Visual Abstract

Metallurgical hydrogen as an indicator and cause of damage of rolled steel

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ABSTRACT. Fatigue tests and measurements of the volumetric distribution of metallurgical hydrogen in specimens cut from rolled I-beam 60Sh3 made of steel 10KhSND were carried out. Fatigue tests show a 20% reduction in fatigue limits compared to similar sheet material. On the fractures of the samples, there are flock-like defects in the areas of interface of the flanges of the I-beam or in the so-called zones of difficult deformation. The concentration of metallurgical hydrogen is unevenly distributed and varies from 0.17 ppm to 1.8 ppm. Large concentrations of hydrogen are observed in the zones of difficult deformation, which indicates the hydrogen nature of the metal defects observed at the fracture. The result of mechanical tests and hydrogen diagnostics is a manufacturing defect of rolled products that cannot be corrected. Hydrogen diagnostics using metallurgical hydrogen (without hydrogen charging samples) requires essentially less time than mechanical tests and yields the adequate result.

KEYWORDS. I-beam, Fatigue, Hydrogen diagnostics, Metallurgical hydrogen.

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INTRODUCTION

The strong influence of hydrogen on the mechanical properties of structural metals has been studied for about 150 years. As a rule, all studies of this effect on metals include preliminary saturation or "charging" of samples with hydrogen in a hydrogen-containing environment. Such saturation is standardized [1-3]. Tests for hydrogen

induced cracking or resistance to hydrogen cracking are also standard [4]. The study of the effect of natural, so-called "metallurgical" hydrogen, has long passed into the field of industrial testing [6] and is currently being studied only in the weld metal [7, 8]. In other cases, for each type of alloy there are maximum allowable concentrations of hydrogen which are controlled, most often, directly in the molten metal at the production stage. We do not have information about modern scientific research on "metallurgical" hydrogen and its effect on the mechanical properties of metals. As a rule, the hydrogen concentration changes significantly at various processing stages: crystallization of ingots, rolling, forging. This is the general practice of a single control for each type of products. For example, during the production of steel products it is controlled only in the melt, during the production of aluminum it is controlled only in the ingot.

It is also difficult to find studies on the effect of hydrogen on the deformation and destruction of structural metals in a conventional "non-aggressive" environment. At the same time, over the years that have passed since the discovery of the hydrogen problem, the influence of hydrogen dissolved in metals on its mechanical properties has greatly increased. Modern structural alloys begin to “feel” this effect starting from hydrogen concentrations of 0.1 ppm [9].

It is generally accepted that hydrogen is located inside the metal in traps of various nature [10]. In this case, each type of trap corresponds to a certain binding energy of hydrogen [11]. The most popular procedure for measuring the degree of occupancy of traps with hydrogen and their binding energies is based on the method of thermal desorption spectra (TDS) [12], which is lengthy and is almost never applied to “metallurgical hydrogen”, since it is too small to measure the spectrum [13]. These difficulties lead to the fact that all hydrogen accumulated in the metal is usually divided into two classes: diffusible hydrogen and bound hydrogen. Together they form the total hydrogen concentration.

There is no single approach in the methods of dividing hydrogen into diffusible and bound ones. The standard [5] defines diffusible hydrogen with the help of the method of its extraction. “The primary method for the measurement of diffusible hydrogen in ferritic arc weld metal is based upon collection and measurement, over mercury, of the hydrogen evolved from a standard-sized weld sample. The evolution takes place at room temperature and consequently the collection time is typically about 14 d.” In other sources, it is considered to be hydrogen with a binding energy or diffusion activation energy of less than 0.3 - 0.4 eV cf.[14]. It is postulated in [15] that the diffusible H content is determined by hot extraction at 300°C.

In our work [16], we showed that using the model of multichannel diffusion of hydrogen in a solid it is possible to determine the distribution of its concentration over binding energy levels based on the results of standard measurements by the hot vacuum extraction method. The AV-1 industrial mass-spectrometric analyzer of hydrogen makes it possible to obtain the dependence of hydrogen flows from metal samples on time. This relationship is referred to as the extraction curve. The volume of hydrogen is proportional to the integral of the flow (of the extraction curve). We have shown that the uniform distribution of hydrogen inside the sample is associated with a certain energy level of the hydrogen bond in each peak., see [16].

Thus, metallurgical hydrogen has several diagnostic features at once:

- total concentration,
- population of various energy levels or distribution of concentration by binding energy levels,
- the form of the distribution of the total, diffusible and bound hydrogen concentration inside the metal.

The relationship of these features with the mechanical state of structures will allow the development and practical application of hydrogen diagnostics of structural metals.

MATERIALS AND EXPERIMENTAL EQUIPMENT

Mechanical fatigue tests and studies of the distribution of hydrogen in the material of the rolled I-beam No. 60Sh3 from steel 10KhSND were carried out. The chemical composition of steel is given in Tab. 1.

C	Si	Mn	Ni	S	P	Cr	N	Cu	As	Fe
0.12	0.8-1.1	0.5-0.8	0.5-0.8	< 0.04	< 0.035	0.6-0.9	< 0.008	0.4-0.6	< 0.04	96

Table 1: Chemical composition (in%) of steel 10KhSND.

For mechanical testing, 12 standard corset samples were cut from the lower and upper flanges of the I-beam with the length, width and thickness of the working part 420x75x40 mm³. The main dimensions of the samples are shown in Fig.1.

The thickness of the lower and upper flanges of the beam is 24 mm; therefore, a part of the vertical flange about 15 mm high was preserved on the samples.

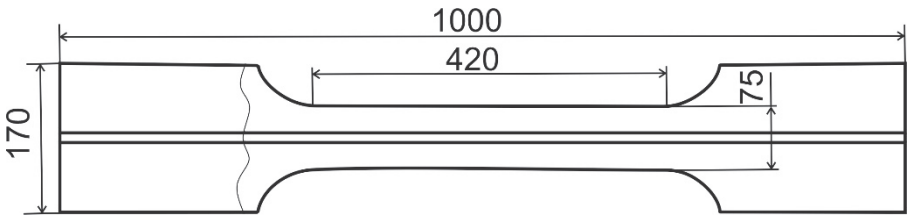

Figure 1: Corset test sample cut from the I-beam flange.

Fatigue tests were carried out on a CDM-200 PU pulsator press (see Fig. 2.) at a frequency of 324 cycles per minute based on 2 million load cycles. The cycle characteristic for all the samples is as follows

$$\rho = \frac{\sigma_{min}}{\sigma_{max}} = 0.1$$

Here σ_{min}, σ_{max} are the minimal and maximal tension stresses. The stresses in the samples during the tests were determined by the tensometric sensors and the test load.

Figure 2: Tests of a corset specimen cut from the I-beam flange

For comparison, the similar corset samples were made and tested from rolled sheet steel 10KhSND with a thickness of 30 mm.

To measure the distribution of hydrogen concentration in the metal of the I-beam, an industrial mass-spectrometric hydrogen analyzer AV-1 was used. It is designed to measure the hydrogen concentration in metals and alloys in the factory laboratory during the final control of castings from various alloys [16-18].

For measurements, prismatic samples were cut out with dimensions of 6x6x25 mm^3 or 6x6x40 mm^3 (depending on the thickness of the metal). The cutting of samples for measuring the distribution of hydrogen concentration was carried out with a hand saw so that their temperature did not rise higher than 50 – 60°C.

One set of samples was cut from the corset sample (I-beam) which collapsed during testing at the clamping point (the fracture line is shown schematically in Fig. 1). The scheme of sample cutting is shown in Fig. 3. Samples in which the hydrogen measurements were carried out are marked on the diagram with the symbol "X".

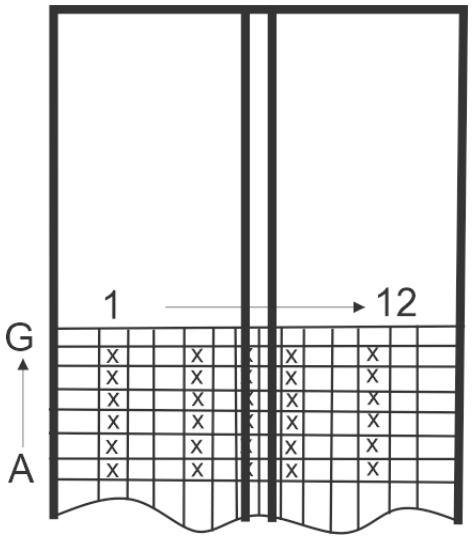

Figure 3: Scheme of cutting samples for the analysis of hydrogen content.

We also studied the distribution of hydrogen concentrations over the cross section of the I-beam "as is" without preloading. The scheme of sampling (cutting samples) is shown in Fig. 4.

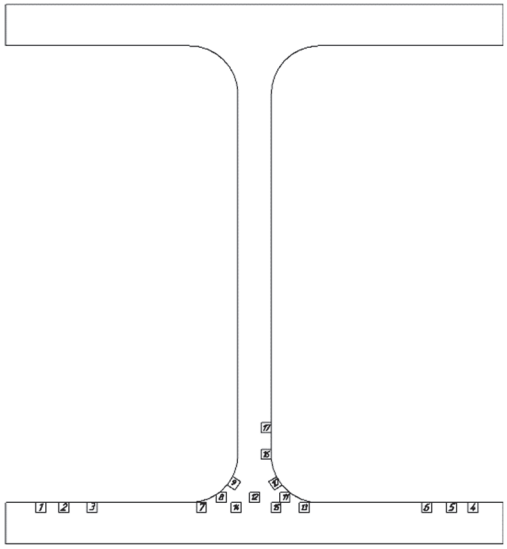

Figure 4: Scheme of sampling (cutting samples) from the I-beam

EXPERIMENTAL RESULTS

The dependences of the maximum applied mechanical stress on the number of the test cycles for specimens cut from the I-beam and specimens cut from a sheet are shown in Fig. 5.

An analysis of the fracture surfaces of samples made from 60Sh3 beams indicates the presence of defects in all tested samples (see Fig. 6.). No defect was observed in the samples cut from a 30 mm sheet.

Fig. 7 shows the distribution of hydrogen concentrations over the area of the sample destroyed at the clamping point (the sampling scheme is shown in Fig. 3). Points 1 and 11 correspond to the left and right borders of the sample, respectively.

The distribution of hydrogen over the cross section of the I-beam was measured according to the cutting scheme. (see Fig. 4.). The map of the positions of samples with color-coded hydrogen concentrations is shown in Fig. 8.

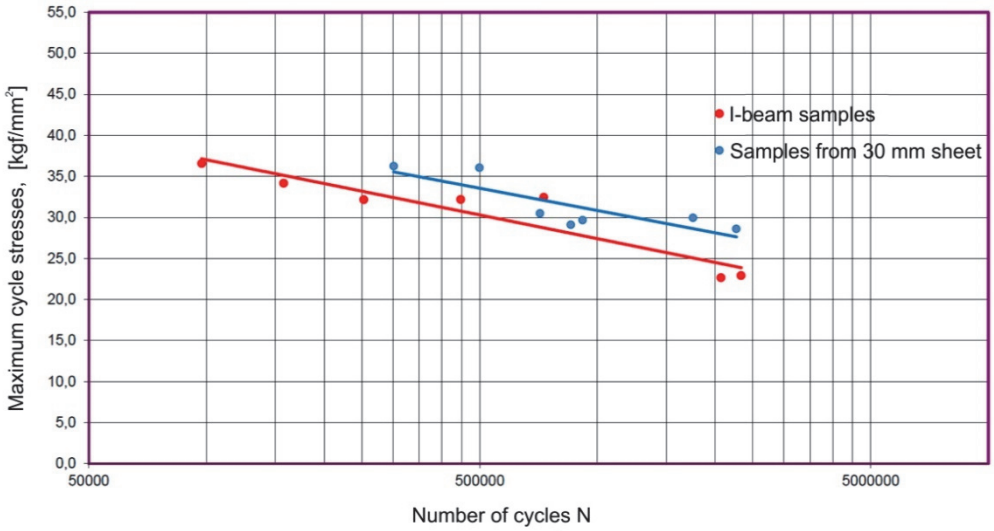

Figure 5: Test results of specimens cut from I-beam 60Sh3 flanges and from 30 mm rolled sheet.

Figure 6: Photograph of fracture of a sample cut from the I-beam.

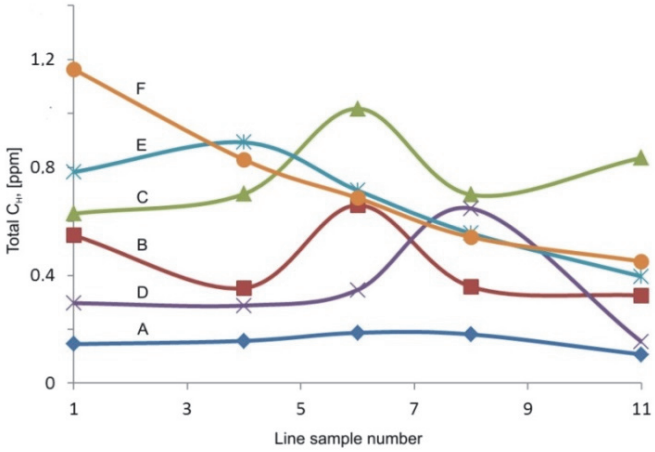

Figure 7: Distribution of total hydrogen concentrations C_H in a sample cut from the I-beam after its break, see Fig.3 for the sample's code.

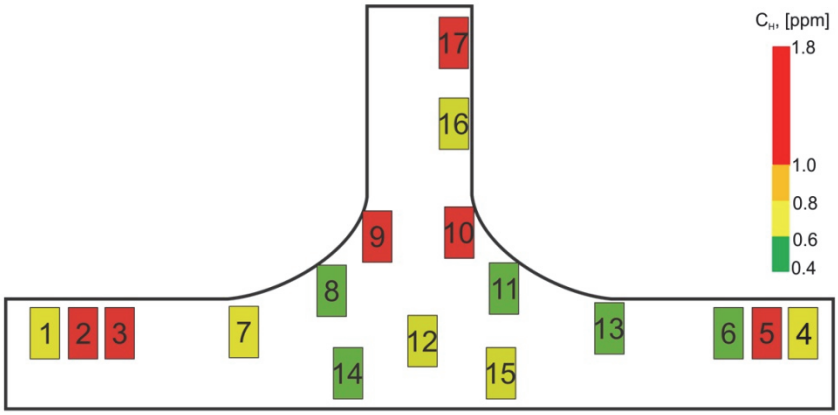

Figure 8: Distribution map of the total hydrogen concentration C_H over the cross section of the I-beam.

Discussion of results

All defects on the fractures of the samples are concentrated in the so-called zone of difficult deformation, where the metal is deformed with the lower compression forces. The causes of these defects may include:

- poor calibration of rolls of section rolling mills,
- insufficient heating of the metal before hot rolling,
- cooldown of the metal during rolling on the last passes in the finishing stands,
- violation of the regime of hot plastic deformation by rolling,
- high concentrations of hydrogen in the metal unevenly distributed in the slab.

This manufacturing defect is final and cannot be eliminated by any heat treatment, without plastic deformation.

The distribution of hydrogen both over the cross section of the I-beam and over the area of the flange is extremely uneven. It significantly exceeds the average level in zones of complex strain (see Fig. 7.8). We can unambiguously say that the cause of defects at the sample fracture is the hydrogen porosity. In the most technical requirements and specifications for structural steels, the concentration of hydrogen in rolled products is not standardized; the hydrogen control is carried out on a sample of about 15 g cut from the molten metal. Such an approach, as this study shows, does not fully characterize the quality of the rolled products because of the multiple difference in the measured values of hydrogen concentration in the cold products. The uneven distribution of hydrogen concentrations in the cold metal can be associated with the distribution of non-metallic particles that could not be removed from the molten metal due to their adhesion to small hydrogen bubbles. This phenomenon is especially important in the case of extensive metal recycling and requires additional research.

Due to the standard requirements the maximum permissible concentration of hydrogen in steels is normalized at the level of 2-4 ppm. But it is necessary to consider the specifics of sampling during the standard industrial testing. Very rarely, the measurements of hydrogen concentration are carried out in solid cold rolled products. The data of numerous studies [8,19-22] show that the hydrogen concentration 0.5 - 1.5 ppm in the cold metals is critical for the strength of modern structural steels, [8,20].

Mechanical testing is very time consuming. For example, in this study each of the 12 samples was tested from 12 to 96 hours depending on the number of load cycles. Due to the large scatter of fatigue test results, at least four samples are needed to obtain the average results.

Hydrogen diagnostics is much faster and cheaper, the time for measuring the hydrogen concentration in one sample is about an hour, and the same statistical reliability is reached ten times faster.

In this study, we used the total hydrogen concentration as the single indicator. The distribution over binding energies can provide additional information, [17]. For example, diffusive hydrogen in steels is much more dangerous for the mechanical characteristics of the metal than the bound hydrogen, and its concentrations in the zone of localization of structural defects can be tens times higher than the average values.

Conclusions

A comprehensive study of a rolled steel I-beam was carried out consisting of the fatigue tests and the hydrogen diagnostics. The distribution of hydrogen concentrations over the volume of the I-beam is measured. The dependences of the cyclic maximum mechanical stresses on the number of load cycles to the destruction of corset specimens cut from the I-beam were obtained.

We observe a good correlation between zones of the high hydrogen concentration and the places of sample fracture. High hydrogen concentrations explain both the defect nature and decrease in the fatigue limits of the metal in 60Sh3 beam compared to the sheet.

Technical testing using the hydrogen diagnostics is faster and cheaper than the traditional mechanical testing. This indicates the advantages of hydrogen diagnostics.

The data obtained from studies of industrial rolled products indicate the insufficiency of monitoring the concentration of hydrogen in samples from the molten metal.

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