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HEAT TREATMENTS INFLUENCE FOR MICROSCOPIC HYDROGEN DIFFUSION IN METALS

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Lucrarea prezintă aspecte noi privind difuzia hidrogenului la scară microscopică (corpul grăunților şi spațiul intergranular) pentru epruvete tratate termic şi anume epruvete normalizate, călite şi supraîncălzite. De asemenea, se fac comparații între cantitățile de hidrogen difuzibil la scară microscopică pentru corpul grăunților, respectiv spațiul intergranular, pentru cele trei tipuri de epruvete tratate termic. In finalul lucrării sunt prezentate concluzii referitoare la procesul de difuzie a hidrogenului la scară microscopică corespunzător tratamentelor termice aplicate epruvetei din S235JR (SREN 10027-1).

This research presents some of the very new aspects concerning microscopic hydrogen diffusion for thermally treated samples: normalized, heated and overheated specimens. In addition, this article presents comparisons between microscopic diffusible hydrogen quantities for grain bodies and for space between grains, for the all three analyzed samples. In the final part of the paper, the authors present the conclusions regarding the hydrogen diffusion process, at a microscopic level, corresponding to heat treatments for the S235JR (SREN 10027-1) sample.

Key words: hydrogen diffusion, grain limit, heat treated sample, microscopic observation

1. Introduction

The hydrogen is easier solving in metals and diffuses by an interstitial mechanism [1]. In this mechanism, the atoms of the solve element jump from one place of the network to another, with implications on the local stage stress. If the interstitial atom does not “wait” to be taken by a network trouble (vacancy, grain limit, dislocation) for jump, the diffusion coefficient can be relatively high [2, 3, 4].

Due to the surrounding atoms, the activation energy becomes bigger and bigger while the rate of diffusion is relatively low. For all that, the atoms can diffuse along the grain limits, interfaces and free material surfaces (cracks, voids) [5, 6].

Hydrogen steel diffusion is influenced by the following factors [7]: concentration gradient, mechanic stress gradient, temperature gradient and electric

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potential gradient. Some other diffusion causes are dislocations migration process (molecular hydrogen catalytic resolution in atomic hydrogen) respectively hydrogen ions transport by dislocations over inside metal [8] and existence of hydrogen trapping (reversible and irreversible) respectively diffusion coefficient dependence between coupling energy and temperature [9].

Having as a starting point these facts, this paper proposes a microscopic hydrogen diffusion study for S235JR samples, thermally treated (normalized, hardened and overheated), using a simplified hypothesis consisting in hydrogen trapping elimination.

2. Experimental device for the electrolytic charging

The experimental device [10] for the electrolytic charging for the S235JR (SREN 10027-1) thermally heat treated homogeneous sample, is presented in Figure 1. This is composed by: a glace container; 8 graffito elements serially connected to a d.c. power supply with 2.5V voltage and 0.7A current; a S235JR (SREN 10027-1) sample connected to the graffito elements. To realize the electrolytic charging process the sample is considered as being the anode while the graffito electrodes represent the cathode of the battery. The sample is immersed in a distilled water solution. This electrolytic charging was realized in about 6 hours.

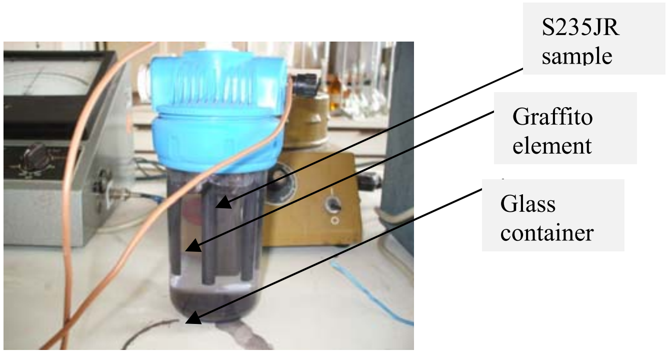

Fig. 1. Experimental device.

The next considerations will study the heat treatments influence on the microscopic hydrogen diffusion; mainly, we will be interested to highlight the mass transfer process influence on the granulation modifications after the heat treatments [11, 12, 13]

3. Microscopic observations on hydrogen diffusion for the normalized and electrolytically charged S235JR sample

The microscopic observations were made for the S235JR (SREN 10027-1) sample normalized treated. The thermal treatment consists of heating the sample up to 960 Celsius degrees, keeping the temperature constant for 30 minutes and then cooling the sample in air flow. The sample was electrolytically charged after this process.

At the end of the charging period, the sample was extracted from the electrolytic bath, dry cleaned in air flow and deeply eroded with nittal (2.3 % HNO_3). Then, the sample was microscopically analyzed with a performing microscope with immersive objective OLYMPUS BX 60 M model, with photo digital camera OLYMPUS 5050. On the sample surface one single cider oil drop was added; this oil has hydrogen capture properties and it can increase the rate of microscope visibility by 500:1. It can be mentioned that the real dimension of grain is 5 – 7 according to ISO 643.

The microscopic observations were made for 5 grains (Figure 2); for each of them the number of hydrogen bubbles, which appears on the grain surface, was counted; also, the number of hydrogen bubbles in the space between grains was found. All these in the time gap from 5 to 720 minutes. The values are presented in Table 1.

Table 1

Numbers of hydrogen bubbles on the grains surface Gi (i=1…5) and also in the space between grains, Ii (i=1…5)

Time [min]	Nr. of bubbles G1	Nr. of bubbles I1	Nr. of bubbles G2	Nr. of bubbles I2	Nr. of bubbles G3	Nr. of bubbles I3	Nr. of bubbles G4	Nr. of bubbles I4	Nr. of bubbles G5	Nr. of bubbles I5
5	15	12	10	9	18	7	11	6	27	19
15	15	14	12	10	20	7	13	9	31	22
30	19	15	14	10	23	11	15	9	32	24
60	21	17	16	12	25	13	16	12	35	27
120	25	20	17	13	26	14	16	13	35	27
360	29	21	19	16	28	16	19	15	37	29
720	32	24	23	18	33	20	22	18	38	33

For each grain, the grains surfaces and the spaces between grains surfaces have been calculated and they are presented in table 2. These values have been obtained by using the measure scale from an image by surface integral calculus.

Table 2

Grains surface Gi (i=1…5) and surface of space between grains Ii (i=1…5)

Grains	**Grain surface [μm^2]**	**Space between grains**	**Surface of space between grains [μm^2]**
G1	400	I1	13
G2	140	I2	9
G3	450	I3	13.5
G4	390	I4	12.5
G5	815	I5	38

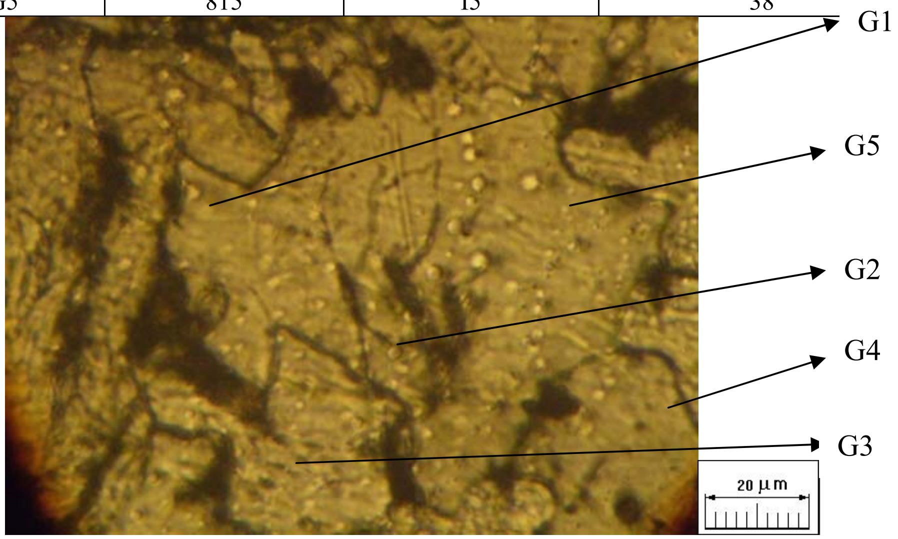

Fig. 2. The 5 analyzed grains.

The calculated hydrogen quantities in the grain body and in the space between grains, relative to the surface [cm^3/cm^2] are presented in Table 3. In table 3 was calculated the quantities of hydrogen in the body of grain and on space between grains, reported on that surfaces [cm^3/cm^2]:

Table 3

Quantities of hydrogen x 10^{-7} in the body of grain and in the space between grains, relative to the surfaces [cm^3/cm^2]

Time [min]	**Grains**					**Space between grains**				
	G1	**G2**	**G3**	**G4**	**G5**	**I1**	**I2**	**I3**	**I4**	**I5**
5	1.5675	2.985	1.6704	1.178	1.35	385.2	41.76	21.63	20.04	20.9
15	1.5675	3.582	1.856	1.3923	1.55	449.4	46.44	21.63	30.06	24.2
30	1.9855	4.175	2.1344	1.6065	1.6	481.5	46.44	33.99	30.06	26.4
60	2.1945	4.776	2.32	1.7136	1.75	545.7	55.68	40.17	40.08	29.7
120	2.6125	5.074	2.412	1.7136	1.75	642	60.372	43.26	43.42	29.7
360	3.0305	5.671	2.598	2.0345	1.85	674.1	74.24	49.44	50.1	31.9
720	3.0305	6.865	3.062	2.3562	1.9	770.4	83.592	61.8	60.12	31.9

In Table 4 we present the experimental distribution ratio **Ii/Gi** of diffusible hydrogen in the same time gap, 5 … 720 min.

Table 4

Ii/Gi ratio for $i = 1,...,5$

Time[min]	I1/G1	I2/G2	I3/G3	I4/G4	I5/G5
5	24.6153	14.0002	12.9493	17.0189	15.0917
15	89.0426	12.9629	11.6518	21.6	15.2196
30	25.9104	11.1111	15.9373	18.72	16.0843
60	24.9077	11.6666	17.3282	23.4	16.5438
120	24.6149	11.8954	17.9434	25.35	16.5438
360	22.2807	13.0994	19.0420	24.6315	16.8744
720	23.0764	12.1739	20.1960	25.5272	18.6965

Following this analysis one can say that the diffusion process on grain surfaces follows the diffusion equation, but some remarks should be made:

- in the time gap 5…100 min there is a distribution of hydrogen quantities in the grain body relative to the surface of 1.17 … 4.77 × 10^{-7} cm^3/cm^2;

- in the time gap 100…400 min one can observe a medium increment of the hydrogen quantities in the grain body of 1.7 … 5.6 × 10^{-7} cm^3/cm^2;

- between 400…720 min the increment of the hydrogen quantities in the grain body remains constant (see Table 3 and Table 4).

Concerning the diffusion process in the space between grains, the experiments revealed an accentuated migration tendency of hydrogen atoms between 5….100 min. The hydrogen quantity is of 20.04…545.7 × 10^{-7} cm^3/cm^2. Between 100…720 min the diffusion process has a similar ascendant course for the all five analysed grains, being of 43.42 … 770.4 × 10^{-6} cm^3/cm^2.

Referring to diffusion process on space between grains, we can saw a accentuate tendency of hydrogen atoms for migration, in the interval 5…100 minutes. The value of hydrogen quantity is between 20.04 … 545.7 × 10^{-7} cm^3/cm^2. In the interval 100…720 minutes, the diffusion process is, mathematically speaking, an ascendant course, similar for the five analyzed grains, the hydrogen quantity being 43.42 … 770.4 × 10^{-6} cm^3/cm^2.

From Table 4, one can observe that the hydrogen quantity relative to the space surface between grains increases comparing to the hydrogen quantity relative to the grain surface, in the time gap 150…720 min; This ratio has values of 11.81…24.83. Therefore, one can see a more important influx (quantity) of hydrogen in the area between grains and a lower diffusion process in the grain zone, for the same time interval.

In the time interval 5…150 min the hydrogen mobility doesn't follow a rule or a mathematical law and this and this can have as a result bigger fluctuations for this ratio (11.1…89.02).

In order to make a comparison between the hydrogen distribution inside the grains and in the space between grains, we will analyze the ratio of hydrogen atoms to the total surface of the analyzed grains and to the areas between grains (Figure 3).

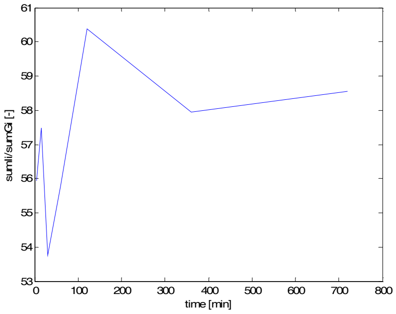

Fig.3. Rapport ∑Ii/∑Gi, i=1…5, for normalized sample.

One can see that between 20…720 min the hydrogen diffusion (quantity) is much bigger in the spaces between grains than in the grain surfaces, especially between 20…100 min. Then, the ∑Ii/∑Gi ratio has smaller values (between 100…720 min).

4. Microscopic observations about the hydrogen diffusion for the hardened and electrolytically charged S235JR sample

The microscopic observations were made for a S235JR (SREN 10027-1) sample hardened treated. The heat treatment consists of heating up to 860 Celsius degrees, keeping the temperature constant for 40 minutes and then cooling the sample in water flow. After that, the sample was electrolytically charged.

The microscopic observations were made for 3 grains (figure 4) and for each of them the number of hydrogen bubbles, which appears on the grain surface and in the space between grains, has been calculated. The time gap was 5…720 min and the results are presented in Table 5.

Table 5

Numbers of hydrogen bubbles on the grains surface Gi (i=1…3) and also in the space between grains, Ii (i=1…3)

Timp[min]						
	Nr. of bubbles G1	**Nr. of bubbles G2**	**Nr. of bubbles G3**	**Nr. of bubbles I1**	**Nr. of bubbles I2**	**Nr. of bubbles I3**
5	7	4	8	7	8	10
15	10	6	9	9	11	13
30	12	8	13	10	15	15
60	12	8	13	11	15	17
120	14	10	14	13	17	19
360	16	10	14	13	17	19
720	16	10	14	13	17	19

The surface of each grain and the surfaces between grains have been calculated; they are all presented in Table 6.

Table 6

Grain surface Gi (i=1…3) and the surface of the space between grains Ii (i=1…3)

Grain	**Surface [µm^2]**	**Space between grains[µm^2]**
G1	1750	24
G2	750	16
G3	1500	22

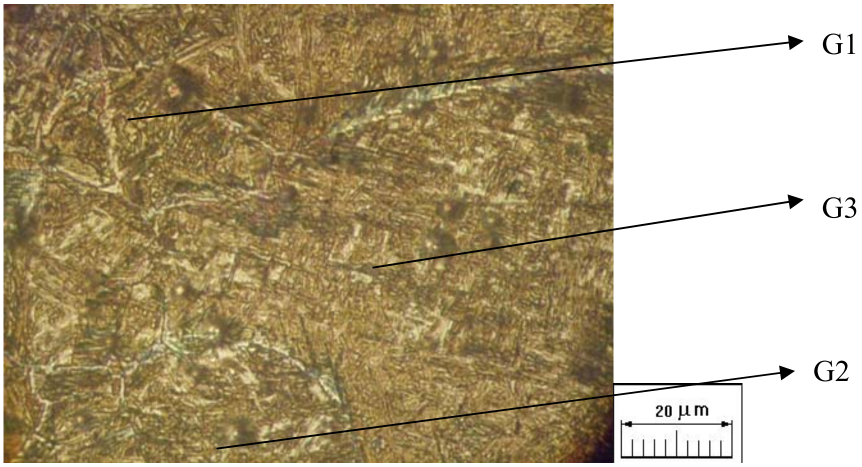

Fig. 4. The 3 analyzed grains.

The hydrogen quantities in the grain bodies and in the space between grains have been calculated and the ratio between them and the surfaces [cm^3/cm^2] is presented in Table 7.

Table 7

Quantities of hydrogen x 10^{-7} in the body of grain and on the space between grains, relative to their surfaces [cm^3/cm^2]

Time[min]	**G1**	**G2**	**G3**	**I1**	**I2**	**I3**
5	10.71	14.28	50.96	781.48	1339.68	1217.9
15	15.3	21.42	57.33	1004.76	1842.06	1583.27
30	18.36	28.56	82.81	1116.4	2511.9	1826.85
60	18.36	28.56	82.81	1228.04	2511.9	2070.43
120	21.42	35.7	89.18	1451.32	2846.82	2314.01
360	24.48	35.7	89.18	1451.32	2846.82	2314.01
720	24.48	35.7	89.18	1451.32	2846.82	2314.01

In Table 7 there are presented the diffusible hydrogen local distributions in the analyzed grain surfaces (5…720 min) and the diffusible hydrogen local distributions in the space between the analyzed grain surfaces (5…720 min).

The following remarks can be done:

- in the time gap 5…50 min the graphic has an ascendant evolution and one can observe a ratio of hydrogen quantities in the grain bodies and the surfaces of 10.71 … 82.81 × 10^{-7} cm^3/cm^2;
- in the time gap 50…100 min a stagnation of the diffusion process took place;
- in the time gap 100…200 min the diffusible hydrogen quantity was dramatically increasing to 18.5…89.18 × 10^{-7} cm^3/cm^2 (see the tables).

After 200 minutes, the diffusion process will be stoped, wich means that the geometrical configuration of the sample is composed of regular shapes and the methalographic sample structure allows a slow diffusion process in the granular level and also in the space between grains level.

Referring to diffusion process in the space between grains, one can observe an accentuate migration tendency of the hydrogen atoms, in the interval 5…120 minutes. The value of hydrogen quantity is between 781.4 … 2846.8 × 10^{-7} cm^3/cm^2. After that, the diffusion process becomes slow (even constant), which means that, at the microscopic level, the diffusion process is practically stopped. Analyzing the Ii/Gi diagrams, i=1…3, one can see that between 5 … 50 min this ratio became low, which means a bigger mobility of the hydrogen atoms in the grains corps reported to the space between grains), while for interval 100 ...720 minutes the ratio is constant, the hydrogen is uniformely distributed (59.29 … 99.09 cm^3/cm^2).

To make a comparison of the hydrogen distribution inside the grains and in the space between grains, the distribution of hydrogen atoms relative to the total surfaces of the analyzed grains and to the spaces between grains should be analyzed (Figure 5).

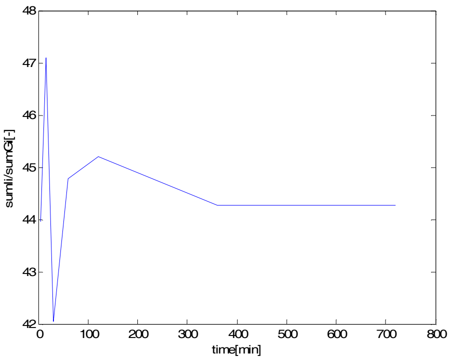

Fig. 5. Rapport ∑Ii/∑Gi, i=1…3, for hardened sample.

One can see that in the time gap 5…20 min the quantity of diffusion hydrogen is much bigger at the grain surfaces than in the spaces between grains, having values of 43.9…47.1. Then, in 20…100 min the diffusion process is inverted??? After that, in the time gap 100…350 min the diffusion process is more accentuate at the grain surfaces than in the spaces between grains. In the interval 350 … 720 minutes one can see an equilibrate distribution of hydrogen atoms in the both microscopic spaces considered.

5. Microscopic observations about hydrogen diffusion for the overheated and electrolytically charged S235JR (SREN 10027-1) sample

The microscopic observations were made for the S235JR (SREN 10027-1) sample treated in overheating conditions. The treatment consists of heating the sample up to 1150 Celsius degrees, keeping o this temperature constant for 20 minutes and then cooling the specimen in air flow. After that, the sample was electrolytically charged.

The microscopic observations have been made for 3 grains (figure 6). For each of them the number of hydrogen bubbles at the grain surface as well as the number of hydrogen bubbles in the space between grains has been counted. The values are presented in Table 8, for 5 to 720 min.

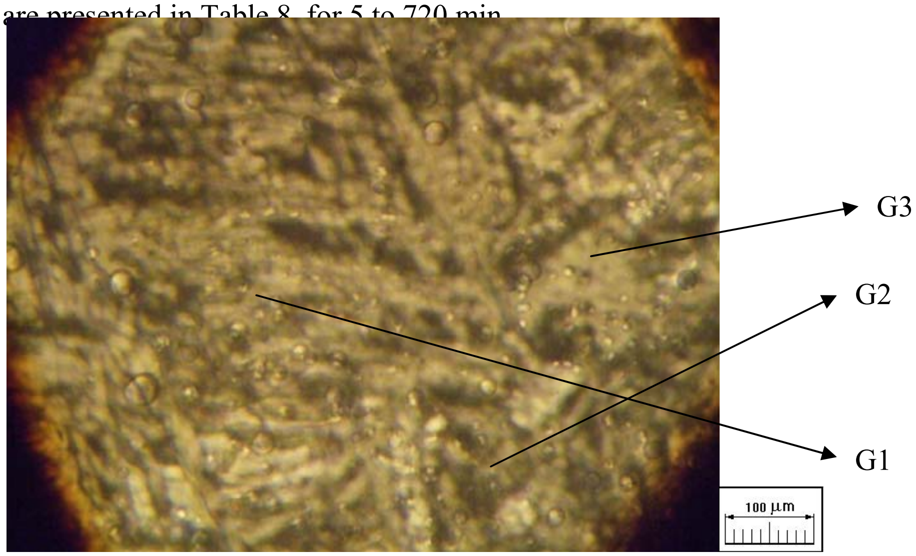

Fig. 6. The analyzed grains.

Table 8

Numbers of hydrogen bubbles on the grains surface Gi (i=1…3) and in the space between grains, Ii (i=1…3)

Grain	**Grain surface [µm^2]**	**Space between grains [µm^2]**
G1	3000	400
G2	520	75
G3	1400	230

The hydrogen quantities in the grain bodies and in the space between grains have been calculated and the ratios between them and the surfaces [cm^3/cm^2] are presented in Table 9.

Table 9

Quantities of hydrogen x 10^{-7} in the grain body and in the space between grains, relative to the surfaces [cm^3/cm^2]

Time[min]	**G1**	**G2**	**G3**	**I1**	**I2**	**I3**
5	15.13	5.15	9.55	133.8	178.62	104.84
15	17.8	25.75	17.19	140.49	285.76	127.6
30	19.58	36.05	19.1	160.56	357.2	139.2
60	22.25	51.5	24.83	180.63	428.64	162.4
120	26.7	72.1	24.83	187.32	428.64	174
360	27.59	72.1	32.47	200.7	500.08	197.2
720	27.59	77.25	32.47	200.7	500.08	197.2

In Table 8 and Table 9 are presented the diffusible hydrogen local distributions in the analyzed grain surfaces (5…720 min) and the diffusible hydrogen local distributions in the space between the analyzed grain surfaces (5…720 min).

The following remarks can be done:

- in the time gap 5…100 min the graphic has an ascendant evolution and one can observe a ratio of hydrogen quantities in the grain bodies and the surfaces of 5.15 … 26.7 × 10^{-7} cm^3/cm^2;

- in the time gap 120…720 min a stagnation of the diffusion process took place; after overheating the sample, the metallographic and geometric structure of grains is modified and this means that the grains and the spaces between them grew up; all these guide to a decrease in the hydrogen quantity relative to the surface unit.

After 200 minutes, the diffusion process will be stoped, wich means that the geometrical configuration of the sample is composed by regular shapes and the methalographic sample structure allows a slow diffusion process at the granular level and also in the space between grains level.

The same remarks as for the grain case can be done about the diffusion process in the space between grains.

In order to obtain a comparison of the hydrogen distribution inside the grains and in the space between grains, we will analyze the distribution of hydrogen atoms relative to the total surfaces of the analyzed grains and also to the spaces between grains (Figure 7).

One can see that between 5 and 120 min, the hydrogen diffusion (quantity) is much bigger at the grain surfaces than in the space between grains, with values between 6.5 … 14.4. Then, in the time interval 120 …350 minutes, the diffusion process is reversed. In the time interval 350 … 720 minutes, the diffusion process is more accentuated at the grain surfaces than in the spaces between grains.

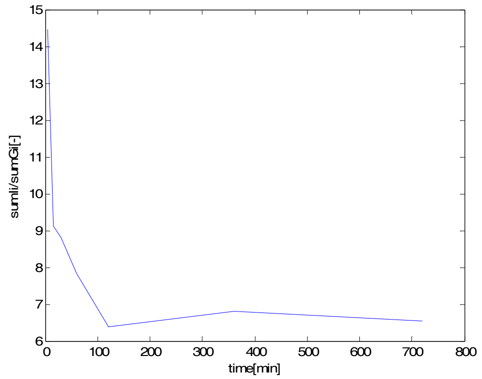

Fig. 7. Rapport ∑Ii/∑Gi, i=1…3, for superheating sample.

6. Conclusions

During this research, the authors used an original method for hydrogen microscopic capture, using a small drop of cedar oil, applied on the sample surface, which was initially metallographic polished.

All the experimental results were processed using MATLAB 7.1.
Concerning the period of electrolitycally charging, one can observe that the period is the same for the three samples.

In the case of the normalized sample, the hydrogen mobility in the spaces between grains is ten times bigger than the mobility for the other two samples. This can be explained by the finest and more uniform structure of the normalized metalllic grains.

For the normalized and overheated samples, the ratio of the diffusible hydrogen quantity at the granular level and the space between the grain levels is 10^2.

One could see a similarity between the diffusible hydrogen quantity for hardened samples and for overheated samples, at the microscopic level, in the grain bodies and in the spaces between grains. The values have the magnitude order of 10^{-7}. In the same time, the ratio between the diffusible hydrogen quantity in the total space between grains and the diffusible hydrogen quantity at the total grain surface is 4-5 times bigger in favor of the hardened samples. The hardened sample grain limits are very small comparing to the overheated sample grain limits.

For the thermally treated specimen one could observe that the hydrogen diffusion process for the analized zones becames very slow, for the interval 360 – 720 minutes.

The inter-granular diffusion values have an important role in hydrogen diffusion in steels.

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