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CHANGES IN HYDROGEN CONTENT DURING STEELMAKING

ZMIANY ZAWARTOŚCI WODORU W KĄPIELI METALOWEJ PODCZAS PROCESU STALOWNICZEGO

Štore Steel produces steel grades for spring, forging and engineering industry applications. Steelmaking technology consists of scrap melting in Electric Arc Furnace (EAF), secondary metallurgy in Ladle Furnace (LF) and continuous casting of billets (CC). Hydrogen content during steelmaking of various steel grades and steelmaking technologies was measured. Samples of steel melt from EAF, LF and CC were collected and investigated. Sampling from Electric Arc Furnace and Ladle Furnace was carried out using vacuum pin tubes. Regular measurements of hydrogen content in steel melt were made using Hydris device. Hydrogen content results measured in tundish by Hydris device were compared with results from pin tube samples. Based on the measurement results it was established that hydrogen content during steelmaking increases. The highest values were determined in tundish during casting. Factors that influence the hydrogen content in liquid steel the most were steelmaking technology and alloying elements.

Keywords: hydrogen content, pin tubes, tundish, deoxidation

Stalownia Štore Steel produkuje gatunki stali sprężynowych, stali do kucia oraz stali do innych zastosowań przemysłowych. Linia technologiczna obejmuje elektryczny piec łukowy (EAF), rafinację pozapiecową w piecu kadziowym (LF) oraz maszynę do ciągłego odlewania kęsów (COS). Badaniom poddana została zmienność zawartości wodoru w stali w zależności od gatunku stali i wybranej linii technologicznej. Zgromadzono bazę danych w postaci próbek pobieranych z pieca łukowego, pieca kadziowego oraz maszyny COS. Próbki z pieca łukowego oraz pieca kadziowego pobierano za pomocą rurek próżniowych. Przeprowadzano regularnie pomiary zawartości wodoru w stali za pomocą urządzenia Hydris. Mierzoną zawartość wodoru w kadzi pośredniej za pomocą urządzenia Hydris porównywano z zawartością wodoru w próbkach pobranych za pomocą rurek próżniowych. Bazując na opisanych pomiarach stwierdzono wzrost zawartości wodoru w stali w czasie realizowanego procesu stalowniczego. Najwyższe zawartości stwierdzono w kadzi pośredniej urządzenia COS. Czynnikami mającymi największy wpływ na zawartość wodoru w ciekłej stali była zastosowana technologia wytapiania oraz pierwiastki stopowe.

1. Introduction

The hydrogen atom is the smallest and simplest of all the elements. It comes in into the steel melt from moisture in atmosphere, deoxidation and alloying elements, slag additives or refractory materials. Hydrogen diffusion is due to the small atom size ten to fifty times faster compared to diffusion of other gases.

Hydrogen is a harmful element in steel. Even a very small amount, a few ppm of hydrogen in steel melt, has later in solidified steel a negative effect. It decreases mechanical properties and causes defects such as hydrogen embrittlement, pinholes, blowholes, fish eyes, blistering and others [1-3].

Solubility of hydrogen in steel is described by Sieverts' law [4]:

$$\frac{1}{2}H2(g) = [H] \qquad (1)$$

$$K = \frac{[ppmH]}{(pH2)^{1/2}} \qquad (2)$$

K – equilibrium constant
p_{H2} – partial pressure oh hydrogen
ppmH – hydrogen content in ppm

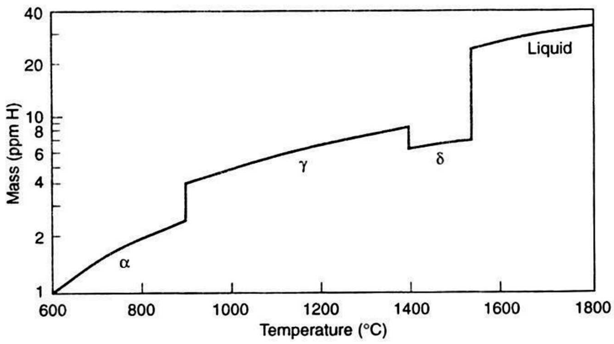

Fig. 1. Hydrogen solubility in pure iron at 1 atm pressure of H2 [4]

Figure 1 shows that hydrogen solubility increases with temperature and is the highest in liquid steel. As a result of

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lower solubility in solid steel, during solidification and cooling diatomic hydrogen is formed. It causes pressure in the cubic lattice which can lead to defects or material failure [5].

To prevent damage from too high hydrogen content various methods for hydrogen sampling and determination were developed and used already in the past. Some of the sampling tubes and molds are presented in Figure 2.

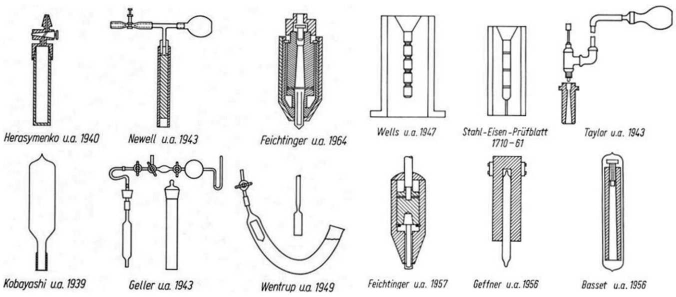

Fig. 2. Different types of molds and tubes for fast cooling of liquid steel samples [8]

Nowadays two methods of hydrogen determination are used, a conventional method, where hydrogen is analyzed from a solid steel sample, cooled in liquid nitrogen and a direct method where hydrogen is determined directly from the steel melt [6,7]. Today mostly direct method is used, where the result of a measurement is known in minutes.

Sampling and measuring of hydrogen in steel with conventional method is demanding because of high diffusion coefficient of hydrogen. For determination of hydrogen from solid samples usually vacuum pin tubes are in use and double sampling is performed in case of a sample porosity.

Measurements of various parameters in the industry can be used as valuable data for verification of numerical models which are used for the better understanding of the steelmaking process [9,10].

2. Experimental work

Steelmaking process in Štore Steel consists of scrap melting in EAF, alloying and secondary refining in LF and continuous casting of billets on a three strand casting machine. Due to a large variety of steel grades with very different chemical composition and application different steelmaking technologies are used in Štore Steel: KL, ACF, EXEM, SM and SMCF. In KL technology aluminium is used for deoxidation, ACF is aluminium and calcium free technology, EXEM is for free machining steels and in SM technology slag with lower basicity is used.

Direct and indirect (conventional) method were used for hydrogen determination. In tundish hydrogen was measured during casting using Hydris device and vacuum pin tubes, while hydrogen in the steel melt from EAF and LF was measured with application of pin tubes and analysed with LECO RH-402 analyser.

In order to study changes in hydrogen content during steelmaking technological process sampling with pin tubes was done at different stages: in EAF before tapping, in various stages of LF treatment and in tundish during casting. Solid samples were stored in liquid nitrogen to prevent diffusion. Because sampling with vacuum pin tubes in Štore Steel was not regularly used in production practice, this method first of all had to be introduced with series of measurements. First results of measurements on different steel grades showed that steel from EAF has to be killed with aluminium before sampling. This measure decreases the possibility of forming porosity.

3. Results and discussion

HYDROGEN DETERMINATION FROM SOLID STEEL SAMPLES

Results from the first series of measurements were not comparable because of big fluctuation. Table 1 shows measuring events where hydrogen was measured with vacuum pin tubes. Figure 3 presents changes in hydrogen content during processing of three heats of the same steel grade (51CrV4). The chemical composition of steel 51CrV4 is written in Table 2.

These three heats were produced with KL technology and cast in sequence. Due to low temperature and porosity of some samples content of hydrogen in EAF and in LF after heating could not be measured. Results of measurements show that hydrogen content in steel increases during steelmaking and reaches the highest value during casting. Comparison of samples, taken at the same time indicates good repeatability of results.

TABLE 1

Measuring events for hydrogen determination [11]

MEASURING POINT	SAMPLE MARK
EAF before tapping	EAF
LF after heating	LF-1
LF after CaSi wire addition	LF-2
LF at the end of treatment	LF-3
CC after 30 minutes of casting	CC

TABLE 2

Chemical composition of 51CrV4 steel grade [12]

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	Nb	V	Sn	As	Pb
Min. [%]	0.49	0.20	0.90			0.90						0.10			
Max. [%]	0.54	0.40	1.10	0.015	0.015	1.20	0.06	0.20	0.011	0.25	0.06	0.20	0.02	0.04	0.02

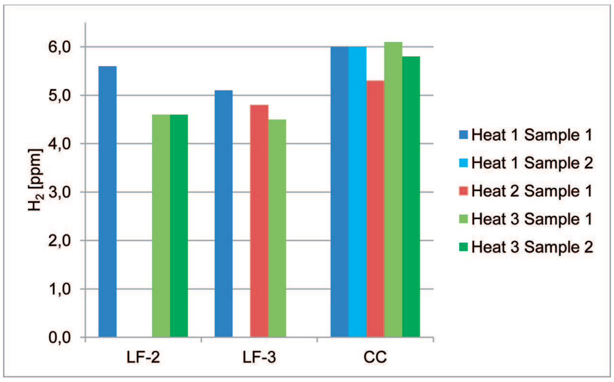

Fig. 3. Hydrogen content in 51CrV4 steel grade during steelmaking

HYDRIS MEASUREMENTS

From December to the end of August intensive measuring of hydrogen content during casting was carried out with Hydris device. In this period more than 1500 measurements were obtained (Figure 4).

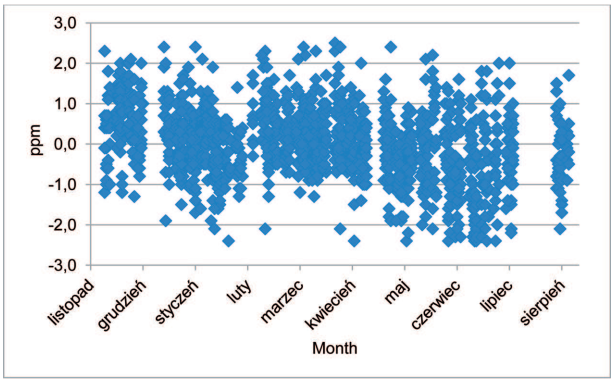

Fig. 4. Deviations from average hydrogen content in tundish after 30 minutes of casting

The influence of steelmaking technology on hydrogen content in tundish is presented in Figure 5. In KL technology heats where steel is aluminium killed, contents of hydrogen in tundish are higher compared to the ACF technology heats where silicon is used for deoxidation (Table 3).

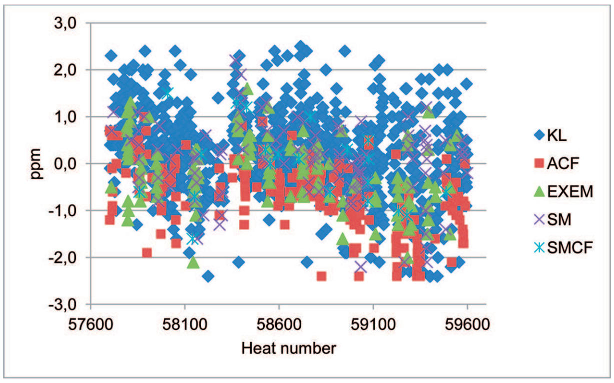

Fig. 5. Deviations from average hydrogen content in tundish after 30 minutes of casting for different steelmaking technologies

Deviations from average hydrogen contents in steel melt during casting for eight most frequently produced steel grades in Štore Steel are presented in Table 4. Highest average value has C45 KL steel grade and the lowest 70MnVS4 ACF steel grade.

TABLE 3

Deviations from average hydrogen content in tundish after 30 minutes of casting for different steelmaking technologies (1514 heats)

Steelmaking technology	Number of measurements	Deviation from average [ppm]
KL	1019	+0.2
ACF	217	-0.7
EXEM	134	-0.2
SM	123	0.0
SMCF	21	0.0

TABLE 4

Deviations from average hydrogen content in tundish after 30 minutes of casting for eight most frequently produced steel grades

Steel grade	KL technology	ACF technology	EXEM technology	SM technology
51CrV4	+0, 1	-0,6		
52CrMoV4	+0, 1			
30MnVS6	+0, 1			
38MnVS6	0			
70MnVS4		**-1,1**		
C45	**+0,6**	-0,5	-0,7	0
C70S6		-0,7		
16MnCrS5	+0, 1		0	+0, 1

Misra, Motlagh at.al. studied the influence of humidity on hydrogen content in steel and detected higher hydrogen values during humid summer months[13]. This trend was not confirmed in Štore Steel (Figure 6).

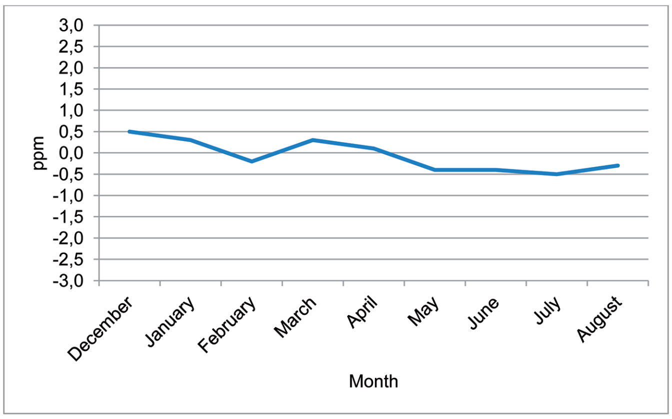

Fig. 6. Average deviation from average hydrogen content for nine months

COMPARISON OF MEASUREMENT METHODS

In Figure 7 comparison of measurements done with Hydris device and vacuum pin tubes is shown. All the measurements were taken in tundish after 30 minutes of casting.

Measured hydrogen content established with vacuum pin tubes was in average for 0,7 ppm lower then average obtained with direct method.

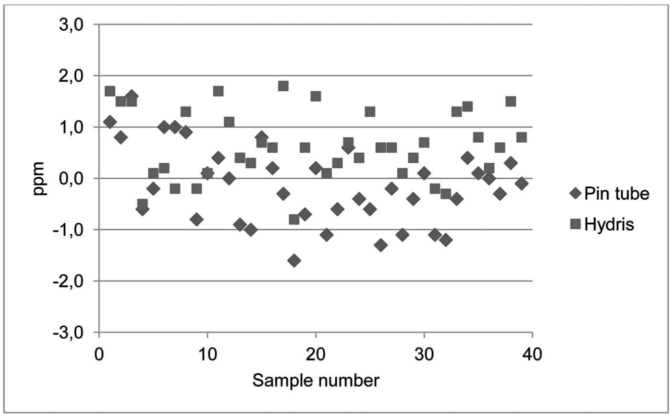

Fig. 7. Deviations from average hydrogen content in tundish after 30 minutes of casting for 51CrV4 steel grade

OUR EXPERIENCES WITH CHANGES IN HYDROGEN CONTENT IN OTHER STEEL PLANT

Measurements of hydrogen content during steelmaking were performed also in other steel plant with different steelmaking technology [14-16]. The technology in this steel plant is more common for modern steelmaking. It contains usage of electric arc furnace (EAF) for melting of steel scrap and ladle furnace/vacuum degassing (LF/VD) as refining aggregate.

Most of the measurements were made with Hydris measuring device after vacuum degasing. Total number of records in data base was about 35,000 written in 2,500 data vectors [17].

For analysis of such a big amount of data it is very important to use reliable and flexible numerical tool. Because of our experiences with even bigger data bases we decided to use MLP neuronal networks [17-20]. This method enable us to select most influential parameters at the beginning of the analysis and latter to find rules which can describe how they effect hydrogen content in steel melt.

The results of this analysis have confirmed that a absolute humidity of air is most influential factor despite the fact that steel melt was vacuum treated for 40 minutes. Because the most influential parameter is also very season dependent the same pattern in hydrogen content change was observed as was described in literature [1].

4. Conclusions

- Multiple series of measurements with pin tubes showed that sampling from EAF melt without aluminium-killing was not possible.
- Hydrogen content increases during whole steelmaking process and reaches the highest value during casting in tundish.
- Lower hydrogen content in steel was determined in case of use of ACF steelmaking technology in comparison to KL steelmaking technology. This rule was verified during casting with both measuring methods, Hydris and pin tubes. Lower hydrogen content of ACF heats was influenced by type of deoxidizer and by slag additives. The highest hydrogen average has C45 steel grade, produced by KL technology and the lowest average has 70MnVS4 steel grade produced by ACF technology.
- Influence of higher values of air humidity during summer months on hydrogen content in steel melt were not detected although in this period intensive measuring of hydrogen in tundish with Hydris device was made.
- Hydris measurements are faster and more accurate than conventional method, but can be used in Štore Steel only during casting. They are also more expensive. Although results obtained with pin tubes are in average slightly lower they are comparable with Hydris and can be used in every day practice.
- Sampling with pin tubes is after successful implementation of the method now regularly used in Štore Steel steelmaking practice.

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