HYDROGEN CONTROL AT ÇEMTAŞ STEEL PLANT

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ABSTRACT

HYDROGEN CONTROL AT ÇEMTAŞ STEEL PLANT

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ÇEMTAŞ Steel Plant produces alloy steels used principally by the automotive industry. For this industry, cleanliness of steel is a crucial criterion. In order to satisfy the demands of customers for cleaner steels and decrease the production losses a master thesis named "Inclusion control at ÇEMTAŞ Steel Plant" was started and completed. According to the results obtained in this study, it was concluded that inclusions are not the only cause of defects in the final product and that hydrogen is another important factor. Steelmaking process was investigated with regards to hydrogen. It was found that steel picks up hydrogen after vacuum degassing and hydrogen content of steel is high just before continuous casting. In order to decrease hydrogen content of steel, some parameters of steelmaking process in ladle treatment like vacuum duration, quantities of additives, and in continuous casting such as tundish and casting powders were studied. As a result, the phases that acts as a source of hydrogen and a proper operation procedure which would decrease hydrogen pick-up were determined.

Keywords: Steel, hydrogen, degassing, ladle metallurgy, continuous casting

ÖZ

ÇEMTAŞ ÇELİK FABRİKASINDA HİDROJEN KONTROLÜ

Suna, Hazal

Yüksek Lisans, Metalurji ve Malzeme Mühendisliği Bölümü

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ÇEMTAŞ Çelik Fabrikası başlıca otomotiv endüstrisi tarafından kullanılan çelikleri üretir. Otomotiv endüstrisi için çelik temizliği önemli kriterlerdendir. Müşterilerin daha temiz çelik kriterlerini karşılamak ve oluşan üretim kayıplarını azaltmak amacıyla "ÇEMTAŞ Çelik Fabrikası'nda Kalıntı Kontrolü" isimli tez çalışması başlatılmış ve bitirilmiştir. Bu çalışma çerçevesinde yapılan iyileştirmeler sonrasında, üründeki hataları etkileyen faktörün sadece çelik içerisindeki kalıntılar olmadığı bulgusuna varılıp, diğer bir faktörün de hidrojen olduğu görülmüştür. Çelik üretim süreci, çeliğin hidrojen miktarı açısından incelenmiştir. İnceleme sonucunda, çeliğin vakumdan sonra hidrojen kaptığı ve sürekli döküm aşamasında çelikteki hidrojen miktarının yüksek olduğu bulgusuna varılmıştır. Çelik üretim süreci boyunca hidrojen miktarını azaltmak amacıyla vakum süresi, eklenen malzeme miktarı ve tandiş parametreleri gibi süreç parametreleri gözden geçirilmiştir. Sonuç olarak, çeliğin temas duruma gelip hidrojen kaptığı fazlar belirlenmiş ve etkilerinin azaltılması çalışmaları yapılmıştır.

Anahtar Kelimeler: Çelik, hidrojen, gaz giderme, pota metalürjisi, sürekli döküm

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CHAPTER 1

INTRODUCTION

Steel is an important product that is used in a great variety of industries such as construction, energy, medical, automotive and other transportation etc. Among these, steel products that are produced for automotive industry are generally considered as safety parts. This necessitates precise control of the products for defects that can cause failure in service. As a result, the criteria for defects that would be considered as production losses are considerably tight. In addition to the demands of the costumers, increasing competitiveness between the producers caused producers to focus on producing defect-free steel products and tightening the control criteria.

ÇEMTAŞ is one of the important quality steel producers in Turkey. The main customer of it is automotive industry thus the control criteria for defects are considerably tight. In ÇEMTAŞ round products can be controlled for surface, subsurface and internal defects by non-destructive tests. Among these defects, it is possible to remove shallow surface defects by grinding operations but internal defects cannot be removed thus they are separated and considered as production losses. Inevitably, production loss amounts increase when the control criteria are tightened. In order to attain lower production loss amounts cleaner, defect-free steels must be produced. Hence, a study for determining and eliminating the sources of the defects was started. At the beginning, it was determined that non-metallic inclusions are the main cause of internal defects. Accordingly project called "Inclusion Control at ÇEMTAŞ Steel Plant" was conducted as the first phase of the study. As a result

of this project, the steelmaking process was optimized and the amount of defects due to nonmetallic inclusions was decreased. However, the production losses due to internal defects were not completely eliminated which have revealed presence of another source of defects; hydrogen. As a result, the need for controlling the steelmaking process with regard to hydrogen have become necessary and this project was started as the second phase of the study.

The main aim of this thesis is to decrease amount of internal defects caused by hydrogen in the final product, to decrease the production losses and to increase the quality of steel. For this purpose, firstly, the critical steps of steelmaking process with regard to hydrogen content of steel and present hydrogen amounts are determined. Accordingly, the factors that influence the hydrogen content during these steps were identified and necessary precautions were taken for decreasing hydrogen pick-up of steel. As a result the hydrogen content of steel was decreased. Also by sulfur addition the production losses due to internal defects caused by hydrogen were considerably decreased.

CHAPTER 2

LITERATURE REVIEW

2.1 Solubility of Hydrogen in Steel

Hydrogen is an element that can be present in steel. The presence of hydrogen does not have any practical advantage, on the contrary beyond a critical level it would affect the properties of steel adversely due its solubility characteristics. Therefore it is only acceptable to very low levels.

Hydrogen is soluble in steel in elemental form which is the case for all of the diatomic gasses. The dissolution process of hydrogen obeys the Sievert's law. This law states that in ideal solutions the concentration of the dissolved element is directly proportional to the square root of the partial pressure of the same element in its diatomic gas state. This process for hydrogen takes place according to Equation 1 below. The equilibrium constant K for this reaction is shown in Equation 2 [1]. At equilibrium state, at a definite temperature, hydrogen that can generate a pressure up to the pressure of the atmosphere surrounding the system, can be present in steel. For open systems the pressure of the system could be taken as the atmospheric pressure.

$$\frac{1}{2}H_2(g)(atm) = [H](ppm) \tag{1}$$
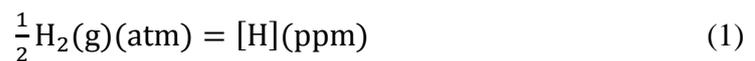
$$K = \frac{ppm\ H \times f_H}{(P_{H_2})^{0.5}} \tag{2}$$

Moreover, the solubility of hydrogen in different phases of iron is different since the equilibrium constant (K) depends on temperature via the Equations 3 (a), (b) and (c).

$$\log K_{\propto,\delta} = -\frac{1418}{T} + 1.628 \qquad (3a)$$

$$\log K_{\gamma} = -\frac{1182}{T} + 1.628 \qquad (3b)$$

$$\log K_{l} = -\frac{1900}{T} + 2.423 \qquad (3c)$$

The temperature dependence of solubility of hydrogen in steel could be summarized in a temperature-mass plot, shown below in Figure 2.1 [1]. The activity coefficient, f_H was taken as unity in this plot, which is suitable for low alloy steels. The temperature of liquid steel remains in the vicinity of 1600 °C during steelmaking process. Accordingly, in liquid steel at steelmaking temperatures maximum 25.6 ppm of hydrogen can be present, in the systems open to atmosphere.
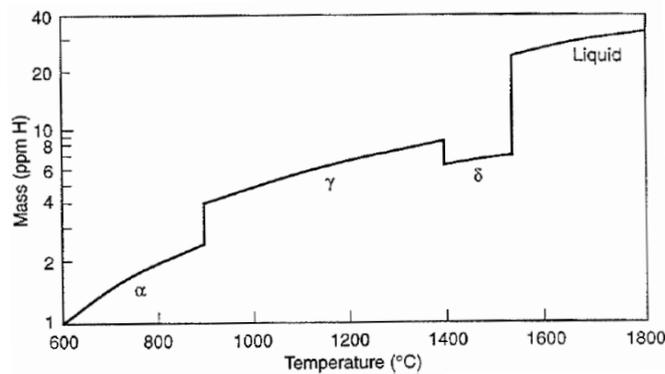
Figure 2. 1 Solubility of hydrogen vs. temperature [1]

In this plot, it can be observed that, the solubility of hydrogen is lower in solid phases ($\propto, \gamma, \delta$) than the liquid phase and it generally decreases as the temperature decreases, even though it is slightly higher in the γ phase, relative to δ. The defects caused by

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hydrogen that is present in liquid steel can be ascribed to decrease in the solubility of hydrogen with temperature.

As a matter of fact, the alloying elements have either increasing or decreasing influence on the solubility of the hydrogen in steel. The value of activity coefficient, f_H differs from unity depending on the chemical composition of steel according to interaction coefficients (e_i^j) of the elements. It can be stated that the solubility and the activity coefficient of hydrogen are inversely proportional at a certain temperature. Thus, elements that increase value of the activity coefficient; would decrease the solubility of hydrogen and vice versa. In the Figure 2.2, the effect of elements to the solubility of hydrogen is given [2].
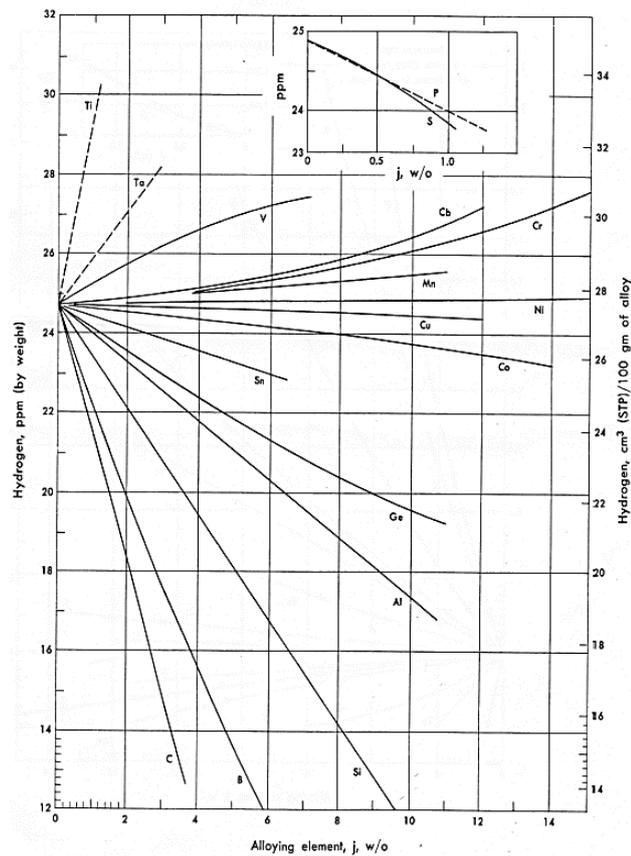
Figure 2. 2 Effect of alloying elements on solubility of hydrogen in steel [2]

It can be seen that B, C and Si are the most effective elements that decrease and Ti, Ta, V and Cb are the most affective elements that increase the solubility of hydrogen. However, their effect becomes considerable when their contents are high. Also some elements do not affect the solubility at a practical level whether they are present in high amount or not, among these Ni, Mn and Cu can be listed.

2.2 Behavior and Effects of Hydrogen in Steel

Hydrogen is soluble in liquid steel and it can be present to a high degree at steelmaking temperatures as stated in Section 2.1. After steelmaking process, liquid steel can be continuously cast into slabs, billets or blooms or cast into ingots (Ingot casting is not in the scope of this thesis.). During continuous casting, due to temperature decrease, solubility of hydrogen decreases. Consequently, hydrogen that is present in liquid steel tends to form hydrogen gas. Hydrogen gas that accumulates during solidification and in the solidified steel can create problems such as sticker breakouts, subsurface blowholes and cracks. The possibility of formation of defects increases with the increase in the hydrogen content of the liquid steel; as the pressure that can be generated by accumulating hydrogen gas that could be formed would increase. For instance at 1400 ^{o}C the maximum pressure that can be generated by 2 ppm and 8 ppm hydrogen are 0.058 atm and 0.9 atm, respectively. Those could increase to 10.4 atm and 166.5 atm when temperature decreases to 500 ^{o}C. This indicates both change in pressure with decrease in temperature and with increase in hydrogen content [1]. In the following sections, the defects that can be formed during solidification and in solidified steel are explained in detail.

2.2.1 Behavior and Effects of Hydrogen during Solidification

During solidification, solute atoms in steel which is an iron alloy, rearrange between solid and liquid phases. For the solute atoms that are generally present in steel such as C, Mn, H and Al the equilibrium between solid-liquid phases requires a liquid phase with higher solute concentration and a solid phase with lower solute concentration than the original alloy composition. The ratio of solute atoms in solid

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to liquid is called distribution coefficient k and in this case the value of k is lower than one. During solidification of steel, the solute atoms that fit this situation are rejected from the solidified steel. As a result, the composition of liquid in front of the solid-liquid interface increases. This is called solute enrichment. Thus melting point of the liquid with new composition decreases below the actual melting point; resulting with formation of a supercooled zone. This situation is shown in Figure 2.3 below. If the supercooled zone that develops in the liquid phase is large enough, dendritic growth would occur because the planar interface would be unstable. This would make interdendritic microsegregation possible, since the solutes that were rejected can be captured between the dendrite arms [1, 3, 4].
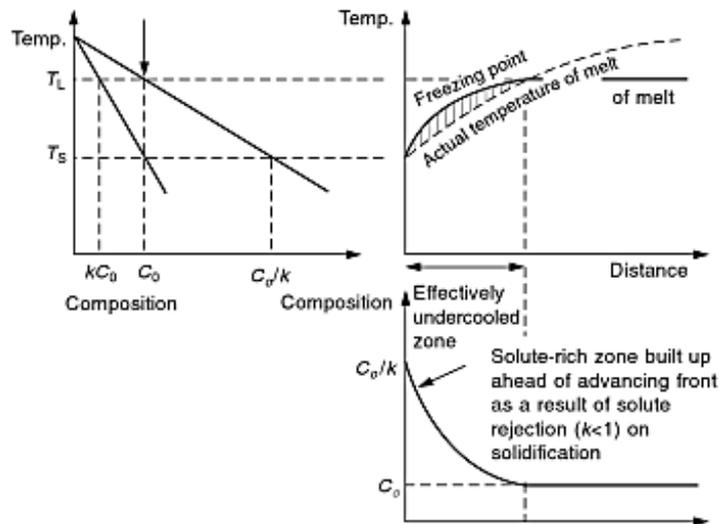
Figure 2. 3 Solute enrichment mechanism during solidification of steel [4]

Formation of subsurface blowholes is a consequence of solute enrichment of gas forming elements H, N, C and O when they are present in high concentrations. The criteria for formation of blowholes is given in Equation 4 which states that, the total pressure generated by these elements must exceed a critical value for gas bubble formation.

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$$P_{H_2} + P_{N_2} + P_{CO} > P_S + P_f + \frac{2\sigma}{r} \qquad (4)$$

This critical value is the sum of atmospheric pressure, ferrostatic pressure near the blowholes and surface tension at the blowhole - steel interface. The contribution of ferrostatic pressure and the surface tension are very small because blowholes form at the beginning of solidification and they are very small in size. In the Figure 2.4 (a) and (b), conditions for blowhole formation, due to the gas accumulation in the liquid phase between the dendrites are given for killed and semi-killed steels with different grades, respectively. The critical pressure for subsurface blowhole formation which is 1.05 atm is shown with horizontal dashed lines. It was stated that hydrogen levels above 6 ppm can pose a risk of blowhole formation for semi-killed steel with high nitrogen content. Hydrogen levels above 8 ppm are above the critical level for both killed and semi-killed steels with different nitrogen contents [1].
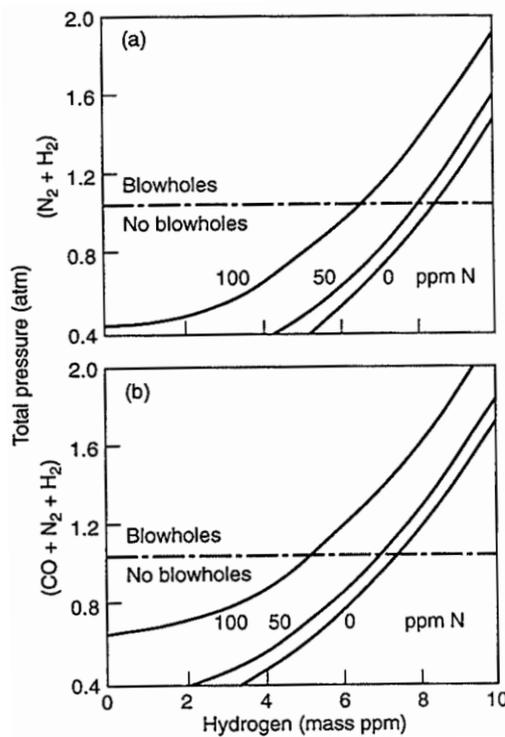
Figure 2. 4 Blowhole formation criteria for steel deoxidized with **(a)** Al **(b)** Si-Mn [1]

Blowholes are undesired because they are likely to cause surface defects. Blowholes that form near the surface enable oxidizing gases to diffuse into the steel, while steel is being heated. As a result, a scale layer is formed under the surface which is one of the cases for longitudinal surface defect formation during hot rolling of steel. In addition to decreasing total gas content of steel, EMS current and superheat of casting could also be modified to prevent blowhole formation [1, 5].

Hydrogen induced sticker breakout is another problem that can occur during solidification of steel in continuous casting mold. Sticker breakout is rupturing of the solidified steel layer followed by spilling of unsolidified steel due to sticking of upper solidified shell to the mold while the rest of the shell is withdrawn during casting. It is a severe problem and extremely undesirable since it does not only interrupts the production, but also it is detrimental for the continuous casting equipment. Hydrogen induced sticker breakout takes place due to the fact that gas bubbles present between the solidified steel and mold, decrease the friction between mold and steel. There are different statements about the sources of the gas bubbles which are dissolved hydrogen in steel and water vapor in air which are explained below [6, 7, 8].

First of all, Mizukami et al. [7] have stated that, during solidification some part of the hydrogen gas is entrapped in solid steel forming blowholes and the remaining is generated from the outer surface of the steel. The volume of hydrogen gas, accordingly the volume of gas generated and entrapped increases with increasing hydrogen content as shown in Figure 2.5.
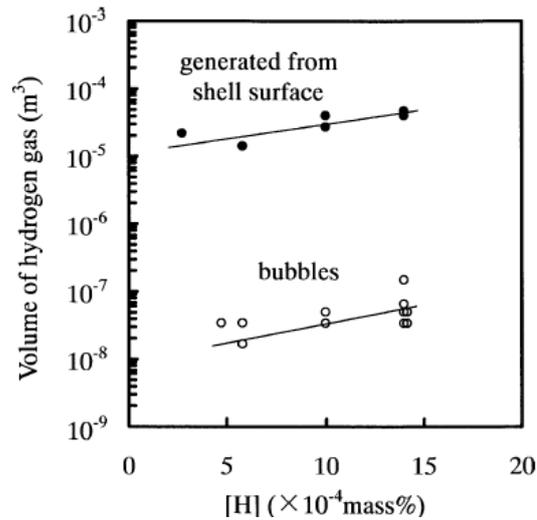
Figure 2. 5 Hydrogen gas formation during continuous casting of steel [7]

The presence of bubbles between the solidified steel shell and the continuous casting mould decreases the lubrication by means of preventing the mould powder inlet. This would eventually result with sticking of shell to mold wall. In conclusion it was found that, there is a critical amount of hydrogen dissolved in steel that could generate necessary pressure for inducing sticker breakout and it is about $7-8$ ppm [7].

In addition to dissolved hydrogen in steel, it was proposed by Kajitani et al. [8] that hydrogen caused sticker breakout can also be a result of hydroxyl ions present in molten flux which forms water vapor. The genesis of these hydroxyl ions are the dissolution of water vapor that is present in air, in the molten flux. In this case, in addition to hydrogen content of steel, the extent of deoxidation, deoxidizing agent and humidity are important factors. According to this mechanism, the water vapor in air would dissolve in the flux, in the form of OH^- ions, introducing two possibilities; one of which is formation of gases that consists hydrogen in the solidified shell and the other is passing of hydrogen to steel, according to the Equations 5 and 6 respectively.

$$2(OH)^- = H_2O(g) + (O)^{2-} \qquad (5)$$

$$2(OH)^- = 2[H](ppm) + [O](\%) + (O)^{2-} \qquad (6)$$
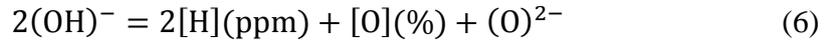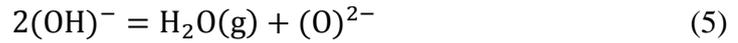
In the case of deoxidation with a strong deoxidizing agent, the hydroxyl ions would be reduced according to Equation 6 and the extent of micropore formation would be lower. In the other case, in which a weak deoxidizing agent is used the amount of hydroxyl ions that are reduced would be lower thus, there would remain hydroxyl ions to form water vapor in the mold flux. Different from the first mechanism, it was stated that micropores are due to vaporization of hydroxyl ions that are dissolved in mold flux as shown in the Figure 2.6 below. Here the Al-K and Si-K represents highly and weakly deoxidized steels respectively.
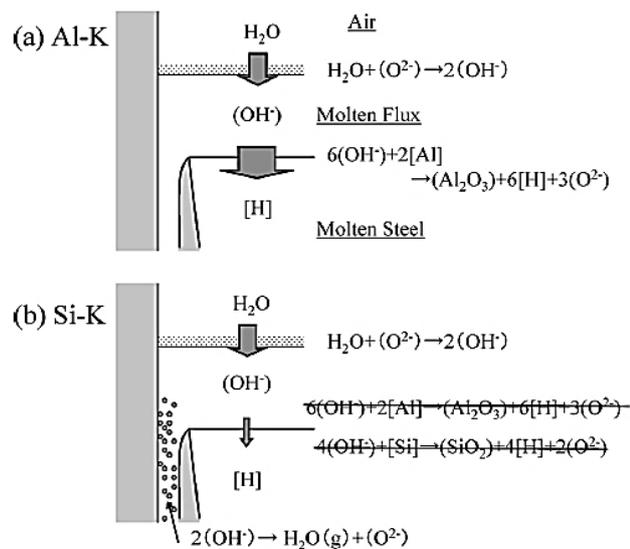
Figure 2. 6 Mechanism of gas bubble formation in mold powder during continuous casting of **(a)** Al-killed **(b)** Si-killed steel [8]

Although it can be thought that the extent of micropore formation is independent of initial dissolved hydrogen value; it was found that, the increase in the initial hydrogen content of steel would increase the hydroxyl ions in the flux according to

the Equation 6 for both weak and strong deoxidizing agents. Thus it increases the risk of sticker breakout formation [8]. Consequently, the initial hydrogen content should be kept under control and a suitable mold powder should be used in order to decrease the possibility of sticker breakout formation.

2.2.2 Behavior and Effects of Hydrogen in Solid Steel

In solid steel, due to low solubility, hydrogen atoms dissolved in liquid steel tend to diffuse out of the steel. During diffusion, hydrogen atoms can encounter discontinuities namely *traps* which are potential accumulation sites for hydrogen. In this case, hydrogen gas would be formed in these traps and result with pressure generation. Traps can be categorized as reversible or irreversible according to the behavior of hydrogen in them. Dislocations, grain boundaries and some of the substitutional atoms are examples of reversible traps where interfaces of inclusions like MnS and TiC and interfaces of ferrite and cementite phases are irreversible traps. [9, 10, 11, 12]. Pressouyre have stated that "Irreversible traps will always act as sinks for hydrogen. On the contrary reversible traps will play a mixed role (sink or source) since, by definition, they can take or give hydrogen." [12]. The amount, kinds and distribution of the traps are effective on the extent of the damage caused by hydrogen. In the case of low amount of traps with heterogeneous distribution, the possibility of the pressure generated by hydrogen gas to overcome the strength of the steel is higher than the case where there are homogenously distributed traps with appropriate amount. Luckemeyer-Hasse and Schenck had studied internal pressures that can be generated by different amounts of hydrogen at different temperatures and compared them with the corresponding tensile strength of steel at those temperatures, given in Figure 2.7 as cited by Zapffe and Sims. It can be seen from this figure that, pressures generated (shown by continuous lines) even by a very low hydrogen amount can be higher than tensile strength of steel (shown by shaded line) [12, 13, 14, 15].
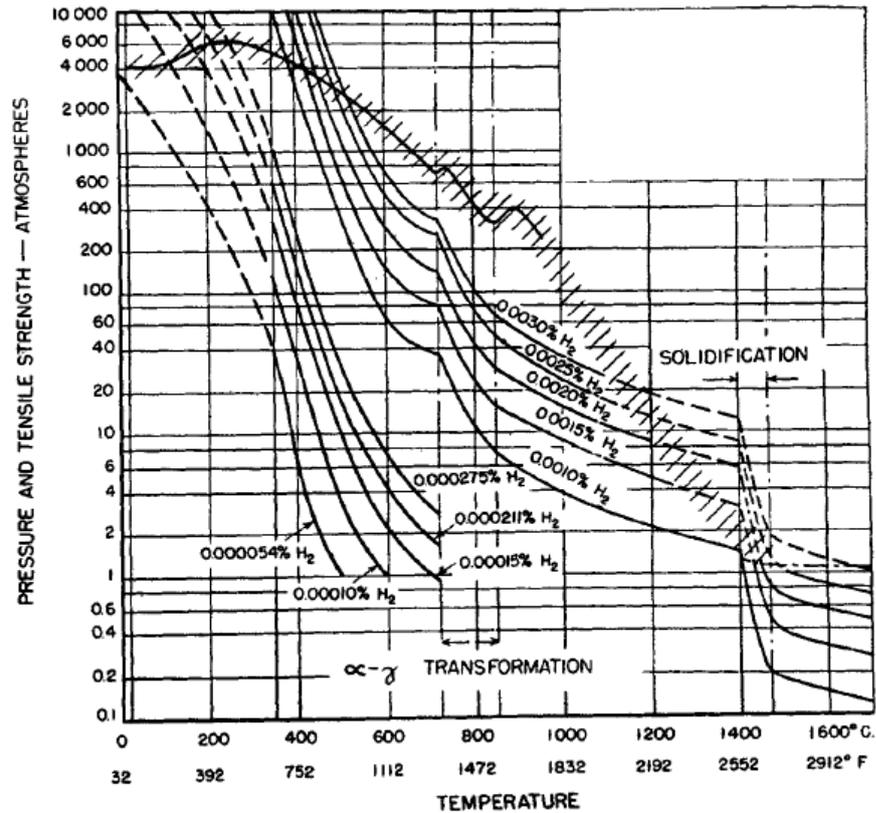
Figure 2. 7 Comparison of pressure generated by hydrogen accumulated in steel (shown by continuous lines) with tensile strength of steel (shown by shaded line) [15]

Shatter cracks, flakes and *fish eyes* are defects that can be formed in solid steel due to presence of hydrogen in liquid steel due to steelmaking operations. Among these fish eyes are defects that occur under tensile loading generally during service, which means that there is a risk of failure due to hydrogen in the products that are nondestructively tested and regarded as defect-free. Flakes form parallel to the rolling or casting direction, due to residual stresses resulted from forging or rolling process. Shatter cracks are multidirectional defects which also form due to presence hydrogen and stresses [15, 16, 17]. In addition, swelling of slabs are another problem that can be come across due to the gas formation near the surface of the steel products when the amount of gas forming elements such as hydrogen and nitrogen is high [10].

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In the case of homogenously distributed traps with adequate amount, the amount of defects due to hydrogen can be decreased or formation of them can be delayed. Pressouyre and Bernstein stated that the presence of homogenously distributed TiC particles which are irreversible traps delays the cracking and increase in the amount of Ti atoms which are reversible traps decreases the amount of cracked area in the steel [14]. MnS inclusions also act as hydrogen traps whose reversibility increases with increasing coherency, nevertheless both reversible and irreversible traps have advantageous effects on preventing hydrogen cracking, provided that their distribution is homogenous. Fruehan have stated that, attaining low sulfur levels would decrease the hydrogen content above which cracks would form. For the reason that, in low sulfur steels, the amount of MnS inclusions would also be low and the pressure that can be generated by hydrogen accumulation in the inclusion-matrix interface would be higher than it is for high sulfur steels. Thus attaining very low sulfur levels should be avoided unless it is not essential for other properties of steel [12, 13].

Therefore, attaining the lowest possible hydrogen content during production of the steel and arranging the amount and type of inclusions would decrease hydrogen caused defects which can occur during casting, during production of the final parts or in service use.

2.3 Removal of Hydrogen from Liquid Steel

During steelmaking, liquid steel can come into contact with several hydrogen-bearing phases which would result with entering of hydrogen to liquid steel (The mechanism of hydrogen pick-up is mentioned in detail in following section.). Considering the solubility level of hydrogen in steelmaking conditions, hydrogen level that is much higher than acceptable can be reached in liquid steel. On the contrary, regarding to adverse effects of hydrogen, during casting or in solid steel attaining very low hydrogen content is essential. For this reason, hydrogen should be removed as much as possible prior to casting. Vacuum degassing is a very efficient

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way of decreasing hydrogen content of steel to very low levels that is generally used for removal of hydrogen from liquid steel.

The removal of hydrogen is governed by first order differential equation which is given for hydrogen in Equation 7. In this equation, k, ρ, M and A represent mass transfer coefficient, density of steel, weight of steel and the area of interface between gas and liquid phases, respectively.

$$\frac{d[\%H]}{dt} = -\frac{k\rho A}{M}\left[[\%H] - [\%H]_{eq}\right] \tag{7}$$

When this equation is solved for hydrogen and k_H is used as overall rate constant instead of $\frac{k\rho A}{M}$ term, the Equation 8 is attained [18].

$$\ln\left(\frac{[\%H]_t - [\%H]_{eq}}{[\%H]_o - [\%H]_{eq}}\right) = -k_H t \tag{8}$$

According to Equation 8, the increase in the area of gas-liquid interface and time and the decrease in the equilibrium hydrogen content favor attaining lower hydrogen amounts. Accordingly, the principle of vacuum degassing is decreasing the pressure on the top of the steel, so decreasing the solubility of hydrogen in steel. In addition by argon stirring, increasing the gas-liquid interface. Stirring would also circulate the steel in ladle which would carry the steel at the bottom to the top where the vacuum actually affects, since at the bottom ferrostatic pressure is dominant and the pressure is not decreased. This can be explained by the process of removal of hydrogen during the vacuum degassing. At the beginning, when the inert gas bubbles free of hydrogen enter the steel that is under vacuum, hydrogen atoms in liquid steel diffuse to the gas-liquid interface and form hydrogen gas to reach equilibrium. However the ferrostatic pressure at the bottom of the ladle is relatively high, hence hydrogen gas formation is limited. Bubbles would rise towards the surface as their volume increase and as the steel is continuously stirred. The pressure above the

bubble decreases during rising, thus more hydrogen can enter the bubble forming hydrogen gas in order to maintain equilibrium. Actually, the other gas forming elements are also removed during vacuum in the same manner but this is out of the scope of this thesis [1, 9, 18]. Consistently, Nebosov et al. [19] have stated that hydrogen removal from steel takes place mostly near the surface of the liquid steel where the bubbles grow very rapidly as shown in the plot of extent of gas removal for different levels in the ladle sketched for one argon bubble in Figure 2.8.
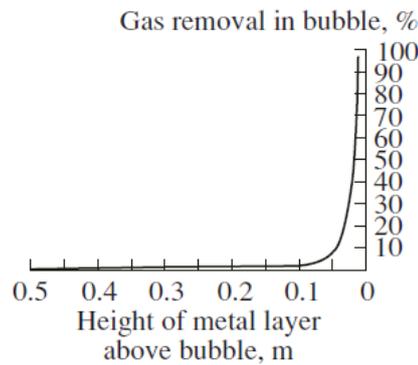
Figure 2. 8 Influence of liquid steel above the bubble to the hydrogen removal amount [19]

Therefore, the pressure above the steel and the argon stirring intensity are important parameters that affect the final hydrogen content. Hydrogen gas formation would be more favored under lower pressures since the solubility of hydrogen in steel decreases with decreasing pressure. Below in the Figure 2.9 resulting hydrogen contents of steels that are exposed to vacuum of different pressures and for different argon stirring intensities are shown [9]. It can be seen from this figure that the initial hydrogen contents do not have influence on the final hydrogen contents, keeping the vacuum pressure constant. Also it can be seen that vacuum below 10 mbar is enough for decreasing hydrogen under 1 ppm and the increase in amount of stirring gas enhances the removal of hydrogen from liquid steel.

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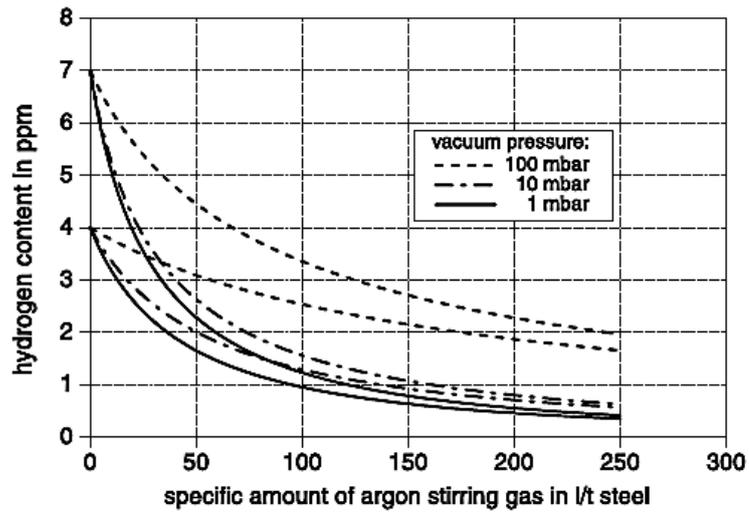
Figure 2. 9 Effect of initial hydrogen content, vacuum pressure and amount of argon used on degree of dehydrogenization of steel [9]

In addition to the pressure and argon stirring intensity, the duration of vacuum degassing is another important parameter that affects the resulting hydrogen content of the steel. In a study conducted by Jha et al. [20] in Durgapur steel plant it was determined that, as shown in Figure 2.10, under pressures lower than 5 mbar with intense argon stirring of 2 Nl/min/ton, the hydrogen content that is achieved at the end of the process decreases with the increasing vacuum duration.
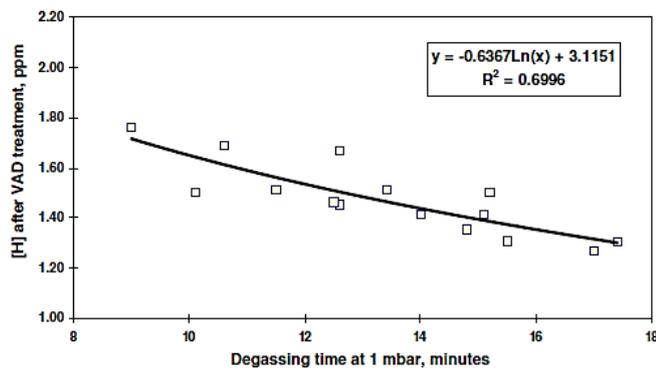
Figure 2. 10 Effect of vacuum degassing duration to hydrogen content of steel [20]

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In addition Steneholm et al. [18] stated that the removal is completed to a large extent in 10 minutes of vacuum then the removal rate decreases and 10 minutes of vacuum is sufficient for reaching suitable hydrogen contents.

There are different kinds of vacuum degassing systems, all based on same principle; keeping the steel under low pressure for a definite time and stirring it in the meantime. These systems are briefly described in the Section 2.3.1.

2.3.1 Vacuum Degassing Systems

Degassing systems can be divided into two groups as recirculation and tank degassing systems. In recirculation degassing systems, part of the heat is degassed at a time. It is applied by forcing that part of liquid steel to fill an evacuated vessel where it is degassed and to turn back to ladle, through snorkels of the vessel that is dipped into the steel in ladle. Circulation of steel between the evacuated vessel and ladle is necessary since only the part of steel that filled the vessel is degassed. There are three different kinds of this system; DH (Dortmund-Hoerder), RH (Ruhrstahl-Heraeus) and RH-OB degasser. The vacuum chamber of DH degasser has one snorkel dipped into the steel. The recirculation is achieved by moving the snorkel up and down in the ladle. In RH system which is shown schematically in Figure 2.11 (a), there are two snorkels of the vacuum chamber dipped into the steel and instead of changing the level of the snorkels, through one of the snorkel, argon bubbles are sent and they pull the steel to the vacuum chamber. Then the degassed steel turns back to the ladle through the other snorkel. The degassing principle of RH-OB system which is shown in Figure 2.11 (b), is as same as the RH system. In this system in addition to degassing, steel is decarburized and reheated by injecting oxygen to the steel in the evacuated vessel.
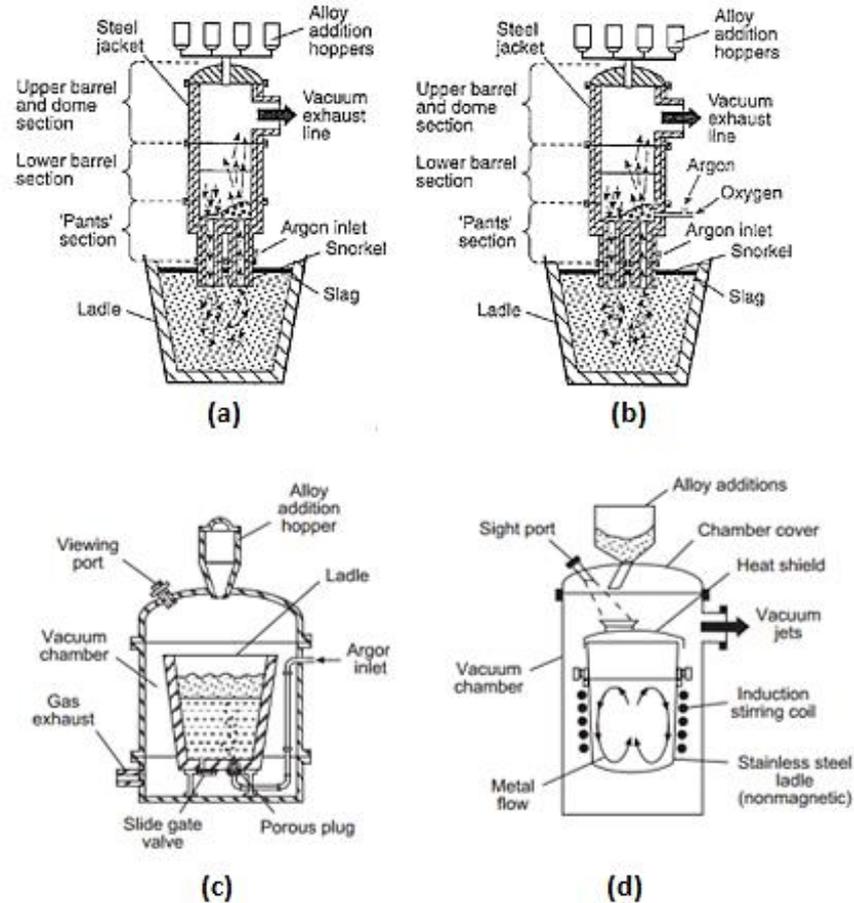
Figure 2. 11 Vacuum degassing systems **(a)** RH system **(b)** RH-OB system **(c)** Tank degassing system with argon stirring **(d)** Tank degassing system with induction stirring [1]

In vacuum tank degassing and vacuum arc degassing, ladle is placed in the vacuum tank which is then evacuated. In these systems, steel is stirred either by argon inlet from the bottom of the ladle or by induction as shown in Figure 2.11 (c) and (d) respectively. Here in addition to removal of gas forming elements, removal of inclusions and desulfurization take place. In the vacuum arc degassing it is also possible to heat the steel during vacuum. This eliminates the reheating the steel after vacuum, or tapping the steel from electric arc furnace after reaching higher temperatures than needed [1, 21].

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2.4 Hydrogen Pick-up during Steelmaking

Hydrogen atoms can enter the liquid steel through contact of steel with phases that contain hydrogen or hydrogen bearing compounds such as water vapor and organic binders. There are several phases which are potential hydrogen sources for steel such as; scrap, limestone that is used for slag making, slag, coke, deoxidation agents, ferroalloys, casting powders, refractory materials, air etc. The removal of hydrogen is achieved to a great extent by vacuum degassing but after it, the removal of hydrogen is almost impossible. Therefore, controlling the hydrogen pick up after vacuum degassing is essential.

The most important hydrogen bearing compound that is present in the phases listed above is water vapor. Hydrogen enters the steel from water vapor according to the Equation 9. The equilibrium constant of this reaction is given by Equation 10, here steel is considered as low alloy and activity coefficients f_H and f_O are taken as unity.

$$H_2O(g)(atm) = 2[H](ppm) + [O](\%) \tag{9}$$
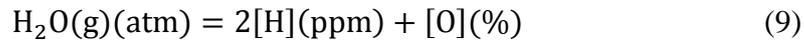
$$K = \frac{(ppmH)^2 \times (\%O)}{P_{H_2O}} \tag{10}$$

It can be deduced from the Equations 9 and 10 that, increase in partial pressure of water vapor and temperature and decrease in oxygen contents favors increase in hydrogen content of steel. Epstein, Chipman and Grant have summarized the relationship between the hydrogen and oxygen concentrations for different H_2-H_2O mixtures at 1600 °C in the Figure 2.12 as cited by Elliott, Gleiser and Ramakrishna [2]. It can be seen from this figure that, for a particular oxygen content the hydrogen level increases with increase in water vapor pressure and at a certain water vapor pressure, hydrogen concentration increases with decrease in dissolved oxygen amount. Consistently, Fruehan have stated that hydrogen pick-up is more favorable for deoxidized steels in the atmospheres with high water vapor content [13].
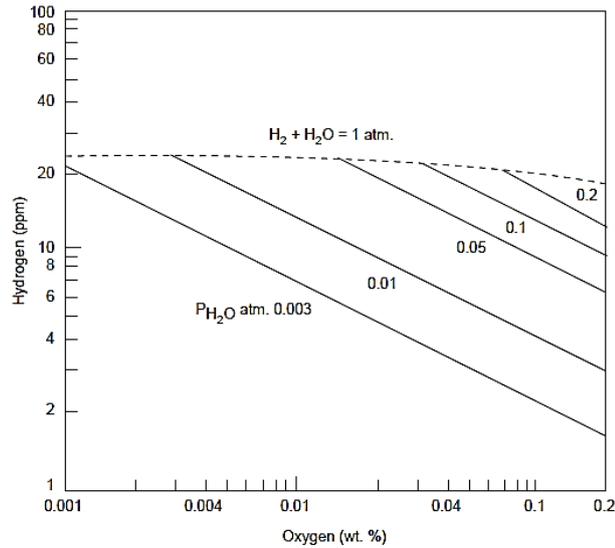
Figure 2. 12 Equilibrium between dissolved oxygen and hydrogen in liquid iron at different vapor pressures [2]

The effect of water vapor in the air was clearly presented by Misra et al. [22] which is shown graphically in Figure 2.13. According to the measurement results of hydrogen contents of non-degassed steel produced in U.S. steel over a year, it was determined that the hydrogen amount of the steel that is produced during summer days is higher than it is in winter days. This is due to the fact that the water vapor content of air is higher in summer than it is in winter. Moreover, it was stated that, the frequency of sticker breakout formation is higher in the summer months, which shows the severity of effect of the water vapor in the air.
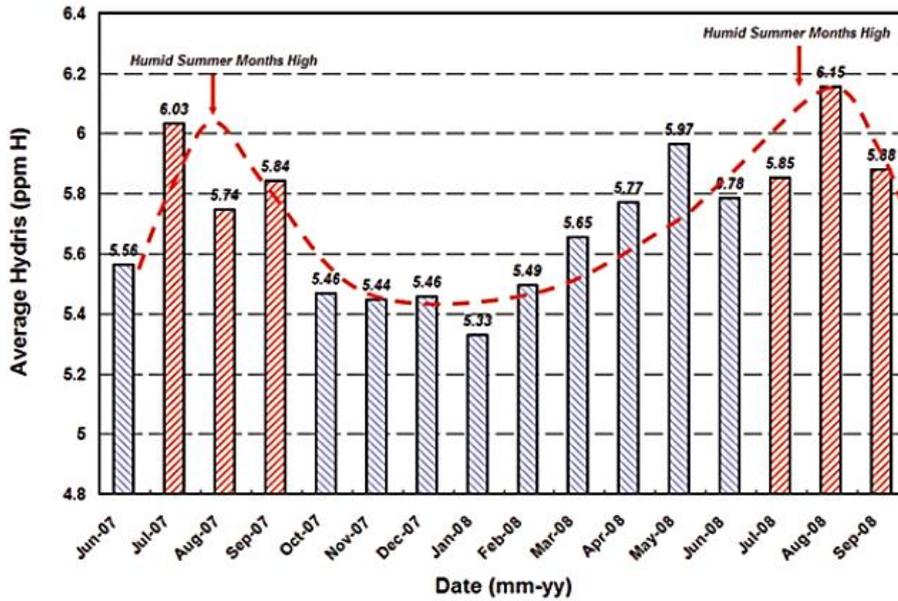
Figure 2. 13 Effect of seasons (humidity) on hydrogen concentration of steel [22]

Dew point is an indicator of humidity level of the air. It is the temperature at which the rate of condensation and evaporation rates of water vapor are equal to each other. It increases as the amount of water vapor in the air increases and when the relative humidity is %100 the dew point would be equal to current temperature. Consequently, its value can also be used for analysis of effect of water vapor in the air to the hydrogen content of the steel. Harris et al. [23] analyzed the relationship between the hydrogen content of steels with different deoxidation practices and the dew point of the air. As a result, it was found that the hydrogen contents of steel are higher for higher dew points. Furthermore, it was found that the hydrogen content of Al-killed steel is higher than Si-Mn killed steels for same dew points which shows the increasing effect of strong deoxidation on hydrogen content of steel.

Elimination of water vapor in the air is impossible during the steel production, as the steel plants are open to atmosphere. In addition strong deoxidation is essential for the most cases. Therefore contact of steel with air must be prevented as much as possible and hydrogen pick-up from the other sources should be controlled.

2.4.1 Hydrogen Pick-Up during Secondary Steelmaking

Secondary steelmaking is the refining step of the process that takes place in ladle furnace. It involves deoxidation, alloying, degassing, desulfurization, composition and temperature homogenization and inclusion shape control of steel. During tapping or ladle process deoxidizers, ferroalloys and wires may be added to steel. In addition, slag makers are used for creating a slag on top of the steel, which would serve the purpose of collecting deoxidation products and effective desulfurization. Homogenization, decarburization and degassing are provided by stirring with argon throughout the process [24]. During this process, hydrogen content of the steel can increase due to hydrogen present in the additives or slag. In this section, firstly the contribution of additives, then importance of slag would be discussed.

Adjustment of carbon content of the steel is often a part of the process in ladle furnace. For this purpose coke or carbon wire are frequently used. It was determined that, hydrogen content of liquid steel increases with the increase in the amount of these additions. Thus, coke and carbon wire can be considered as sources of hydrogen [22, 25]. In Figure 2.14 the relationship between hydrogen pick-up and amount of injected carbon wire to ladle furnace in U.S. steel is shown where the effect of carbon wire additions can be seen clearly. This increase can be ascribed to physical and chemical water and hydrogen content of the carbon wire, which were determined in the same study by Misra et al.. Consequently, a new procedure for carbon amount adjustment was developed which involves lowering late additions in ladle and adjusting the carbon content during tapping and it was resulted with decrease in hydrogen content of steel [22].
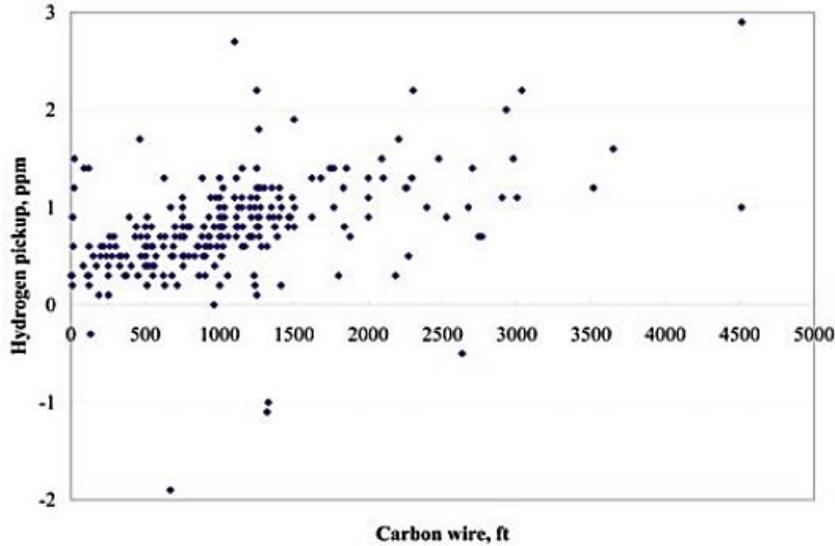
Figure 2. 14 Hydrogen pick up amount vs amount of carbon wire addition [22]

In addition to carbon containing materials, several ferroalloys such as ferrosilicon, ferromanganese, ferrochromium, ferrovanadium etc. are used for producing steel with desired properties. The effect of ferroalloy addition was studied by Zinchenko et al. [26] in Severstal Company. It was found that, ferroalloys are one of the important hydrogen sources and there is a direct proportion between the amounts of ferroalloys added. Similarly, the effect of ladle additions were also studied in CitiSteel whose results are given in Figure 2.15. In this figure two groups of steels are compared separately. In the first group hydrogen contents with respect to ladle additions are compared. It can be seen that, the hydrogen content of the steel with higher amount of alloy (FeSi and C) addition is higher. In the second group, the effect of lime based desulfurizing material is investigated which shows that the slagmaking additives also contribute to hydrogen pick-up of steel [23].
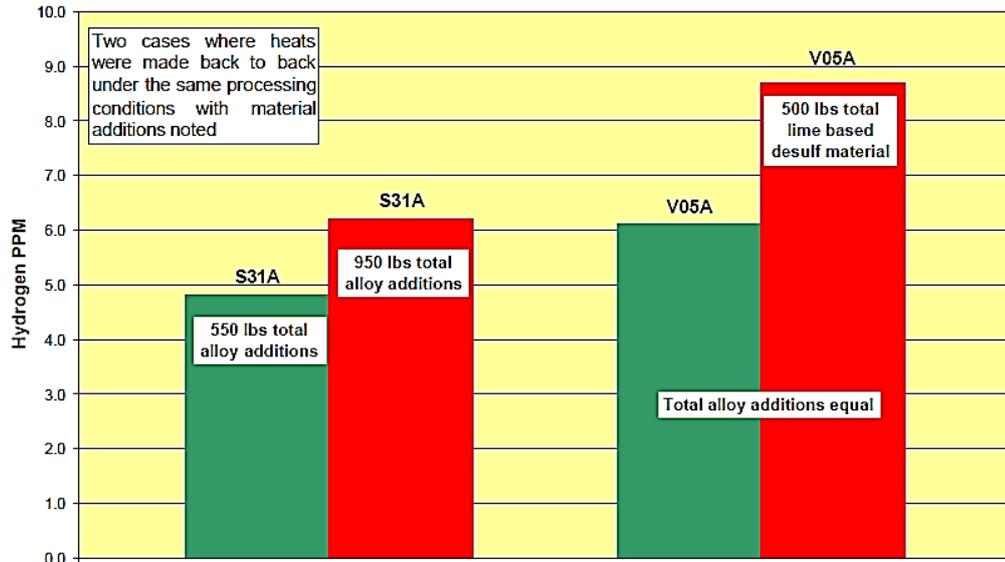
Figure 2. 15 Effect of ferroalloy (left-green) and desulfurization material (right-red) addition to hydrogen content of steel [23]

Throughout the steelmaking process, a slag phase is present on top of liquid steel. In electric arc furnace, a basic slag is necessary for dephosphorization. In ladle furnace, electric arc furnace slag can cause reoxidation thus a different slag is formed which is suitable for covering the surface of steel and preventing hydrogen pick-up and assisting desulfurization and removal of inclusions. Thus, the properties such as basicity of slag is important with regard to hydrogen, sulfur and oxygen content of steel. Yoon et al. [27] indicated that CaO saturated slags are thermodynamically appropriate for inclusion removal but the high melting point is a disadvantage. It was stated that instead of CaF_2 addition, keeping the ratio of CaO/Al_2O_3 in the 1.7-1.8 range would be ideal for inclusion removal. In the case of desulfurization CaO saturated calcium-aluminate slags are stated to be appropriate [1].

The properties of slag are important also for hydrogen control of liquid steel. Elemental hydrogen is not soluble in slag, unlike it is in liquid steel. Instead, it is present as hydroxyl ions or radicals in basic and acidic steelmaking slags, respectively. In acidic slags, a reaction between bonded oxygen and water vapor

takes place according to Equation 11, consequently hydroxyl radicals are formed. In the case of basic slags, water vapor dissolves according to Equation 12 and hydroxyl ions are formed.

$$(\equiv Si - O - Si \equiv) + H_2O(g) = 2(\equiv Si - OH) \tag{11}$$

$$(O^{2-}) + H_2O(g) = 2(OH^-) \tag{12}$$
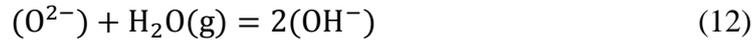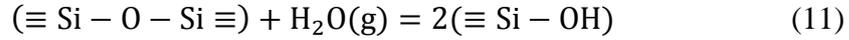
As a matter of fact, in both cases the ability of slag to dissolve water vapor is important. This ability is called *water capacity (C_{OH}),* given in Equation 13 which is valid for both acidic and basic slags [1, 28, 29].

$$C_{OH} = \frac{(ppm\ H_2O)}{P_{H_2O}^{0.5}} \tag{13}$$

C_{OH} term in Equation 13 involves the equilibrium constant of dissolution of water in slag, activity of oxygen ion and activity coefficient of hydroxyl ion thus, it depends on temperature and composition of the slag. Accordingly, the amount of hydrogen that can dissolve in slag depends on the water vapor pressure and the composition of slag, so the basicity of the slag. The temperature dependence is also expectable but it was revealed to be ineffective [30, 31, 32]. Composition and water vapor pressure dependence of solubility of water vapor was studied by Schwerdtfeger et al. [32] for CaO-Al_2O_3 slags. It was determined that the hydrogen amount is directly proportional to square root of water vapor pressure for a definite slag as can be seen from the Figure 2.16. In addition it increases with increasing CaO amount in CaO-Al_2O_3 slags, namely with increasing basicity of the slag.
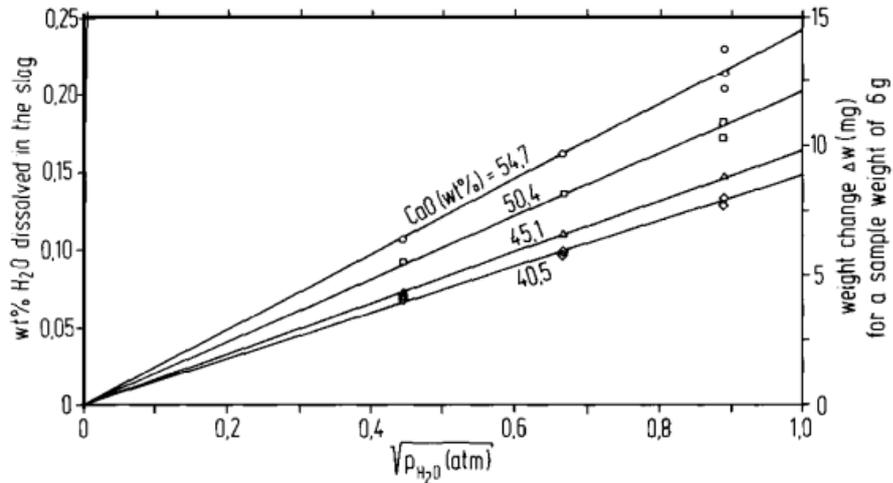
Figure 2. 16 Amount of H_2O dissolved in slag as a function of water vapor pressure for different CaO contents in slag [32]

Steelmaking slags can also contain SiO_2 and MgO in addition to CaO, Al_2O_3. The water capacities of these slags are studied by Brandberg et al. and Jo et al.. The results of both studies given by Brandberg et.al [30] shown in the Figure 2. 17 below. The compositions shown with Arabic numbers belong to study of Brandberg and compositions shown with Roman numbers belong to the study of Jo. It was stated that, water capacities of quaternary slags are not substantially affected from the change in slag composition unless the slag is saturated with CaO. It can be seen from the Figure 2.17 that between the water capacity values remain between 1 x 10^3 and 2 x 10^3 except for the slags having a composition nearly saturated to CaO for both of the studies. In that case the water capacities are remarkably higher and can reach the levels of 3 x 10^3 .
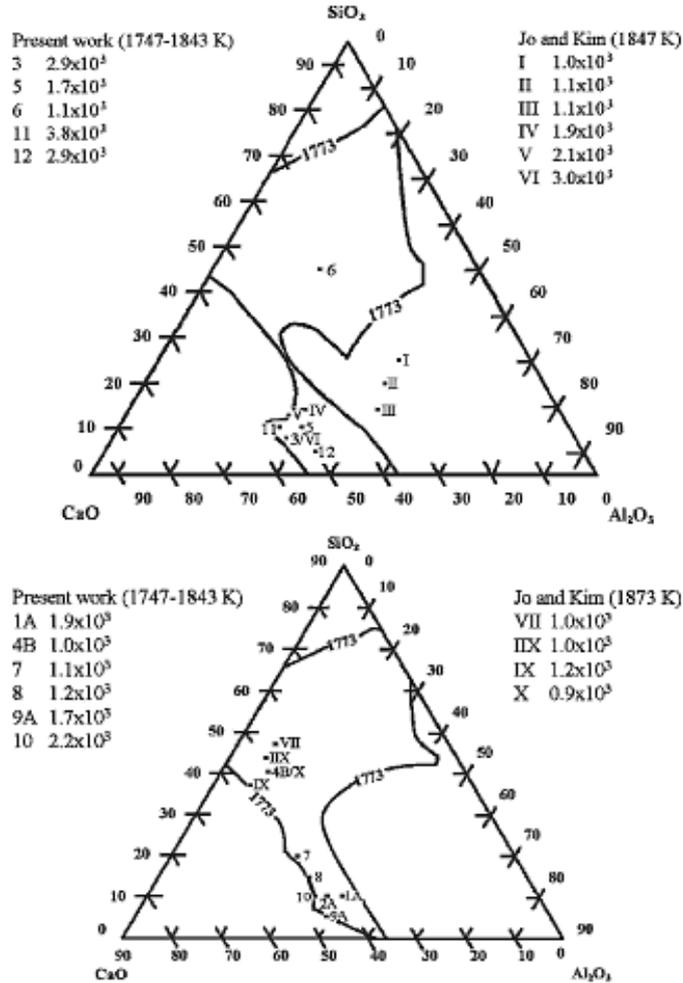
Figure 2. 17 Water capacity of slags with different compositions (top) 5% MgO (bottom) 10% MgO [30]

The water capacity of slag is an important property as the hydroxyl ions that are present in slag pass to steel and increase the hydrogen content of the steel. The reaction between slag and metal takes place according to Equation 14. It can be seen that dissolved hydrogen content of steel would increase with increasing amount of hydroxyl ions and this would take place more severely in the highly deoxidized steel [8, 28].

$$2(OH^-) = 2[H](ppm) + [O](\%) + (O^{2-}) \tag{14}$$
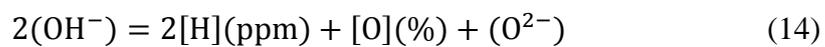
In addition, making of steelmaking slags in the ladle process involves addition of CaO which is a material that can easily be hydrated and provide hydrogen to steel. This situation can also be seen from the red group of columns of Figure 2.15. Moreover, Fruehan and Misra found that, the sequence of CaO addition is important for the extent of picked-up hydrogen which is lower when CaO is added on the top of the slag than in the case that slag involving CaO is used [23, 26, 33].

As stated before, the composition of slag is not only important for hydrogen content of steel but it is also important for inclusion removal and desulfurization. Thus, altering the composition by only considering the hydrogen content of steel may not be preferred in every case. Instead, the surface of slag was covered with MgO in a study by Jha et al. in Durgapur steel plant, which made the slag surface heterogeneous and increase the viscosity. As a result the hydrogen pick-up was decreased to lower values than 0.5 ppm [20].

2.4.2 Hydrogen Pick-Up during Continuous Casting

The last stage of steelmaking process is continuous casting of steel whose properties such as composition and temperature were brought to desired levels. In this stage liquid steel in ladle is transferred to tundish through a refractory tube called shroud that is placed between the bottom gate of the ladle and the tundish. Tundish is a refractory lined vessel which keeps the speed of steel flow constant while steel is distributed to the continuous casting molds. Flow with constant speed is attained by keeping steel level in the tundish constant throughout the casting. In this stage, contact of steel with air is prevented by covering the surface of steel with casting powders in tundish and by using tubes during flow of steel between ladle, tundish and molds. Furthermore, casting powders that cover the surface of steel forms a liquid phase on the top of the steel which also aids the collection of inclusions. Accordingly, during continuous casting, steel comes into contact with phases that can be potential hydrogen sources. Lachmund et al. [9] have determined the hydrogen sources for liquid steel in the continuous casting step as water vapor or

organic binders that are attached to casting materials; shrouding tube, tundish covering agents, tundish lining material, casting powder, sliding gate sand and air. Among these the effect of sliding gate sand was ignored due to very low consumption amounts. In the Figure 2.18, the contributions of these sources to the hydrogen content of steel is given according to the average results of 9000 heats. It was stated that tundish lining and shroud provide hydrogen to steel at most where the casting powder and air is less effective. In this figure, the decrease of hydrogen pick-up due to tundish lining shows the elimination of hydrated phases in the lining during casting sequence which would be mentioned later in this section.
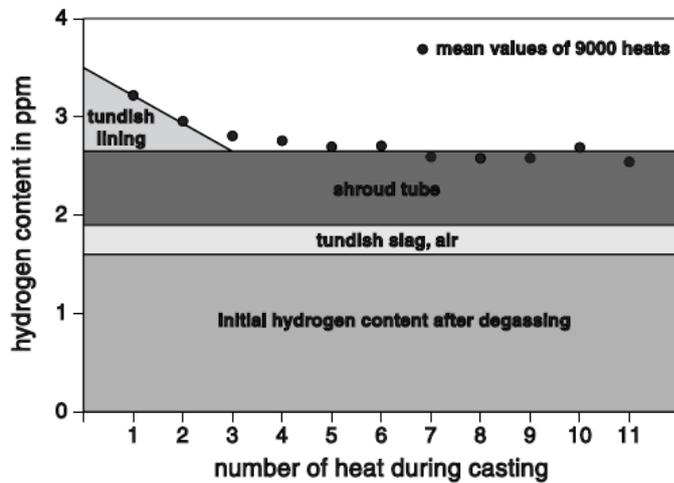
Figure 2. 18 Hydrogen sources and hydrogen pick up amount of steel during continuous casting [9]

Likewise, Bragança et al. [34] determined an increase in hydrogen content of steel cast with unused tundish and conducted thermal analysis of materials that are used in continuous casting. It was found that, during heating of tundish lining materials and powders, hydrogen content of these materials are decreased which is more severe for casting powder. Furthermore chemical analysis revealed that powders contain hydrated phase of $Ca(OH)_2$ which can be the source of hydrogen. This shows that, these materials can be considered as hydrogen sources especially in the first heats of

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a sequence when tundish, shroud and powders are new. Since the main source is physically and chemically bound water, preheating the aforementioned materials or using materials with different chemical composition were considered to be the solution of preventing hydrogen pick-up [9, 34].

Actually, heating of tundish beforehand is an ordinary preparation step of a tundish for casting for removal of hydrated phases and preventing the sharp decrease of temperature of steel. In this case, sufficiency of the heating cycle with regards to duration and temperature is important. Harris et al. [23] determined that, doubling the heating duration decreases the hydrogen pick-up in tundish. In this study the decrease of hydrogen content of steel during casting was investigated for heats cast by using unused tundish with different preparation practices. It can be stated according to the results of this study which was given in Figure 2.19 that there is a lower degree of decrease in the casts for those double heated tundish were used than for the casts for those normally heated tundish were used.
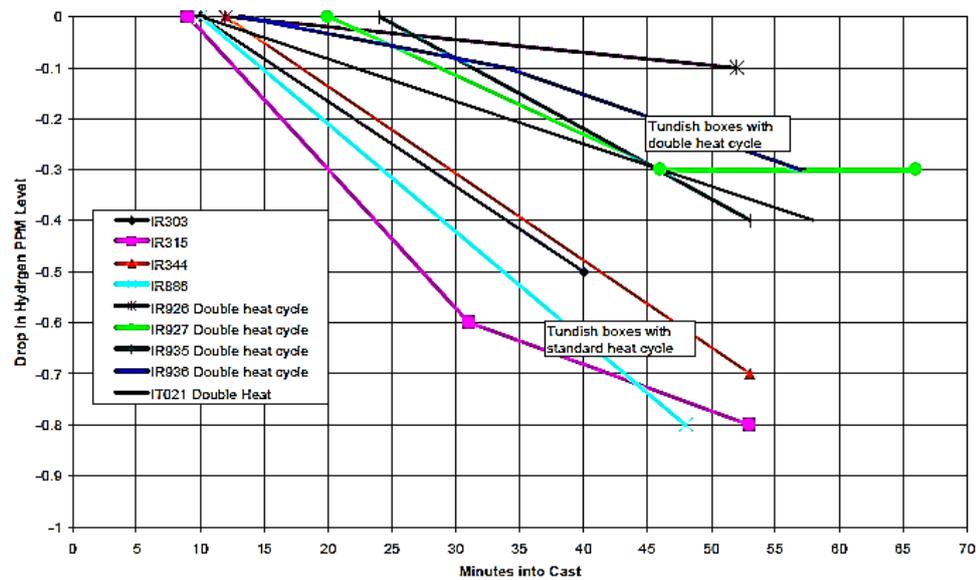
Figure 2. 19 Decrease of hydrogen contents of steel cast with tundish with standard and double heating cycle, during continuous casting [23]

The lower degree of decrease indicates the lower degree of hydrogen pick-up at the first opening of the heat [23]. This indicates the normal cycle's insufficiency to remove the hydrogen present in the tundish lining.

In continuous casting, one tundish can be used for more than one heat having similar grades which are being cast subsequently. This is called sequence casting. As stated before in this section, sequence casting eliminates the contribution of tundish lining material to hydrogen content of liquid steel [10, 23, 35]. The beneficial effect of sequence casting on hydrogen content of steel is shown in Figure 2.20. In that study the hydrogen pick-up of steel after vacuum degassing in tundish was analyzed according to the sequence of heat taken with same tundish in Arcelor Mittal Ruhrort GmbH steel plant.

The plot shows data with the fitted equation $y = 0.97x^{-1.10}$, $R^2 = 0.86$. The x-axis is labeled "Position of heat in casting sequence" and the y-axis is labeled "Hydrogen pick-up in ppm".
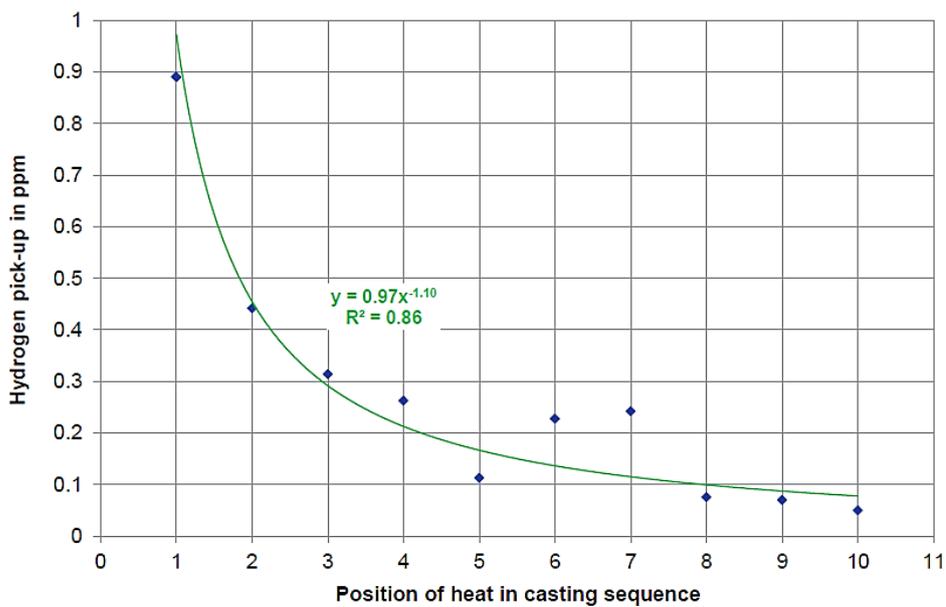
Figure 2. 20 Hydrogen contents of heats cast in a sequence [35]

It can be obviously seen that, the amount of hydrogen pick-up decreases sharply after the first heat and a smoother decrease proceeds for all the sequence heats. The reason

for this situation is the diminishing of water or other hydrated phases present in the tundish refractory material heat by heat and removal of higher amount of water at the first contact [35].

In Gerdau Steel, hydrogen measurements were conducted from four heats of a sequence during each heat in order to investigate the hydrogen pick-up amount in tundish and the effects of sequence casting to that. As can be seen from the Figure 2.21 hydrogen amounts decrease during sequence casting however the manner of decrease is different from the results of the study mentioned before. It can be seen that, there is an increase in the beginning of every cast shown by blue circles, still being lower than first measurement of the preceding cast. This incident was ascribed to two cases; one of which was the use of casting powders at the beginning of the heats, which are possible hydrogen sources as mentioned before. The other possible reason that was offered was that the passing of steel through the shroud a little time period after slide gate of the ladle was opened which causes the steel to have contact with air during this period of teeming [36].
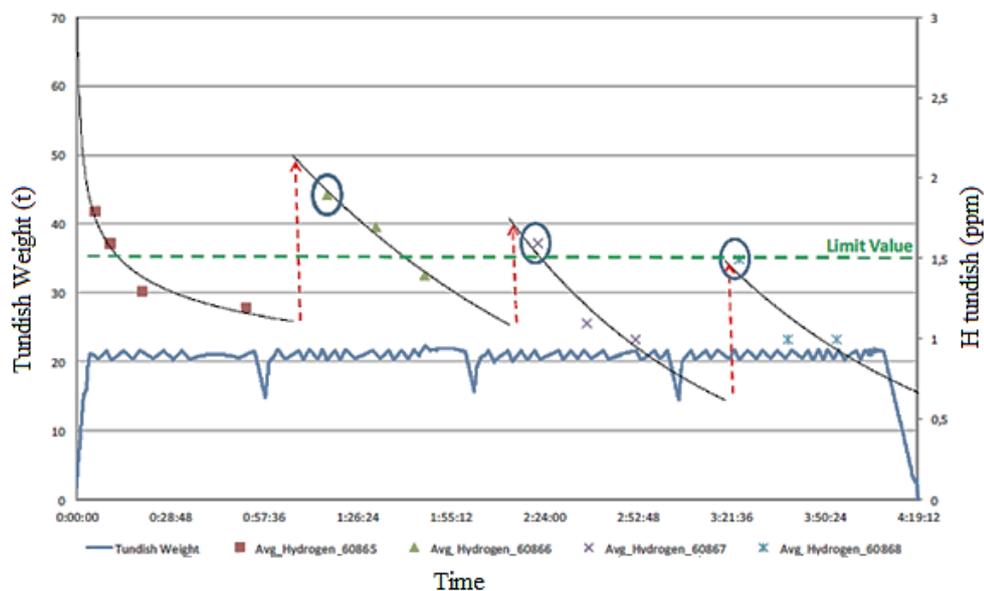
Figure 2. 21 Decrease in hydrogen contents of heats during sequence cast [36]

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To sum up, hydrogen is an undesired element that can be present in liquid steel and cause problems due to its solubility characteristics. It can enter the steel via several phases that steel come into contact during steelmaking process. The main source of hydrogen that is present in these phases is water vapor. Removal of hydrogen is attained to a great extent with vacuum degassing however after vacuum steel can still encounter hydrated phases and without vacuum degassing, removal of hydrogen is almost impossible. Accordingly, determination of possible sources of hydrogen during the process and preventing hydrogen pick-up is necessary for producing quality steel.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Description of ÇEMTAŞ Steel Plant

ÇEMTAŞ Çelik Makina Sanayi ve Ticaret A.Ş. was founded in early 1970s in the Industrial district of Bursa, Turkey with the intention of producing quality steel from scrap. Since the establishment, with several investments and developments, ÇEMTAŞ has become an important quality steel producer that can fulfill the demands of customers.

Starting with ingot casting of steel produced by electric arc furnace in 1970s, until early 1990s ÇEMTAŞ had increased its technology by firstly acquiring rolling mill and continuous casting system, followed by modernization of the electric arc furnace, investments about ladle furnace, vacuum degassing unit and wire injection units. In 1990s a new continuous casting system was installed, rolling mill was revamped and ÇEMTAŞ had reached its present state. Owing to all of the investments and developments, ÇEMTAŞ can today produce 153000 tons/year in the steel mill and 228000 tons/year in the rolling mill. In the upcoming days, there would be other renovations on continuous casting system and roughing mill; first part of the rolling mill.

3.2 Steel Production Process of ÇEMTAŞ

The production process and the equipment used today are briefly explained in this section starting from the steel mill, continued with the rolling mill and the non-destructive test units.

Billets which are intermediate products are produced in steel mill; here the process starts with melting the scrap and ends with continuous casting. In rolling mill the billets are rolled into the bars with desired dimensions which are the final products.

3.2.1 Electric Arc Furnace

The steelmaking process in ÇEMTAŞ starts with charging mostly automotive industry originated scraps, to the electric arc furnace and melting them by creating an arc between the electrodes and scrap. The present electric arc furnace is a 30 tons capacity eccentric bottom tapping furnace of DEMAG. The scrap is charged in three parts, with a certain amount of lime added to the first part. In the melt carbon-boil takes place, which is oxidation of carbon and formation of carbon monoxide gas. By this means, oxygen content of steel is decreased, the temperature of the steel is homogenized, hydrogen and nitrogen contents are decreased by the flushing effect of the bubbles and the steel is dephosphorized. In addition, C and O_2 are injected to the metal-slag interface by manipulators, which ensure a significant amount of CO gas formation there. By this means a foamy slag is created which is necessary for efficient use of electrical energy and disposal of the slag that consists P_2O_5.

Along entire steelmaking process, starting with the liquid steel in the EAF, lollypop samples are taken and chemical analysis of steel is done by optical emission spectrometer which is important for adjusting the composition of steel. After attaining desired temperature, which is in the vicinity of 1650°C steel is tapped to the ladle without carry-over slag. During tapping, deoxidizers (mostly aluminum) are added when one-third of the ladle is full.

3.2.2 Ladle Furnace I

For ladle refining DEMAG Ladle Furnace with 30 tons capacity is used, with wire injection and automatic alloying systems. Here, in the ladle furnace step, firstly creation of a new slag with a definite composition by addition of slag making additives (CaO, CaF_2, etc.) takes place. Then composition of steel is adjusted according to standards and costumer demands. In addition to chemical composition, the dissolved oxygen and hydrogen amounts are checked by Celox and Hydris systems of Electro-Nite, respectively. Along the entire process, steel is stirred by argon or nitrogen gas injected from the bottom of the ladle through a porous plug. This accelerates the removal of inclusions by floating and passing to slag. Also by stirring, composition and temperature of steel are homogenized.

3.2.3 Vacuum Degassing

After reaching a definite composition, ladle is taken to the vacuum degassing station. In ÇEMTAŞ tank type vacuum degassing system is present with 30 ton capacity product of MESSO. Steel is kept under 1 mbar pressure for a definite time. Here, the gas forming elements like hydrogen and nitrogen are removed. During vacuum, vigorous stirring with argon is applied in order to get rid of the remaining deoxidation products by passing them to slag, increase the efficiency of degassing and desulfurize the steel by increasing the area of slag metal interface.

3.2.4 Ladle Furnace II

After vacuum, the ladle is taken to the second ladle furnace, which is also 30 tons capacity unit of CVC. Here wire additions are done in order to make small adjustments of composition, to carry out alloying that should be done after vacuum, to ensure appropriate microstructure in the products and to modify the shape of inclusions. The wires that can be added are Al, C, MnN, B, Ti, S, Ca and CaSi. Furthermore, in ladle furnace II, the temperature of steel which had decreased during

vacuum is increased to the casting temperature and also the gas stirring from the bottom of the ladle with argon or nitrogen continues gently during entire process.

3.2.5 Continuous Casting

In ÇEMTAŞ closed continuous casting is applied by CONCAST system of 2 strands which can be decreased to 1 or increased to 3. Full ladle is taken to the turret and slide gate at the bottom of the ladle is opened in order to allow the steel to flow through shroud to the tundish. The flow of steel to molds is controlled by stopper system that is assembled to the tundish. After filling the tundish, steel is allowed to flow through submerged entry shrouds, thus distributed to the molds of generally 140 mm and 160 mm square cross sections. During flow through the copper molds it is electromagnetically stirred.

ÇEMTAŞ is capable of producing square cross sectioned billets with 100, 120, 130, 140, 150 and 160 mm side lengths today and 200 mm square cross sectioned billets would be produced with the aforementioned investment.

3.2.6 Rolling Mill

The billets are marked against the possibility of mixing and processed in the following stations of rolling mill successively; reheating furnace, descaler, roughing mill, continuous rolling mill, shot peening and straightening stations.

The rolling process starts in the walking hearth reheating furnace of THYSSEN with 50 tons/hour capacity. Here the billets are heated to 1250 $^{\circ}$C in a controlled atmosphere. Then scale on the billets is removed by descaling unit. The descaled billets firstly, go through rouging mill with three stands then they are given their final shapes and cross-sectional dimensions by the continuous rolling mill. Roughing and rolling mills are both products of DEMAG. At the end of the rolling, dimensions are measured by a laser system. During rolling the temperature of the round or spring steel bars would decrease by about 200 $^{\circ}$C, then they are taken to the controlled

cooling bed where their temperature would drop slowly about another 200 °C. The bars are then taken from the cooling bed and left to cool to room temperature in air.

The round bars between 15 – 80 mm diameter and spring steel bars having several profiles with several combinations of dimensions can be produced. The round bars are then subjected to the non-destructive tests.

3.2.7 Non-Destructive Testing Unit

ÇEMTAŞ has the technology and equipment of non-destructively testing of only the round products. By these tests internal, subsurface and surface defects can be detected. All of these three kinds can be detected by ultrasonic testing machine of GE IT (KRAUTKRAMER). The probes of the ultrasonic testing machines create ultrasonic sound waves and these sound waves propagate through the steel bar. When there is a discontinuity along the way, the sound waves are reflected and they are sensed by the probes. Surface defects are also detected by circoflux testing machine of FOERSTER Company, by creating magnetic flux around the bars. Surface defects are detected by the magnetic sensors that detect flux leakage.

There are three of each type of machines which are integrated so all kinds of defects are detected at the same time. The defected areas are marked with different colors according to type of defects. Finally, the marked parts, especially internally defected parts are separated from the products as production losses and analyzed microscopically and macroscopically in the laboratory.

3.2.8 Heat Treatment and Peeling

There are two optional processes that ÇEMTAŞ is also capable of. The first one is heat treatments for stress relieving, softening and cold shearability annealing. The second one is peeling of round bars.

3.3 Experimental Procedure

In this study, several heats were chosen as experimental heats and during production of these heats, data such as time, temperature, quantities of additives were noted. Hydrogen contents were determined both in the ladle and tundish by using HYDRIS device, a design of Heraeus-Electro Nite. The principal of HYDRIS (hydrogen direct reading immersion system) is sending nitrogen to the molten steel through a lance immersed into the steel with a probe on it and sending the nitrogen to the pneumatic unit of the system after retracting it from steel. This loop continues until there is equilibrium between the liquid steel and the nitrogen bubbles regarding to the dissolved hydrogen content as hydrogen in steel would pass to nitrogen bubbles until there is equilibrium. Then the partial pressure of hydrogen (in hPa) in the bubbles are determined by thermal conductivity detector. The difference between the thermal conductivities of hydrogen (1.816 mW/cm ^{o}K) and nitrogen (0.252 mW/cm ^{o}K) makes distinguishing hydrogen and determining the partial pressure of hydrogen possible. Hydrogen content of the liquid steel is determined by using Sieverts law by using the partial pressure value [37]. For chemical analysis of the steel ARL 4460 optical emission spectrometer was used. For this analysis, lollypop samples were taken from the molten steel at different stages of process.

As in normal production practice, the round bars were tested for surface, subsurface and internal defects by non-destructive testing techniques. All of the defected areas that are determined are marked with different colors and parts with internal defects are separated for macroscopic and microscopic analysis. In the scope of this thesis, mostly macro examination was done by blue fracture and macroetching test according to ASTM E-381 and SEP 1584, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This is the second phase of a study undertaken at ÇEMTAŞ Steel Plant with the objective of decreasing production losses related to defects. ÇEMTAŞ produces low alloy flat and round bars to be used primarily by the automotive industry. The specifications for the products are quite strict and all round bars are controlled by using magnetic flux and ultrasonic non-destructive testing methods to detect surface, subsurface and internal defects. Laborious grinding operations are required for surface and subsurface defects. Presence of internal defects necessitates cutting operations, which result in production losses. The study was undertaken primarily to investigate the reasons for internal defects and to take measures directed to decreasing production losses resulting from these defects. An example to internal defects resulting in production losses is given in Figure 4.1 where blue fracture test samples taken from a part in one of the final round bar products of heat number 4761. The internal defects, marked in red circles, are seen to be located in a region between the mid-radius and the surface of the rod and are found to continue for several centimeters in the direction of rolling. SEM observations and EDS analysis indicated presence of non-metallic inclusions in these defects. It was therefore concluded that one of the causes of defects was non-metallic inclusions. Certain precautions explained in the M.S. thesis of Şahin [38] were taken in order to decrease inclusion contents of the steel.
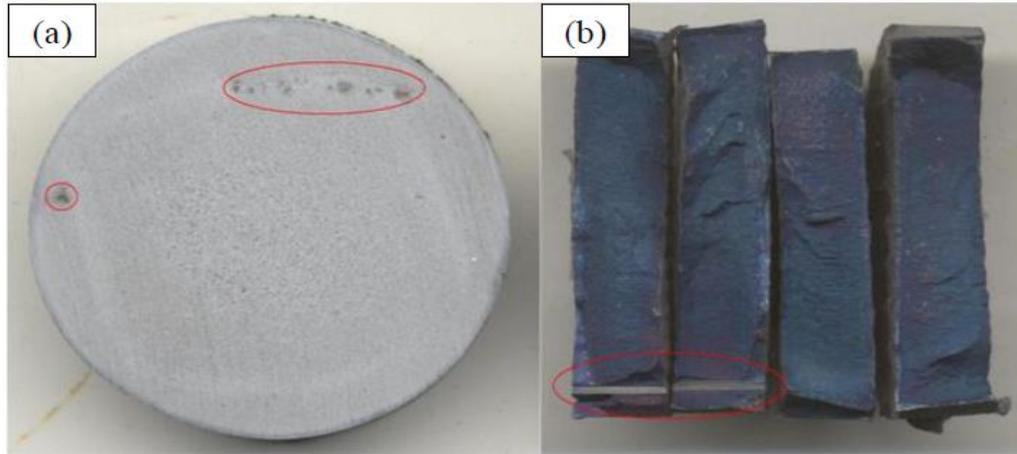
Figure 4. 1 Nonmetallic inclusions in **(a)** macroetching and **(b)** blue fracture samples [38].

These precautions were very effective and production losses were significantly decreased and defects similar to that illustrated in Figure 4.1 were almost completely eliminated. This is illustrated in Figure 4.2 where blue fracture test samples taken from defective parts of the final round bar products of heats Exp. Heat 06 (Experimental Heat 06) and Exp. Heat 07 are shown. Decrease in inclusion contents of heats resulted in significant decrease in production losses but production losses due to internal defects were not completely eliminated. Microscopic examination of blue fracture test samples like those shown in Figure 4.2 revealed presence of microcracks located primarily at the central part of the round products. Production losses due to internal defects were also found to decrease with decrease in the diameters of the round products. The fact that round bars of smaller diameters are produced by more extensive rolling indicates that rolling decreases microcracks. These were taken as signs of internal defects not related to inclusions to be due to hydrogen contents of the heats and the present study was initiated.

Figure 4. 2 Blue fracture samples taken from defected areas which does not contain inclusion (left) Exp. Heat 07 - Ø72 mm, (right) Exp. Heat 06 – Ø 75 mm

4.2 Determination of Hydrogen Levels

Liquid steel picks hydrogen from hydrogen containing species like H_2O, hydrocarbons, OH^-, etc. contained in air, refractories, slags, fluxes etc. and elemental hydrogen contained in metallic additives when it comes in contact with these phases. As such liquid steel can pick hydrogen in the furnace, in the ladle, in the tundish, in the mold and during transfer from one vessel to another like from furnace to ladle, from ladle to tundish, from tundish to mold. Hydrogen levels at various stages of steelmaking should therefore be known in a study directed to hydrogen control. Hydrogen is best eliminated from liquid steel by vacuum treatment. A vacuum treatment facility is present in plants producing low-hydrogen steels and such a facility exists in ÇEMTAŞ. It is the hydrogen level after the vacuum treatment which is important in such plants. With this understanding the study was concentrated on hydrogen levels during and after vacuum treatment.

The study was started with determination of hydrogen levels of liquid steel before and after vacuum treatment. Such a study was already made in the previous phase of

the study where the objective was control of oxygen. In vacuum, not only the gas forming elements but also the non-metallic inclusions which have not floated yet are removed from the liquid steel to a large extent. Therefore, studies were conducted to determine the optimum durations of vacuum considering oxygen and hydrogen contents in the previous project. It was found that for decreasing oxygen amounts, 10-15 minutes are optimum under 1 mbar pressure with vigorous argon stirring and after this period there is an increase in oxygen contents due to reoxidation as can be seen from the Figure 4.3.
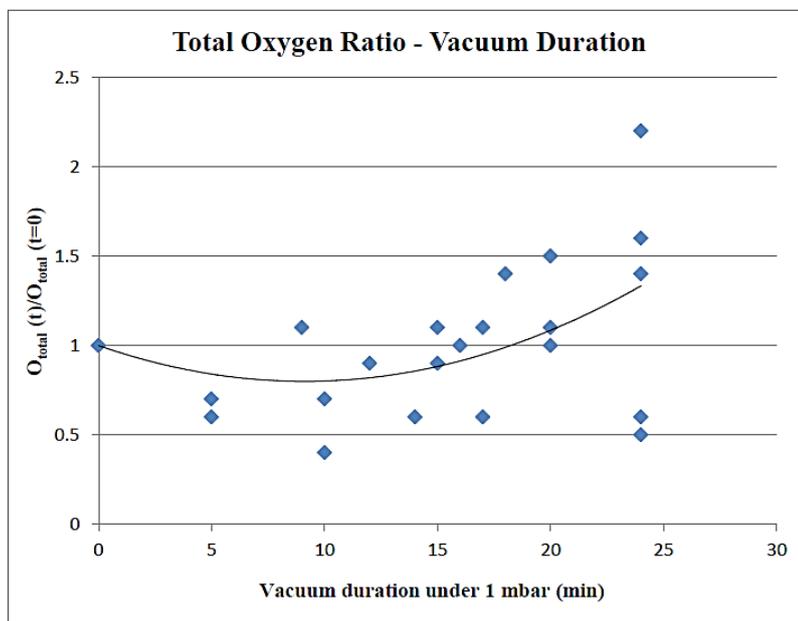
Figure 4. 3 Change in total oxygen content of heats as a function of vacuum duration [38]

As stated before, during the determination of optimum vacuum degassing durations, hydrogen contents were also considered. It was found that by the vacuum durations that are suitable for decreasing oxygen contents which are 10-15 minutes, hydrogen contents of steel can be decreased from 7.5-8.5 ppm to the vicinity of 1 ppm [38]. In Table 4.1, the dissolved hydrogen amounts of several heats that were taken

throughout the study, before and after vacuum degassing and the vacuum durations are given. Here the first five heats were taken during the previous project but their data of hydrogen contents before vacuum were not given there. After a few hydrogen measurements it was understood that the hydrogen levels are nearly same for all heats and here it can be seen that hydrogen amounts can be decreased from 7.5 ppm levels to 1 ppm level by about 15 minutes of vacuum degassing.

Table 4. 1 Hydrogen values before and after vacuum degassing for different steel grades

Heat No	Grade	Steel Standard	Vacuum Duration (min)	H - before Vacuum (ppm)	H - after Vacuum (ppm)
Exp. Heat 01	23MnNiMoCr52	DIN 17115	20	7.1	1.2
Exp. Heat 02	51CrV4	EN 10089	14	8.5	1.3
Exp. Heat 03	51CrV4	EN 10089	12	8.0	1.1
Exp. Heat 04	51CrV4	EN 10089	17	8.0	1.1
Exp. Heat 05	51CrV4	EN 10089	10	8.0	1.1
Exp. Heat 40	28CrS4	EN 10084	16	7.5	0.7
Exp. Heat 41	28CrS4	EN 10084	16	7.2	0.8
Exp. Heat 42	28CrS4	EN 10084	16	-	0.8
Exp. Heat 43	5120H	SAE J 1268	16	6.2	0.7
Exp. Heat 44	5120H	SAE J 1268	16	-	0.9
Exp. Heat 45	28CrS4	EN 10084	16	-	0.6
Exp. Heat 46	5120H	SAE J 1268	17	-	0.6
Exp. Heat 49	5120H	SAE J 1268	15	-	0.6
Exp. Heat 50	1040	SAE J 403	12	-	1.0
Exp. Heat 51	1040	SAE J 403	12	-	0.8
Exp. Heat 52	51CrV4	EN 10089	13	-	0.7
Exp. Heat 53	51CrV4	EN 10089	18	-	0.8
Exp. Heat 54	5120H	SAE J 1268	16	-	0.5
Exp. Heat 55	5120H	SAE J 1268	16	-	0.6
Exp. Heat 59	51CrV4	EN 10089	14	-	0.9
Exp. Heat 60	51CrV4	EN 10089	14	-	0.9
Exp. Heat 61	51CrV4	EN 10089	12	-	1.1
Exp. Heat 62	51CrV4	EN 10089	12	-	1.0
Exp. Heat 63	51CrV4	EN 10089	12	-	0.9
Exp. Heat 64	42CrMo4	EN 10083	19	-	0.8
Exp. Heat 65	45NiCrMo16	EN ISO 4957	20	-	0.8

Table 4.1 (continued)

Exp. Heat 66	51CrV4	EN 10089	12	-	1.0
Exp. Heat 68	51CrV4	EN 10089	13	-	1.1
Exp. Heat 69	55Cr3	EN 10089	13	-	0.9
Exp. Heat 71	51CrV4	EN 10089	15	-	1.0
Exp. Heat 72	51CrV4	EN 10089	14	-	0.8
Exp. Heat 73	55Cr3	EN 10089	12	-	1.0
Exp. Heat 74	51CrV4	EN 10089	15	-	0.9
Exp. Heat 75	S355J2	EN 10025	15	-	0.9
Exp. Heat 76	34CrNiMo6	EN 10083	20	-	1.2
Exp. Heat 77	38MnS6	-	16	-	0.9
Exp. Heat 78	42CrMoS4	EN 10083	18	-	1.0
Average			15	7.6	0.9

The effect of vacuum durations on hydrogen contents is also given in the Figure 4.4. According to this figure, after 15 minutes of vacuum hydrogen contents remain between 0.5 to 1 ppm. Considering Figures 4.3 and 4.4 together, it can be stated that 12 to 15 minutes of vacuum is optimum for both hydrogen and oxygen contents of steel.
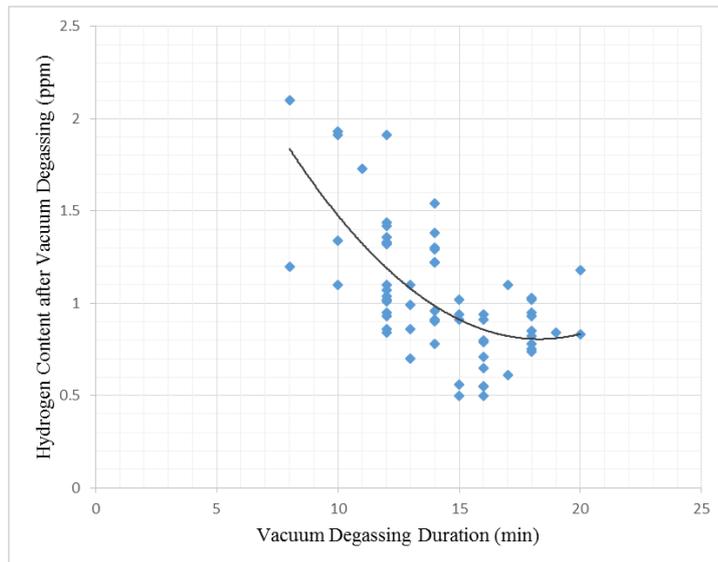
Figure 4. 4 Effect of vacuum degassing duration to hydrogen contents of steel

After vacuum, steel is treated in ladle for temperature and composition adjustment and then taken to the continuous casting. Hydrogen has no effect on processing of liquid steel and the detrimental effects of hydrogen arise during and after solidification as stated in Chapter 2. Consequently it is the hydrogen concentration just before solidification which is the most important. Measurement of hydrogen content of liquid steel in the continuous casting mold was not possible due to space constraints and also due to possibility that such a measurement may give rise to defects in the final billet. The tundish, the last possible place to take measurement from liquid steel, thus becomes the vessel where concentration of hydrogen is the most important. The results of hydrogen measurements in the tundish for 6 heats are given in Table 4.2. Two measurements were taken for 4 of the heats as shown in this table. Considering hydrogen levels of these heats to be about 1 ppm after vacuum, as concluded above, the results indicate that there is hydrogen pick-up of nearly 3.5 ppm after vacuum. This is a severe pick up amount, because 4 – 5 ppm hydrogen in tundish could easily cause defects due to the pressure generated by formation of hydrogen gas after solidification of steel. For instance, according to Equations 1, 2 and 3 ppm of hydrogen in liquid steel at 1550 $^{\circ}$C would be in equilibrium with 0.028 atm of H_2 gas but when temperature of this steel decreases to 200 $^{\circ}$C the equilibrium hydrogen gas pressure would increase to 9686 atm which is an enormous pressure value.

Table 4. 2 Hydrogen contents of different grades of steels in tundish

Heat Number	Grade	Steel Standard	H (1st measurement in tundish-ppm)	H (2nd measurement in tundish-ppm)
Exp. Heat 08	4340	SAE J 404	4.2	2.7
Exp. Heat 09	30CrNiMo8	EN 10083	4.9	3.3
Exp. Heat 11	80CrV2	EN 10132	3.6	3.0
Exp. Heat 12	58CrV4	-	4.3	2.7
Exp. Heat 13	50CrV4	EN 10089	4.7	-
Exp. Heat 18	51CrV4	EN 10089	4.7	-

After ascertaining that there was hydrogen pick-up after vacuum, hydrogen concentrations of three heats before vacuum treatment (BV), after vacuum treatment (AV), at the end of ladle treatment after vacuum (EL) and in the tundish at different times (TN1, TN2 etc.) were determined to find the location(s) of hydrogen pick up. The results of these measurements are given in Figure 4.5.

	BV	AV	EL	TN1	TN2	TN3
Exp. Heat 40	7.5	0.7	1.7	3.2	3.3	
Exp. Heat 41	7.2	0.8	1.1	1.8	1.7	1.5
Exp. Heat 43	6.2	0.7	1.4	2.6	2.2	
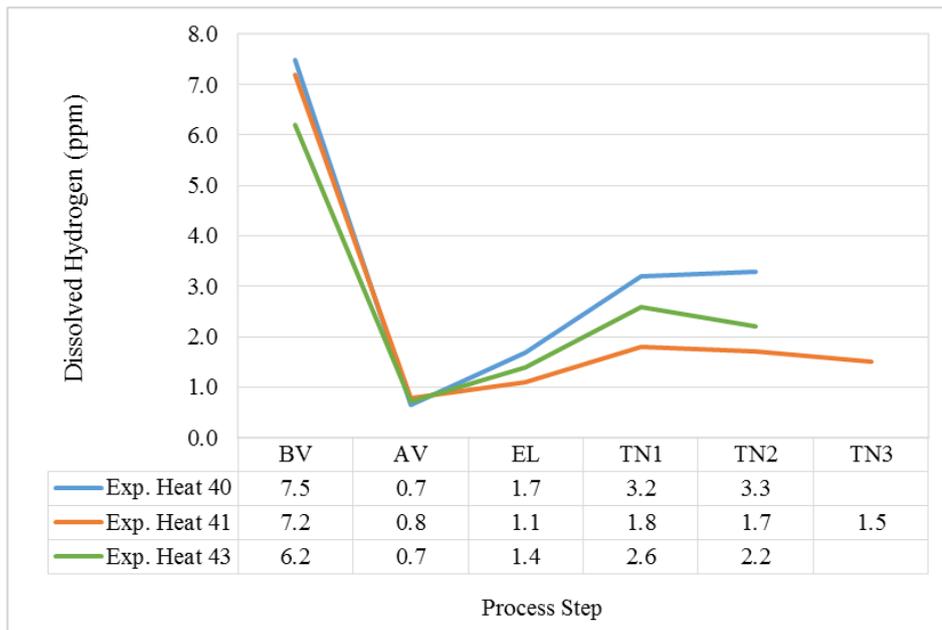
Figure 4. 5 Change in hydrogen content of steel during steelmaking

The results in the Figure 4.5 are in accord with the previous findings that hydrogen decreases to less than 1 ppm at the end of vacuum treatment irrespective of the initial amount and that steel picks up hydrogen after vacuum treatment. The Figure 4.5 shows that there was some hydrogen pick up after the vacuum during ladle treatment and a more severe pick up during transfer of steel from the ladle to the tundish. The Figure 4.5 also shows that hydrogen content in the tundish decreases with time.

After vacuum, in ladle furnace, wire feeding is applied and the temperature of steel is increased for casting. In the next step, liquid steel in the ladle, is transferred to the

tundish through shroud tube and then by the aid of tundish steel is introduced to the molds. There can be hydrogen pick-up during both of the processes due to the contact of steel with hydrogen containing compounds. In ladle furnace, the probable sources of hydrogen pick up could be the hydrogen containing compounds in the wires that are fed, the slag, the gas phase above the slag, the water vapor in air etc. In continuous casting the hydrogen present in hydrogen containing compounds in shroud, tundish lining, casting powders the water vapor in air etc.

In this study the continuous casting step was investigated in the first place as the hydrogen pick-up amount is higher here.

4.3 Hydrogen Pick-up during Continuous Casting

Tundish is the container into which the steel in the ladle is poured, through a refractory tube called shroud and from which the steel flows to the molds through refractory tubes called submerged entry nozzles which can be more than one depending on the number of strands in the casting. The stationary level of steel in tundish ensures the flow to molds with a constant speed. In addition, tundish is also a buffer, which acts as a source of liquid steel while the empty ladle is changed with a full one for sequence casting as tundish is used more than once in sequence casting.

Hydrogen measurements were made in tundish at different time intervals during casting of heats. The results for Exp. Heat 09 are shown in Figure 4.6. Here hydrogen content of steel in the tundish is seen to be about 5 ppm at the 12th minute of the casting but to decrease to about 3 ppm at about 50 minutes. These results are similar to those shown in Figure 4.5. Figures 4.5 and 4.6 indicate that steel picks hydrogen during transfer of steel from the ladle to the tundish and that hydrogen content in the tundish decreases with time. During transfer of steel from ladle to tundish liquid steel comes into contact with the shroud, tundish lining and the tundish slag. Hydrogen containing species that are present in these phases result in pick-up of hydrogen by liquid steel. This pick up is expected to be pronounced at the beginning of casting

when quantity of hydrogen containing species in these phases are highest. Quantity of these species will decrease with time which will result in less hydrogen pick-up in later stages of casting. The results given in Figures 4.5 and 4.6 are in accord with these expectations.
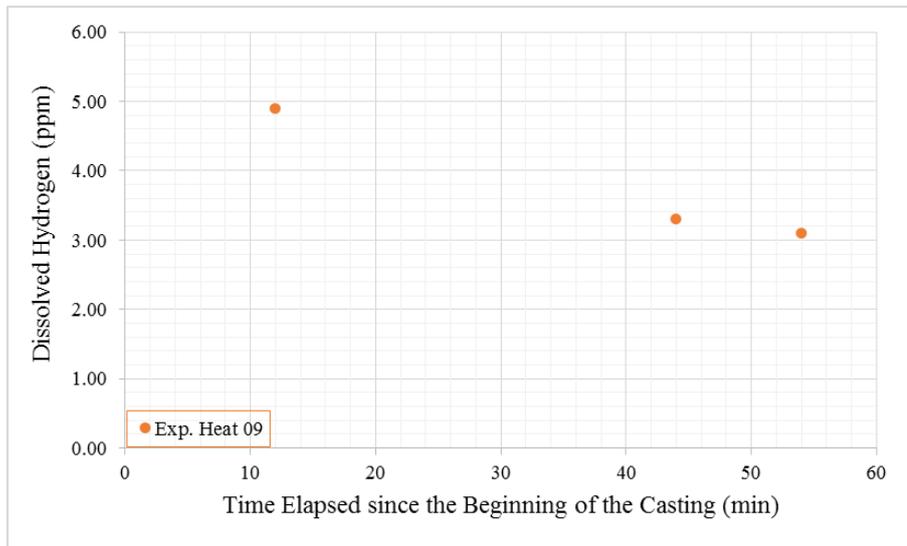
Figure 4. 6 Change in hydrogen content of steel during continuous casting in tundish

When the quantity of a certain grade of steel to be cast is more than the capacity of one ladle, several ladles are cast with only one tundish. This is referred to sequence casting. In the light of the finding that quantities of hydrogen containing species in the phases that liquid steel comes into contact decrease with time, hydrogen pick-up in the first cast expected to be more pronounced than those in subsequent casts. Hydrogen measurements in the tundish at different times for heats Exp. Heat 09 and 10, the first and second casts in a sequence casting are given in Table 4.3.

Table 4. 3 Hydrogen contents and measurement times of heats of two-heat sequence cast (30CrNiMo8- EN 10083)

Heat Number	Time Elapsed Since the Beg. of Casting (min)	Steel in Ladle (tons)	Dissolved H (ppm)
Exp. Heat 09	12	22	4.9
Exp. Heat 09	44	9	3.3
Exp. Heat 09	54	0	3.1
Exp. Heat 10	75	20	2.2
Exp. Heat 10	92	12	1.8
Exp. Heat 10	114	2	1.9

The results presented in Table 4.3 are shown graphically in Figure 4.7. Figure 4.7 indicates that hydrogen contents in the tundish in the second cast is less than those in the first cast and that hydrogen content in the tundish decreases with time in the first as well as second casts of a sequence casting.
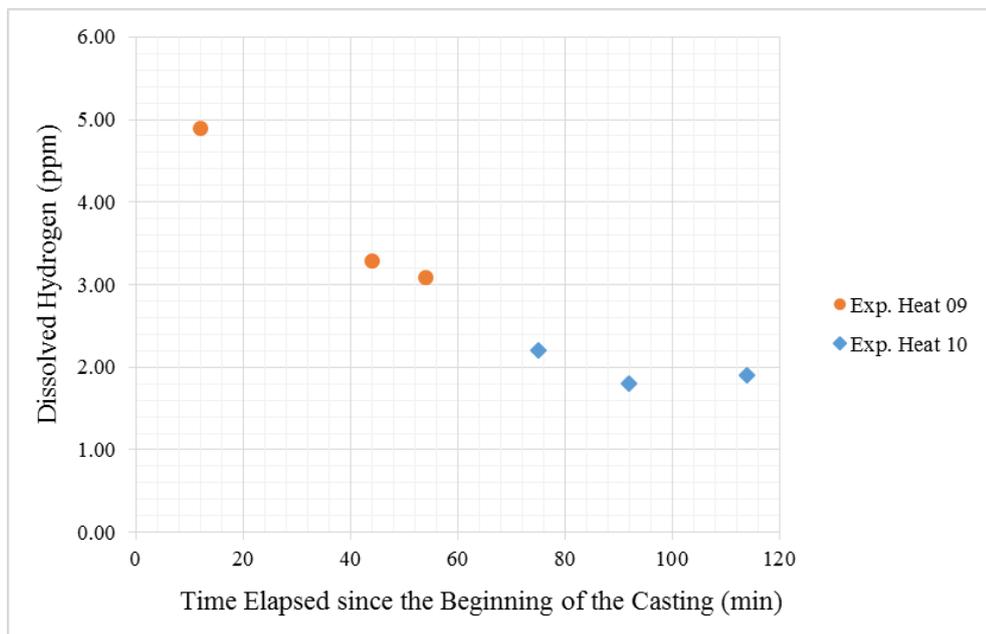
Figure 4. 7 Change in hydrogen content in two-heat sequence casting

These results indicate that, hydrogen pick-up is mostly at the beginning of the casting due to the first contact of the steel with tundish and casting powders and shroud. Furthermore, results of sequence heats reveal one of the advantages of sequence casting which is attaining low hydrogen levels in later heats. Other advantages of using the same tundish for more than one heat are due to economical point of view and increase in the production rate. Therefore, effort is being made in order to use sequence casting as much as possible and amount of sequence cast heats was increased from 2012 to 2014.

Hydrogen pick up of steel during transfer from ladle to tundish may be due to hydrogen containing species in the tundish lining and tundish casting powders as stated before. To determine the effects of these phases on hydrogen pick up, studies were concentrated on these phases separately. In the experiments directed to the effect of one of these phases on hydrogen pick up, care was taken to keep the states of the other phases not to be different.

4.3.1 Effect of Casting Powders

During continuous casting of steel, different kinds of powders are used in the tundish. These are tundish covering powder and insulating powder. At the beginning of the transfer of steel from ladle to tundish firstly the surface is covered with tundish covering powder and then insulation is provided by insulating powder. The use of these powders can be one of the reasons for hydrogen pick up of steel. In this section, the results of studies directed to the effects of these powders on hydrogen pick up are presented.

Tundish covering powder

Examination of the powders started with tundish covering powder which is used in the single heats and in the first heats of a sequence casting. It is used for multiple purposes;

- Covering surface of steel and blocking its contact with air to prevent reoxidation and hydrogen pick up by forming a continuous liquid phase,
- Removal of inclusions by keeping the ones that have risen to the surface of the steel, in the liquid phase formed by the powder,
- Assisting heat insulation.

In order to fulfill these tasks the tundish covering powder should have a suitable chemical composition. In the studies for which the results were presented up to this point, the tundish covering powder was a commercial powder (to be referred to as powder A) having the composition given in Table 4.4. This powder is seen to contain high amounts of CaO and MgO and its melting point is given as 1550 $^{\circ}$C by the producer.

Table 4. 4 Information about tundish covering powders used

Properties	Powder A	Powder B
MgO (wt. %)	40-55	12-14
CaO (wt. %)	40-55	41-43
SiO$_2$ (wt. %)	2-4	22-24
Fe$_2$O$_3$ (wt. %)	1-2	< 3
Al$_2$O$_3$ (wt. %)	1-2	16-18
Na$_2$O + K$_2$O (wt. %)	1-3	<2
Moisture (wt. %)	< 1	<0.8
Grain size (mm)	< 0.3	<0.9
Melting Point ($^{\circ}$C)	≈1550	≈1400

The temperature of steel in the tundish is generally in the vicinity of 1550 $^{\circ}$C. The tundish covering Powder A, due to its high magnesium oxide content is expected to have a high melting point, when formation of a homogenous liquid phase will be difficult. Visual observations indicated that this powder did not form a fully molten slag on the steel in the tundish and could not form a continuous barrier between the liquid steel and air. Based on these, a different commercial powder was decided to be used and studies were continued with this powder (referred to as powder B). The

composition of this powder is also given in Table 4.4. This powder can form a liquid phase on the steel.

Hydrogen contents in the tundish of 4 heats cast with powder A and 4 heats cast with powder B are tabulated in Table 4.5 and presented graphically in Figure 4.8. TN_1 and TN_2, in this table represent measurements taken at the beginning and towards the end of the casting, respectively.

Table 4. 5 Results of hydrogen measurements in tundish of heats cast with different tundish covering powder

Heat Number	Grade	Steel Grade	Tundish covering powder	H-TN_1 (ppm)	H-TN_2 (ppm)
Exp. Heat 09	4340	SAE J 404	A	4.2	2.7
Exp. Heat 11	80CrV2	EN 10132	A	3.6	3.0
Exp. Heat 12	58CrV4	-	A	4.3	2.7
Exp. Heat 18	51CrV4	EN 10089	A	4.7	-
Exp. Heat 19	100Cr6	DIN 17230	B	2.5	2.5
Exp. Heat 20	46MnVS6	EN 10267	B	2.6	1.9
Exp. Heat 21	42CrMoS4	EN 10083	B	3.1	3.0
Exp. Heat 22	20NiCrMoS6	EN 10084	B	3.2	2.2

It is clearly seen from Table 4.5 and Figure 4.8 that the initial H-concentrations (TN_1 values) of heats cast by use of Powder B is less than those cast by use of Powder A.
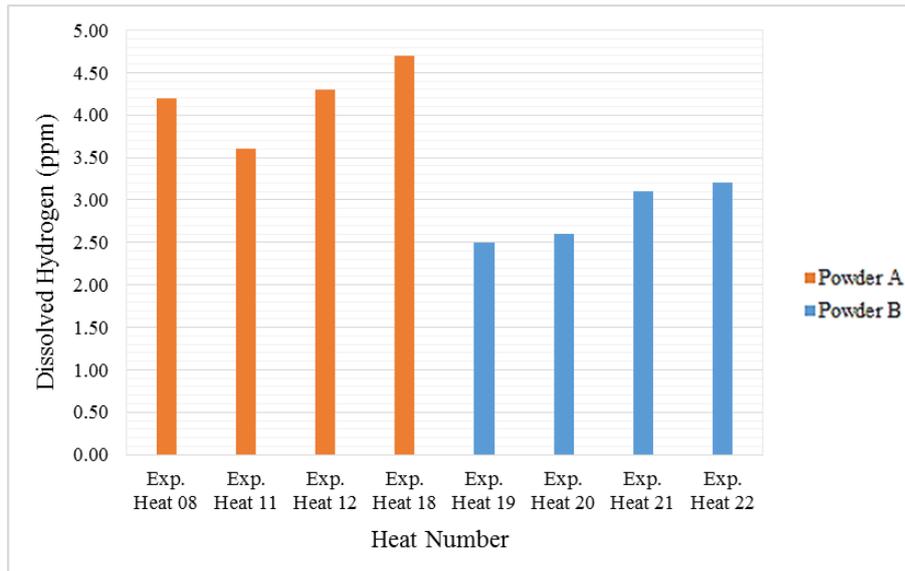
Figure 4. 8 Hydrogen contents of heats cast with different tundish covering powder

The average of TN_1 values of heats cast by use of Powder B is 2.85 ppm while that of heats cast by use of Powder A is 4.2 ppm. This difference, 1.35 ppm is quite significant and type of tundish covering powder used is seen to be very important for hydrogen pick-up. This decrease can both be attributed to the type of powder and the ability of Powder B of forming a liquid phase and blocking the contact with air.

Hydrogen measurements in the tundish were made in a 5-heat sequence casting by use of powder A and in a 4-heat sequence casting by use of powder B. The results of these measurements are tabulated in Table 4.6 and presented graphically in Figures 4.9 (a) and (b). It can be seen that, the hydrogen contents of the heats cast with Powder B is lower than those cast with powder A.

Table 4. 6 Hydrogen contents of sequence heats cast with Powder A and Powder B

Tundish Covering Powder	Heat Number	Grade	Steel Grade	Time Elapsed since the Beg. of Casting (min)	Steel in Ladle (tons)	H – TN (ppm)
Powder A	Exp. Heat 13	51CrV4	EN 10089	29	9	4.7
	Exp. Heat 14	51CrV4	EN 10089	81	21	2.7
	Exp. Heat 15	50CrV4	EN 10089	147	24	2
	Exp. Heat 16	50CrV4	EN 10089	216	21	2.1
	Exp. Heat 17	51CrV4	EN 10089	238	24	2.2
Powder B	Exp. Heat 22	20NiCrMoS6	EN 10084	8	21	3.2
	Exp. Heat 22	20NiCrMoS6	EN 10084	38	4	2.2
	Exp. Heat 23	20NiCrMoS6	EN 10084	88	11	1.6
	Exp. Heat 24	20NiCrMoS6	EN 10084	168	16	1.4
	Exp. Heat 25	20NiCrMoS6	EN 10084	228	20	1.4
	Exp. Heat 25	20NiCrMoS6	EN 10084	258	4	1.5

Figure 4.9 (a) and (b) also show that hydrogen pick up is highest in the first cast and is less in the second and even less in the third casts. Hydrogen pick-up remains essentially constant for later casts.
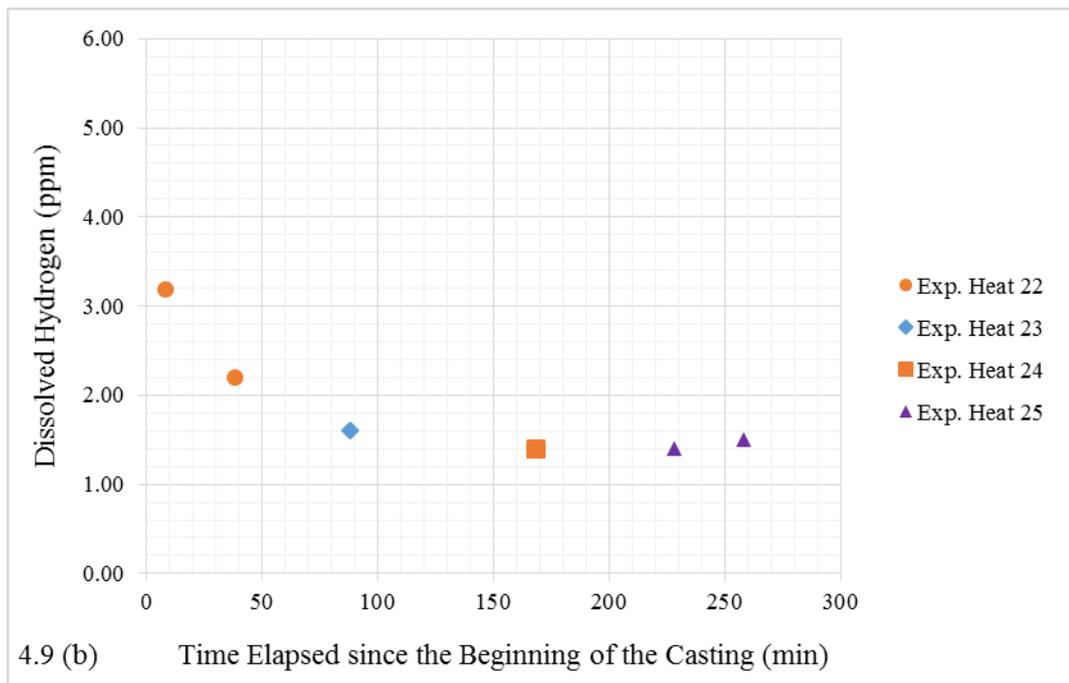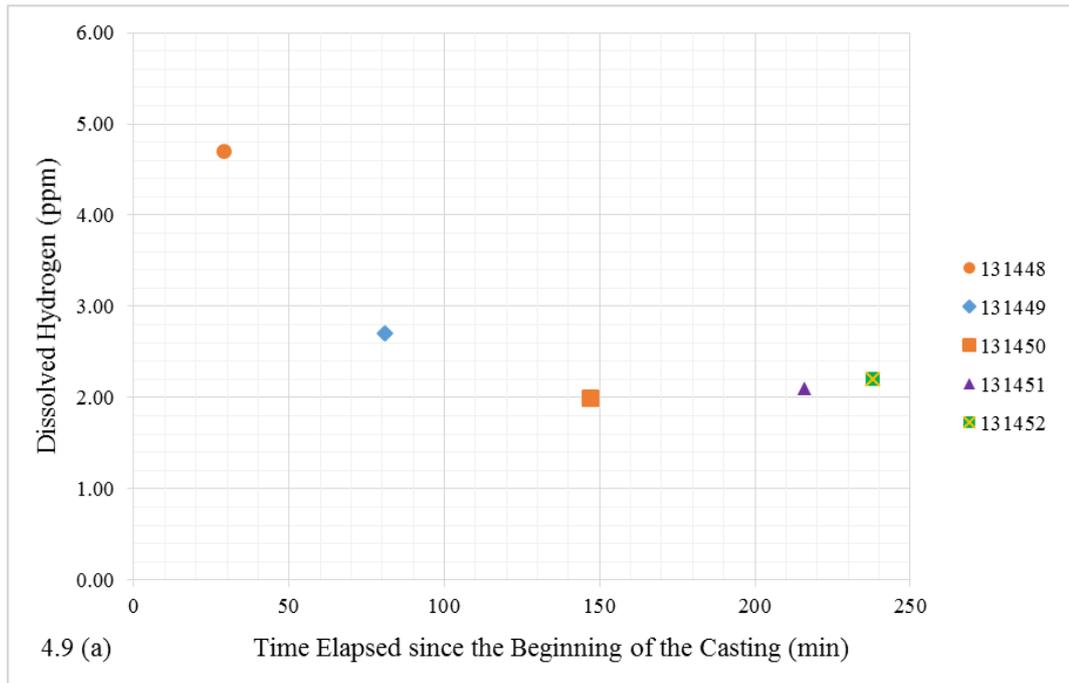
Figure 4. 9 Hydrogen measurements taken from heats of a sequence cast with **(a)** Powder A **(b)** Powder B

Based on these findings, usage of Powder A was abandoned and Powder B was started to be used. The results of studies to be presented in later sections are for heats cast by using Powder B.

Insulating Material

During casting, as expected temperature of steel in the tundish continuously drops due to heat losses. In order to prevent rapid heat loss, after the top of steel in tundish is covered with tundish covering powder, it is also covered by an insulating material. In ÇEMTAŞ for this purpose, rice husk is used. Rice husk is an organic material and it contains hydrogen and due to the delivery conditions it could be wet. Both of these pose a risk for increasing the hydrogen content of steel. When rice husk is spread on the steel, it immediately burns and ash is formed which covers the surface. The insulating duty is fulfilled by ash form of this material. Actually, there are commercially available products in the form of rice husk ash, one of which is tried during this study.

Rice husk ash mainly consists of silica (≈85% according to producer) and it is kept in sealed packs. It can be used instead of rice husk as insulating material, because it is the ash form of the rice husk that carries out the insulating duty. Due to its low bulk density, rice husk ash easily spreads over the surface of the steel. Especially due to its very low organic and moisture contents (<1%), the usage of it is expected to be advantageous for hydrogen pick-up issue.

A number of heats were cast by use of rice husk and rice husk ash and the hydrogen contents of these heats were compared. Below results of this comparison is given graphically in Figure 4.10. In this graph orange columns represent the heats with rice husk (RH) usage, and the blue ones represent the heats with rice husk ash (RHA) usage. As the insulating material is used in all heats of a sequence casting series, unlike tundish covering powder, rice husk ash was also tested in at least second and if possible third heats of a sequence. The heat series are grouped together and the

first column of every group represents the first heat and subsequent ones represent subsequent heats. Also information about state of shroud (number of times used) is also given as there may be pick up of hydrogen from the shroud in its first use. It can be seen from this graph that the hydrogen contents of first heats cast with RHA are lower than the hydrogen contents of heats cast with RH. Average of the hydrogen levels in the first heats cast by use of RH for three heats given in Figure 4.10 (3.6 ppm, 3.9 ppm and 2.6 ppm) is about 3.4 ppm while that of the heats cast by use of RHA is (2.6 ppm, 3.2 ppm and 2.3 ppm) is 2.7 ppm. Use of RHA instead of RH did not have an effect on the heats other than the first. This may be due to presence of layers of liquid tundish covering powder and insulating powder formed during the previous heat, on which the new one is added. So there would be less contact of the heat with insulating powder than the contact of previous heat.
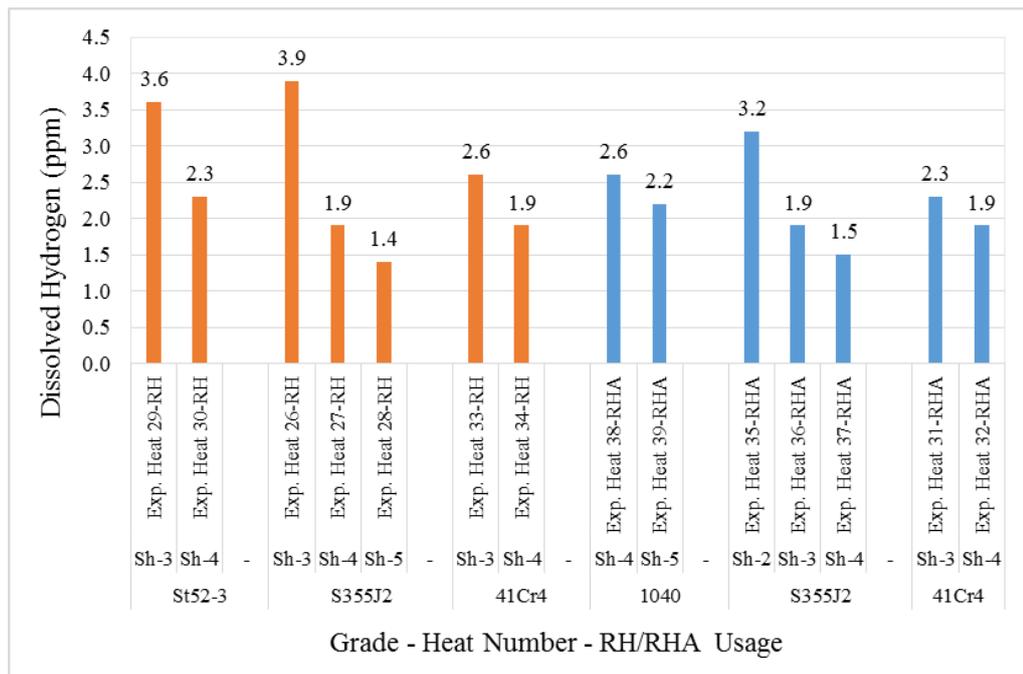
Figure 4. 10 Effect of insulating material (RH/RHA) on hydrogen contents of steel in tundish

The hydrogen levels in tundish also depend on hydrogen levels in the ladle. Comparison of difference between hydrogen levels in the ladle (EL) and in the tundish (TN1) is the measure of hydrogen pick-up. With this understanding, (TN1-EL values) are examined for a number of heats in Figure 4.11. Information about shroud is also given. The average of hydrogen pick up for heats cast by use of RH (1.5 ppm, 1.8 ppm and 1.8 ppm) is about 1.7 ppm while that for heats cast by use of RHA (1.6 ppm, 1.1 ppm, 1.4 ppm, 1.6 ppm and 1.5 ppm) is 1.4 ppm. These result indicate that steel picks up hydrogen from the insulating powder but difference in hydrogen pick-up values by use of RH or RHA is slight. The hydrogen pick-up values of heats cast by use RH or RHA are about the same in heats other than the first heats of a sequence casting.
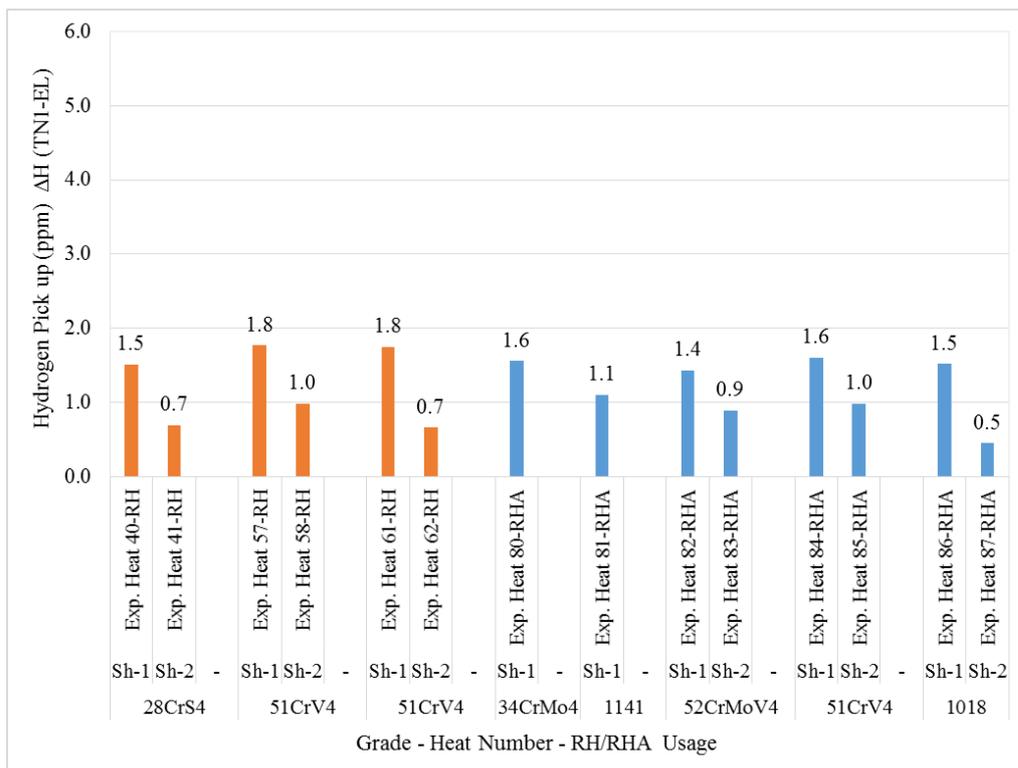
Figure 4. 11 Effect of insulating material (RH/RHA) on hydrogen pick-up values of steel in tundish

On the basis of these findings, it was concluded that, insulating powder is a source of hydrogen and rice husk ash usage instead of rice husk has a slight effect on decreasing hydrogen pick up amounts of first heats and it was decided to use RHA instead of RH. But during this project, rice husk was used in the trial heats.

4.3.2 Effect of Shroud

As indicated before, every phase that steel comes in contact with may be a source of hydrogen. Air is one of the most important phases from which steel may pick up hydrogen (and also oxygen). To avoid contact of steel with air during continuous casting, steel is transferred to the tundish from the ladle by use of refractory tubes called shroud which is mainly composed of Al_2O_3, SiO_2 and C. The shroud may be a source of hydrogen as there may be H_2O and volatile hydrocarbons present in it.

In order to understand whether there is an effect of shroud, H_2O and volatiles in it should be removed and the change in the hydrogen pick-up should be compared. One of the ways of removal of H_2O and volatiles is preheating the shroud or the other one is using the shroud for more than one heat, similar to using tundish in more than one heat. The latter is already being applied during usual practice, so comparison of hydrogen pick-up contents of heats with used and unused shrouds was made.

Hydrogen concentrations in the tundish (TN_1) and in the ladle (EL) were measured for 39 sequence-cast heats. Averages of hydrogen pick-up (TN_1-EL) values of the first heats and subsequent heats by 1st, 2nd, 3rd and 4th use of shrouds are presented graphically in Figure 4.12. Average H pick-up values in the first heats of sequence casting shown by orange columns are seen to be 1.67 ppm, 1.40 ppm, 1.15 ppm and 1.13 ppm in the first, second, third and fourth use of shroud respectively. Average hydrogen pick-up values in the second and later heats of sequence casting, shown by blue columns, are also given in Figure 4.12. Average hydrogen pick-up values in these heats are seen to be 0.94 ppm, 0.73 ppm, 0.59 ppm and 0.57 ppm in the first, second, third and fourth use of the shroud, respectively. It can be seen that, for both

first and subsequent heats the highest hydrogen pick up amounts belong to heats for which shroud is used for the first time. This may be taken as an indication of shroud being a hydrogen source. Supporting this, the hydrogen pick up amounts decrease with increase in shroud usage.
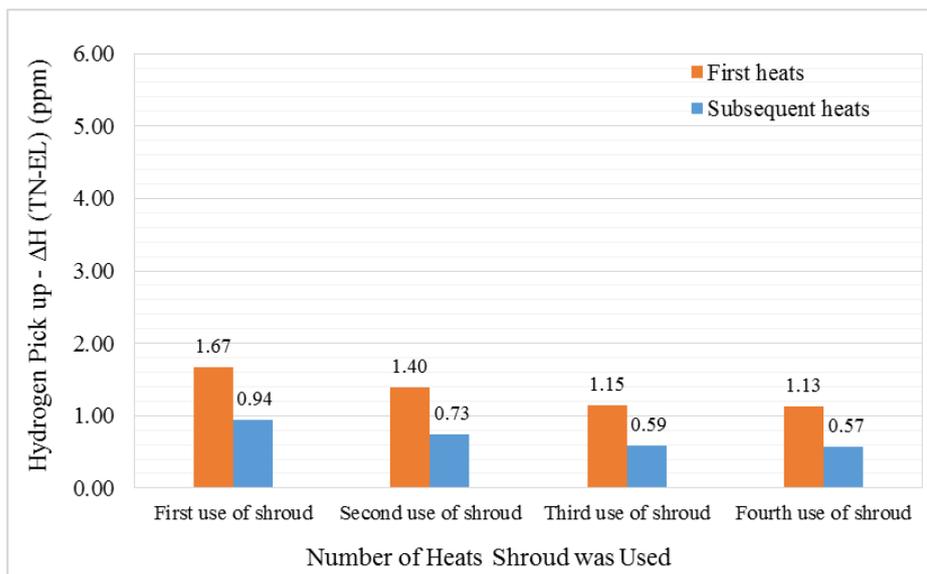
Figure 4. 12 Effect of shroud usage on hydrogen pick up of steel for first and subsequent heats

Heating of the shroud before its first use may be beneficial in decreasing hydrogen pick-up but this was not possible in present study due to absence of a facility for heating of the shroud.

4.3.3 Effect of Tundish Lining

Another phase that liquid steel comes in contact with and from which it can pick up hydrogen is the tundish lining. Tundish that will be used for casting is firstly prepared. First of all, a thin lining of tundish lining material is applied to surface of tundish. Then the walls and base are covered with alumina refractory bricks and dried. Afterwards, the tundish nozzles are mounted. Finally, the tundish is lined with

tundish lining material composed of MgO (> %70), SiO_2, CaO and Al_2O_3 which was mixed with water beforehand. The prepared tundish is first slowly heated to approximately 1000 °C then with the stopper mechanism attached to approximately 1200 °C at which temperature it is kept for 120 to 150 minutes. H_2O or volatile materials in the tundish lining and the stopper mechanism is expected to be removed to a large extent during this heating but any hydrogen containing species remaining may be a source of hydrogen. With this understanding heating durations of tundish are prolonged and hydrogen contents of liquid steel in the tundish in its first use were measured and hydrogen pick-up in the tundish (TN1 – EL) values were determined for normally and prolonged heated tundish. Figure 4.13 shows hydrogen pick-up in the tundish with use of new (unused shrouds). Heat numbers and duration of heating of the tundish are shown on the x-axis. The hydrogen values indicate that prolonged heating of the tundish did not have an effect on hydrogen pick-up. In fact the average of the hydrogen pick-up values with prolonged heating, 1.99 ppm is higher than that with usual heating program, 1.72 ppm, which is not reasonable.
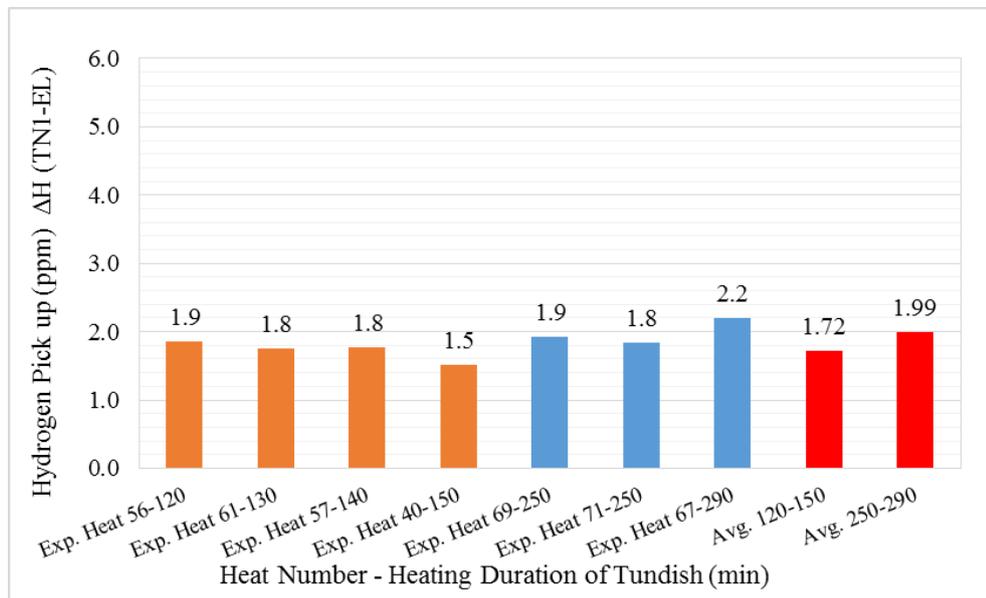
Figure 4. 13 Hydrogen pick-up amounts of heats cast with normally and extendedly heated tundish (First heats - unused shrouds)

Hydrogen pick up values in the tundish with use of used shrouds are shown in Figure 4.14. Again there is not a significant difference between heats cast with tundish prepared with normal heating program and those cast with tundish prepared with prolonged heating.
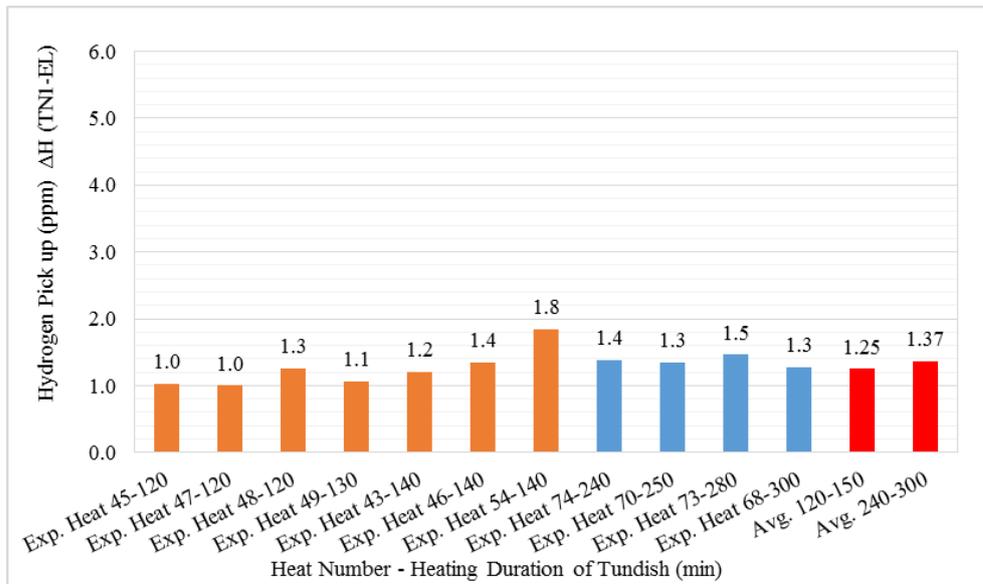
Figure 4. 14 Hydrogen pick-up amounts of heats cast with normally and extendedly heated tundish (First heats - used shrouds)

Based on these results prolonged heating was decided not to affect the hydrogen pick up. Also, drying durations of tundish were prolonged and the hydrogen measurements were conducted from heats cast with these tundish. The results are similar to the results of the trials of extending heating durations. From these results two possible deductions can be made. The first one is heating and drying for two hours is sufficient and the second is that four hours may still not be enough. Extending the durations beyond 4 hours was not possible as that would affect productivity of the plant.

As a consequence, it was seen that in tundish hydrogen pick-up amounts can be decreased down to 0.67 ppm which is the average hydrogen pick-up value for sequence heats cast with used shrouds. In this case average hydrogen content of steel in tundish at the beginning of casting is 2 ppm. For the first heats cast with using unused shrouds and rice husk as insulating powder the average hydrogen pick up is 1.67 ppm and the average hydrogen content at the beginning of casting is 3 ppm. The hydrogen contents of first heats can be decreased further by using used or heated shrouds and rice husk ash.

4.4 Hydrogen Pick-up during Ladle Treatment

It was indicated and graphically shown in Figure 4.5 that steel picks up hydrogen during treatment in the ladle furnace following the vacuum treatment. Additional data were collected to find the extent of hydrogen pick up in the ladle furnace. These data are presented for 41 heats graphically in Figure 4.15 where hydrogen pick-up values in the ladle, differences between hydrogen levels at the end of the ladle treatment (EL) and at the end of the vacuum treatment (EV) are plotted versus duration of ladle treatment. The data show measured hydrogen levels for the heats which were treated between 21 to 76 minutes. The average hydrogen pick-up of these heats are 0.45 ppm and the trend of hydrogen pick up shows nearly a linear relationship with the process time. Within ÇEMTAŞ Steel Plant, the average ladle treatment duration for heats taken during 2013 and 2014 is 30 minutes. The previous studies and experience show that the pick-up levels at the continuous casting process dominate when the two processes are considered together. This could be simply reasoned to the average ladle treatment time mentioned above, which is relatively short for hydrogen pick-up. Nevertheless, studies concerning the ladle treatment are directed to determine the source of hydrogen and to reduce the pick-up levels.
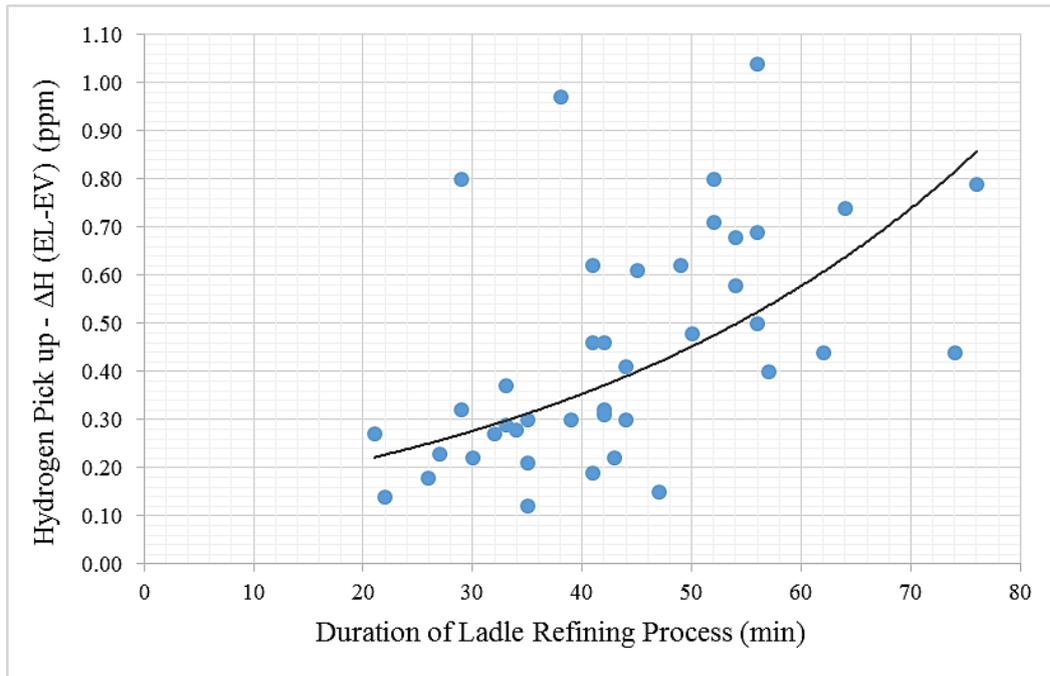
Figure 4. 15 Hydrogen pick up vs. duration of ladle refining process

Ladle treatment after vacuum degassing is the step of steelmaking process where final adjustments are carried out before casting. These adjustments involve; compositional adjustments by wire injection, heating by electrodes for casting and gentle stirring with gas (argon or nitrogen depending on the desired composition of steel) for homogenization of steel and elimination of the inclusions that have not floated to slag yet. Each of these processes within ladle treatment could be named as possible sources of hydrogen pick-up. Within the scope of this thesis each of the consumables and phases that steel comes into contact with were examined.

First of all, the effects of wire injection process were investigated. Wire injection is known as an efficient way of making additions to steel melt. The elements or alloys that would be added are either in powder form which are encapsulated in a steel wire or in metallic form. In steel production process of ÇEMTAŞ, different kinds of injections could be given to steel with different purposes. These are briefly listed below;

- C, S, MnN, B, Ti etc. for compositional adjustments like microalloying and resulfurization, depending on the customers' demands
- Al for grain size control,
- CaSi for inclusion shape control for castability and manipulating the behavior of the sulfur inclusions during hot rolling.

Generally, after vacuum wire injection becomes necessary but in certain cases depending on the chemical analysis of liquid steel, wire injection would not be required for any of the purposes listed above or only CaSi wire is added at the end of the ladle treatment. The most frequently used wires are Al, C and CaSi wires.

Moisture held on these cored or metallic wires are thus thought as a possible source of hydrogen in steel. In order to find out the extent of hydrogen pick-up due to wire feeding, measurements were performed before and after each injection. The measurements were taken for the most frequently used wires mentioned above and individual effects of these were examined. The results are presented graphically in Figures 4.16 (a) to (c) as the difference in the amount of hydrogen before and after the injection. It can be concluded that, even for the wire feeding amounts up to 40 meters in length, the hydrogen pick-up behavior stays at a level that could be neglected.
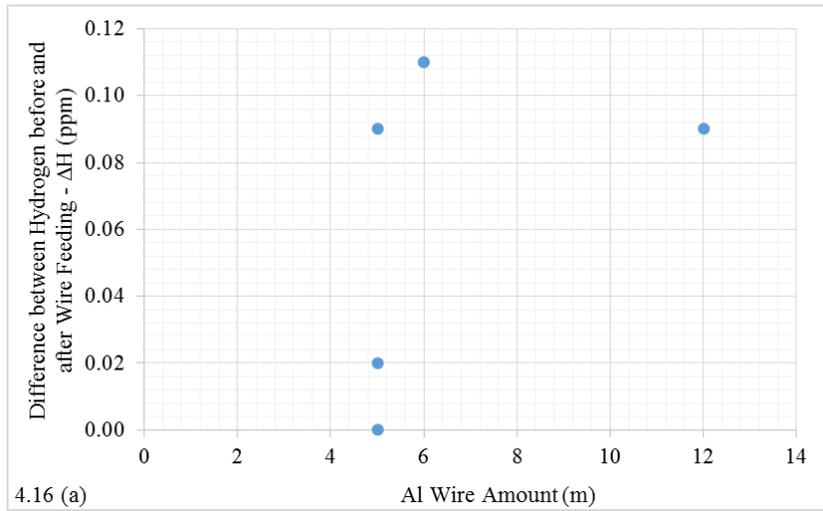
4.16 (a)
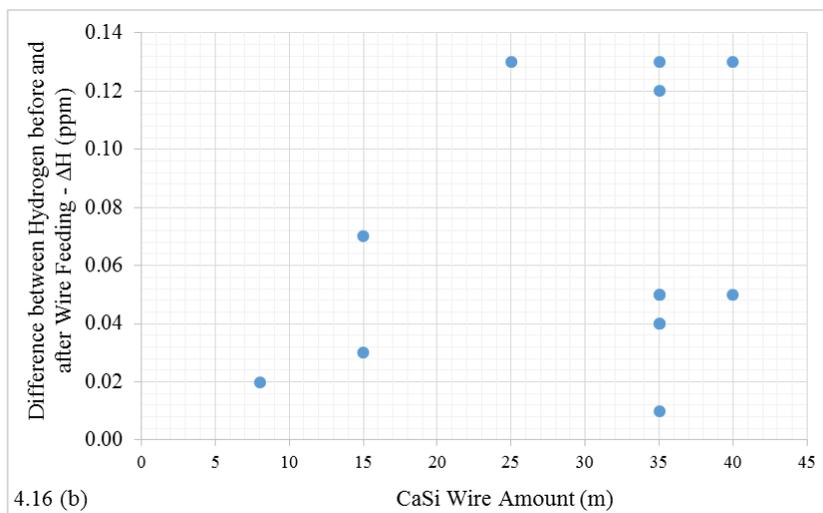
4.16 (b)
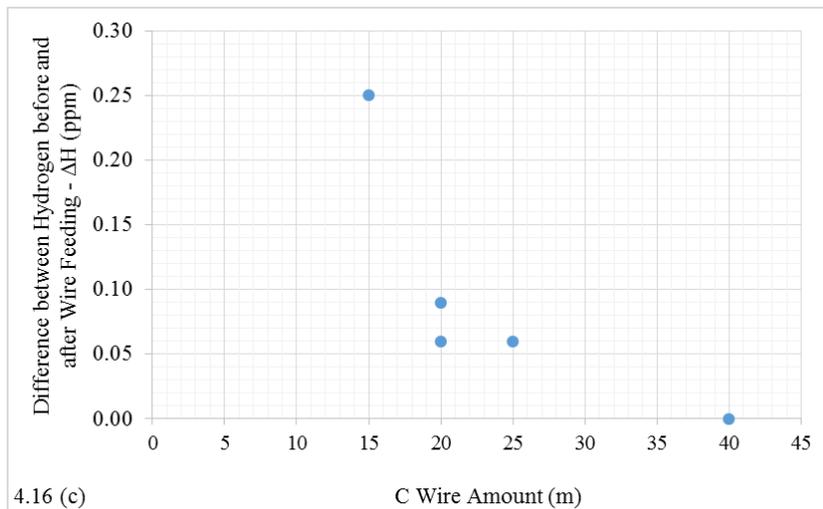
4.16 (c)

Figure 4. 16 Effect of **(a)** Al **(b)** CaSi **(c)** C wire injections to hydrogen pick up amount

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In addition to the investigation of the most frequently used wires, the other types of wires such as S, MnN were tested. However in this case, instead of their individual contribution, the change of hydrogen content was tracked as a function of the total amount of wire injected. The results are presented in Figure 4.17. These results include the previous results obtained for the most frequently used wires as well. It can be understood that, the hydrogen pick-up levels due to wire injection are in the vicinity of 0.15 ppm.
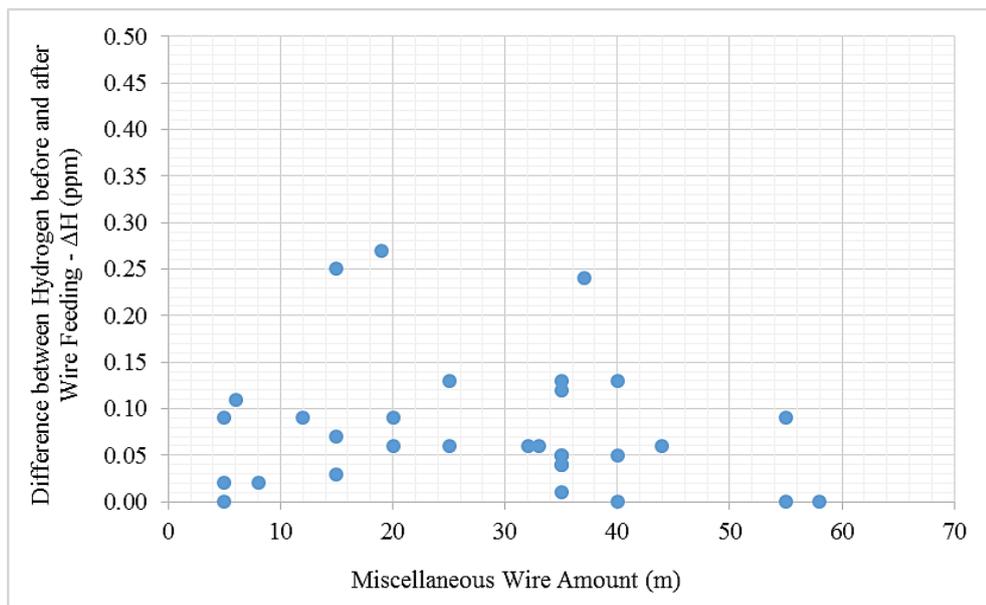
Figure 4. 17 Effect of various wire additions to hydrogen pick up amount

Between the measurements before and after wire injection approximately 10 minutes have passed. In order to reveal whether this pick-up is due to wires or not, hydrogen measurements were done at the beginning and end of ten-minute periods of ladle treatment without injecting wires to steel. It was found that there is still average hydrogen pick-up of 0.15 ppm. Based on these, it can be concluded that the wire injection during ladle treatment does not have a practical significance from the hydrogen pick-up point of view. In addition, to verify the hydrogen pick-up of the

heats which does not require wire injection (or requiring just CaSi wire injection at the end of the process); measurements were taken just after the vacuum treatment, just before the CaSi injection (if exists) and/or just at the end of the ladle treatment. The comparison of these values also revealed an increase in the amount of hydrogen with ladle treatment duration even if there is not additional wire injection. In Figure 4.18, the hydrogen pick-up amounts of different heats with respect to the duration of ladle treatment are given. This indicates the heats that were subject to only heating and gentle gas stirring with a slag phase on the top were prone to hydrogen contamination as well. This is thought to have a relation with the time spent at the ladle treatment, since the longer the process takes the longer steel remains in contact with these phases.
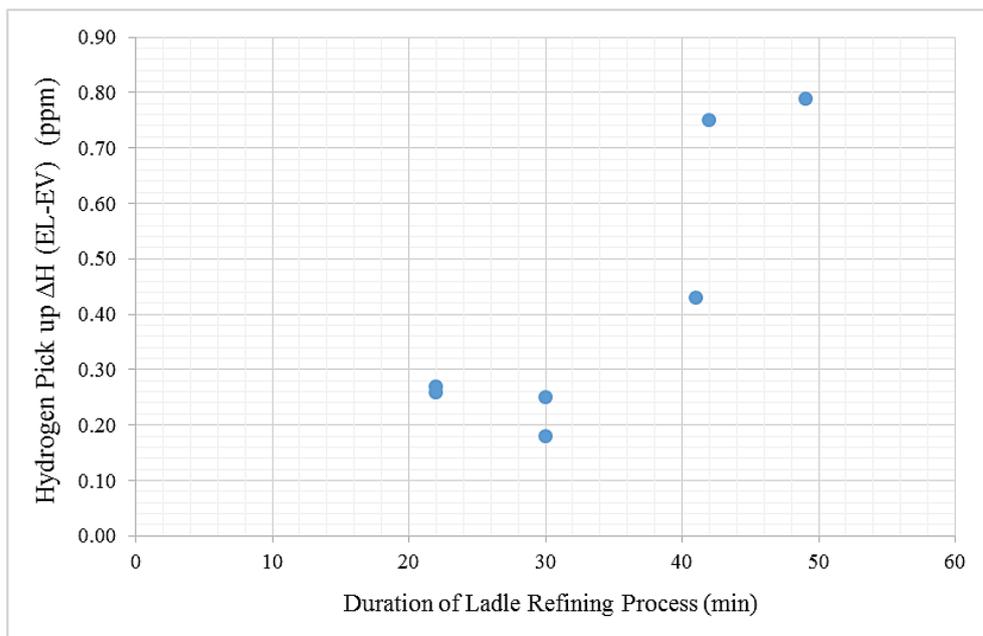
Figure 4. 18 Hydrogen pick-up of heats without wire injection as a function of ladle refining process duration

As stated before, during ladle treatment steel comes into contact with different phases other than wires which can also act as a hydrogen source. Among these, the contact

with slag and stirrer gas remains during the entire ladle treatment process. The contact with air occurs intermittently owing to the absence of slag on top of the steel. The direct contact can occur when slag cannot cover the surface if it cannot form a continuous phase. This can be due to the stirring process that can create spout eyes in the slag. As a matter of fact, slag is a source of hydrogen due to its ability to contain hydrogen in the form of hydroxyl ions which can pass to steel according to Equation 14 given in Chapter 2. In this case the main source of hydrogen is water vapor in the air. In order to understand the relationship between the moisture content of the surrounding atmosphere and hydrogen content of the steel at the end of the ladle treatment, the track of the humidity level was recorded throughout the processes. In Figure 4.19, hydrogen pick-up amounts with respect to the partial pressure of water vapor in air are shown.
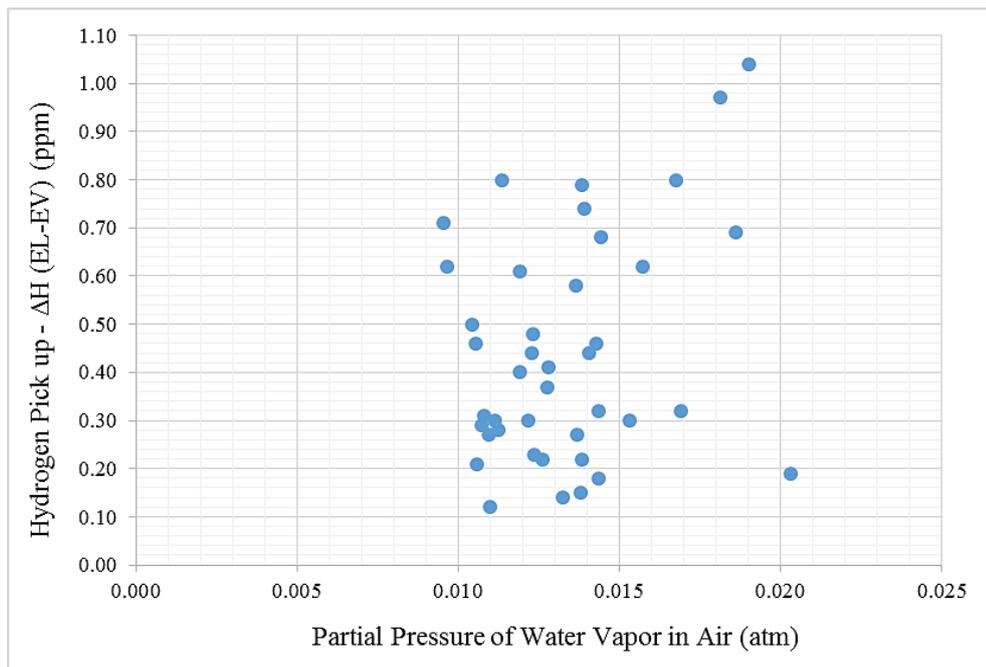
Figure 4. 19 Change in hydrogen pick-up amount in ladle furnace with partial pressure of water vapor in air

It can be stated that, the hydrogen pick-up amount tends to increase with increase in partial pressure of water vapor in air. However it is not possible to determine the reason strictly since both the extent of hydrogen pick up through slag and hydrogen pick up due to direct contact would increase with increasing partial pressure of water. Moreover direct contact interface between the surrounding atmosphere and the liquid steel continuously changes due to the causing mechanisms explained above which hinders detection of the exact duration of direct contact. Thus, studies directed to determining effect of slag on hydrogen increase had been conducted primarily.

The composition of slag has a great effect on hydrogen pick-up behavior of the liquid steel due to its ability to contain hydroxyl ions. Compositional effects were investigated to understand the correlation with the pick-up behavior. To this end, hydrogen measurements were conducted for 12 heats and slag samples were analyzed by XRF technique. The analysis results are given below in Table 4.7. Here the amounts of oxides that forms the slag are given in weight percent. The outstanding fact about the composition of the slag is the high amounts of CaO present in them. Therefore the hydroxyl capacities of the slag are expected to be high (the exact values are not known) which would make the slag a source of hydrogen for steel. On the other hand the composition of slag is also important for eliminating inclusions and desulfurization of the steel and refractory life. This slag composition was determined according to experience and studies that were conducted before. Thus, the composition was not changed even though it was not suitable for preventing hydrogen pick up of steel. Instead covering the surface of slag with another oxide was tried. First of all, insulating powder RHA was used as covering agent but it did not have a considerable effect on neither the characteristics of the slag nor the hydrogen pick-up amounts of steel. Secondly MgO was tried as covering agent which also did not have an positive effect on hydrogen pick-up amounts. On the contrary, in some of the MgO trials, slag did not form a continuous phase on the liquid steel and the hydrogen pick-up amounts of these heats were higher than expected depending on the treatment duration which was on average 0.96 ppm in 49 minutes of ladle treatment.

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Table 4. 7 Composition of ladle slag of different heats

Heat No	Grade	Steel Standard	SiO$_2$ (%)	Al$_2$O$_3$ (%)	CaO (%)	MgO (%)
Exp. Heat 66	51CrV4	EN 10089	20	13	61	5
Exp. Heat 68	51CrV4	EN 10089	16	15	61	6
Exp. Heat 69	55Cr3	EN 10089	12	17	66	4
Exp. Heat 70	5160H	SAE J 1268	11	16	68	3
Exp. Heat 71	51CrV4	EN 10089	13	16	65	4
Exp. Heat 72	51CrV4	EN 10089	15	15	67	4
Exp. Heat 73	55Cr3	EN 10089	14	16	65	4
Exp. Heat 74	51CrV4	EN 10089	14	15	67	3
Exp. Heat 75	S355J2	EN 10025	12	17	61	5
Exp. Heat 76	34CrNiMo6	EN 10083	12	19	60	5
Exp. Heat 78	42CrMoS4	EN 10083	15	18	59	5
Exp. Heat 79	51CrV4	EN 10089	14	18	61	4
AVERAGE			14	16	63	4

During ladle treatment bottom stirring with argon or nitrogen gas is applied. This is essential for eliminating the inclusions and homogenization of composition and temperature of the steel. Gas stirring is also a way of removing hydrogen but it also is another possible reason of the increase of hydrogen content during ladle treatment since the gas that is used can hold moisture and creates spout eyes as it leaves the steel. In ÇEMTAŞ steel plant, the flow rate of gas is on average 30 Nl/min and it is nearly constant for every heat. Thus, more gas would be used for longer ladle treatments. On that account hydrogen pick-up amounts of heats with the total gas amount that is used during the ladle treatment are compared in Figure 4.20. This comparison have revealed that even if there is not a direct relationship, hydrogen pick-up amount slightly increases with increasing gas amount.
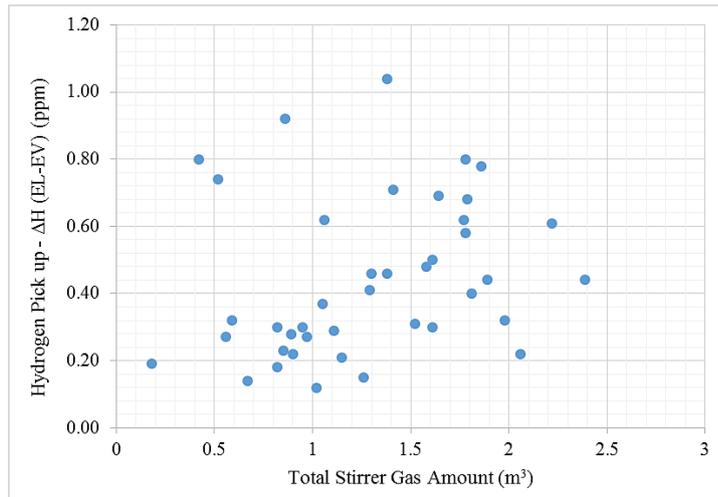
Figure 4. 20 Hydrogen pick-up of steel in ladle furnace as a function of gas amount used for stirring

In addition it was found that there is a relation between hydrogen pick-up amount and the temperature increase during ladle treatment as shown in Figure 4.21. This was concluded to be related with ladle treatment duration as the temperature increase during the treatment is directly proportional to duration of heating which is longer for longer ladle treatments.
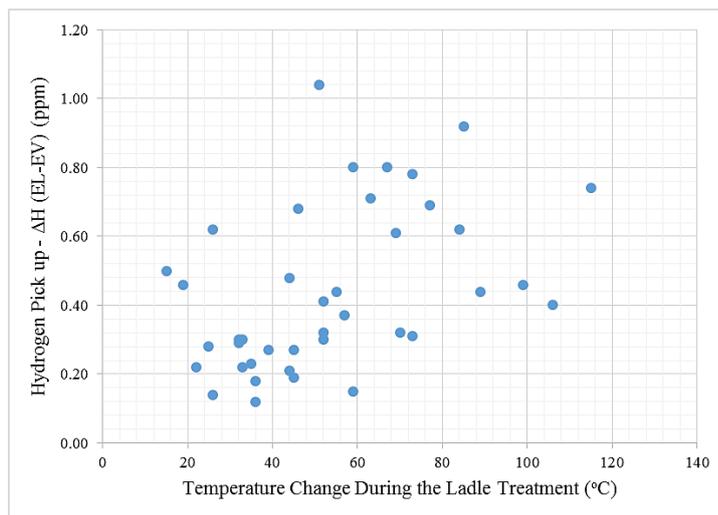
Figure 4. 21 Hydrogen pick-up vs. temperature change during ladle treatment

According to these findings, it can be stated that, the separate contribution amounts of sources of hydrogen during ladle treatment cannot be determined exactly since the effect of one cannot be eliminated during investigation of the effect of other one; for example argon stirring cannot be stopped during treatment or slag cannot be removed. Moreover, it was found that hydrogen pick up amount is higher in the heats with lower hydrogen contents at the end of the vacuum as shown in the Figure 4.22 below. Since the lower hydrogen contents are more desired at the end of the vacuum, it is very important to be cautious about preventing hydrogen pick-up during ladle treatment.
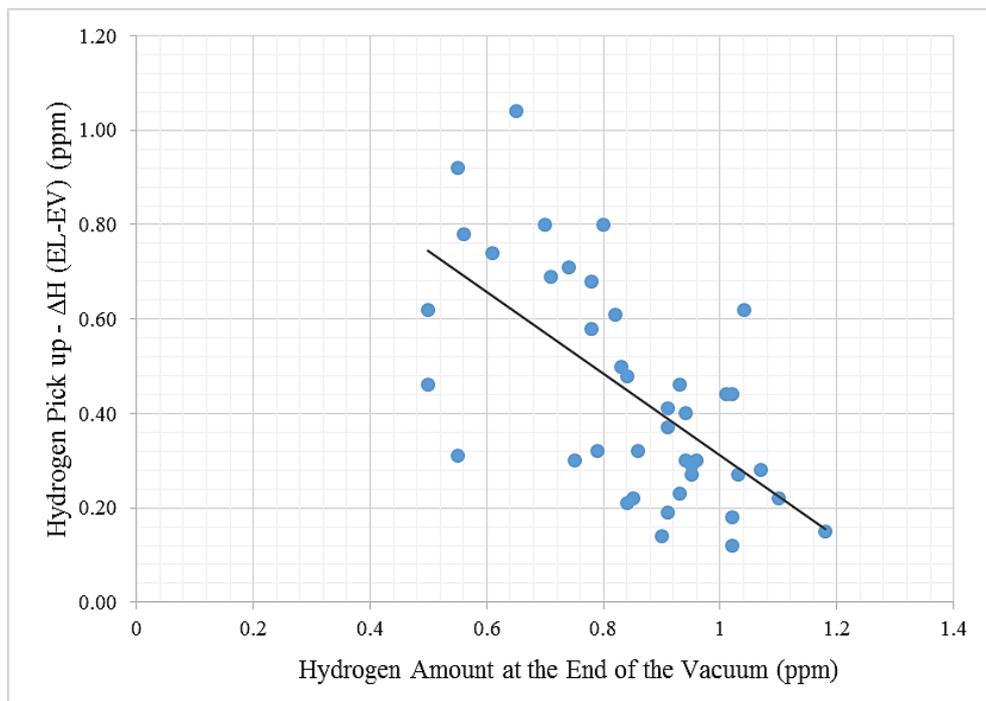
Figure 4. 22 Hydrogen pick-up vs hydrogen amount at the end of vacuum degassing

It can be concluded that, in order to decrease hydrogen pick-up amount in ladle, after vacuum steel should not be kept for a long time in ladle furnace, slag should cover the surface of steel and steel and the argon stirring should be kept very gentle in order not to form spout eyes in slags surface.

4.5 Other Applications in ÇEMTAŞ to Decrease Production Losses Due To Hydrogen

The operation of the ladle furnace is very efficient in ÇEMTAŞ and sulfur levels are normally below 0.005 % which is much lower than the maximum specified in the standards. The products of ÇEMTAŞ are mostly used in the manufacture of automobile parts and are therefore subject to machining. Some customers want the sulfur contents of the products to be higher than what ordinarily is supplied by ÇEMTAŞ. Under these conditions sulfur is added to liquid steel after vacuum treatment to bring sulfur to the maximum specified by the standards. So several steel grades are produced with or without sulfur addition depending on customer demands. Analysis of amounts of internal defects in products produced with sulfur addition and those produced without sulfur addition revealed that sulfur addition resulted in decrease of amount of production loss amounts due to internal defects as can be seen from Figures 4.23 (a) and (b) where indexed amounts of production losses due to internal defects and sulfur contents of 20MnCr(S)5 and C45E steel grades are shown for several heats. The beneficial effect of sulfur in decreasing the amount of internal defects was concluded to be related with hydrogen. Sulfur forms sulfide inclusions as stated in Section 2. Hydrogen diffuses to these inclusions and forms H_2 gas in voids present in the inclusions. As volume of void in which H_2 is formed cannot increase, pressure of hydrogen gas (P_{H_2}) increases with increase in the amount hydrogen that forms hydrogen gas. When P_{H_2} reaches a certain value, it gives rise to formation of cracks. Quantity of hydrogen that forms H_2 in one inclusion and hence P_{H_2} increases with decrease in the number of sulfide inclusions. Accordingly, possibility of crack formation due to hydrogen increases with decrease in number of sulfide inclusions. Since the number of sulfide inclusions increase with increase in sulfur content, the possibility of crack formation due to hydrogen would decrease with increase in Sulfur content. That very low sulfur levels increase the possibility of crack formation due to hydrogen was mentioned by Fruehan. The results of the present study are in accord with what is stated above and that mentioned by Fruehan [13].
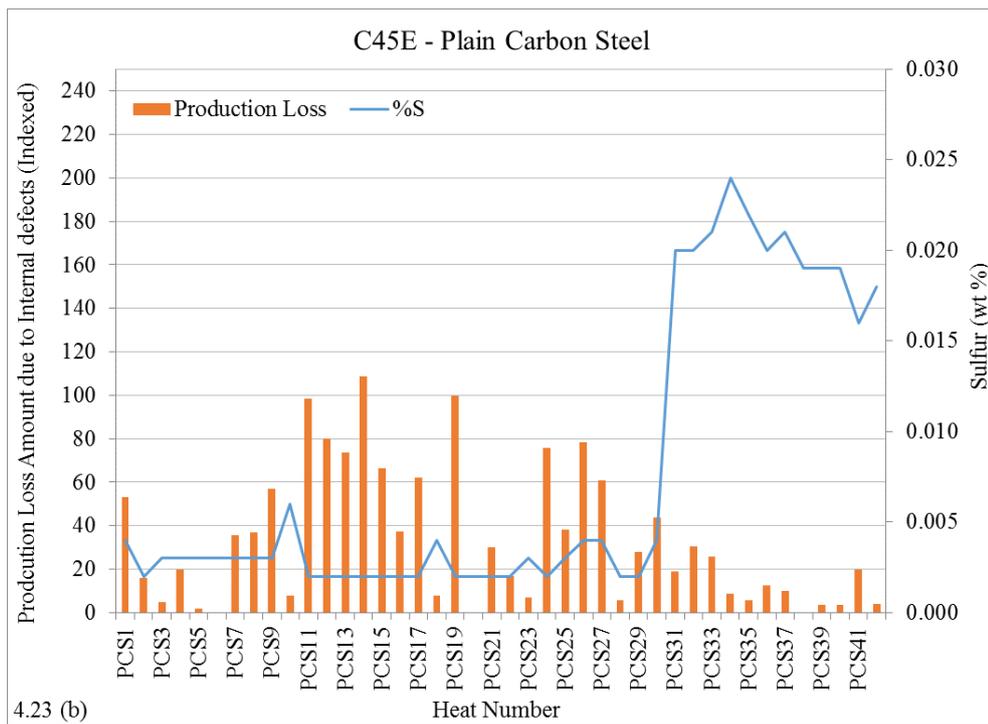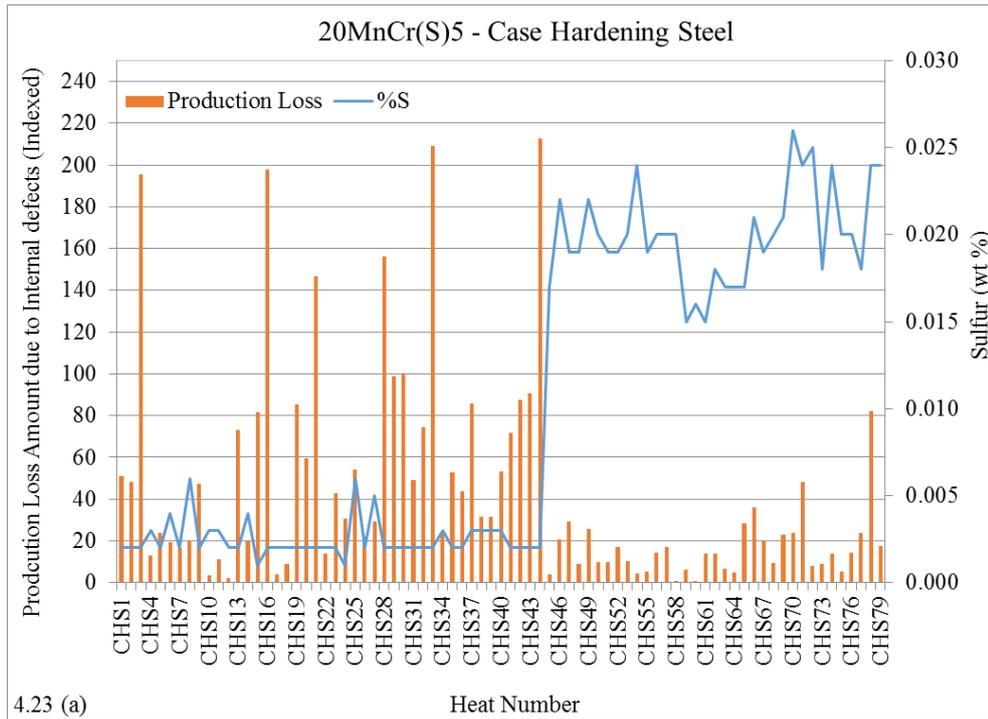
Figure 4. 23 Production loss amounts of different grades of steels with different sulfur contents **(a)** 20MnCr(S)5 **(b)** C45E

After being certain about the effect of sulfur, this application was widened to all possible steel grades that are nondestructively tested, amount limited by the relevant steel standards and the result was consistent for all of the trials.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Hydrogen Control at ÇEMTAŞ steel plant was the second part of the study that was started with the aim of determining the origin of internal defects and eliminating them by improving steelmaking process in order to increase the amount of defect-free products. In the first part; "Inclusion Control at ÇEMTAŞ Steel Plant", by the measures taken, non-metallic inclusions in steel which were the outstanding source of defects were eliminated to a large extent. As a result, the defect amount was decreased. However, defected parts were continued to be detected by NDTs on which macroscopic examinations were conducted. As a result, it was concluded that hydrogen found in molten steel is one of the causes of the defects formed in the final products. Accordingly, the current study was started with the aim of decreasing hydrogen contents of liquid steel and defect formation in the final products.

At the beginning of the study, present hydrogen levels before and after vacuum were determined. It was found that $7.5 - 8.5$ ppm of hydrogen is present in steel before vacuum and it can be decreased to about 1 ppm by $12 - 15$ minutes of vacuum degassing. However hydrogen content increase up to $4 - 5$ ppm during subsequent operations. In order to determine sources of hydrogen and to prevent hydrogen pick-up, hydrogen measurements from the molten steel were carried out during steelmaking process following vacuum degassing. Consequently, the change in hydrogen contents, possible sources and precautions that can be taken to decrease hydrogen pick-up during steelmaking were determined as listed below:

- After vacuum degassing, there was hydrogen pick-up during both ladle treatment and continuous casting and it was more severe during continuous casting.

- Hydrogen levels were higher at the beginning of the casting due to the first contact with phases that contain hydrogen and decrease during casting. Correspondingly, hydrogen contents of sequence cast heats were lower than those of first heats of a sequence. Thus, more heats should be cast by sequence casting.

- Two types of tundish covering powder were tried and with the powder that can form a liquid phase hydrogen contents of the first heats were decreased by 1.35 ppm on average. This decrease can be attributed to both the powder itself and the effective prevention of air contact.

- Using rice husk ash as an insulating powder instead of rice husk slightly decreased the hydrogen contents of the first heats and did not affect the sequence heats.

- Shroud, the tube that steel flows through during transfer from ladle to tundish was determined to be a source of hydrogen. The hydrogen pick-up amounts of heats were highest for which the unused shrouds were used and it decreases with increase in the number of heats shroud was used.

- Heating and drying durations of the tundish were extended but neither of those trials made a difference in hydrogen pick up amounts. The reason for these is that either the present practice was sufficient for removing hydrogen present in tundish lining or it could not be removed by prolonged heating or drying.

- During the ladle treatment steel picks up hydrogen up to 1 ppm. The pick-up level increases with increase in duration of ladle treatment. Therefore duration of ladle treatment should be kept at minimum. The average ladle treatment duration of ÇEMTAŞ during 2013 and 2014 was 30 minutes which is admissible.

- Hydrogen pick-up in the ladle was found to increase with decrease in hydrogen content after vacuum.

- Wire injection did not have a significant effect on hydrogen pick-up amounts of steel.

- The hydrogen pick-up amount in ladle tend to increase with the increase in water vapor pressure in the air. This can be due to ability of slag to dissolve water vapor or air contact than can occur when slag could not cover the surface of steel.

- Composition of slag was high in CaO, which would make water capacity of slag to be high. However, the composition could not be arranged considering only hydrogen. Thus, covering the surface with rice husk ash and MgO were tried but these did not have an effect on hydrogen pick-up amounts. Visual observations showed that the hydrogen content increases more than expected when the whole surface of the steel was not covered with slag.

- Hydrogen pick-up amount increases with increase in the volume of gas used for stirring and increase in temperature increase during ladle treatment.

For this particular study, the following conclusions can be drawn; the main reasons of hydrogen pick-up for steel after vacuum degassing were determined as contact with casting powders, shroud, tundish lining and long ladle treatment. By taking precautions hydrogen content of the first heats at the beginning of casting hydrogen were decreased to 3 ppm on average. In the case of sequence casts average hydrogen content of steel in tundish at the beginning of casting is 2 ppm. In addition. sulfur addition application was widened to all possible steel grades that are nondestructively tested, amount limited by the relevant steel standards which resulted in decrease of amount of production losses due to internal defects.

To sum up, in order to prevent hydrogen pick-up after the vacuum process, the ladle treatment duration should be kept at minimum and during the treatment the surface of steel should be covered with slag. During continuous casting, the tundish covering

powder should cover the surface of steel in tundish and shrouds should be heated before use. In addition rice husk ash should be preferred to the rice husk as insulating powder. Together with these, sulfur addition application should proceed in order to prevent defect formation due to hydrogen.

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