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The influence of chemical composition on the dimensions change of hardened steels in nanofluids

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ABSTRACT

The paper presents the influences of nanofluids, which are used in hardening process, to dimension changes, hardness and microstructure of hardened construction of steel samples. An analysis was also carried out with the use of English methods of cooling abilities of nanofluids environments based on water, solid nanoparticles of Al_2O_3 and ammoniac water. The results of this experiment show, that only one of specific dimensions of cooled samples, in the distilled water, changed for about 9%, but when using nanofluids this change was smaller. The hardness of alloy materials got a few percent more when nanofluids were used in comparasion to using the distilled water. The gained results allow to conclude the positive influence of nanofluids on parameters of the hardened materials.

1. INTRODUCTION

The matter of heat conductivity and cooling is a key problem for industry progress which specializes in: metal products manufacturing, energy supply, transport and electronics. In the past few years, various guided experiments which were targeted at finding a new medium with better parameters of heat penetrability were carried out.

In the case of closed systems, the aim was to improve the efficiency of industrial machines, for example: engines or solar collectors. Instead, in opened mediums, that means in the case of heat treatment (hardening and supersaturation), it endeavored to manipulate cooling speed in narrowed range of austenite area, what is equal to increasing and decreasing of cooling speed of treated samples.

One of the possibilities, allowing the implementation of these tasks, was connecting the base of cooling substance, which is appearing to be water, with solid which is nanoparticles. The small dimension of the last one provides a big supporting surface, which is the reason of getting high heat conductivity of nanofluids. This mix, because of big potential, intrigues scientists, who saw the chance to replace the classic cooling materials by better ones.

Furthermore, nanofluids are characterized by [1]:

- smaller need for the power necessary for fluid pumping, which is required in getting proper value of heat permeation,
- better control of thermodynamic parameters and transporting properties, which depend on particle properties: accumulation, material, size and shape.
- rised stability of the mix.

At this moment three phenomena have been described, which are probably the reason for properties of nanfoluids listed earliers: Brown Motion, Liquid Layering and Nanoparticle Aggregation. However, nowadays there is no unequivocal confirmation, which one, from the listed phenomena, is the most important [1].

At the beginning the idea of nanofluids application was directed at improving heat exchange, what is equal to better efficiency, in closed systems. An example of this kind of nanofluids application is their usage in solar collectors, to improve their efficiency almost about 10%, in comparison to plane collectors [2].

The next step was to research on the nanofluids application as a cooling medium in the liquid stream form.

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One of the conclusions of the science experiment was that nanofluids are better cooling medium than water. However the improvement value of nanofluids is dependent i.a. on nanoparticles amount in base fluid [3].

Next, tests were implemented and the usage of beneficial nanofluids properties in material heat treatment as hardening. It was proven, that during the multiple heating and cooling process of experimental sphere, with a diameter of 10mm, the cooling of its core was accelerated with every iteration. According to the scientists, parts of particles were mounted on a metal element and caused boost of cooling efficiency in next probes. After seven iterations, metal component was cooled in about 30 seconds, that means a half of the original time. This was possible by using nanofluids which contain SiO_2 particles [4].

In the past few years, nanofluids gained a big scientist public, in 2001 the amount of releases about them was about ten, but 10 years later it had almost eight hundred releases. [1] There were a lot of reasons which explain this situation i.a. add-on of solid nano particles in various fluids improve their heat conductivity, that means a cooling ability, what gives a chance to discover new, better medium to, for example: industry machine cooling or hardening process.

However, the value of cooling speed improvement depends on nanonfluids: chemical composition, nano particles amount and cooled material. Undoubtedly, in many articles it has been proven, that nanofluids can be better colling medium than the very popular water. But, because there is a big amount of materials, which can be used as nano particles, and their concentration values, scientists make experiments, in purpose to find the best nanofluid with the highest cooling speed.

2. EXPERIMENT DESCRIPTION

2.1. Used materials

In experiments, there were used two kinds of materials: low carbon steel C10 (0.09%C; 0.57%Mn; 0.19%Si; 0,08%Cr), which chemical composition was corresponding with PN-EN 10277 – 2:2008 [5] and low alloy steel 16MnCr5 (0.18%C; 1.22%Mn; 0.23%Si; 0,92%Cr) which composition was corresponding with PN-EN 10084 : 2008 [6]. From the described materials, Navy C-ring samples were made.

As a quenching medium the distilled water was used, which provides parameters repetitively from chemical-physic side. Al_2O_3 nano participles, which form was spheroidal and size did not exceed 50nm were used. The ammonia water, in which ammonia concentration was about 25% was used as well. The aforementioned ingredients allowed to create nanofluid of about 1% concentration of nano particles and 10% concentration of ammonia water [7,8].

2.2. Examination of hardening medium properties

The experiment of cooling properties was made based on the English method, which is described in norm: ISO 9950 (PN-ISO 9950:2014-12) [9].

In this process a probe is used, made from heat-resistance alloy: Inconel 600. The chrome-nickel alloy is characterized by good resistance on corrosion cracking, which is the result of chloride ions activity and oxidation in high temperatures. Important experimental element dimensions are: diameter, which is 12,5mm, and length, which is equal 60mm. Inside of the element there is jacketed thermocouple made from NiCrAl [9].

The measurement probe was heated to 850°C, cooled in the examined quenching medium. Data registration, with a computer, allow to get information in the temperature-time system. However, the extra mathematical analysis gives the possibility to remove noise from the system and show data not only in the temperature-time diagram but in the temperature-cooling speed, too.

2.3. Heat treatment process

Navy C-ring probe and prepared quenching mediums let implement hardening process, every variant of which is presented in Tab. ***1***.

Tab. 1. Heat treatment variants.

The process variant	**The grade of steel**	**The heat treatment process**	**The quenching medium**
W1	C10	-	**-**
W2	C10	Hardening	The distilled water
W3	C10		The distilled water + 1% Al_2O_3 + 10% NH_3*H_2O
W4	16MnCr5	-	-
W5	16MnCr5	Hardening	The distilled water
W6	16MnCr5		The distilled water + 1% Al_2O_3 + 10% NH_3*H_2O

In the hardening process, the austenitizing stages were carried out in a tube, a flow furnace. The probes were heated to temperature of 860°C and left for 0,6h.

To eliminate any harmful external influences on the hardened material, a gas protection was used - it was technical nitrogen.

The material was placed in the heat chamber with a gap directed to the bottom and it was placed in the same way in cooling medium.

2.4. The research of dimension change

The treated probes allow to make an experiment of dimension change, which was carried out by measuring every parameter before and after the heat treatment. These parameters were (Fig. 1.):

- thickness *g_L* and *g_P*,
- gap width *h* from numbered site and not numbered,
- external diameter in two axis,
- internal diameter in two axis.

The dimensional difference between hardening before and after, and the value of dimension change for h gap is described by equations:

$$\Delta h = h_H - h_{IS} \tag{1}$$

$$\Delta h_{RC} = \left|\frac{h_H - h_{IS}}{h_{IS}}\right| \qquad (2)$$

where:
Δh - change of dimension [mm],
h_H - dimension after hardening [mm],
h_{IS} - dimension in initial state[mm],
Δh_{RC} – relative change of dimension [%].

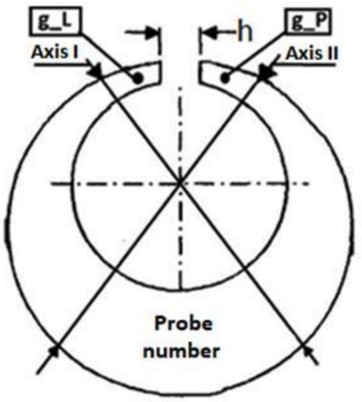


Fig. 1. The Navy C-ring probe.

2.5. The hardness research

The hardness research was carried out on the probe surface before and after hardening using Vickers method, under the load of 98,1N (10kG), according to PN-EN ISO 6507-1:2007 [10] on Zwick company hardness.

Also the hardness on cross section was measured, again by Vickers method, but this time under the load of 0,98N (0,1kG) [10], by using the same measurement machine.

2.6. The metallographical observations

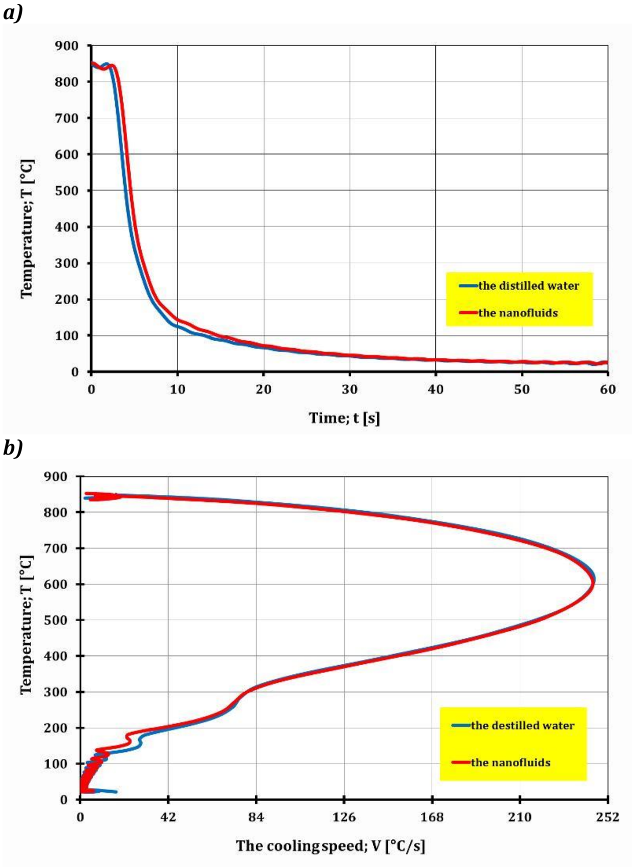
The microstructure research was done using Opta-Tech LAB40 microscope with a digital camera conneceted with PC computer to vision registration. The microstructure was observed using two types of objectives with: 5x and 50x zoom. Metallographic probes were analysed with 2% Nital solution. The structural constituent (phase) was verified using the work [11].

3. THE RESEARCH RESULTS

The obtained results from the research of quenching medium are presented in figure 2 in two coordinate systems: temperature (T) – time (t) (Fig. 2a) and temperature (T) – cooling speed (V) (Fig. 2b).

It was affirmed, on the basis of the cooling curvature, that slowing down in cooling of nanofluids is clearly observed only in the arrangement of the temperature - time system (Fig. 2a). However, we do not clearly observe this in the arrangement of the temperature - cooling speed system (Fig. 2b), because the differences obtained are smaller than in the previous arrangement of coordinates between individual media.

The comparison of number values results shows, that at the beginning phase of cooling, which lasted to 2,25s, nanofluids are characterized with slower cooling speed relative to distilled water. Also nanofluids are not the cause of cooling speed increment and shorten the treatment time.


a)

b)

Fig. 2. The cooling abilities of research quenching mediums in coordination system: a) temperature – time ; b) temperature – cooling speed.

In the first stage the probes were analysed from the macroscopic site before and after the hardening, which shows lack of any defects: lack of material and cracks.

The results of the gap *h* research, before and after the heat treatment, are presented in table 2.

The table shows, that the probe hardening, for both steels, causes very small dimension changes and most of them do not exceed 0,2mm. When comparing dimensions changes, from the type of used cooling form, it can be seen that higher dimension changes were gained for the probes cooled in the distilled water. Minus in values means, that the result of the heat treatment was the reduction of the parameter.

The percentage changes of dimensions of low carbon steel, treated with distilled water were equaled about 9%. For both cooled materials with nanofluids difference in dimensions, changes were smaller.

To sum up, the important dimension change was only in *h* gap, which became narrowed, in one case almost 9% in water and 3÷5,5% change by using nanofluids.

The results of the hardness measurements on the surfaces of the elements are presented in Tab. ***3*** and Fig. ***3***.

The difference of hardness in the initial state between these steels results from the chemical composition what causes the different quantity in the microstructure of ferrite and pearlite phase.

Tab. 2. The dimensions of h gap in initial and hardened state as well as value of change after hardening process

The process variant	h_{IS} [mm]	h_H [mm]	Δh [mm]	Δh_{RC} [%]
W1	2,17	-	-	-
W2	2,26	2,05	-0,21	9,09
W3	2,19	2,12	-0,07	3,20
W4	2,22	-	-	-
W5	2,22	2,07	-0,16	6,98
W6	2,35	2,48	0,13	5,54

Tab. 3. The hardness of probes in initial or hardened state

The process variant	The hardness of HV10	
	The initial state	The hardened state
W1	61,4	-
W2	48,3	80,8
W3	55,8	81,7
W4	68,8	-
W5	72,8	161,8
W6	66,3	168,7

The C10 steel gets the microstructure, which is composed of ferrite and perlite near the small content of the carbon and the vestigial quantities of alloy elements. In the case of the 16MnCr5 steel, the carbon content and the enlarged content of manganese and chrome let obtain the pearlite-ferrite microstructure. Because the pearlite shows larger hardness from the ferrite, so 16MnCr5 steel, its larger part in the microstructure, lets get higher hardness in the initial state.

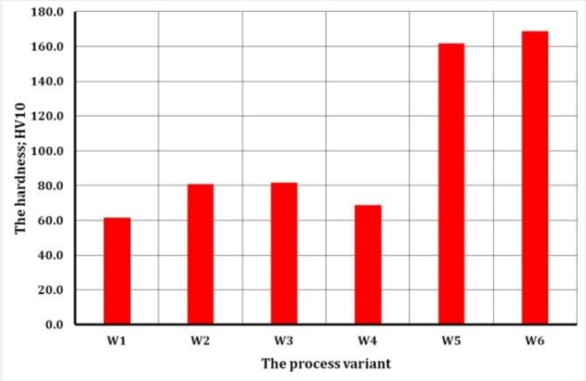


Fig. 3. The HV10 hardness on surface obtained in initial or hardened state.

Furthermore, there are presented figures 4 and 5 with the values of microhardness parameter *HV0.1* which is dependent on the measurement distance from the cross section surface.

The obtained hardness results show that carbon steel did not gain too much after the hardening process. In the distilled water, the cooling raise *HV10* hardness only about 33 points and in nanofluids about 25 points. That means, that in the probes there would be only little phase changes in comparison to the initial state. Hardened low alloy steel gained much more in comparison to the initial state. The probes cooled in nanofluids increased their hardness about 102 *HV10* points and 89 points in the case of distilled water.

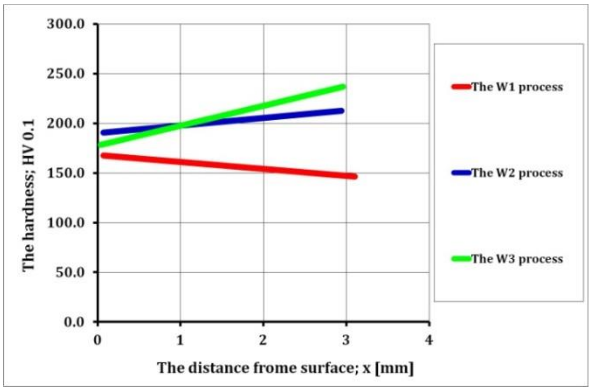


Fig. 4.The HV0.1 hardness on cross section probes of C10 steel after W1, W2, W3 process.

Higher low alloy steel hardness could be a result of extra alloy additives (Mn and Cr) and higher amount of carbon in chemical composition, compared to low carbon steel, what improved hardenability of treated steel.

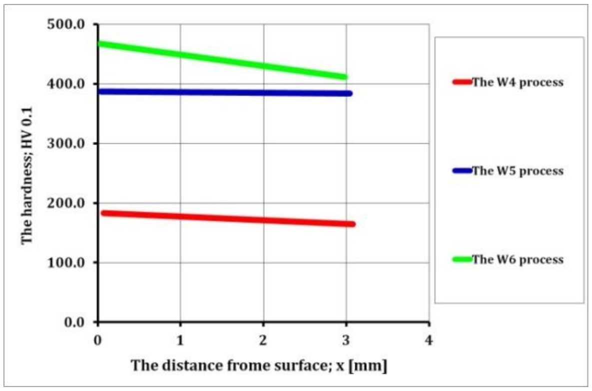


Fig. 5. The HV0.1 hardness on cross section probes of 16MnCr5 steel after W4, W5, W6 process.

The increased hardness from the surface to the core in *HV0.1* hardness analysis is probably a result of the ineffective influence, protection atmosphere, what could lead to decarbonizing of the top layer of the material. The described phenomenon did not have place in low carbon steel case.

In Fig. ***6*** to Fig. ***11*** the microstructures of probes after different processes are presented, which parameters are presented in Table 1.

Figure 6 presents the microstructure of a probe with C10 steel after W1process, that is in the initial state. This microstructure is composed of ferrite and small quantity of pearlite. However, the microstructure of the probe with 16MnCr5 steel in the initial state (W4 process) is presented in figure 9. The microstructure of this steel is composed of the ferrite and pearlite mixture.

In Fig. ***7*** (W2 process), as a result of the hardening process, it is obtained on ferrite grain boundaries (supersaturated ferrite) martensite or bainite precipitation, what is confirmed in a low hardness increase. In the next figures (Fig. 8), the microstructure of C10 steel hardened in nanofluids is presented, which also contains supersaturated ferrite phase and smaller martensite or bainite precipitation on its boundaries.

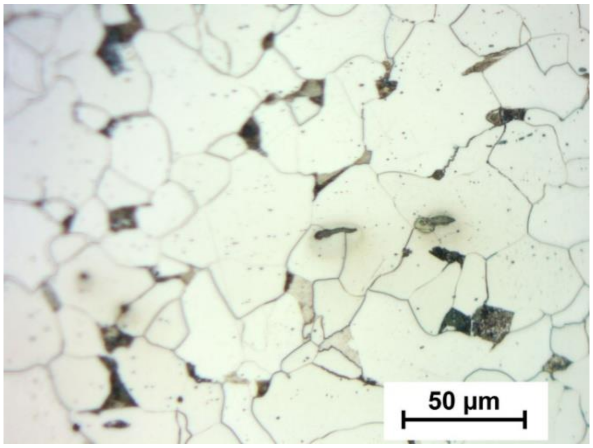


Fig. 6. The microstructure of probe with C10 steel after W1 process.

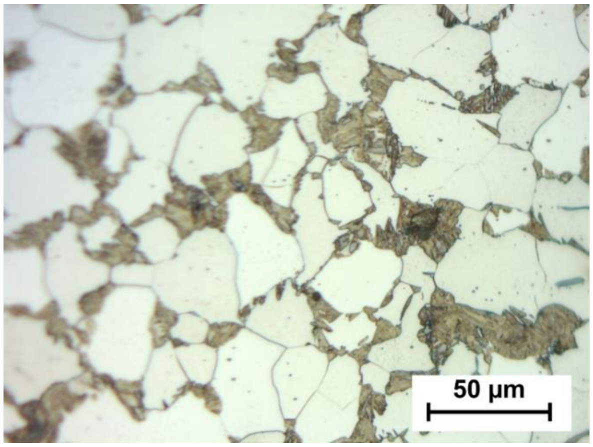


Fig. 7. The microstructure of probe with C10 steel after W2 process.

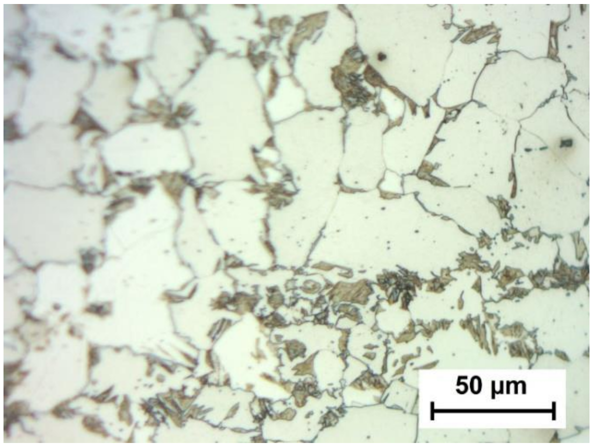


Fig. 8. The microstructure of probe with C10 steel after W3 process.

This is the reason of the lower increase of hardness in this probe.

Low alloy steel microstructure hardened in the distilled water (W5 process) is presented in figure 10. It is a martensite and bainite mix with a little amount of supersaturated ferrite precipitation. It is confirmed by the hardness results.

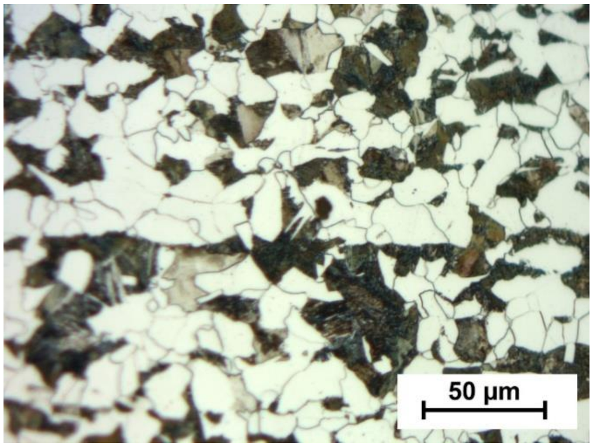


Fig. 9. The microstructure of probe with 16MnCr5 steel after W4 process.

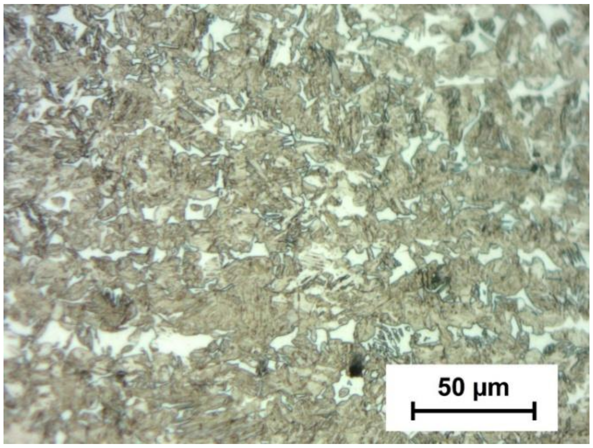


Fig. 10. The microstructure of probe with 16MnCr5 steel after W5 process.

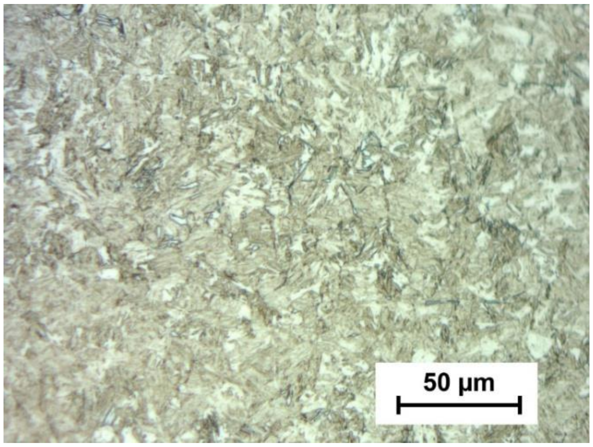


Fig. 11. The microstructure of probe with 16MnCr5 steel after W6 process.

The 16MnCr5 steel which was hardened in nanofluids (W6 process) is characterized by the microstructure which contains martensite and bainite with low amount of supersaturated ferrite, what fits to the hardness parameter. This microstructure is presented in figure 11.

On the basis of the obtained results, we can at last certify that the use of nanofluids (process W3 and W6) during hardening of low carbon (C10) steel or low alloy (16MnCr5) steel lets get the microstructure assuring high hardness near minimum dimension changes.

4. SUMMARY

Conclusions from the experiment are listed below:

- addition of solid nanoparticles in nanofluids has a very little influence on cooling speed in comparison to the distilled water,
- the biggest dimension changes in Navy C-ring hardened probes occur for *h* gap. The difference between the initial and the hardened form was about 3% and 5,5% for nanofluids and for the distilled water it was about 9%,
- the hardness gained after cooling with the distilled water and nanofluids is comparable in the same type of considered material and does not exceed 5%,
- microstructure of the hardened probes confirms the obtained results in the experiment. Low carbon steel probes after the hardening process are characterized by supersaturated ferrite with martensite and bainite precipitation on grain boundaries. However, low alloy steel probes in the hardening process gained the microstructure with the mix of martenstie and bainite and a little amount of supersaturated ferrite precipitation.

Based on the experiment and the literature analysis, it can be seen, that using nanofluids with the chemical composition: water + 1% Al_2O_3 + 10% NH_3*H_2O has a positive influence on a treated material in comparison to the hardening process carried out with the distilled water. Also, there was a smaller dimension change when we used nanofluids, than with the use of the distilled water, for both kinds of analysed materials. However, the presented here experiment, is the beginning for a deeper analysis of this topic, therefore it requires more research with wider spectrum of rating of gained hardened materials parameters.

Acknowledgements

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