out most of the pieces. To separate the ones with very similar composition from each other visual cues and their dimension was used to link them to each other and to the right steel type. It was possible to determine which pieces that contained defects by visual markings distinguishable when sorted in groups of each steel type.

5.3. Defect examination

The final cutting of the pieces with defects was made so that they were of the appropriate size for grinding. These were then grinded approximately 0.3mm at a time with 320P grinding paper. After grinding 0.3mm a 800P grinding paper was used to create a finer surface. The surface was then examined in an optical microscope to search for internal defects. This was repeated until a surface with defects was found. Example pictures were taken with the optical microscope of the found defects.

If the defect found was in the form of a crack or cracks the specimen were grinded with 1200P grinding paper to create a finer surface and then etched with a 3% Nital solution. If the defect was in the form of a pit or pits the specimen was not grinded further or etched. These samples were then examined in a scanning electron microscope and the compositions of the bulk material as well as any interesting defects found were analyzed with energy-dispersive X-ray spectroscopy.

5.4. Hardness testing

Pieces without defect were cut from each of the original specimens except one. The two specimens from the steel type 826B proved hard to cut because of their hardness. To cut out a piece from one of them an angle grinder was forced to be used. Cooling by water could only be made while not cutting which made the possibility of heating effects higher. Therefore only one of the original specimens was cut up. These pieces were cut into the appropriate size and baked into bakelite pucks. These steel specimens were then tested for their hardness by two methods. HRC with a HRC LECO KT-240 hardness tester with a load of 150kg and HV with a Vickers Matsu Zawa MxT50 Micro hardness tester with a load of 1Kg.

For HRC five test of each specimen was done and an average calculated. For HV three tests were done for each specimen with an average calculated. From the HV values an estimated tensile strength were calculated.

6. Results

6.1. Hardness testing

Measured hardness values and tensile strength estimated from the HV value are shown in Table 7 and Table 8.

Table 7: Measured hardness value in HRC for the tested specimens.

Ovako charge number	Steel type	HRC1	HRC2	HRC3	HRC4	HRC5	Average HRC
V9083	157C	10	16	38	14	38	23
V7817	157B	51	20	35	32	21	32
V6337	157B	20	19	19	25	33	23
D1103	826B	37	36	37	37	45	38
D1051	281P	5	9	7	24	25	14
V5845	281T	13	18	19	22	16	18

Table 8: Measured hardness value in HV and estimated tensile strength for the tested specimens.

Ovako charge number	Steel type	HV1	HV2	HV3	Average HV	Estimated tensile strength (3,33*HV) [18]
V9083	157C	260.6	234.3	253.6	250,0	833
V7817	157B	264.3	265.6	264.3	265,0	882
V6337	157B	272.7	258.1	246.1	259,0	863
D1103	826B	380	390	324.8	365,0	1216
D1051	281P	250.1	272.1	243.8	255,0	849
V5845	281T	263.7	280.5	239.1	261,0	869

6.2. Ultrasonic testing

Four of the seven selected bars showed signs of defects when using ultrasonic testing at Ovako. The cut out pieces from the same bars also showed defects when tested at Högskolan Dalarna. These can be seen in in Table 9.

Table 9: This table shows which of the seven bars that showed signs of defects when using ultrasonic testing at Ovako and Högskolan Dalarna and if the signal came from a single point or from an area

Ovako charge number	Steel type	Defect found at Ovako (ultrasonic testing)	Defect found at Högskolan Dalarna (ultrasonic testing)
V9083	157C	Yes	Yes (signal from one point)
V7817	157B	Yes	Yes (signal from an area)
V6337	157B	Yes	Yes (signal from an area)
D1103	826B	No	No
V5265	826B	No	No
D1051	281P	Yes	Yes (signal from an area)
V5845	281T	No	No

In Figure 17-Figure 23 the results from the ultrasonic testing in the lab at Ovako are shown. The test is calibrated so that 100% = 0.2 mm flat bottom hole.
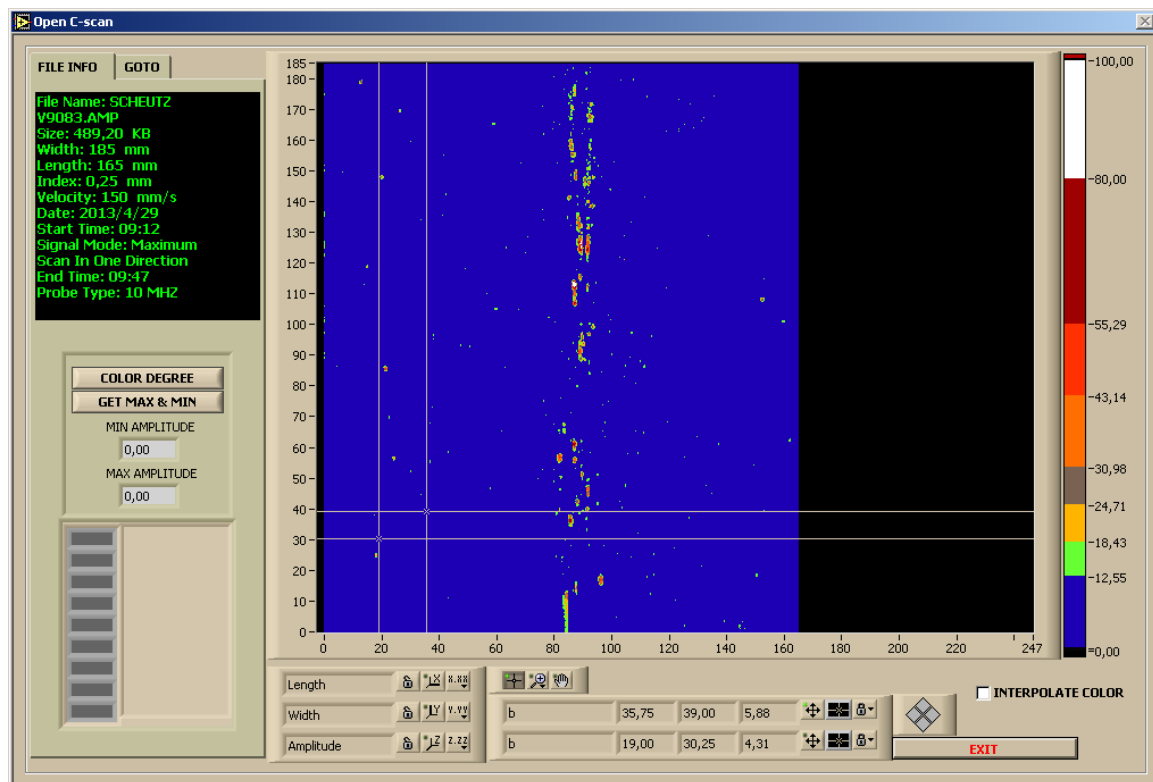
Figure 17: Ultrasonic testing in the lab at Ovako for steel specimen with charge number v9083, steel type 157C and rolling date 2012-11-12
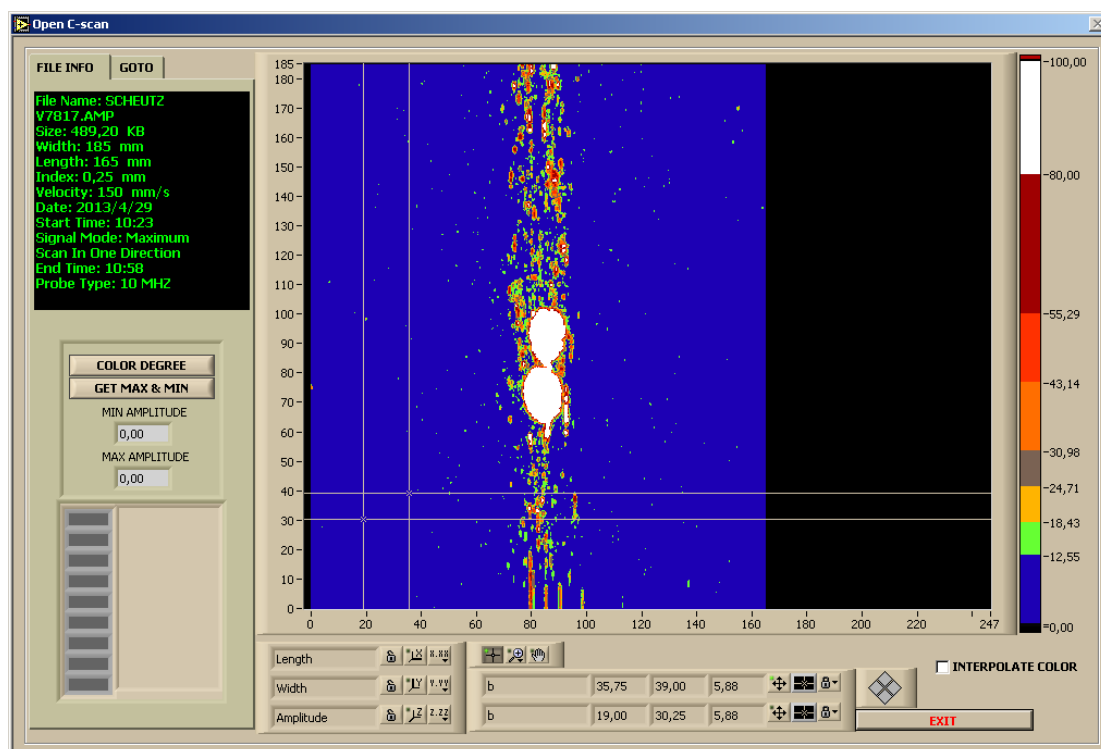

Figure 18: Ultrasonic testing in the lab at Ovako for steel specimen with charge number v7817, steel type 157B and rolling date 2012-06-03
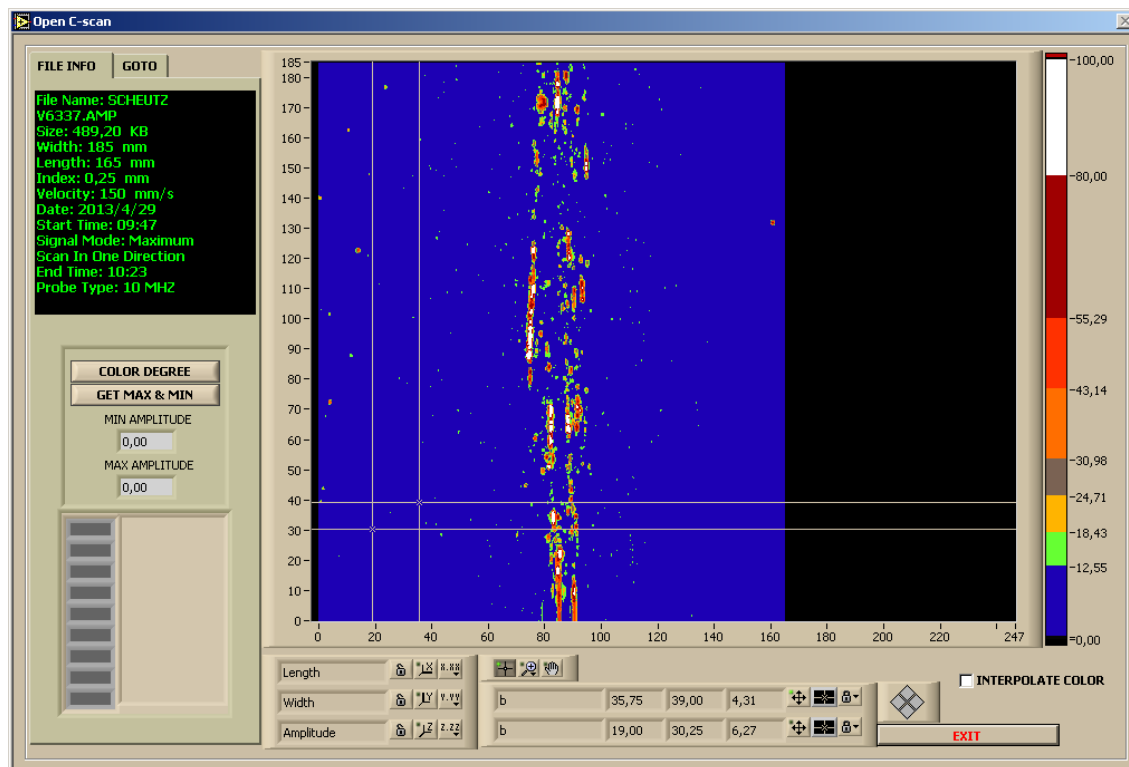
Figure 19: Ultrasonic testing in the lab at Ovako for steel specimen with charge number v6337, steel type 157B and rolling date 2012-03-10

Figure 20: Ultrasonic testing in the lab at Ovako for steel specimen with charge number D1103, steel type 826B and rolling date 2013-03-13

Figure 21: Ultrasonic testing in the lab at Ovako for steel specimen with charge number v5265, steel type 826B and rolling date 2011-10-23
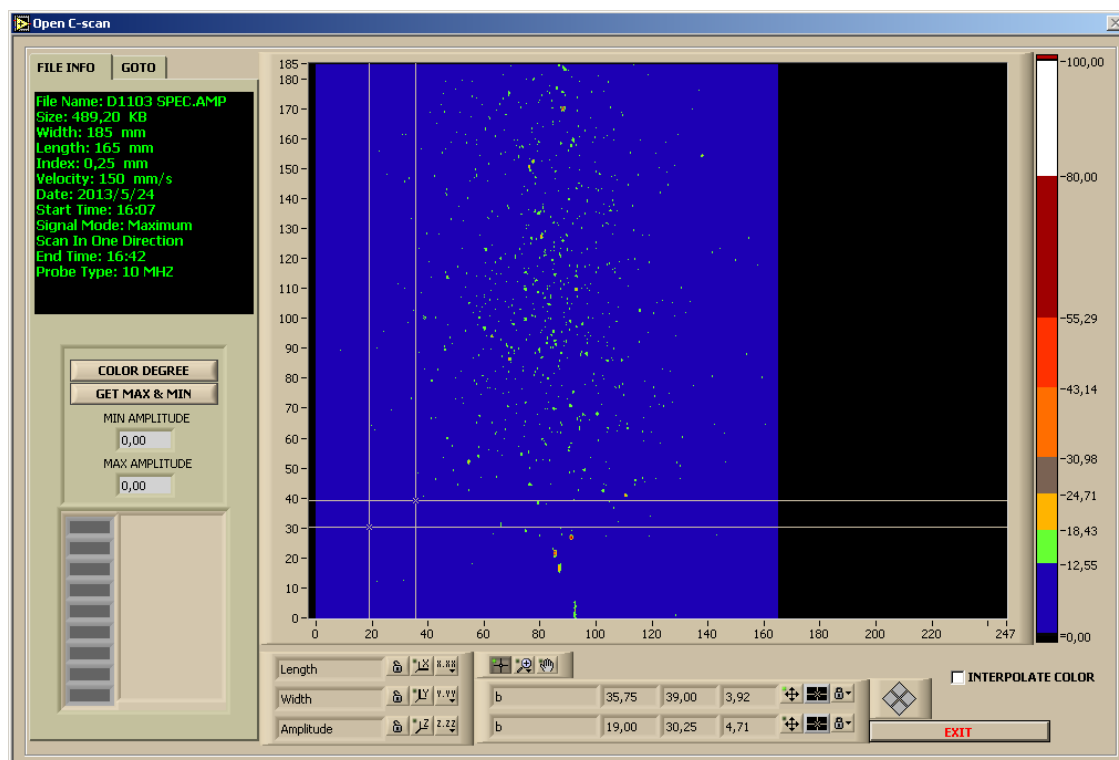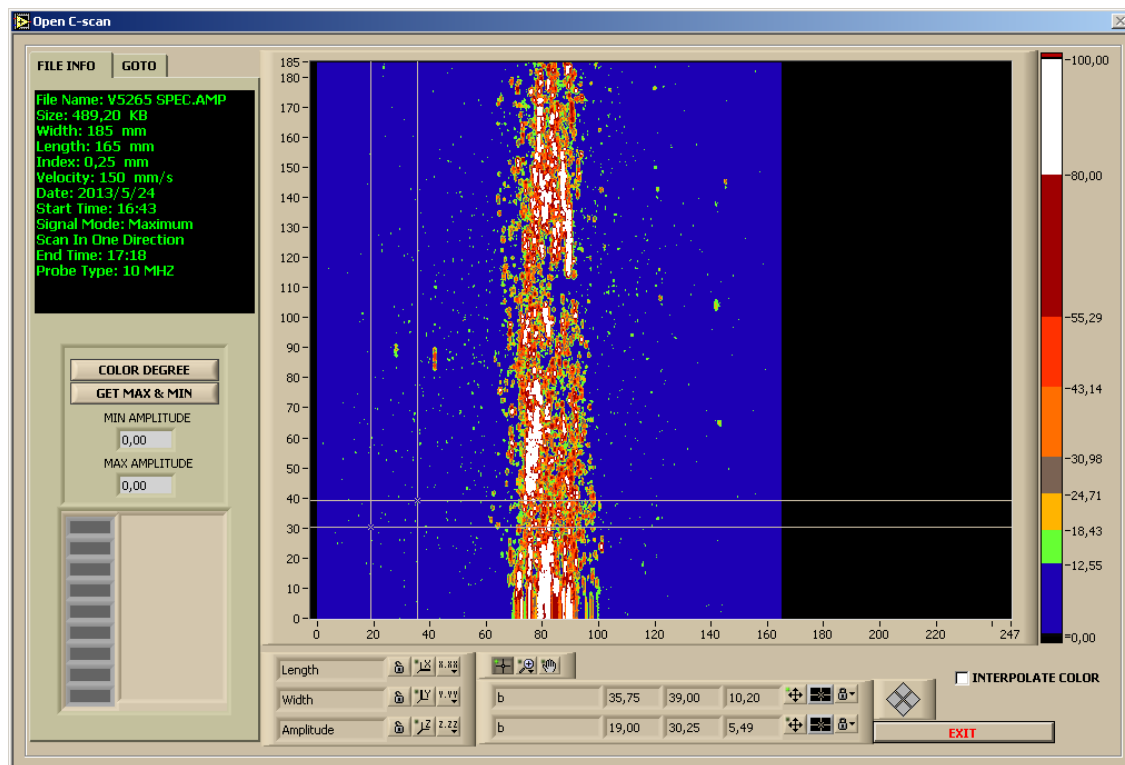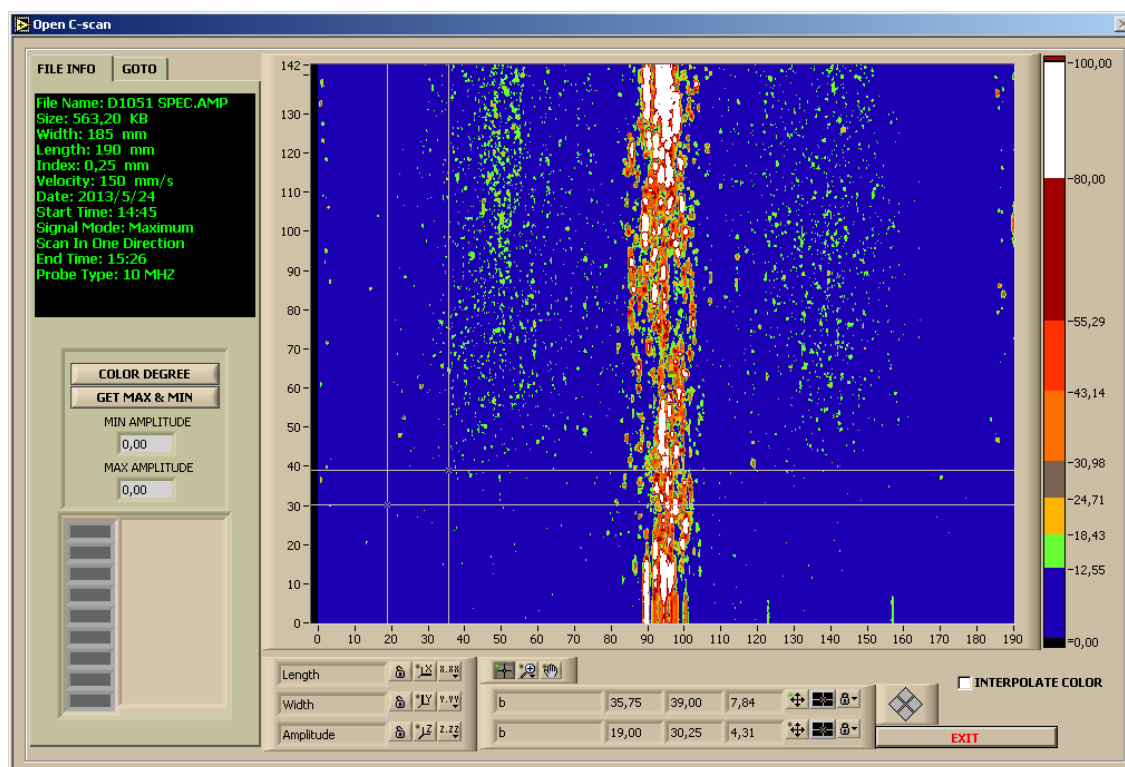

Figure 22: Ultrasonic testing in the lab at Ovako for steel specimen with charge number D1051, steel type 281P and rolling date 2013-03-06
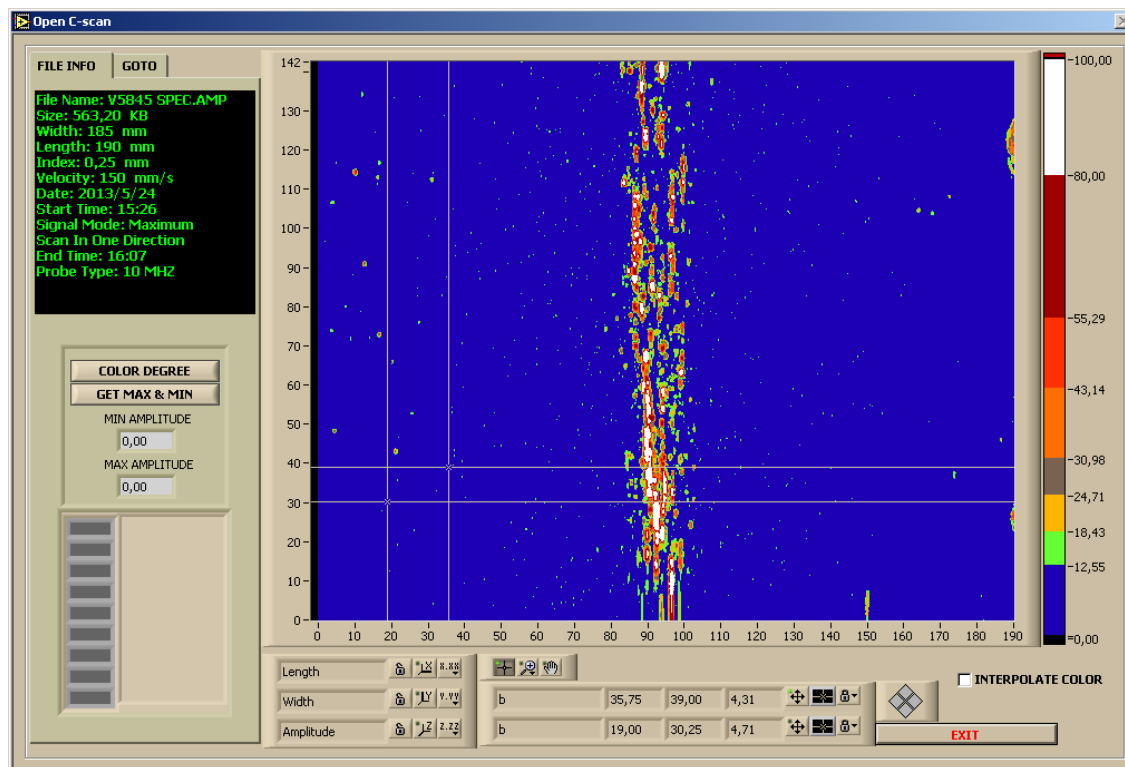
Figure 23: Ultrasonic testing in the lab at Ovako for steel specimen with charge number v5845, steel type 281T and rolling date 2011-12-11

6.3.XRF analysis

Table 10 shows the results from the XRF analysis of the pieces that were mixed together. From this information and from visual comparison it was possible to figure out which pieces that was from the same charge number. The ones named are the reference pieces or pieces possible to identify with visual cues. The latter ones are the ones whose names are followed by a 2.

Table 10: Results from the XRF analysis of the mixed together specimens and the reference pieces.

SAMPLE	Fe	Cr	Ni	Mn	Mo	Cu	V
unknown1	96.17	0.52	1.72	0.60	0.27	0.06	-
unknown2	95.99	0.45	1.84	0.52	0.97	0.19	-
unknown3	96.13	0.43	1.74	0.51	0.98	0.17	-
unknown4	97.89	0.23	0.10	1.41	0.04	0.20	0.12
unknown5	97.54	0.24	0.13	1.40	0.03	0.14	0.13
unknown6	96.14	0.43	1.70	0.52	1.00	0.18	-
d1051	97.89	0.23	0.10	1.41	0.04	0.15	0.11
d1051,2	97.86	0.25	0.12	1.42	0.04	0.17	0.10
v6337	96.05	0.44	1.78	0.49	0.96	0.18	-
v6337,2	95.96	0.43	1.83	0.51	1.00	0.20	-
v7817	96.03	0.44	1.69	0.53	1.01	0.15	-
v9083	96.17	0.51	1.64	0.63	0.27	0.07	-
v9083,2	96.06	0.52	1.78	0.60	0.26	0.07	-

6.4. Optical microscope analysis

Pictures taken in optical microscope of the defects surfaces examined further are shown in Figure 24-Figure 27.

Figure 24: Picture from optical microscope showing a defect in the steel with charge number v9083. The picture width is 210 µm
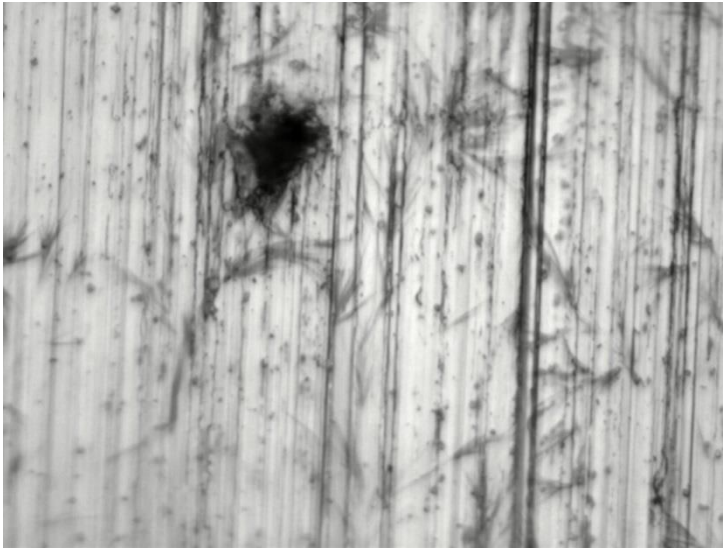

Figure 25: Picture from optical microscope showing defects in the steel with charge number v7817. The picture width is 520 µm

Figure 26: Picture from optical microscope showing defects in the steel with charge number v6337. The picture width is 1030 μm

Figure 27: Picture from optical microscope showing defects in the steel with charge number d1051. The picture width is 210 μm

6.5. Electron scanning microscope analysis

6.5.1. Steel specimen with charge number v9083

In this specimen one defect was found. EDX analysis of the bulk material was made in an area and on one point in the defect. The results are shown in Figure 28 and Table 11.

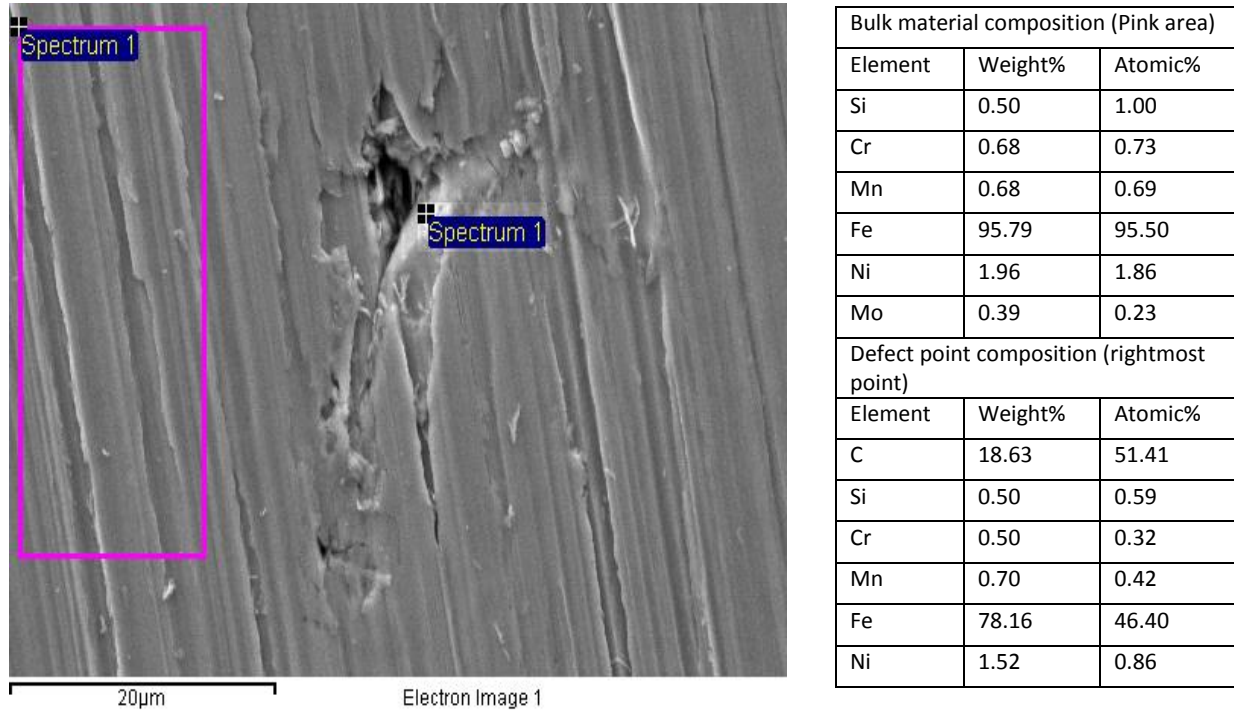**Table 11: Bulk Material and defect EDX analysis and compositions**

Bulk material composition (Pink area)		
Element	Weight%	Atomic%
Si	0.50	1.00
Cr	0.68	0.73
Mn	0.68	0.69
Fe	95.79	95.50
Ni	1.96	1.86
Mo	0.39	0.23
Defect point composition (rightmost point)		
Element	Weight%	Atomic%
C	18.63	51.41
Si	0.50	0.59
Cr	0.50	0.32
Mn	0.70	0.42
Fe	78.16	46.40
Ni	1.52	0.86

Figure 28: Bulk Material and defect EDX analysis and compositions

6.5.2. Steel specimen with charge number v7817

In this specimen one chain of defects were found as well as several smaller defects. EDX analysis of the bulk material as well as on representative defects was made. A SEM picture of a chain of defects in the sample is shown in Figure 30. The defect length is in the rolling direction. The results from the EDX analyses are shown in Figure 29, Figure 31, Table 12 and Table 13.

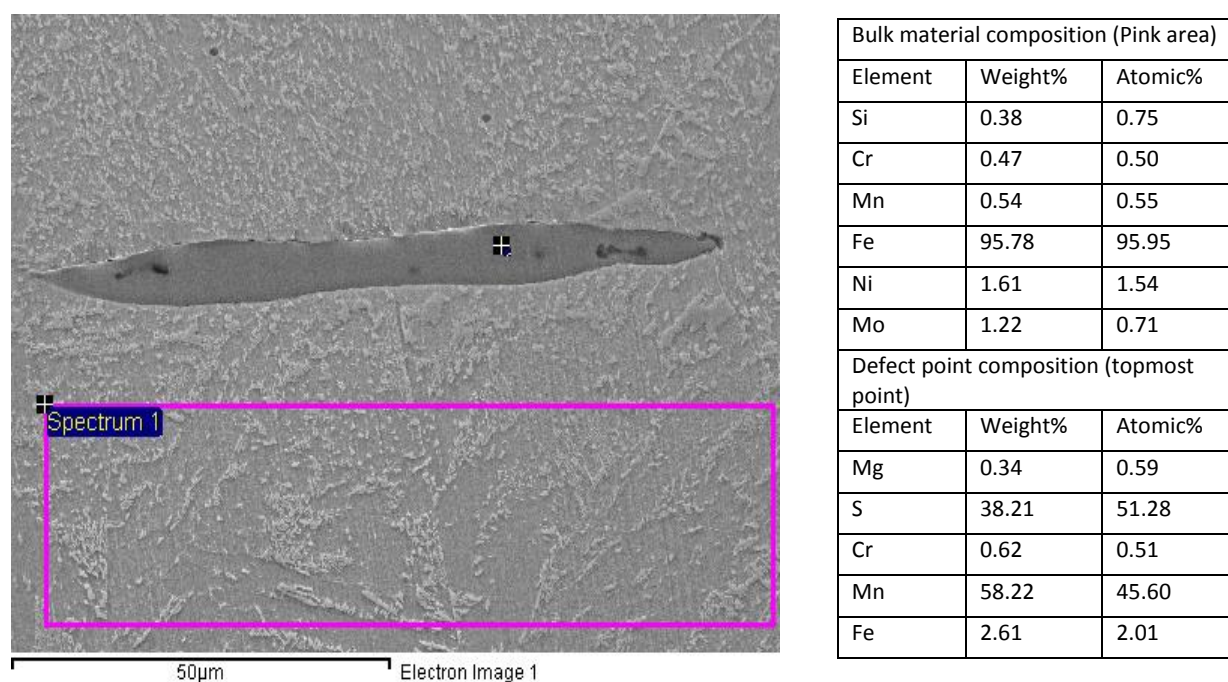**Table 12: Bulk Material and defect EDX analysis and compositions for steel specimen with charge number v7817**

Bulk material composition (Pink area)		
Element	Weight%	Atomic%
Si	0.38	0.75
Cr	0.47	0.50
Mn	0.54	0.55
Fe	95.78	95.95
Ni	1.61	1.54
Mo	1.22	0.71
Defect point composition (topmost point)		
Element	Weight%	Atomic%
Mg	0.34	0.59
S	38.21	51.28
Cr	0.62	0.51
Mn	58.22	45.60
Fe	2.61	2.01

Figure 29: Bulk Material and defect EDX analysis and compositions for steel specimen with charge number v7817
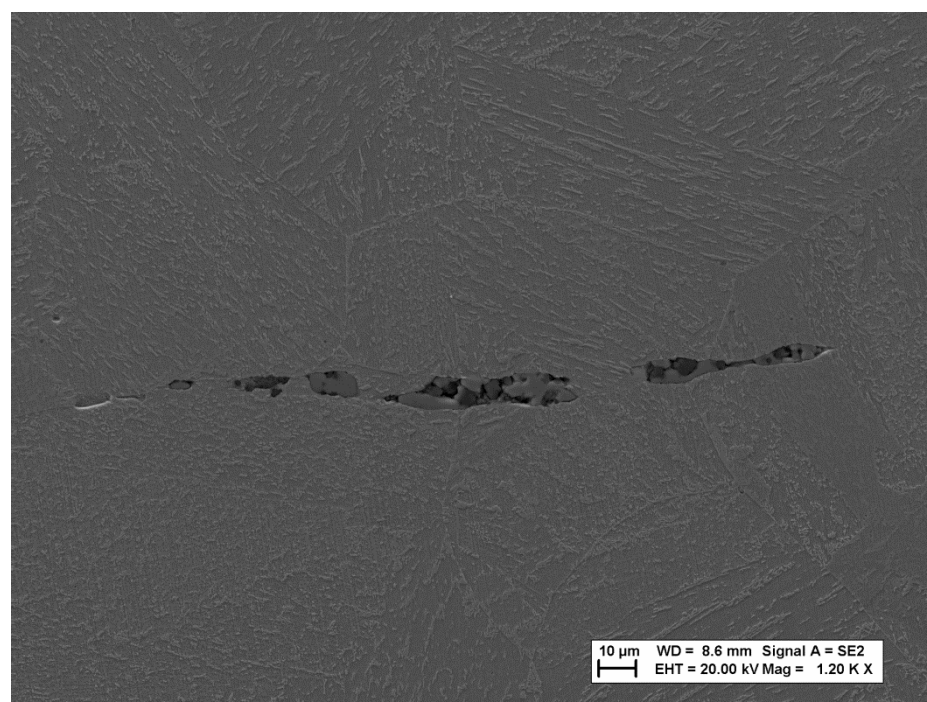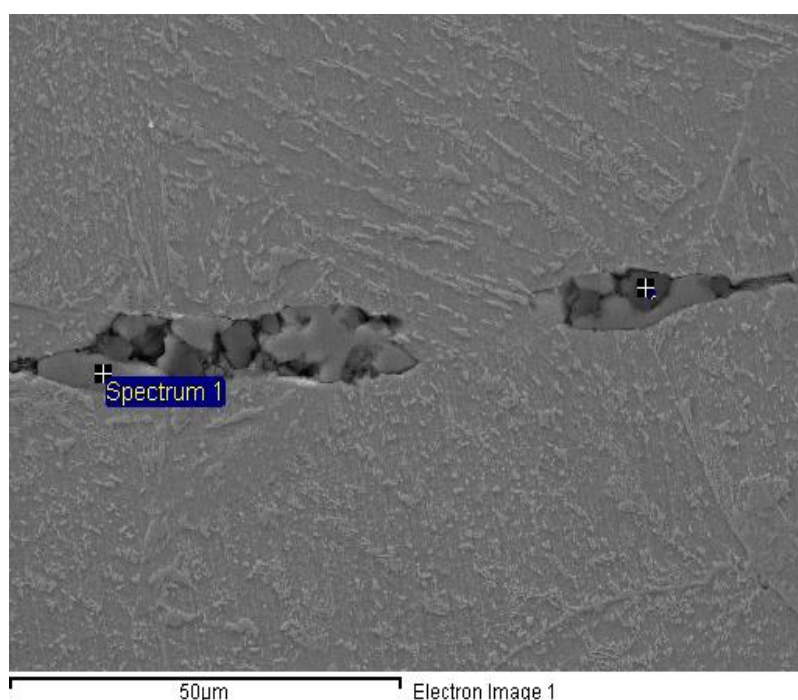

Figure 30: SEM picture of a chain of defects in steel specimen with charge number v7817. Picture width is 250 µm.

Table 13: EDX analysis of two points in the defect in Figure 30

Composition at the left point		
Element	Weight%	Atomic%
Mg	2.22	3.83
Al	0.65	1.00
Si	0.19	0.28
S	38.25	49.93
Ca	0.95	0.99
Cr	0.34	0.27
Mn	54.97	41.88
Fe	2.43	1.82
Composition at the right point		
Element	Weight%	Atomic%
O	46.07	59.93
Mg	9.13	7.82
Al	37.62	29.02
S	1.94	1.26
Mn	3.44	1.30
Fe	1.80	0.67

Figure 31: EDX analysis of two points in the defect in Figure 30

6.5.3. Steel specimen with charge number v6337

In this specimen several chains of defects were found. Three pictures of three of them can be found in Figure 32-Figure 34. The defect length is in the rolling direction. EDX analysis of the bulk material as well as on two representative parts of the defects was made. The results of the analysis of the bulk material and the defects are shown in Figure 35, Figure 36, Table 14 and Table 15. There were also small darker defects in this sample that is not captured in the pictures.
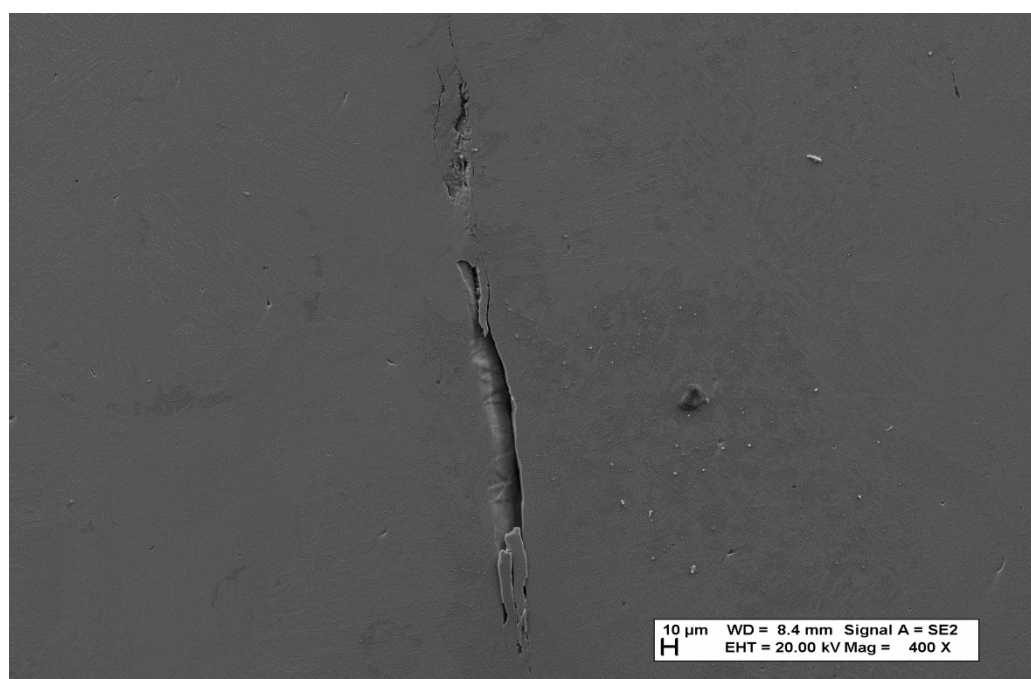

Figure 32: SEM picture of a chain of defects in steel specimen with charge number v6337. Picture width is 730 μm.
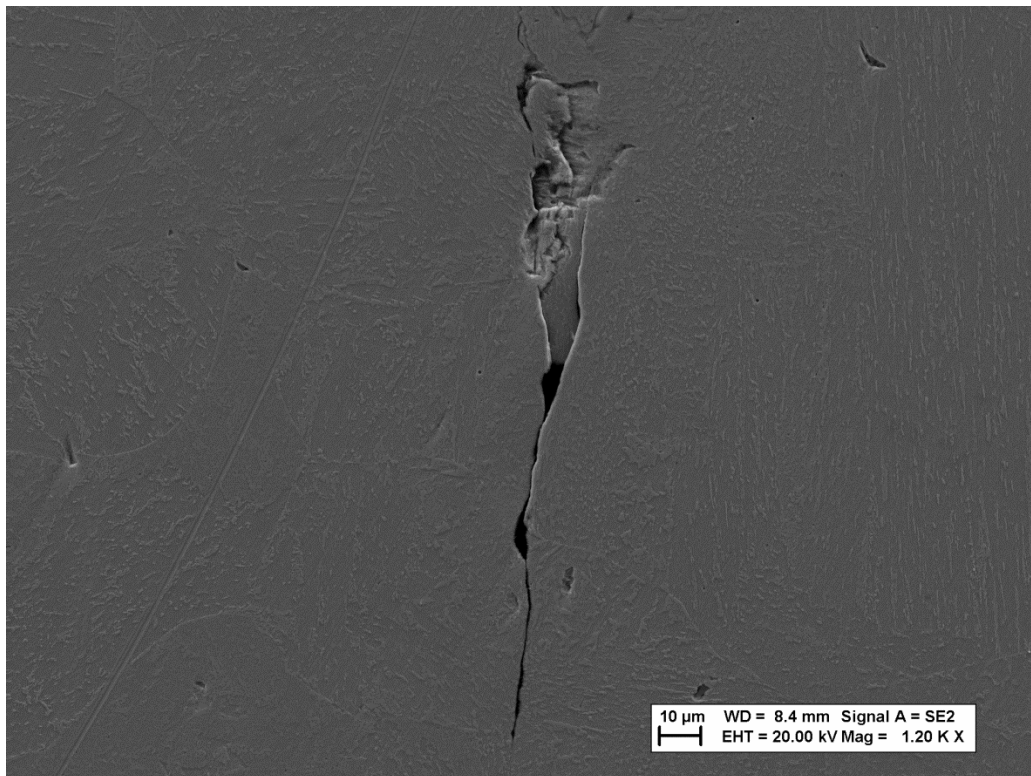
Figure 33: SEM picture of a chain of defects in steel specimen with charge number v6337. Picture width is 250 µm.
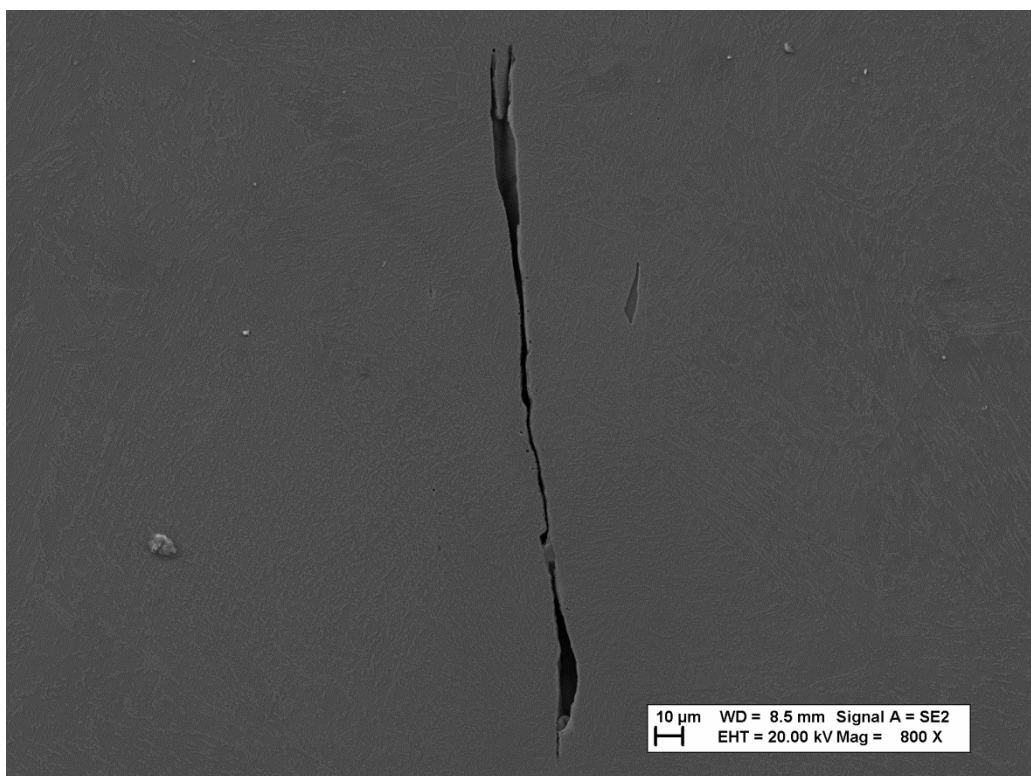

Figure 34: SEM picture of a chain of defects in steel specimen with charge number v6337. Picture width is 370 µm.

Table 14: Bulk Material and defect EDX analysis and compositions for steel specimen with charge number v6337

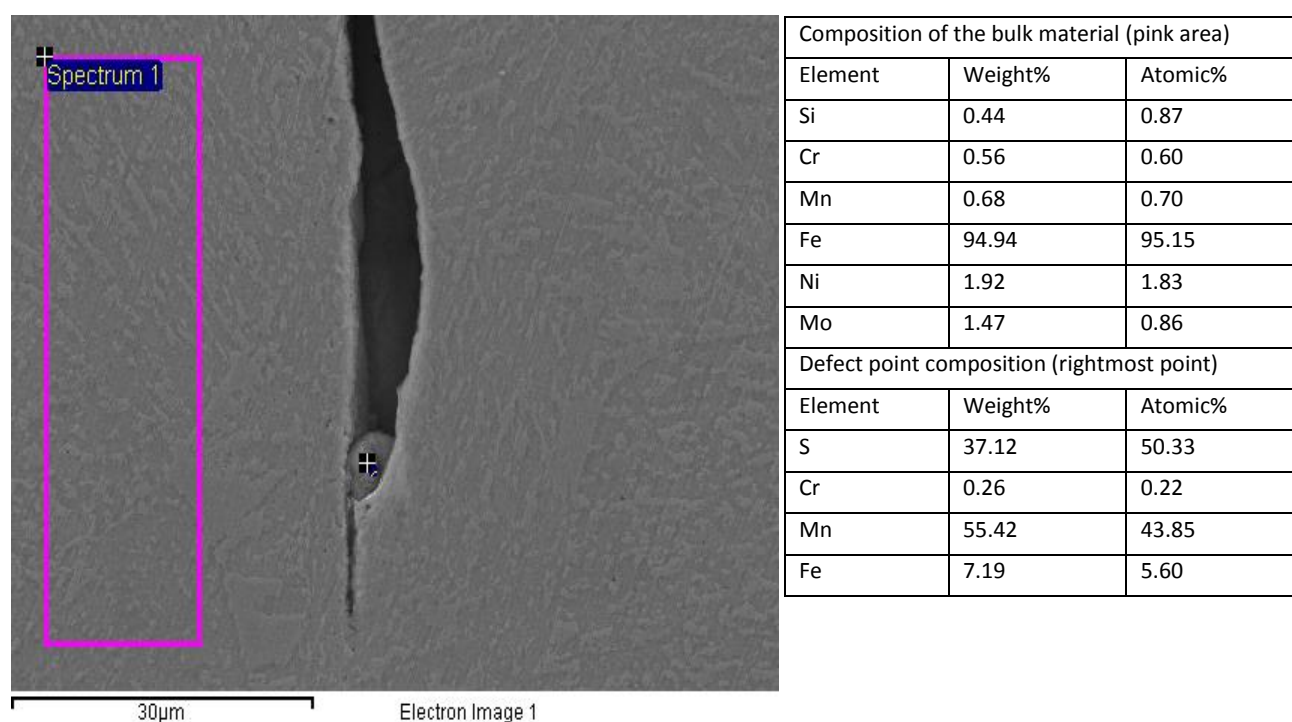| Composition of the bulk material (pink area)		
Element	Weight%	Atomic%
Si	0.44	0.87
Cr	0.56	0.60
Mn	0.68	0.70
Fe	94.94	95.15
Ni	1.92	1.83
Mo	1.47	0.86
Defect point composition (rightmost point)		
Element	Weight%	Atomic%
S	37.12	50.33
Cr	0.26	0.22
Mn	55.42	43.85
Fe	7.19	5.60

Figure 35: Bulk Material and defect EDX analysis and compositions for steel specimen with charge number v6337

Table 15: EDX analysis of the defect point and its compositions for steel specimen with charge number v6337

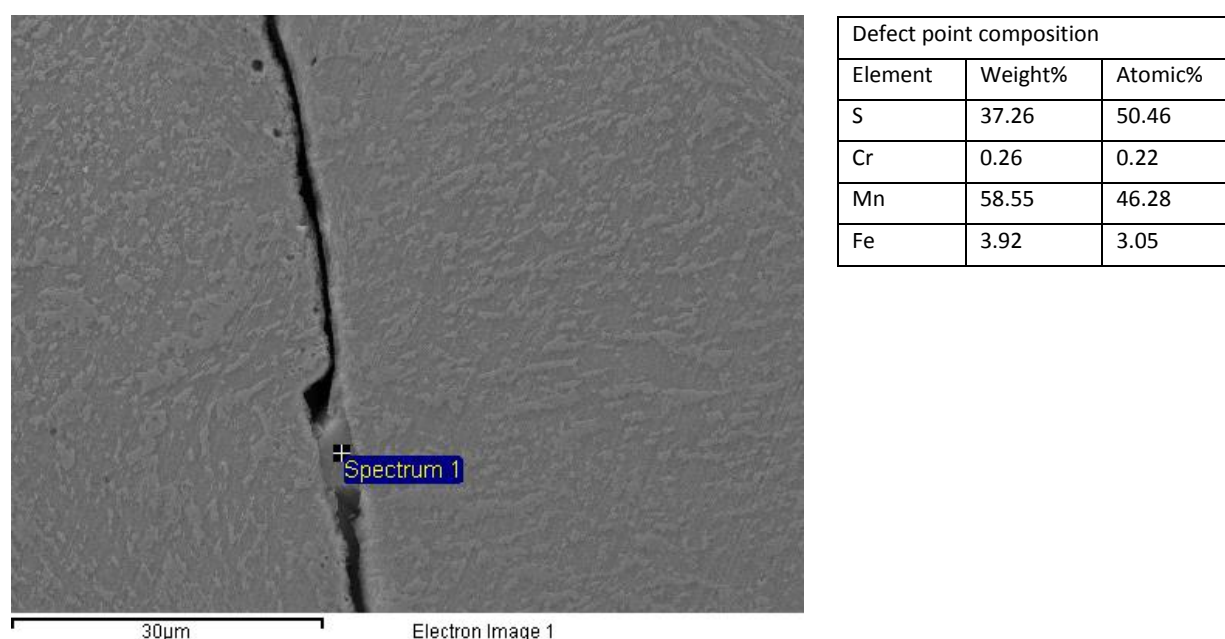| Defect point composition		
Element	Weight%	Atomic%
S	37.26	50.46
Cr	0.26	0.22
Mn	58.55	46.28
Fe	3.92	3.05

Figure 36: EDX analysis of the defect point and its compositions for steel specimen with charge number v6337

6.5.4. Steel specimen with charge number D1051

In this specimen a lot of defects were scattered about on the surface. A SEM picture is shown in Figure 37. EDX analysis of the bulk material as well as on two representative defects was made. The results of the analysis of the bulk material and a few representative analyses of the defects are shown in Figure 38 and Table 16.
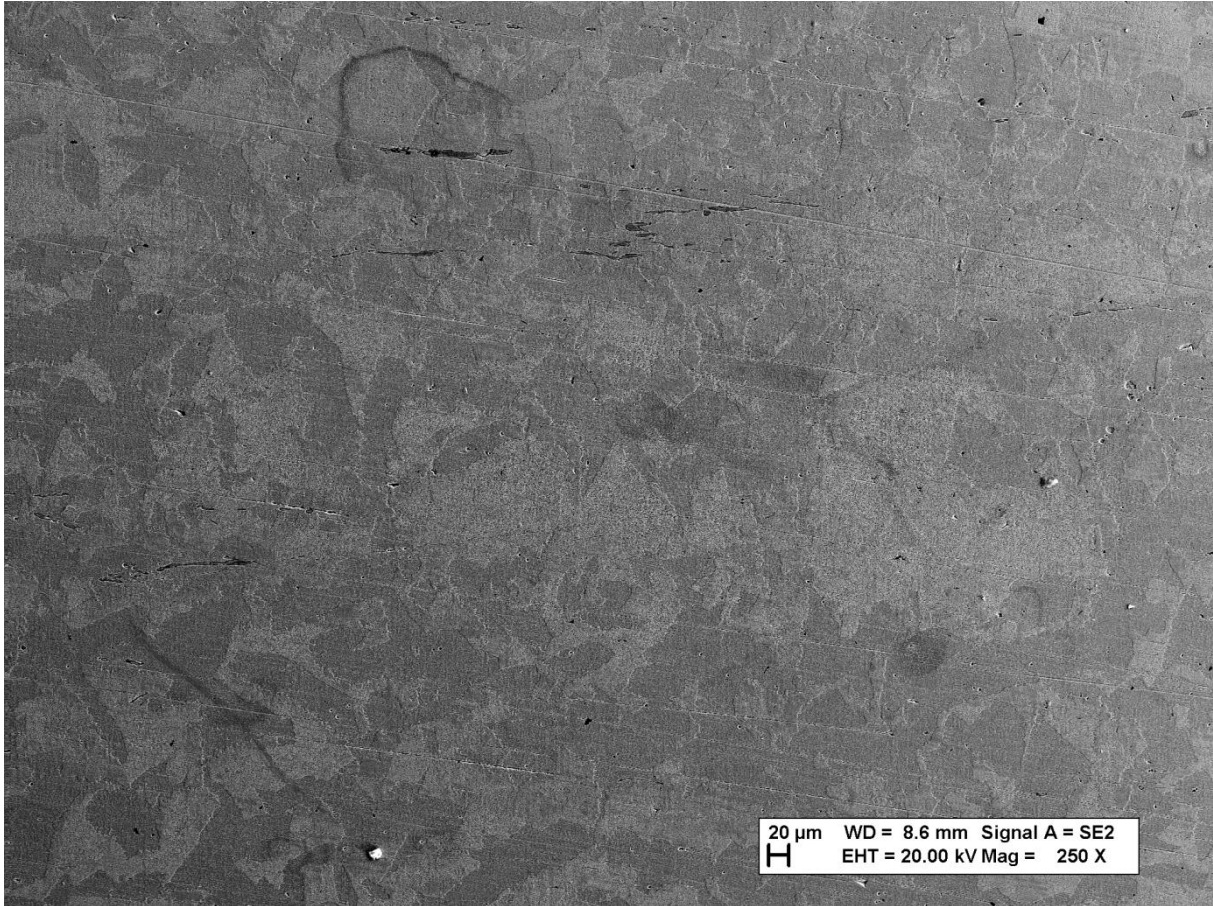

Figure 37: SEM picture of steel specimen with charge number D1051. Picture width is 1180 µm.

Table 16: Bulk Material and defect EDX analysis and compositions for steel specimen with charge number D1051
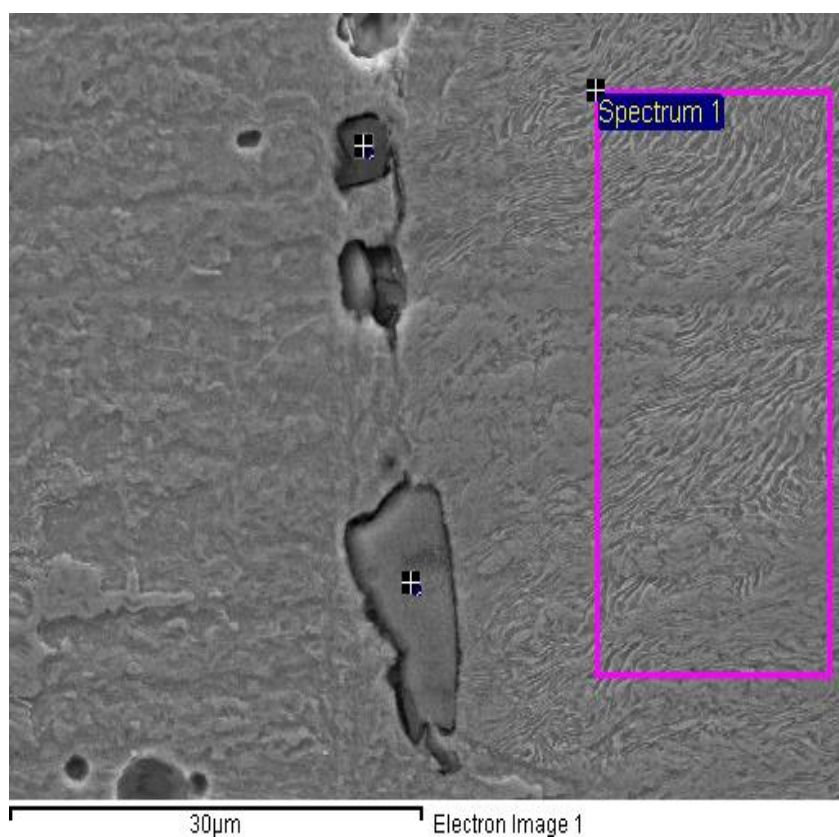

Figure 38: Bulk Material and defect EDX analysis and compositions for steel specimen with charge number D1051

Composition of the bulk material (pink area)		
Element	Weight%	Atomic%
Si	0.42	0.82
Cr	0.35	0.37
Mn	1.60	1.62
Fe	97.64	97.19
Defect point composition (bottommost point)		
Element	Weight%	Atomic%
Mg	0.72	1.27
Al	0.44	0.70
S	37.65	50.25
Ca	0.62	0.67
Mn	56.88	44.30
Fe	3.68	2.82
Defect point composition (topmost point)		
Element	Weight%	Atomic%
O	47.31	60.87
Mg	8.62	7.30
Al	39.55	30.17
Fe	4.51	1.66

7. Discussion

7.1. Theoretical study of hydrogen damage, creep and porosity

When evaluating hydrogen damage two kinds are applicable to this situation, hydrogen stress cracking and shatter cracks. For hydrogen stress cracking the main mechanism is internal diffusion to stress concentrations where crack initiation leads to failure. The steels that were examined contained between 0.7 and 1.7 ppm hydrogen and HSC can occur with as little as 0.1 ppm hydrogen content. All the tested steels had HRC values above the minimum of 22 and estimated tensile strength above 800 MPa. All this and the fact that this is observed between -100° and 100° Celsius make it a theoretically possible phenomenon for the situation. [7, 8]

Shatter cracks typically occur in forgings and castings. The source of hydrogen is most often water vapor that reacts with the molten steel. Since Ovako do not preheat the scrap metal before melting this could be a source for that water vapor. Other sources could be water from the slag or from the refractory material in the furnace. Excess hydrogen created from its lower solubility in bcc than fcc diffuse to internal defects like voids or inclusions where the hydrogen atoms form hydrogen molecules. The pressure can then give the stresses necessary to form internal defects known as flakes. [7, 8]

Except for lowering the hydrogen content the ways to avoid these two hydrogen damage types differ a bit. For HSC baking is usable as long as irreversible damage has not yet occurred. If possible it is also a good idea to choose materials below 22 HRC and 1000 MPa tensile strength. For shatter cracks minimizing inclusions and voids is important. Sulfides are also important to consider since they increase the potential of the hydrogen. Slowing down the cooling rate also decreases the risk of shatter cracks. [7, 8]

Room temperature creep is a mechanism that can facilitate hydrogen diffusion which could increase the risk of hydrogen damage. RTC itself does not pose a big threat because it does not propagate cracks on its own. Avoiding pores could be a good way to decrease the available defects to which the hydrogen diffuses. Pores in themselves do not apply any tension since they are just a void in the steel matrix but they are a stress concentration point and therefore sensitive to stresses of different kinds. [3, 6, 11]

The best way to seal pores is to make sure the ingots is deformed enough during forming. To achieve this, bigger ingots could be used. Or it is possible to consider forging instead of rolling for large dimensions since forging deforms the steel more. [4, 5]

7.2. Ultrasonic testing and XRF analysis

When doing the ultrasonic testing at Ovako it was not known which part of the bar the pieces came from. Because of different amounts of segregation in different parts of the ingot after casting it is not possible to compare the ultrasonic analysis to each other. Even if comparing those of the same steel type to each other only those from steel type 826B shows more defects in the older specimen compared to the newer. [2, Figure 17-Figure 23]

When looking at the XRF analysis of the unknown samples (after accidentally mixing them together) it is possible to identify most immediately. Unknown4 and unknown5 both contain vanadium. The only steel type that contains this element is the one with charge number d1051 which means that

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these two are of that steel type. Unknown1 contains 0.27 weight% molybdenum. The only steel type that contains this amount is the one with charge number v9083 which means that this on is of that type. The ones that are left have very equal composition which is not strange because they are of the same steel type. They were separated by visual comparison instead which was possible because of size differences. [Table 5, Table 10]

7.3. Examination in optical and electron scanning microscope

As can be seen in the pictures from the optical microscope, defects were found in all the samples were defects were indicated by ultrasonic testing. The steel specimen with charge number v9083 shows some form of pit or void while the others show one or more cracks. Except in the case of the steel specimen with charge number v9083 the defects on these pictures might not have been the ones studied in the scanning electron microscope. This is because these samples had to be grinded with 1200p paper. This removes some of the material meaning it is not the exact same surface studied in SEM as in optical microscope. [Table 9, Figure 24 - Figure 27]

The SEM analysis of the steel specimen with charge number v9083 shows a pit of some sort. The bulk materials composition is in many cases slightly higher than the given intervals. The analysis of the defect point shows a high amount of carbon. If the fact that the SEM analysis overestimates carbon content is taken into account the analyzed particle is likely to be some kind of iron carbide. The amounts of other alloying elements probably come from the surrounding bulk material. [Table 11, Figure 28]

For the steel specimen with charge number v7817 there seems to be a number of different inclusions. The first one contains manganese, sulfur, magnesium, chromium and iron. The iron and chromium is most likely from the bulk material. The similar atomic percentages of manganese and sulfur indicate a manganese sulfide inclusion. The shape also indicates a ductile inclusion like that one. The magnesium is probably from a magnesium oxide. Unless found in large amounts oxygen is omitted from the analysis since it cannot be quantified accurately. [1, Table 12, Table 13, Figure 29 - Figure 31]

The first point on the second inclusion also contains high amounts of manganese and sulfur which again indicates a manganese sulfide. The iron and chromium is most likely from the bulk. The calcium, aluminum, magnesium and silicon are probably from calcium silicates, calcium aluminates, aluminum and magnesium oxides and/or $MgO-Al_2O_3$-spinels. The second point on the inclusion contains high amounts of aluminum and oxygen. This indicates an aluminum oxide. The iron is from the bulk. The manganese and sulfur probably from a manganese sulfide close by. The magnesium is either from magnesium oxide or from $MgO-Al_2O_3$-spinels or both. [1, Table 12, Table 13, Figure 29 - Figure 31]

The analysis of the other inclusions seen in the pictures was omitted because they have similar composition as the ones already analyzed. The darker ones are aluminum oxide and the lighter ones and manganese sulfides. [1, Table 12, Table 13, Figure 29 - Figure 31]

For the steel specimen with charge number v6337 several cracks were found. Inclusions were only found in one of them. As in the previous specimen those inclusions are manganese sulfides. The darker inclusions in the sample not shown in the pictures are aluminum oxides. For the steel specimen with charge number d1051 there are no cracks but instead there are several areas with

inclusions. As for the previous specimens, the darker inclusions are aluminum oxides and the lighter are manganese sulfides, both with some other elements included. In the bulk material analysis of this specimen there is no vanadium like in the XRF analysis. This could be because the amounts are close to the detection limit for the EDX so it is not detected. [1, Table 10, Table 14 - Table 16, Figure 32 - Figure 38]

All the steel specimens, except for the one with charge number v9083, contain a lot of inclusions. Inclusions are initiation points for crack growth and for hydrogen damage. Minimizing the amount of inclusions in the steel is one way of minimizing shatter cracks. The cracks detected with ultrasonic testing could have been initiated because of the inclusions. Inclusions have a different elastic modulus than steel which gives rise of stresses when deformed. This could be a cause for crack initiation. [1, 7, 8]

8. Conclusions

There are two kinds of hydrogen damage that could be affecting the steel during long term storage, hydrogen stress cracking and/or shatter cracks. More testing is needed to know for sure. But if it is suspected for a certain steel type baking could be considered and inclusions should be kept to a minimum. If possible, lowering the hydrogen content is beneficial.

Pores are initiations point for cracks and hydrogen damage. If possible these should be decreased. This can be done by using bigger ingots or by forging steel types where pores are considered a problem.

The steel specimens contained a lot of inclusions around the areas that showed defects in the ultrasonic examinations. Minimizing these could decrease the amounts of defects found in the steels.

9. Further work

Some of the possible things to work on in the future are the following:

- Determine which of the steel types that Ovako uses that have practical problems with internal defects and find ways to avoid the problems.
- Examine the problem with inclusions further and see if there are inclusions in other steel types including those that do not show any signs of defects.
- Theoretically and/or practically calculate residual tension in the steels after rolling to determine how these affect crack growth.

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