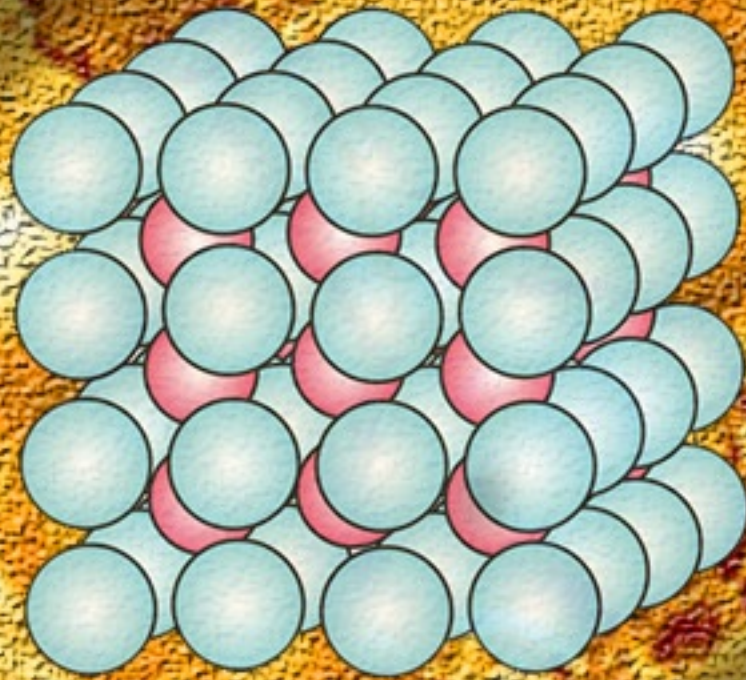


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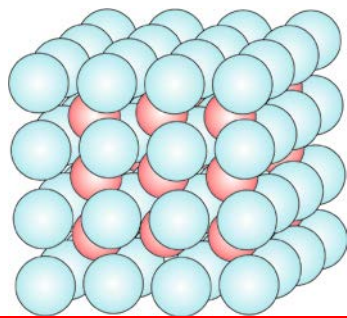
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Effect of inoculation, cooling rate and charge composition on gray iron microstructure

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Abstract: This paper analyses the effect of different charge compositions for melt production, cooling rate (i.e. casting wall thickness) and inoculation on the gray iron microstructure. In this study, three gray iron melts were produced that had almost the same chemical composition. The proportions of steel scrap (SS), pig iron (PI), gray iron return (GIR) and SiC in charge were as follows: melt 1 (10 % SS, 39.4 % PI, 49.2 % GIR, 0.6 % SiC), melt 2 (38.8 % SS, 9.9 % PI, 47.9 % GIR, 1.6 % SiC) and melt 3 (0 % SS, 0 % PI, 99.2 % GIR, 0.06 % SiC). One uninoculated and one inoculated stepped test casting with walls thicknesses of 5, 10, 20, 45 and 65 mm was casted from each melt. The inoculant was added in the melt stream during pouring in the mould in an amount of 0.23 wt.%. The type, size and distribution of graphite flakes in the analysed walls did not significantly depend on the charge compositions. The structure of the metal matrix, carbides precipitation and type, size and distribution of graphite flakes were largely dependent on the wall thickness. As the wall thickness increased, the cooling rate decreased and the type of graphite flakes changed, from D and E through B to A type. Carbide formation has occurred in the edge region of the 5 mm thick walls. With the decrease of the cooling rate and increasing the proportion of D and E type graphite flakes, the ferrite content in the metal matrix increased. The carbide content in the edge region of the 5 mm thick walls was significantly reduced by inoculation. Inoculation increased the proportion of A type graphite flakes in the middle of 5 mm thick wall and in walls with a thickness from 10 to 65 mm. In addition, inoculation significantly reduced the proportion of B, D and E type graphite flakes or were completely eliminated. Wall thickness has affected this effect.

Keywords: GRAY IRON MICROSTRUCTURE, INOCULATION, COOLING RATE, CHARGE COMPOSITION

1. Introduction

Gray iron belongs to the group of cast irons in which carbon precipitates in the form of graphite [1 - 3]. Due to the flake shape of the graphite particles, gray iron has low tensile strength, hardness, toughness, elongation and modulus of elasticity and increased section sensitivity. The positive characteristics of gray iron are good machinability, very good damping of vibration, resistance to heat shocks, good castability and high compressive strength. It is widely used in various fields, such as machine building, production of castings for stoves and furnaces, process industry and energetics, motor vehicle industry, various constructions and decorative castings, and in many other areas.

The properties of gray iron depend on its microstructure. Through changes in the microstructure, different properties can be achieved. Numerous factors influence the microstructure of the gray iron, but the most important are: the chemical composition, the cooling rate of the casting in the mould during and after solidification (i.e., casting section thickness), raw materials for melt production, preconditioning and inoculation [4 - 20].

This article analyses the effect of different charge compositions for melt production, casting wall thickness and inoculation on the microstructure of gray iron.

2. Experimental

Three gray iron melts were produced in a medium-frequency induction furnace. The shares of the components in the charge are shown in Table 1. The chemical composition of the charge components is shown in Table 2.

Table 1: Shares of components in charge.

Component	Share in charge, wt.%		
	Melt 1	Melt 2	Melt 3
Pig iron (PI)	39.4	9.9	0
Steel scrap (SS)	10	38.8	0
Gray iron return (GIR)	49.2	47.9	99.2
SiC	0.6	1.6	0.06
FeP	0.7	0.6	0.06
FeS	0	0.1	0.08
Recarburizer	0.2	1.1	0.6

Table 2: Chemical composition of charge components.

	Share, wt.%						
	PI	SS	GIR	SiC	FeP	FeS	Recarburizer
C	4.41	0.09	3.56	2.90	0.1	0.3	min. 98
Si	1.25	0.13	2.05	-	1.86	0.96	-
Mn	0.13	0.71	0.43	-	1.91	-	-
P	0.08	0.024	0.32	-	25.72	0.01	-
S	0.02	0.014	0.091	0.05	0.04	49.37	max. 1.2
Cu	0.01	0.03	0.19	-	-	-	-
Cr	0.01	0.027	0.071	-	-	-	-
Al	-	-	-	0.06	-	0.01	-
Ti	-	-	-	-	1.2	-	-
SiC	-	-	-	90.04	-	-	-
SiO ₂	-	-	-	2.8	-	-	-
Fe	bal.	bal.	bal.	0.4	bal.	bal.	-

Two stepped test castings (STC) containing 5, 10, 20, 45 and 65 mm thick walls were cast from each melt. One STC was cast without and the other with the addition of inoculant in the melt stream during pouring in the mould. The addition of inoculant was 0.23 wt.%. The inoculant of the following chemical composition was used: 73 - 78 wt.% Si, 0.1 wt.% Ca, 0.6 - 1 wt.% Sr, 0.5 wt.% Al, and the rest is Fe. It follows from the above that the STC 1, 3 and 5 are uninoculated and STC 2, 4 and 6 are inoculated.

Samples for metallographic analysis were cut from the middle of each wall in the STC. In addition, samples were taken from the edge of the wall thickness of 5 mm from all STC. Microstructure was analysed using light metallographic microscope with a digital camera. Samples were etched with 5 % nital.

3. Results and discussion

The chemical composition of the gray iron melts is shown in Table 3. It can be seen that the melts have a very similar chemical composition. This eliminates the influence of differences in chemical composition on the microstructure.

Table 3: Chemical composition of gray iron melts.

	Chemical composition, wt. %							CE
	C	Si	Mn	P	S	Cu	Cr	
Melt 1 (STC 1 and 2)	3.5	2.1	0.46	0.33	0.084	0.15	0.07	4.31
Melt 2 (STC 3 and 4)	3.53	2.12	0.4	0.36	0.1	0.18	0.07	4.36
Melt 3 (STC 5 and 6)	3.57	2.08	0.45	0.32	0.1	0.19	0.1	4.37

Figures 1 and 2 show the microstructure of STC in unetched condition at 100x magnification.

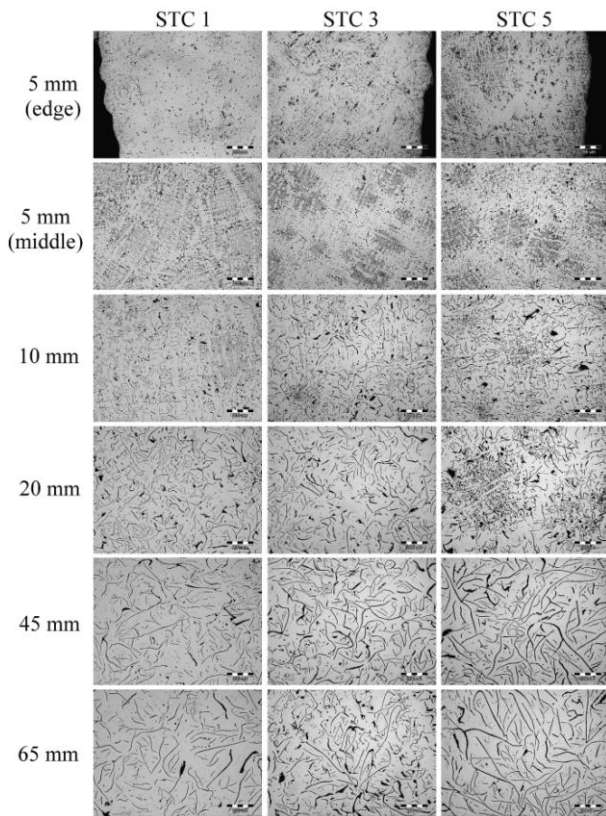
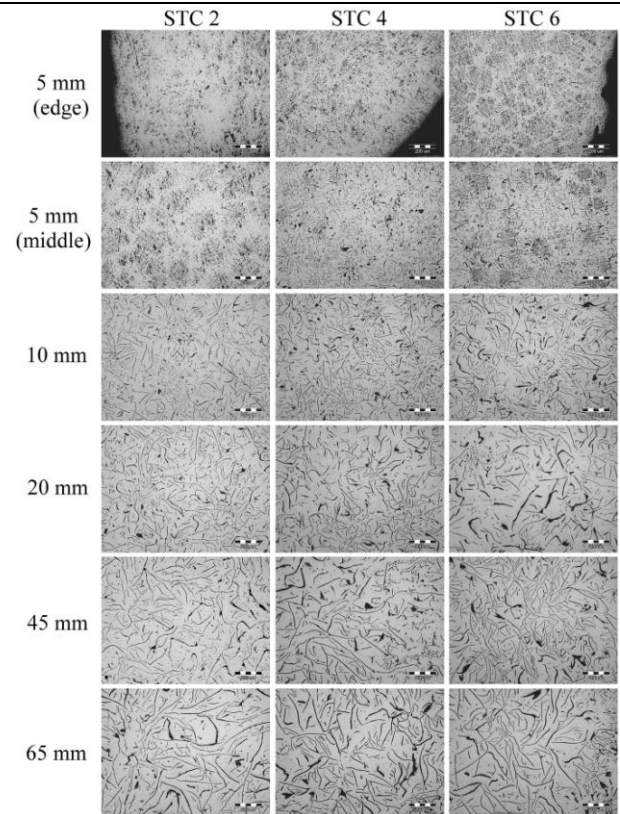
**Fig. 1** Microstructures of uninoculated STC (unetched).

Figure 1 shows that small graphite flakes D and E type and a high proportion of carbides are present in the microstructure of the edge of 5 mm thick wall in uninoculated STC 1, 3 and 5. The highest proportion of carbides and the smallest proportion of graphite particles is present in STC 1, which was cast from the melt produced from the charge with the highest proportion of pig iron. The high solidification rate of the edge zone caused a large undercooling of the melt, which, in combination with inadequate nucleation and graphitization potential (originating from a low content of silicon), resulted in the formation of carbides. In addition, rapid solidification and greater undercooling of the melt favour the creation of D and E type graphite flakes. Inoculation improves the nucleation potential of the melt, which is why the 5 mm thick wall from STC 2, 4 and 6 contains a higher proportion of graphite phase and a smaller proportion of carbides, which are almost completely eliminated in STC 6 (Figure 2). Graphite flakes are still D and E type.

**Fig. 2** Microstructures of inoculated STC (unetched).

In the microstructure of the middle part of the 5 mm thick wall from STC 1, D type graphite flakes predominate, with a smaller proportion of E type graphite flakes (Figure 1). STC 3 and 5 also contain D type graphite flakes, but their proportion is smaller than in STC 1 (Figure 1). In addition, their microstructure contains a certain proportion of A and B type graphite flakes. The presence of graphite flakes A and B type indicates a more favourable nucleation potential and less undercooling of the melt (especially in the case of A type graphite flakes). In the middle of the wall thickness of 5 mm from STC 1, 3 and 5 carbides are not present, although they are not inoculated. Slower solidification of the central part relative to the edge of the wall with a thickness of 5 mm prevented the formation of carbides. Figure 2 shows that the improvement of nucleation potential by inoculation favourably affected the morphology of graphite flakes. STC 2 contains a smaller proportion of D type graphite flakes compared to STC 1. STC 4 contains graphite flakes A and B type, not graphite flakes D type as STC 3, which was cast from the same melt but without the addition of inoculant. STC 6 also contains A and B type graphite flakes and a very small proportion of D type graphite flakes (significantly smaller than in STC 5).

The wall thickness of 10 mm from STC 1 contains A and B type graphite flakes and a smaller proportion of D type graphite flakes (Figure 1). Inoculation eliminated D type graphite flakes and increased the proportion of A type graphite flakes (STC 2, Figure 2). The slower solidification of the wall thickness of 10 mm compared to the wall thickness of 5 mm resulted in a lower undercooling of the melt. This favours the formation of B type graphite flakes, but also the formation of A type graphite flakes if the undercooling is low and the nucleation potential of the melt is favourable. STC 3 and 5 contain A and B type graphite flakes, and a smaller proportion of C type graphite flakes, which appear due to hypereutectic composition of the melt (Figure 1). Inoculation increased the proportion of A type graphite flakes and decreased the proportion of B type graphite flakes (STC 4 and 6, Figure 2).

Type A graphite flakes are present in the microstructure of a 20 mm thick wall from STC 1, 3 and 5 (Figure 1). In addition, the STC 5 also contains a certain proportion of B type graphite flakes (Figure 1). This indicates a favourable nucleation potential and

slower solidification. Improving nucleating potential by inoculation increased the proportion of A type graphite flakes and eliminated B type graphite flakes (Figure 2).

Figure 1 shows that the wall thickness of 45 mm in all STC contains A type graphite flakes and a smaller proportion of C type graphite flakes. The slower cooling and sufficiently suitable nucleation potential of the melt favoured the formation of A type graphite flakes. Inoculation further increased the proportion of A type graphite flakes and reduced their size to some extent (Figure 2).

Figure 1 shows that the wall thickness of 65 mm in all STC contains A and C type graphite flakes. Similar effects as in a 45 mm thick wall were achieved by inoculation.

Comparing the microstructures shown in Figures 1 and 2, it can be seen that increasing the wall thickness results in a change in the type of graphite flakes - from D and E through B to A type. Increasing the wall thickness decreases the cooling rate and the undercooling of the melt. This creates favourable conditions for the formation of A type graphite flakes, which are also the most suitable. In addition, it can be seen that the number of A and C type graphite flakes decreases and their size increases with increasing wall thickness, which is the result of slower solidification.

STC 1 and 2 which are casted from the melt produced from the charge with 39.4 wt.% of pig iron did not prove superior in terms of the morphology of the graphite flakes in comparison to other STC that are made from melts without or with very low content of pig iron in the charge. It should be taken into consideration that the charge for making melt 2 contained the highest proportion of steel scrap, but also the highest proportion of SiC. The strong preconditioning of the melt with SiC had a beneficial effect on its nucleation potential, which ultimately affected the type, size and distribution of graphite flakes and carbide formation.

Figures 3 and 4 show the microstructure of STC in etched condition at 100x magnification.

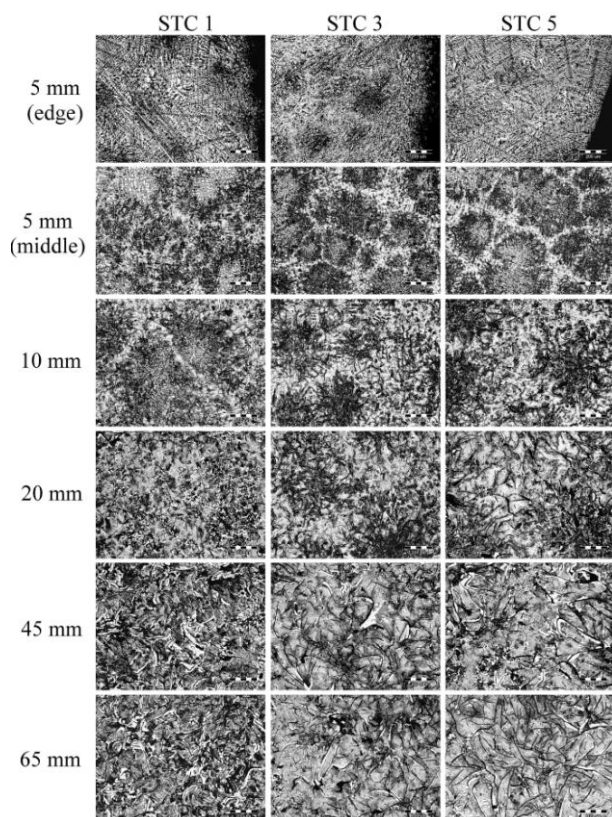


Fig. 3 Microstructures of uninoculated STC (etched).

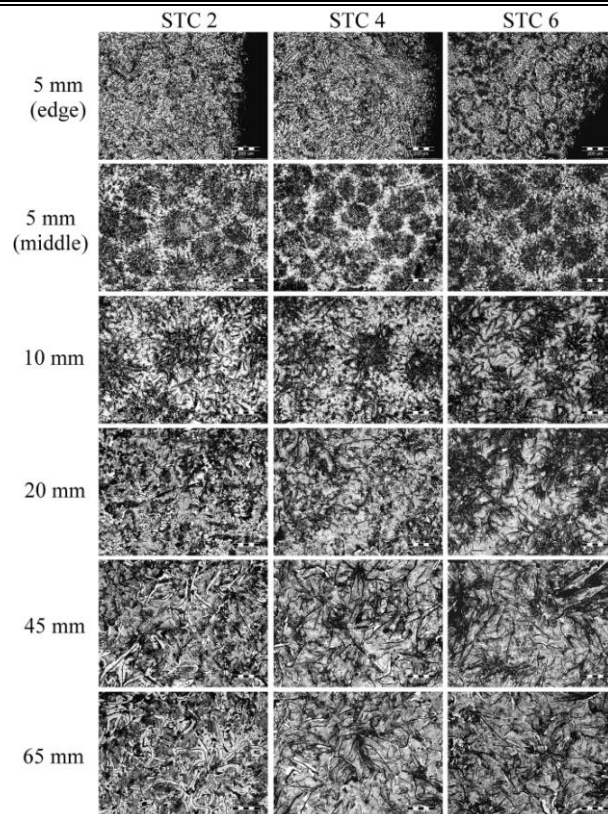


Fig. 4 Microstructures of inoculated STC (etched).

Figure 3 shows that in STC 1, 3 and 5 the edge of the wall thickness of 5 mm has a pearlitic metal matrix, while in STC 2, 4 and 6 the metal matrix is ferritic-pearlitic (Figure 4). Pearlite content is much higher than ferrite content due to high solidification rate. Ferrite is present in areas where D type graphite flakes are found. Because they are extremely small and branched flakes, the carbon diffusion paths from austenite are significantly shortened. This facilitates the reduction of the carbon content in austenite and its transformation into ferrite. In addition to the constituents mentioned above, carbides and a phosphide eutectic network were found in the microstructure. The increased phosphorus content in melts resulted in the formation of a phosphide eutectic.

The middle of the wall thickness of 5 mm in all STC (inoculated and uninoculated) has a pearlitic-ferritic metal matrix (Figures 3 and 4). As well as on the edge, the pearlite content is greater than the ferrite content, which is found around the D type graphite flakes. The phosphide eutectic network can be clearly seen in all samples. Carbides are not present in the middle of this wall, but not in other thicker walls because of slower cooling.

The metal matrix of the wall thickness of 10 mm in all STC contains a high proportion of pearlite (Figures 3 and 4). Ferrite is present in a smaller proportion, mainly in areas where small flakes of graphite are found (B and D type), and to a lesser extent around A type graphite flakes. As in the previous wall, a phosphide eutectic, which is located along the grain boundaries, is also present in this wall.

The wall thickness of 20 mm in all STC has a pearlitic-ferritic metal matrix with a high content of pearlite (Figures 3 and 4). Ferrite is located around graphite flakes. A phosphide eutectic is also present in the microstructure. It is surrounded by pearlite, as in the previously mentioned walls.

The 45 and 65 mm thick walls in all STC also have a pearlitic-ferritic metal matrix and contain a phosphide eutectic (Figures 3 and 4). The ferrite content is higher than in the previous walls due to the slower cooling, which is a result of the greater thickness of the walls.

4. Conclusion

Based on the results of research of the influence of different charge compositions for melt production, casting wall thickness and inoculation on the gray iron microstructure, the following can be concluded:

- the type, size and distribution of graphite flakes in the analysed wall thicknesses of 5, 10, 20, 45 and 65 mm did not significantly depend on the content of pig iron, steel scrap and gray iron return in the charge,
- preconditioning with SiC improves the nucleation potential of the gray iron melt, which is especially evident in the melt made from the charge containing a relatively high proportion of steel scrap (~40 %),
- solidification rate, i.e. the wall thickness, greatly influences the type, size and distribution of graphite flakes, carbide formation and the structure of the metal matrix,
- in thin walls (5 mm), due to the high solidification rate, a large undercooling of the melt is produced, which ultimately results in the formation of D and E type graphite flakes,
- with increasing wall thickness (from 10 to 65 mm), i.e. with decreasing solidification rate, the conditions for the formation of A and B type graphite flakes are created,
- in thin walls (5 mm), the presence of carbides can be expected, especially in the edge region where the solidification rate is greatest,
- with decreasing cooling rate and increasing the proportion of D and E type graphite flakes increases the proportion of ferrite in the metal matrix of gray iron,
- inoculation significantly affects the microstructure of gray iron because it improves the nucleation potential of the melt,
- corresponding addition of inoculant reduces or almost completely eliminates the formation of carbides in thin walls, decreases the proportion of B, D and E type graphite flakes, and increases the proportion of A type graphite flakes,
- phosphorus content > 0.3 wt.% results in the formation of phosphide eutectic in wall thicknesses of 5, 10, 20, 45 and 65 mm.

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The features of recrystallization of steels under laser action

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Abstract. The features of recrystallization of steels with different chemical composition and type of crystal lattice under laser action were investigated. These processes are of great importance in high-speed laser heating and cooling, as well as in the formation of the microstructure of steels under the influence of residual heat.

It was found that recrystallization under laser action has signs of a dynamic process due to an increase in the dislocation density. In addition, the dislocation substructure of steel is inherited from the initial hot-deformed state. It is shown that the mechanism of laser recrystallization depends on the type of steel, chemical composition, and crystal lattice.

In different steels, the development of primary, collective, and secondary recrystallization was observed. In this case, the change in the grain structure of steels took place against the background of an increased density of dislocations and the formation of a cellular dislocation substructure.

KEYWORDS: STEEL, RECRYSTALLIZATION, LASER ACTION, MICROSTRUCTURE, STRESSES, HIGH SPEED RELAXATION

1. Introduction.

Laser processing is widely used to strengthen various steel products. During this treatment, structural and phase transformations in steel proceed at a very high rate. In this case, the critical points of transformations are shifted upward on the temperature scale relative to their equilibrium value by 50...100 °C [1-3]. Numerous studies have established that the effect of strengthening steels under laser irradiation is achieved by high-temperature strengthening, martensitic transformation, obtaining an ultrafine structure, dissolution of carbides and non-metallic inclusions, saturation of the matrix with their components, microchemical inhomogeneity, an increase in the number of defects in the crystal structure and plastic shears [1-11]. All these factors act simultaneously and it is not always possible to separate their influence in the study of steels traditionally subjected to laser processing, especially in steels with a complex structure. The goal of the work was to study the features of high-speed recrystallization

in steels with different chemical composition and type of crystal lattice under laser action.

2. Materials and Procedures.

Specimens made of hot-deformed steels 08Yu, 08Kp, 08H18N10T, E3 were irradiated by laser in GOS-30M and Quantum-16 installations with an excitation voltage of 2,5kV and pulse energy of 18 J at heating rate of 10^5 °C/s and cooling rate of 10^6 °C/s with action time of $3,6 \cdot 10^{-3}$ s. These steels can be considered model alloys because they have a single-phase structure or a structure with a small amount of a second phase and contain little carbon (see tabl. 1). Such a set of research objects made it possible to obtain relatively simple types of matrix with different impurities and crystal lattices. The microstructure of steels in the laser impact zone was studied using a Neophot-31 light microscope and a Tesla electron microscope. The dislocation density, block sizes, and texture in a thin surface layer were evaluated on a DRON-2.0 X-ray diffractometer.

Table 1. Chemical composition of the steels

Steel	Element content, %									
	C	Mn	Si	Cu	Cr	Al	Ti	Ni	S	P
08Kp	0,09	0,32	0,01	0,22	0,05	0,01	-	0,05	0,025	0,009
08Yu	0,07	0,29	0,01	0,07	0,03	0,04	-	0,05	0,022	0,007
E3	0,035	0,10	3,1	0,09	0,05	0,013	-	0,09	0,005	0,005
08H18N10T	0,08	1,2	0,80	0,07	18,0	-	0,6	10,1	0,021	0,006

3. Results and discussion.

In [2, 5], the features of phase transformations, in particular, the austenitization of steels during laser heating, were studied. It has been established that phase transformations are accompanied by polygonization [12] and recrystallization [5] due to internal strengthening and having a static character. It was shown in [13] that the kinetic regularities of recrystallization upon conventional and laser annealing are similar. However, it was established in [2, 14, 15] that, during laser treatment, the dislocation density increases by several orders of magnitude, and the level of microdistortions of the crystal lattice increases by several times, which indicates plastic shears and is directly stated by the authors of [15].

Structural changes in the zone of laser impact in low-carbon steels took place under conditions of high temperature and a powerful shock pulse. The short duration of such a powerful impact inevitably generates shock microwaves. The impact of a laser beam is similar to a microexplosion (thermal shock), shock waves develop huge pressures [2], leading to plastic deformation, which manifests itself in a very short time of shock compression. Under these conditions, the stresses in the thin surface layer of steel exceed

the yield strength and the material is able to flow. As a result, dislocations and vacancies multiply, dislocation reactions occur, and a significant concentration of nonequilibrium vacancies is created.

An analysis of the microstructure of hot-rolled steels showed that in the zone of laser irradiation, the grains become larger by 1 ... 3 points (from 8 to 5 ... 6 points, GOST 5639) compared with the initial state, i.e., collective recrystallization occurs. Steels 08Yu and 08kp differ in the chemical composition by the presence of aluminum in the former. After laser treatment in steel 08Yu, the grain size increased by 1...2 points (from 8...10 to 6...7 points), in steel 08kp - by 2...3 points (from 8 to 5...6 points) (Fig. 1, a, b). Such a difference in the degree of grain size increase is associated with the barrier effect of aluminum nitride particles AlN (Fig. 1c). At the moment of laser exposure, inclusions of aluminum nitrides partially dissolve: in these places, the grain boundaries are capable of migration and the grains grow. The laser exposure zone is characterized by the presence of wavy grain boundaries, which in the surface layers are perpendicular to the sample surface. This is due to the direction of exposure and heat removal and causes the appearance of signs of a columnar structure.

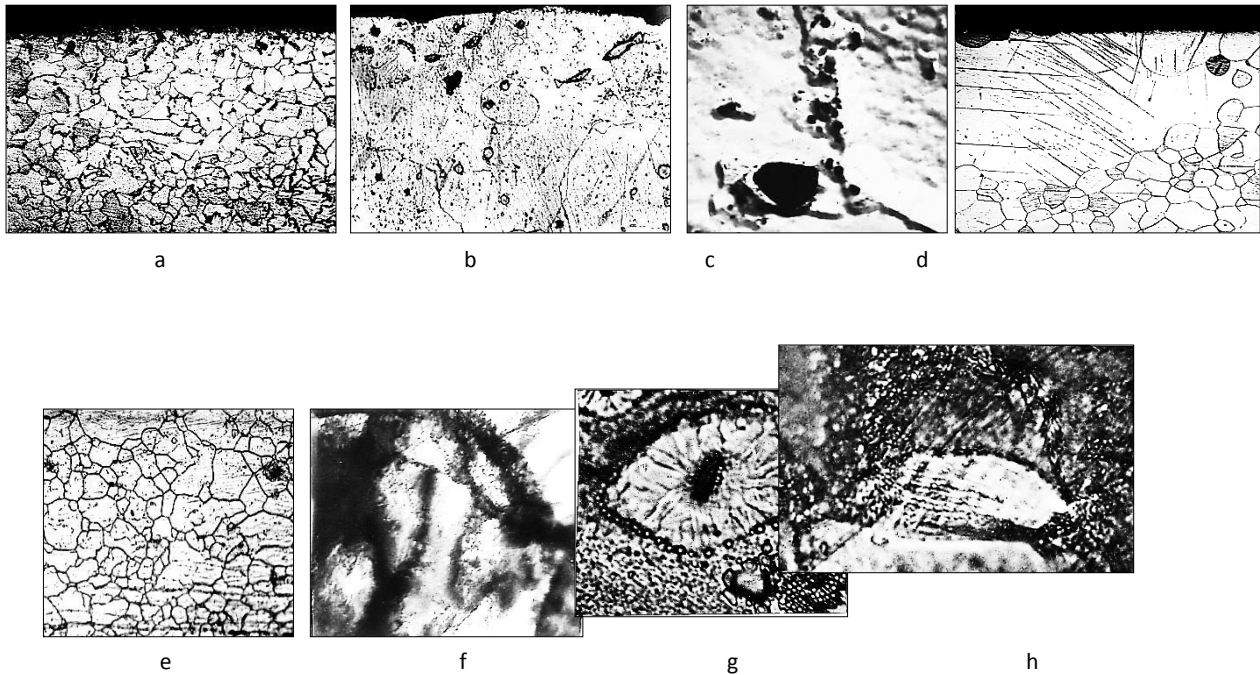


Figure 1. Microstructure of hot-rolled steels 08Yu (a, c, g), 08kp (b, h), E3 (d), 08Kh18N10T (e, f) in the laser impact zone: a, b, d, e, h, $\times 600$, c - $\times 20000$, f - $\times 50000$, g - $\times 1000$.

In E3 steel, ferrite grains increased by one point (from 4 to 3 points). It is known that this steel is practically not prone to collective recrystallization, since the grain boundaries in the alloyed ferrite are inactive due to their fixation by particles of dispersed precipitates and the resulting recrystallization texture [15]. Secondary recrystallization or anomalous grain growth was observed in the zone of laser impact of E3 steel in places with favorably oriented grains (Fig. 1d). In austenitic steel 08H18N10T, the grains also became coarser by 1...2 points (from 9...10 to 7...8 points) in comparison with the initial sizes (Fig. 1, e). In the zone of laser impact, a lot of so-called "dangling" boundaries are visible, which is typical for this steel [16]. In steel 08Yu, fragments of grain boundaries and subboundaries are also visible. Recrystallization under laser action of 08H18N10T and 08Yu steels was accompanied by splitting of the grain boundaries and formation of the special boundaries in their structure. Thus, in the case of laser action, as in conventional annealing, collective recrystallization is suppressed in alloyed ferrite and austenite, but secondary recrystallization develops.

Non-metallic inclusions were the centers of nucleation of recrystallized grains in the steel, as in conventional annealing or any type of high-speed heating [16, 17], while the short time allotted for the relaxation of deformation and thermal stresses creates conditions for the nucleation of several recrystallization nucleus near one inclusion, where recrystallized grains of a specific petal character appear (Fig. 1g).

In the zone of laser impact in all hot-worked steels, the slip lines and microcracks were observed, indicating significant plastic deformation (Fig. 1h). In the grains of E3 steel, a large number of twins of the several systems were found that intersect each other (see Fig. 1, d). In addition, traces of the sliding along several systems were revealed. In some places, the deformation had a clearly vortex (rotational) character, the sliding "torches" were observed at the intersections of twins with each other and with the

grain boundaries, as well as zones of deformation by the dumping. During laser processing, plastic-plastic relaxation in hot-worked steels proceeds by the shear and rotational mechanisms. Observations testify to the high-speed nature of the deformation, which has a number of features: the number of dislocation sources and slip systems increases, and the velocity of dislocations in slip planes increases too [1–4, 15]. The short duration and locality of the laser impact contributes to the constraint of plastic deformation when local plastic rotations of microregions are carried out. The fields of elastic stresses can relax due to plastic rotations of the lattice of conjugated grains. The constraint of plastic stress relaxation under laser irradiation is also due to the specifics of high-speed mass transfer [18, 19], which is realized, in contrast to diffusion processes occurring during conventional heating.

The study of fine structure of steel 08Yu using an electron microscope showed that in the zone of laser action there are areas with dislocation clusters and a developed cellular substructure (Fig. 1f), which occupy 40 and 60% of the area of the studied samples, respectively. The dislocation substructure of steel after laser exposure differs from the initial hot deformation substructure by the presence of small dislocation coils and thin mid-angle subboundaries. The formation of a cellular substructure in the 08Yu steel during laser exposure indicates a significant plastic deformation that has taken place in the grains. In austenitic steel 08H18N10T, the areas of interlacing and flat accumulations of dislocations are also observed, there are zones with a cellular substructure. Table 2 shows the dislocation density in the steels in the hot-rolled state and after laser processing. It can be seen that the density of dislocations in the zone of laser action in all steels increased by two orders of magnitude compared to the hot-rolled state. In addition, laser processing resulted in almost 3-fold refinement of the blocks (from $61 \cdot 10^{-5}$ to $19.5 \cdot 10^{-5}$ cm), which indicates the presence of microdistortions in the crystal lattice of the solid solution.

Table 2. Dislocation density ρ before (1) and after laser exposure (2)

Steel	Dislocation density ρ , cm^{-2}	
	1	2
08Yu	$1,3 \times 10^8$	$3,54 \times 10^{10}$
08Kp	$2,0 \times 10^9$	$1,4 \times 10^{11}$
08H18N10T	$4,6 \times 10^8$	$8,2 \times 10^{10}$

X-ray studies showed that a weakly developed crystallographic texture (110) α arose in the laser impact zone; part of the grains is oriented by this plane parallel to the sample surface.

The mode of laser irradiation used in the present studies was selected empirically in order to exclude heating of the steel above the structure change induced by phase transformation $\alpha \leftrightarrow \gamma$ start point. The proof that no polymorphic transformation occurred under the studied irradiation conditions is evidenced by the following facts:

- steel grains have grown, not crushed. If a polymorphic transformation occurred, and even a double one (during heating and cooling), at such high heating and cooling rates, the many phase transformation centers would arise and the structure would form fine-grained; - the same results were obtained both for steels in which polymorphic transformation is possible (08kp, 08Yu), and for steels where it is excluded (E3, 08KH18N10T), moreover, having a different crystal lattice;
- sulfide inclusions did not melt during heating, but they melt at temperatures above 950 °C [11, 20, 21].

4. Conclusions.

In the zone of laser action of hot-worked steels, structural signs of two processes are observed - collective or secondary recrystallization and high-speed shear or rotational plastic deformation. These processes run in parallel, so it should be considered that at the moment of pulsed laser irradiation, dynamic collective or secondary recrystallization develops in steels. The specific conditions of laser exposure, mainly its short duration and localized powerful energy, ensured the processes of restoring the structure of a dynamic nature.

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Electronic properties of carbon nanostructures

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Abstract: *The properties of an array of carbon nanostructures or a material containing its is differ from the properties of individual components. For bulk array of carbon nanostructures it is unknown to what extent the electrons of each layer participate in conductivity, the role of defects is not defined. properties. So, this work presents some answers to these questions.*

Key words: *carbon nanotubes, electrical properties, composite, mechanical properties*

Introduction

The needs of resources for various industries are growing, this causes resource, technological, environmental and social problems. The exhaustion of fossil fuel and energy sources stimulates the development of methods of using alternative and ecologically safe energy sources, which contributes to their widespread implementation.

Today the shortage of energy resources is partially covered by the use of direct conversion of thermal and radiant energy into electrical energy using photothermoelectric converters (solar cells). But there are a number of limitations here: this type of energy production occupies large areas for its stations. In addition, this type of energy production is conditionally ecological: the production of solar panels and their disposal greatly pollutes the environment.

Carbon nanostructures have a unique anisotropic structure that determines their electronic properties [1-5], a special place is occupied by carbon nanotubes (CNTs), its can be sources of intense self-electron emission [6]. This feature of them, the inertialessness of electron moving along the CNT axis and the tunneling mechanism of their exit, does not require large energy costs. Such materials are of great interest in the field of energy storage and conversion due to their unique properties [7]. It is necessary to descry between the electrical conductivity of individual particles of carbon nanostructures and the conductivity of a composite or material containing such structures.

Today, using of carbon nanomaterials in the energy industry contributes to the improvement of already existing elements and contributed to the development of thermocouples for energy storage systems [8], the main problem of alternative energy sources is that they do not adapt to the demand of energy problems, so the urgent issue is not only in the search for new materials that will expand the possibilities of their application, and it is necessary to simultaneously develop elements for storing this energy. And carbon nanomaterials open up opportunities to solve these problems in both directions [9-13].

Carbon nanomaterials have shown high efficiency when used in solar batteries [14], which confirms the uniqueness of such structures.

Authors of the work [14] showed the possibilities of using carbon nanomaterials in thermoelectric elements. Such materials can serve as thermoelectric generators, and composites based on them increase their characteristics even more.

Defects in CNTs can occur during synthesis (growth defects) or during external exposure, for example, high-energy irradiation.

Experimentally obtained CNTs may contain defects that lead to distortion of their structure and differences in properties. The formation of bent, column-shaped, serpentine CNTs, as well as tubes of variable diameter occurs only in the presence of topological defects, which are associated with

rehybridization and unsaturated bonds [15]. The presence of defects will contribute to the expansion of the spheres of application of carbon nanostructures.

Therefore, the search and research of new materials with increased functional properties for the needs of alternative energy is one of the priority directions for solving the above-mentioned problems. A special place is occupied by carbon-containing materials promising for use in storage devices and direct energy converters.

Experiment

The electrical conductivity of the array of carbon nanotubes was measured in a dielectric cylinder. The latter was filled with nanotubes that were compressed when the piston was lowered. The bottom of the cylinder and the piston were made of copper and served as electrodes. After reaching the maximum compression to a density of $\sim 1.5 \text{ g/cm}^3$, the piston was gradually raised. At the same time, the electrical contact between the nanotubes and the electrodes was maintained, which is due to the elastic relaxation of the previously compressed array of carbon nanotubes. This allowed measuring electrical conductivity during discharge. The termination of the elastic relaxation of nanotubes led to the opening of electrical contacts and a sharp increase in electrical resistance, which was determined by the dependence of electrical conductivity on the density of the material $\sigma(\rho)$.

Multilayer nanotubes in diameter were obtained by chemical vapor deposition (CDV).

Results

Multilayered carbon nanotubes (MCNTs) differ from single-layered ones in a wider variety of shapes and configurations. Most often, these are coaxially nested single-layer nanotubes. Of course, the situation for an array of individual nanotubes or a material consisting of them may be different due to the presence of contacts between adjacent nanotubes, electrodes, contact pressure and other factors. When changing the volume in which an array of electrically conductive CNTs is placed above a certain critical value, the closure of nanotubes may occur with the manifestation of characteristic signs of the percolation transition. The latter, as is known, is a geometric analogue of the metal-insulator transition [16].

The electrical conductivity of multilayer (fig. 1a) and single-layer (fig. 1b) carbon nanotubes was studied. In accordance with the basic assumption of transmission electron microscopy that the contrast intensity of images directly depends on the amount of scattering substance, so darker areas in positive images correspond to thicker areas of the sample or heavier atoms present in the sample, the observed narrow dark bands refer to the walls of the nanotube.

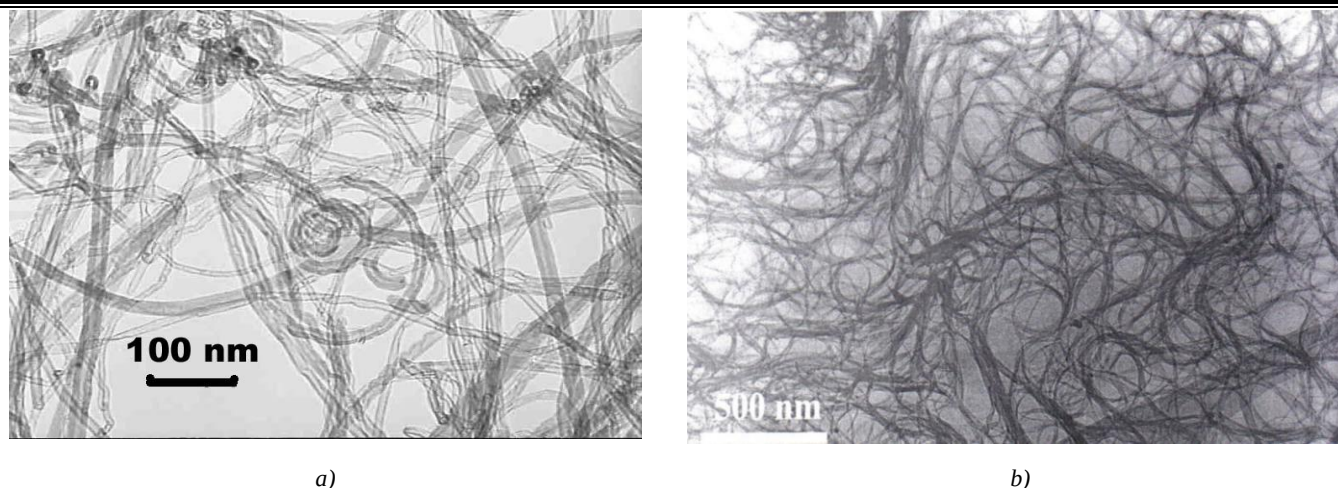


Fig. 1 – TEM image of multilayer (a) and single-layer (b) carbon nanotubes

The statistical distribution of MCNT by outer diameter showed that the diameter of its is in the range of 7-25 nm. Most tubes have a diameter of 9-15 nm. The thickness of the CNT walls varies between 3 and 4 nm. Nanotubes have 5-17 carbon layers, with the most likely value of 9 carbon layers (fig. 1a).

Single-layer CNTs were obtained by electric arc evaporation on a Ni/Y catalyst (fig. 1 b). Cleaning was carried out by oxidation in air and washed in HCl solution, without the use of surface-active substances. The specific gravity of CNT is 93-94%. The main impurities are graphite particles with a size of 2-4 μm and impurities of metals Ni, Y, Cu, Zn ($\Sigma = 1.3\%$). The specific surface area is 375 m^2/g , the proportion of open nanotubes is 24%.

When the volume in which the interacting nanotubes are placed decreases, the electrical circuit closes and the system (nanotube-air) goes into a conductive state, which corresponds to the dielectric-metal transition.

Fig. 2 shows the dependence of the electrical conductivity of an array of arbitrarily oriented CNTs on its density. At the initial stage of compression, the regrouping of nanotubes occurs, the density of their packing increases, which leads to the closing of the electrodes and the appearance of electrical conductivity in the region of the percolation transition. It can be seen that the initial density of the array of interacting CNTs, which is sufficient for measuring electrical conductivity and at which the transition to the conductive state occurs, is 0.13 g/cm^3 .

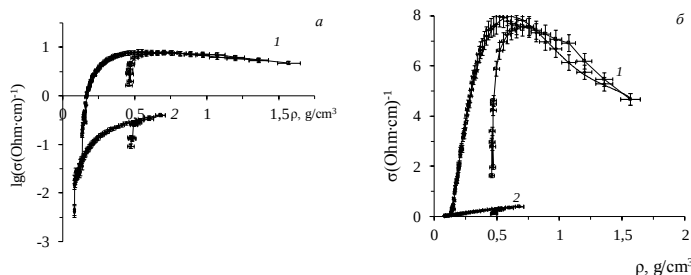


Fig. 2 – Dependence of the electrical conductivity of an array of single-layer and multilayer CNTs in the process of compression deformation. a – along of the ordinate axis is $\lg \sigma$, b – the real value of σ . 1 – SCNT, 2 – MCNT, ♦ - loading, □ - unloading

During the compression under the piston, the electrical conductivity jumps up by 3 orders of magnitude, reaching a maximum value of 8.0 $(\Omega \cdot \text{cm})^{-1}$ at a density of 0.5 g/cm^3 . Subsequent compression to a density of 1.6 g/cm^3 leads to a decrease in electrical conductivity to 4 $(\Omega \cdot \text{cm})^{-1}$. Deformation leads to the appearance of mechanical stresses, which contribute to the appearance of additional potentials, at which conduction electrons are scattered during the passage of current. This causes a drop in electrical conductivity.

The observed effects (fig. 2) are explained by the action of two competing mechanisms: 1) an increase in the total contact area between neighboring CNTs, which contributes to the growth of electrical conductivity; 2) elastic deformation, which contributes to a decrease in electrical conductivity.

After compressing the sample to $\rho \approx 1.6 \text{ g}/\text{cm}^3$, the piston was raised and simultaneously measured the electrical conductivity of the elastically relaxing material, which is restored to the

maximum value and ensures contact with the electrodes. The reverse course of the curve $\sigma(\rho)$ in the process of elastic relaxation of the CNT repeats the course of the curve during compression on a large segment of the piston path. Completion of the relaxation process was recorded by a sharp increase in electrical resistance $\sigma(\rho)$ and opening of the electrical circuit. This process was fixed by the density of the relaxation transition. The appearance of hysteresis between the transition to the conducting state and the relaxation transition is caused by inelastic processes that are associated with the displacement of nanotubes during deformation.

The electrical conductivity of SCNTs was 1.5 orders of magnitude lower than that of MWNTs (fig. 2). The density of the transition to the conducting state decreases to 0.08 g/cm^3 , but they have a much lower elastic limit (30%).

This difference in electrical conductivity is due to the different type of conductivity in CNTs.

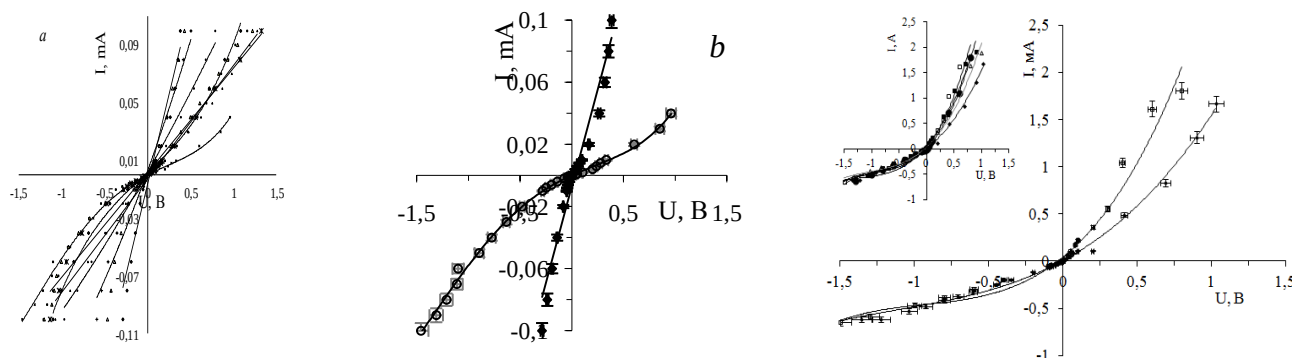


Fig. 3 – VCC of MCNT for different compression densities of the array. *a* – range of densities $\rho=0.13-0.51 \text{ g/cm}^3$, *b* – at minimum and maximum compression density. $\blacktriangle$ – $\rho=0.13 \text{ g/cm}^3$, $\blacksquare$ – $\rho=0.136 \text{ g/cm}^3$, $\triangle$ – $\rho=0.147 \text{ g/cm}^3$, $\circ$ – $\rho=0.15 \text{ g/cm}^3$, $\bullet$ – $\rho=0.155 \text{ g/cm}^3$, $\diamond$ – $\rho=0.18 \text{ g/cm}^3$, $+$ – $\rho=0.26 \text{ g/cm}^3$, Δ – $\rho=0.35 \text{ g/cm}^3$, $\blacklozenge$ – $\rho=0.51 \text{ g/cm}^3$; *c* – SCNT: *a* – current-voltage characteristics for different compression densities of the CNT array $\blacklozenge$ – $\rho=0.51 \text{ g/cm}^3$, Δ – $\rho=0.60 \text{ g/cm}^3$, $\blacksquare$ – $\rho=0.68 \text{ g/cm}^3$, $\bullet$ – $\rho=0.78 \text{ g/cm}^3$, $\square$ – $\rho=0.92 \text{ g/cm}^3$

The study of the current-current characteristics (VCC) for different compression densities of the CNT array showed that the VCC of the bulk MCNT array during the compression process was not always linear in nature: at a density of up to $\rho=0.35 \text{ g/cm}^3$, the VCC has a nonlinear symmetrical appearance, which indicates van der Waals interaction in the array of CNTs at a certain density (fig. 3 *a*). With the subsequent increase in density and maximum compression, the I-V characteristic is linear (fig. 3, *b*). This behavior of the VCC confirms the close relationship between the electrical properties of CNTs and the mechanical load.

SCNT have an asymmetric VCC for all compression densities in the range of $\rho=0.51-0.92 \text{ g/cm}^3$ (Fig. 3c), which indicates the semiconducting nature of the conductivity.

Conclusions

In the process of deformation of an array of unoriented MWNTs, the electrical conductivity jumps up by 3 orders of magnitude, reaches a maximum $(8 \text{ } \Omega \cdot \text{cm})^{-1}$ at a density of $\rho=0.5 \text{ g/cm}^3$ and decreases by a factor of two upon further compression. The observed effects are explained by the action of two competing mechanisms: 1) an increase in the total area of van der Waals contacts between the outer shells of neighboring CNTs, which leads to an increase in electrical conductivity; 2) elastic deformation of CNTs, which leads to a decrease in electrical conductivity.

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Pressure-induced long-time phase transitions in selected chosen vegetable oils

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Abstract: Research on vegetable oils was already carried out in the industrial era. Oils are used not only in the food industry, but also in the cosmetics and pharmaceutical industries. Due to the beneficial effect on the human body, they have been studied more and more thoroughly. The development of high pressure food preservation has further accelerated this process. Due to the use of pressure in the production and preservation of food, it turned out to be important to study the phase transitions induced by pressure in these oils. Due to their long-term nature, these transformations may damage the machines used in the industry. So far well-researched vegetable oils in this regard are castor oil, rapeseed oil, soybean oil, sunflower oil and olive oil. Research on other oils will be conducted in the future.

Introduction

Vegetable oils are one of the substances produced by man for the longest time. In antiquity, they were produced, among others, in China, India, Egypt, Greece and Rome. Even then, their beneficial influence on human health was known. They were an ingredient of many dishes, they were used as a natural medicine and used for body care. The health-promoting effect of vegetable oils on the human body is also widely discussed today [1-4].

Of great importance for example olive oil, the myth of the protection of Athens may prove. The scene depicting this mythical event was presented, among others in the center of the west tympanum of the Parthenon (temple dedicated to the goddess Athena) located on the Acropolis in Athens [5].

The ancient Egyptians also used oils in many ways for example, as a "sunscreen" to protect against sunburn.

Oils were extruded originally using cloth bags, to which sticks were attached and the whole thing was tightly twisted until the juice ran out. Olives placed on canvas, in a stone hole, with wooden hammers, were also churned. The juice, on the other hand, was collected under the cloth. It was also possible to put olives in a cloth, tied bag and tread them [6]. Later, much more productive methods of obtaining oils appeared. Heavy stone rollers were rolled over the seeds or olives. Then, millstones were used to obtain oils [6]. Eventually, presses began to be used for the production of oil. These were lever and screw presses and wedge-shaped and finally hydraulic. With the advent of the industrial revolution, these presses began to be driven mechanically, thermodynamically and eventually electrically. The industrial production of oils resulted in lower prices and greater availability.

All this made people more interested in oils. Their physical, chemical and medical properties began to be explored. It turned out that they can be used not only in the food industry, but also in the cosmetics and pharmaceutical industries.

Research on oils

Vegetable oils were very valuable and very unstable at the same time. They broke quickly. Research has shown that not only microbes and pollution, but also the access of air or sunlight have a negative impact on their condition. For this reason, good quality oils were sealed in dark glass bottles. Research has also begun on how to get rid of microorganisms from oils without depriving them of such valuable nutrients. The use of ultraviolet and then X-rays caused the breakdown of many molecular bonds and impoverished the composition of the oil. The oil was heated as well. Cold-pressed oil is of a higher quality than hot-pressed oil for a reason [7-9]. Additionally, these two pasteurization methods resulted in the formation of new, often poisonous substances in the oil. So other methods of preservation were sought. Ultimately, due to the fact that the oils were produced using pressure, it was decided to check whether this preservation could not be obtained with the high-pressure method. It turned out that this method is not only effective in killing microorganisms, but also (if properly carried out) allows to preserve the nutrients of oils and at the same time does not create new hazardous substances. This resulted in the rapid development of high-pressure food preservation methods, which continues to this day [10-18].

Research on vegetable oils has been conducted at the Warsaw University of Technology since 1975. They were initially devoted to the selection of fluids for piston high pressure standards. Since the rheological parameters of the working fluid constitute a significant part of the formula defining the effective piston cross-section of such a standard, the tests of compressibility and viscosity of castor oil, commonly recommended for this application, were started. These were the classic measurements of density and viscosity carried out in the range up to approx. 0.3 GPa. Initially, these studies did not show any phase transitions. Phase transitions for vegetable oils were observed for the first time in castor oil in 1989 [19].

Phase transitions caused by temperature changes in oils have been known for a long time [20-24], while such a pressure-induced transformation has not been observed before.

Initially, attempts were made to explain the observed transformation with the properties of fatty acids whose acid residues constituted the triglyceride chains of castor oil. For this reason, studies of pressure changes in oleic, linoleic and other acids have been carried out [25-30].

Monoglycerides [31] and diglycerides of fatty acids [32-36] have also been studied.

Initially, the influence of pressure was limited to the study of PVT (pressure-volume-temperature) characteristics [37-38]. Significant progress was later made [39-40] by optical observation of pressure-induced crystallization of triglycerides. The properties of edible oils were also tested in high-pressure laboratories. These experiments were a continuation of previous studies on changes in pressure physical properties of castor oil [41]. Measurements of optical properties of triglycerides [42] showed the occurrence of the first kind of phase transitions. The phenomenon of pressure-induced phase transformation has been studied by many methods, showing discontinuous changes in volume [43], refractive index [42], dielectric permittivity [44] and viscosity [45-48] during the phase transition. Most of these effects are summarized in [41]. Further progress was achieved thanks to the study of pressure changes in the triolein [38, 47, 49-53]. These studies showed similar phase changes as in castor oil. Both of these substances are mixtures of fatty acid triglycerides. On this basis, the occurrence of a phase change was predicted in a wide class of edible oils with the above properties [54-60]. These predictions were confirmed by observations of phase transformations in rapeseed oil [54-55]. Moreover, the measurements of the dependence $V(p)$ (volume from pressure) and $\epsilon(p)$ (relative permittivity from pressure) were performed for soybean oil [56], showing similar behavior. All these transformations taking place in oils showed a long-time character (these transformations lasted much longer than for standard substances - even several days). In the meantime, physical research on the quality of oils (including olive oil) began [61, 62]. Therefore, sunflower oil and olive oil were selected for further high-pressure tests carried out by me. As part of these tests, measurements of mechanical properties were made, which confirmed the occurrence of long-time phase transitions in these oils. Electrical quantities were tested for the same oils (in terms of composition) [63-67]. The previously used method of testing phase transitions in vegetable oils based on the measurement of electric permittivity has been developed much more precisely. The physical causes of changes in the values of electric parameters of oils were established. The

change in the value of electric permittivity was related both to the concentration of molecules, their shape and their mutual position [68]. Resistivity was used for the first time to study phase transitions. Changes in its value have been carefully analyzed and related to changes in the arrangement, shape, size and decay rate of ion channels. Also for the first time to analyze phase changes in vegetable oils, electrical phase diagrams were used along with impedance changes contained in them. These charts are arranged in characteristic shapes resembling triangles. All these electrical methods (based on the measurement of permittivity, resistivity as well as with the use of impedance phase diagrams) showed high sensitivity to physical processes occurring during phase transitions. They also turned out to be resistant to external factors (except the pressure chamber). These methods also turned out to be one of the easiest to use. Providing clear and distinct results, unlike, for example, temperature measurements. This is due to the long-time phase transformations taking place in oils [54-60, 63-67].

Summary and conclusions

Vegetable oils have been produced since ancient times and were valued in many ancient countries [5]. Today they are also valued for their pro-health properties [1-4]. Vegetable oils have always been pressed from seeds or fruit, and the methods of pressing them have evolved over time [6]. At one point, the oils were investigated and it was discovered that the rate of their deterioration was influenced not only by microorganisms but also by light and air. Therefore, appropriate maintenance methods were applied. Some of them based on heating and radiation have turned out to be harmful. For this reason, a method of pressure oil preservation has been developed, which allows to preserve their nutritional value [10-18]. Pressurized extracting and preservation of oils contributed to the acceleration of research on pressure-induced phase transitions in vegetable oils.

So far, the components of vegetable oils, including fatty acids [25-31], diglycerides [32-36], and triglycerides [38-41, 47-52], have been well researched in terms of pressure-induced phase changes. Some oils have also been well researched in this respect, including: castor [19, 42-46], rapeseed [54-55], soybean [56], sunflower [57, 66-67] and olive oil [58-65]. The remaining oils are still not well researched in this regard and will likely be tested in the future.

These studies were carried out using, inter alia, thermodynamic [31, 37, 43, 63, 66], ultrasonic [32, 34, 35, 48, 59], resonance [64], optical [36, 42, 58, 61, 62], x-ray [25] and electric [29, 30, 44, 65, 67] methods.

Due to the long-time nature of phase transformations occurring in vegetable oils, a rapid change in the physical properties of the oil during them and the use of pressure for their extracting and preservation, the constant expansion of knowledge about these changes is crucial for the safe operation of machines, both in the food, cosmetic and pharmaceutical industries.

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The Electrothermal Processes During High-voltage Electric Pulse Consolidation of Refractory Powder Materials

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Abstract: The main features of high-voltage electric pulse consolidation (HVC) of refractory powder materials and the resulting unique capabilities of the method are considered. The electro-thermal processes of HVC at the contacts between powder particles and at the macroscale of the entire consolidated sample are analyzed. The results of experimental studies of the parameters of high-voltage electrical impulse action in the processes of consolidation of high-temperature powder compositions, high-voltage welding of dissimilar materials, as well as high-voltage discharges in liquid are presented. The results of measuring the intensity of thermal radiation of the investigated materials under high-voltage electrical impulse action, recorded by the method of pulse photometry using photodiode sensors, which, together with the Rogowski coil, are components of the measuring complex developed by the authors, are presented.

Keywords: HIGH-VOLTAGE ELECTRIC PULSE CONSOLIDATION, REFRACTORY POWDER MATERIALS, ELECTROTHERMAL PROCESSES

1. Introduction

The method of high-voltage consolidation of powders is effective for the production of refractory composite materials that retain their strength properties at ultrahigh temperatures under aggressive external influences. The short duration of high-temperature exposure in the process of high-voltage consolidation makes it possible to preserve the structural-phase state of the initial powder material in the consolidated compact material. A feature of this method is the high density concentration of the released energy in the area of contacts between powder particles. The initial state of the surface of powder particles (the thickness and structure of oxide films, the presence of foreign impurities, etc.), the shape of powder particles and their sizes significantly affect the regularities of high-voltage consolidation process. Along with the characteristics of the powder, the determining factors are: the rate of input of the energy of the electromagnetic field into the powder material, the magnitude and nature of the mechanical pressure acting on the powder blank during high-voltage consolidation. The high energy density in the particle contact zones leads to a local change in the state of aggregation of the powder substance in these zones. Along with the inhomogeneity of powder heating in interparticle contacts, a macroscopically inhomogeneous distribution of the current density in the volume of the consolidated sample is possible. The formation of the structure of a powder material during high-voltage consolidation is determined by processes of different scales occurring at interparticle contacts, in powder particles, in the bulk of the entire sample, and by the mutual influence of these processes. The advantages of the high-voltage consolidation method can be fully realized with optimal process parameters, since intense electro-thermal action on the powder material can lead to instability of the consolidation process, the formation of an inhomogeneous structure of the material to be consolidated, and even to the destruction of the consolidated sample and technological equipment. The study of electro-thermal phenomena, both in the particle contact zones and on the scale of the entire consolidated sample, makes it possible to establish the optimal parameters of high-voltage consolidation.

2. Theoretical analysis

As a result of theoretical analysis of electro-thermal processes in contacts between powder particles during high-voltage consolidation [1], the threshold value of the current density j^* in the interparticle contact was established, the excess of which causes an electrothermal explosion:

$$j^* = \sqrt{\frac{2\xi\sigma}{\rho h}} T_b^2, \quad (1)$$

where: σ is the Stefan-Boltzmann constant; $\xi \leq 1$; T_b is the boiling point (loss of conductivity) of the powder material, ρ is the resistivity of the material, h is the thickness of the interparticle contact. The validity of criterion (1) was confirmed experimentally on grains of the nickel heat-resistant alloy (EP741), and the results were published in [2]. Non-uniform heating of the powder material in the consolidated sample may be due to the non-uniform distribution of the current density along the radius of the cylindrical sample. This phenomenon is associated with the displacement of the current to the periphery as a result of the skin effect, as well as with a change in the conductivity of the powder during the flow of a powerful current pulse through it. The thickness of the skin layer - Δ is determined by the expression:

$$\Delta = (\sqrt{\mu\mu_0\omega/\rho})^{-1}, \quad (2)$$

where: μ – relative magnetic permeability, $\mu_0=4\pi\cdot 10^{-7}$ H/m, ρ – powder resistivity, ω – current pulse frequency. To obtain a consolidated sample with a uniform density, a uniform distribution of energy over the volume of the sample is necessary. The uniform distribution of the input energy is possible if the condition $R \leq \Delta$ is satisfied, where R is the radius of the cylindrical sample. For example, for current pulses with a discharge frequency $\omega = 10$ kHz, and for samples made of hard alloy powder (WC-Co20%) with a radius $R = 5$ mm, the value of the parameter $R/\Delta = 0.4$, which ensures a fairly uniform distribution of the input energy along the radius of the sample. The temperature distribution along the height of the consolidated sample is determined by heat removal to the punch electrodes. As an example, Figure 1 shows the results of calculating the temperature in a hard alloy sample (WC-Co20%) for various times.

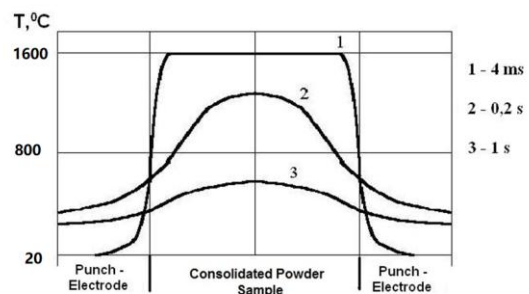


Fig. 1. Temperature distribution along the axis of the consolidated sample.

The calculation results (Figure 1) clearly show that the effect of heat removal during the first 4 ms manifests itself only in a narrow near-surface zone (200–300 microns) of the sample in contact with the punches. The short duration of exposure to high temperatures on

the consolidated powder material prevents grain growth and ensures the preservation of the original microstructure of the powder particles in the consolidated material.

3. Experimental method

High-voltage consolidation uses the constant pressure and high voltage pulse electric current to provide the resistive heating of powder sample by Joule effect. High voltage pulse electric current are generated by experimental equipment described in [3]. Registration of the parameters of a high-voltage current pulse and the intensity of thermal radiation of the consolidated powder materials was carried out using a measuring complex developed by the authors. This complex consists of a Rogowski coil with an integrating circuit, which registers the parameters of a high-voltage current pulse, photodiode sensors that register the intensity of thermal radiation, which is transmitted through a special optical waveguide from the consolidated powder materials, systems for triggering and synchronizing the components of the measuring complex. The radiation during high-voltage electric pulse consolidation of powder materials was recorded by a calibrated photodetector with a maximum sensitivity in the spectral range of 800–900 nm based on a silicon photodiode (FD-21 KP) with a fiber optic light guide diameter 1.5 mm. To calibrate the photodetector, a light-measuring tungsten tape lamp (SI 10-300U No. 70) calibrated for the spectral density of the energy brightness of radiation in the region from 300 nm to 2500 nm was used. A schematic diagram of the measurement of powder thermal radiation is shown in Fig. 2.

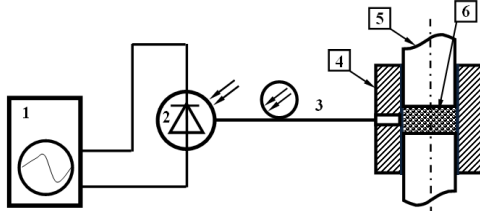


Fig. 2. Scheme for measuring the thermal radiation of a powder during electropulse consolidation.

1 - oscilloscope; 2 - photodiode; 3 - optical fiber (light guide); 4 - dielectric die; 5 - electrodes-punches; 6 - powder

The dielectric die is a hollow ceramic cylinder with a height of 30 mm, an inner diameter of 10 mm, and an outer diameter of 30 mm. The height of the powder filling is 10 mm. The compressive force of the punch electrodes provides a pressure on the powder of 20–25 MPa.

4. Results and Discussion

Testing of the measuring complex for recording electro-thermal parameters of high-voltage consolidation was carried out in experiments with copper powder. Fig. 3 and 4 show synchronous oscillograms of current pulses recorded using a Rogowski coil (in Fig. 3 the maximum value corresponds to current amplitude of 41 kA, and in Fig. 4 - 94 kA) and oscillograms of signals from a photodetector that registers the radiation of a powder material during consolidation process.

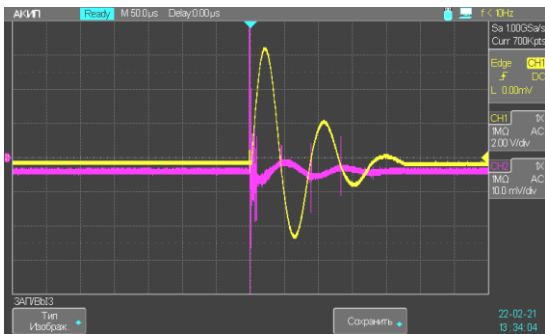


Fig. 3. Synchronous oscillograms of current pulses (CH1) and the radiation of a powder material (CH2) during consolidation process (capacitive energy storage voltage $U_{max} = 1.5$ kV).



Fig. 4. Synchronous oscillograms of current pulses (CH1) and the radiation of a powder material (CH2) during consolidation process (capacitive energy storage voltage $U_{max} = 3$ kV).

The radiation brightness of the studied sample B_{exp} was determined by comparison with the brightness of the reference sample B_{ref} , taking into account the corresponding solid angles Ω_{ref} and Ω_{exp} , the cross sections of the optical fiber (receiver) during calibration S_{et} and in the experiment S_{exp} , as well as the amplitudes of the photodetector signals during calibration U_{ref} and during experiments U_{exp} according to the following formula (3):

$$B_{exp} = B_{ref} \times \frac{\Omega_{ref} \cdot S_{ref} \cdot U_{exp}}{\Omega_{exp} \cdot S_{exp} \cdot U_{ref}} \quad (3)$$

The experimental value of the radiation brightness of the studied sample B_{exp} obtained in this way was compared with the brightness of the black body radiation at the effective wavelength of the calibrated photodetector (900 nm) using the Wien formula, which is true for the conditions of our experiments. Thus, from the ratio for the brightness of black body radiation (Wien's formula):

$$B_{exp} = \frac{2\pi hc^2}{\lambda^5} \times e^{\frac{hc}{\lambda kT}}, \quad (4)$$

where h is Planck's constant, c is the speed of light, λ is the radiation wavelength, k is Boltzmann's constant, and T is the desired brightness temperature of the source under study.

Based on the above approach, when processing the data of test experiments on electropulse consolidation of copper powder when charging the energy storage device to 3 kV, we obtain the amplitude value of the brightness temperature of the sintered sample of 1465 K, which slightly exceeds the value of the copper melting temperature of 1356 K under stationary conditions. When the voltage on the energy storage device decreases to 1.5 kV, the amplitude value of the brightness temperature of the consolidated copper sample, determined by this method, drops to 1366 K, which is only 10 degrees higher than the melting point of copper under stationary conditions.

Testing of the measuring complex capable of recording the electrothermal parameters of the impact on materials by a high-voltage current pulse was also carried out in experiments on high-voltage welding of dissimilar materials and in electric discharges in water.



Fig. 5. Synchronous oscillograms of current pulse (CH1) and the radiation (CH2) of the contact zone of Fe-Cu metal welding (capacitive energy storage voltage $U_{max} = 2.2$ kV).

Fig. 5 shows synchronous oscillograms of a current pulse (the maximum value corresponds to current amplitude of 29 kA) and a photodetector signal that records the radiation of the contact zone of Fe-Cu metal welding.

Certain values of the brightness temperature of the area of resistance welding of Cu-Fe in air are $T = 2048 \pm 50$ K. It should be noted that the obtained values of the brightness temperature in the area of contact welding significantly exceed the melting temperatures of copper and iron under stationary conditions in air.

With an electric pulse discharge in water, an expanding brightly luminous gas-vapor bubble is formed with hot vapors of water and electrode material, the dimensions of which are many times greater than the dimensions of the input window of the photodetector. This leads to an overestimation of the value of the spectral brightness of the discharge region, and, as a result, to an overestimated value of the brightness temperature of the discharge region. In addition, under the conditions of an electric pulse discharge in water, a noticeable contribution from the radiation of the intense spectral line of oxygen at 777 nm is possible, which can also lead to an overestimation of the brightness temperature measured by a calibrated photodiode with a maximum spectral sensitivity of the photodetector in the region of ~ 900 nm. Therefore, the obtained value of the brightness temperature of the electric pulse discharge in water $T = 4140$ K is overestimated.

Fig. 6 shows synchronous oscillograms of a current pulse (the maximum value corresponds to a current amplitude of 8.8 kA) and a photodetector signal that records the radiation of electropulse discharge in water.

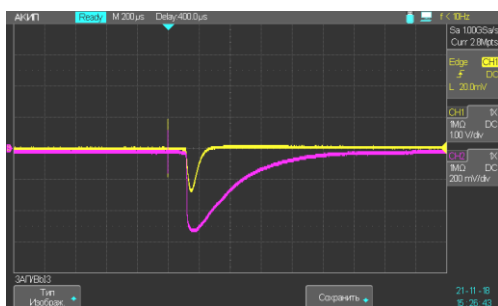


Fig. 6. Synchronous oscillograms of current pulse (CH1) and the radiation (CH2) of the electropulse discharge in water (capacitive energy storage voltage $U_{max} = 1.5$ kV).

Experimental studies of the parameters of high-voltage electric impulse action during the consolidation of high-temperature HfC powder compositions have been carried out. As an example, Fig. 7 and 8 show the microstructures of consolidated HfC samples in various modes of high-voltage consolidation.

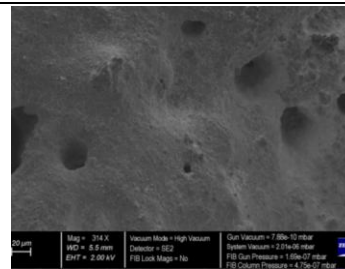


Fig. 7. The structure of HfC consolidated at the cumulative mode.

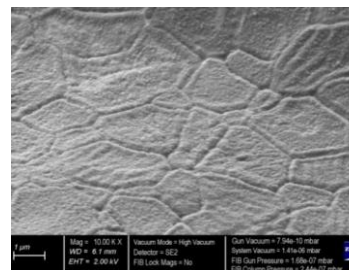


Fig. 8. The structure of HfC consolidated at the optimum mode.

Fig. 7 shows a photograph of the microstructure of a hafnium carbide sample obtained in the cumulative mode [1] of high-voltage consolidation. The optimal mode of high-voltage consolidation of HfC powder makes it possible to obtain a high-density consolidated sample, the microstructure of which is shown in Fig. 8.

5. Conclusion

It is worth mentioning that the fabrication of high-density refractory samples by the HVC method requires accurate identification of the optimal values of the pulsed current amplitude applied to the specimen since the optimal values of this parameter are close to the critical ones, which define the boundary between stable and unstable modes of HVC.

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The effects of graphite additive on hydrogen sorption/desorption behavior by the Mg/C composite

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Abstract: The reactive ball milling technique was applied to fabricate the Mg-based composite with graphite additives. The sorption/desorption kinetics of the composites were investigated under isothermal conditions. The best hydrogen sorption/desorption kinetics was attained for the magnesium-carbon composite synthesized using the low surface area graphite powder as an active additive. This sample is characterised by the best kinetics performance compared to other composites. It releases 4.2 wt.% of hydrogen at 270 °C within ~18 min and uptakes 4.6 wt.% of hydrogen for ~130 min at 200 °C.

Keywords: HYDROGEN STORAGE, Mg, GRAPHITE ADDITIVE, SORPTION/DESORPTION

1. Introduction

The most ecologically clean source of energy is hydrogen. Its combustion in the heated element leads only to the formation of water, which prevents pollution of the environment by combustion products. However, several drawbacks prevent the widespread use of hydrogen. One of these obstacles is the development of efficient and safe hydrogen storage systems, which is associated with its low density (gaseous state $\sim 0.09 \text{ kg/m}^3$), low liquefaction temperature, and high explosiveness [1]. The requirements of the US Department of Energy (DOE) are guided during the development of promising hydrogen storage systems [2]. There are several ways of storing and transporting hydrogen [3, 4], namely in:

- a gaseous state under pressure (high pressure cylinders);
- a liquid state in cryogenic containers;
- the solid-phase bound state in metal hydrides;
- an adsorbed state on cryoadsorbents at low temperatures;
- a chemically bound state in liquid media;
- combined systems.

However, none of the above hydrogen storage methods meets the requirements of the Department of Energy. Developing a safe, efficient, and cost-effective way to store hydrogen is an important task.

The metal/intermetallic hydrides are the most suitable and promising method to store and transport hydrogen in large amounts. Some of these compounds have fast hydrogen uptake/desorption kinetics at near-ambient temperatures, a simple activation process, and moderate hydrogenation pressure. However, most of them have a low hydrogen capacity [5-8].

One of the most promising candidates for long-term hydrogen storage and transport is magnesium due to its high theoretical reversible hydrogen storage capacity (7.6 wt. %) and low cost [9]. Moreover, magnesium is widely distributed in nature, non-toxic and safe to use when preventing its oxidation. The equilibrium modification of MgH_2 is a tetragonal $\alpha\text{-MgH}_2$ phase. Under the high pressure impact, $\alpha\text{-MgH}_2$ undergoes polymorphic transformations with the formation of two modifications: $\gamma\text{-MgH}_2$ and $\beta\text{-MgH}_2$, which have a rhombic structure and a hexagonal structure, respectively [10]. However, some drawbacks limit the practical use of MgH_2 as a hydrogen storage medium. These include high values of operating temperatures $\sim 300^\circ\text{C}$, slow sorption/desorption kinetics, difficulty of activation, and deterioration of properties during cycling [11]. Various methods have been offered to overwhelm the disadvantages pointed out above. The mechanical activation of magnesium with various additives/catalysts attracts particular attention. The mechanical activation process provides the controllable synthesis of the nanosized materials distinguished by "softer" hydrogen sorption/desorption modes. The catalytic additives significantly reduce the operating temperatures and facilitate the kinetics of interaction between hydrogen and magnesium [12-18], also.

In this paper, we used graphite powders with different specific surface areas as an active additive to magnesium. The samples were synthesized by reactive ball milling under a hydrogen atmosphere.

2. Materials and method

The reactive ball milling technique under hydrogen (Fritsch Pulverisette P-6 ball mill) was applied to fabricate Mg-based composites. A special stainless steel milling bowl was designed to execute the mechanical activation procedure under a high-pressure hydrogen medium. The composition of the samples and specific surface area values ($S_{\text{BET}}(\text{C})$) of the used graphitic powders are listed in table 1. The total duration of ball milling process for all samples was 30 hours. The milling process was divided into 15 min intervals to prevent the grinding container from overheating. Every 15 min milling interval was followed by a 1 min pause. The speed of rotation of the grinding container (n) and the ratio of the mass of the balls to the mass of the powder ($m_b : m_p$) were unchanged in all experiments and were $n = 400 \text{ rpm}$. and $m_b : m_p = 30 : 1$, respectively. X-ray diffraction studies are carried out on the standard diffractometer with filtered Co K_α radiations in the Bragg-Brentano geometry. The interaction of magnesium-based composites with hydrogen was investigated on a homemade Sievert-type apparatus under isothermal conditions.

Table 1: Chemical composition of samples.

Sample №	The composition of the composite, wt. %		$S_{\text{BET}}(\text{C})$, m^2/g
	Mg	C (graphite)	
Mg-C0	100	-	-
Mg-C1	90	10	8,135
Mg-C2	90	10	329

3. Result and discussion

The XRD patterns of as-milled Mg-based composite are shown in Fig. 1.

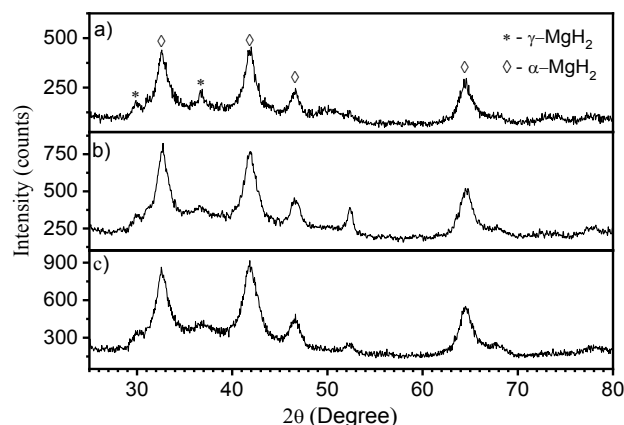


Fig. 1 XRD pattern of as-milled Mg-based composite: a – Mg-C0; b – Mg-C1; c – Mg-C2.

It should be noted the all samples have wide diffraction maximums with positions close to γ -MgH₂ and α -MgH₂ phases. It has been found by the Rietveld refinement procedure the graphite-free sample (Fig. 1, a) contains two phases: ~ 63 wt.% of α -MgH₂ and ~ 37 wt.% of γ -MgH₂. The crystallite sizes are 150 and 100 Å for α -MgH₂ and γ -MgH₂, respectively. Graphite additive with the 8.1 m²/g surface area to magnesium leads to decreases ~ 53 wt.% of α -MgH₂ phase in a composite Mg-C1 (Fig. 1, b). However, the percentage of the γ -MgH₂ phase in the Mg-C1 sample rises to ~ 47 wt.%. The crystallite size for α -MgH₂ and γ -MgH₂ hydrides are 100 and 30 Å, respectively. The Mg-C2 composite which contains graphite additive with the 329 m²/g surface area has ~ 60 wt.% of α -MgH₂ and ~ 40 wt.% γ -MgH₂ phase (Fig. 1, c). The crystallite size for both phases is 100 Å.

The hydrogen sorption/desorption kinetics of the Mg-based composites was examined under isothermal conditions by Sievert's technique for as-milled and activated samples at 300 and 270 °C, respectively. Kinetics measurements were executed for the temperatures when the fastest hydrogen uptake/release processes were.

Fig. 2 shows the hydrogen desorption curves at 300 °C for the as-milled Mg-C composites and pure Mg.

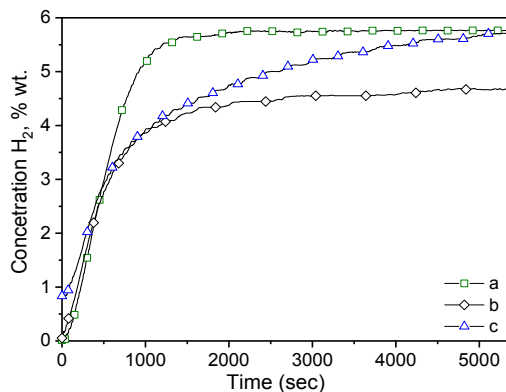


Fig. 2 Desorption of hydrogen in isothermal conditions at $T=300$ °C for as-milled composites: a – Mg-C0; b – Mg-C1; c – Mg-C2.

It is clear, that the best hydrogen kinetics and capacity are for the as-prepared graphite-free sample Mg-C0 (see Fig. 2, a). This sample desorbs 5.7 wt.% of hydrogen within 30 min at 300 °C. In contrast to the graphite-free sample, the graphite-containing ones show sluggish hydrogen release kinetics. So, the graphite containing samples Mg-C1 (Fig. 2, b) and Mg-C2 (Fig. 2, c) desorb 4.65 wt.% and 5.7 wt.% of H₂ more than twice slower for 80 and 85 min, respectively. It is worth noting that as-prepared composites Mg-C1 and Mg-C2 can release less hydrogen capacity and exhibit worse kinetics compared to pure magnesium.

After the activation of the samples, the behaviour of the hydrogen desorption curves is significantly different from the non-activated ones. Fig. 3 shows the hydrogen desorption curves recorded for the activated samples at 270 °C. A catalytic effect of graphite additive with different specific surface areas on the desorption process is noticeable. It can be seen that graphite less sample Mg-C0 (Fig. 3, a) at this temperature can desorb ~ 4.64 wt.% hydrogen for 57 min. Under the same conditions, Mg-C2 composite releases ~ 4.6 wt.% hydrogen within 59 min (Fig. 3, b). Thus, it is clear that the graphite powder with a specific surface area of 329 m²/g affects the hydrogen desorption kinetics negligibly. The composite Mg-C1 with a small surface area of graphite additive ~ 8.1 m²/g demonstrates an increased rate of dehydrogenation compared to other samples (Fig. 3, c). Under isothermal conditions, this sample releases ~ 4.2 wt.% of H₂ at 270 °C within 18 min.

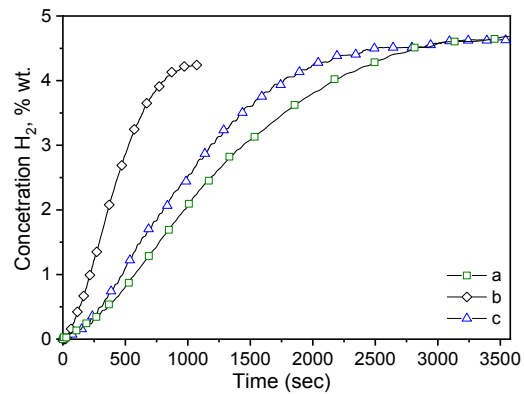


Fig. 3 Desorption of hydrogen in isothermal conditions at $T=270$ °C for activated composites: a – Mg-C0; b – Mg-C1; c – Mg-C2.

The studies of the hydrogen sorption kinetics under isothermal conditions at a temperature of 200 °C have been carried out (Fig. 4).

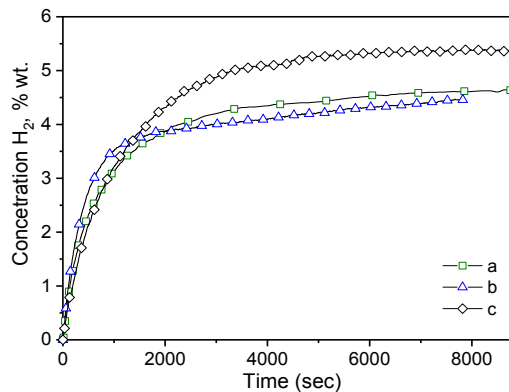


Fig. 4 Sorption of hydrogen in isothermal conditions at $T=200$ °C for activated composites: a – Mg-C0; b – Mg-C1; c – Mg-C2.

The maximum hydrogen storage capacity absorbed by Mg-C0 and Mg-C1 samples within 130 min is about 4.6 wt.% and 4.4 wt.%, respectively (Fig. 4, a and b). The composite Mg-C2 was saturated at a rate higher than Mg-C0 and Mg-C1 samples and reached a higher hydrogen capacity. It was found the Mg-C2 composite with graphite powder (329 m²/g) uptakes 5.3 wt.% of hydrogen for 90 min (Fig. 4, c).

4. Conclusion

The Mg-C composites applying graphite powders with different specific surface areas (8.1 and 329 m²/g) were produced by reactive ball milling technique in a hydrogen gas atmosphere. It was uncovered the surface areas of the graphite powder added to magnesium affect the hydrogen sorption/desorption kinetics of the Mg-based composites. The Mg-C1 composite (surface area of graphite is 8.1 m²/g) shows the best hydrogen desorption kinetics. This sample releases ~ 4.2 wt.% of H₂ at 270 °C within 18 min. Also, the hydrogen sorption curves recorded under isothermal conditions for the 200 °C were analysed. It has been clarified that the Mg-C2 sample (surface area of graphite is 329 m²/g) uptakes ~ 5.3 wt.% of H₂ within 90 min at 200 °C.

5. Acknowledgments

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Modified assembly for spraying fine powder

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Abstract: The results of testing a nozzle with a zero angle of attack for obtaining atomized metal powders are presented, which indicate its increased overhaul life, a satisfactory yield of fine fraction powders with a good spherical powder shape.

KEYWORDS: INSTALLATION FOR OBTAINING POWDERS, SPRAYING UNIT, SHOWER, SPRAYED BRONZE POWDERS

1. Introduction

One of the ways to increase the powders yield of fine fractions obtained by dispersing a metal melt with a gas flow is a nozzle developed on the basis of a Laval nozzle, which ensures an increase in the yield of fine powder fractions up to 80% [1, 2]. However, the developed nozzle has a relatively short overhaul period of the spraying unit, associated with the sticking of melt particles on the lower end of the nozzle for the outflow of the melt jet, and therefore, it is necessary to stop work and replace the part in the spraying unit. As a result, the output of fine powder per shift due to time losses is no more than 6 kg (which corresponds to the weight of the melt in one crucible).

Work purpose - study of the possibility of increasing the overhaul life of the nozzle, developed on the basis of the Laval nozzle, by changing the direction of the gas flow.

2. Experiment results and their discussion

To solve this issue, a small-sized installation was developed to study the processes of obtaining and producing copper-based powders (Fig. 1).

For the experiments, a spray assembly was made, in which the nozzle had a zero angle of attack (Figure 1). It was assumed that this would prevent sticking of metal to the end of the pipe for the outflow of the melt jet, and the process of dispersion of the melt jet would occur due to ejection and a sharp expansion of the air flow.

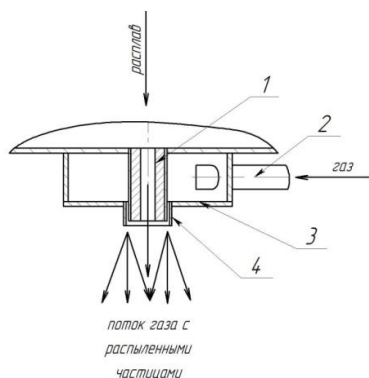


Fig. 1. The design of the spray unit: 1 - ceramic branch pipe for the outflow of the melt jet; 2 - branch pipe for supplying gas-energy carrier; 3 - nozzle; 4 - nozzle

Approbation of the nozzle design was carried out as part of a laboratory installation with a metal receiver capacity of up to 10 kg (nominal volume 6 kg).

The appearance of the installation during the spraying process is shown in Figure 2.



Fig. 2. The process of spraying copper-based powders

The experiments were carried out in the preparation of powders of tin-phosphorous bronze of the BrO10F1 grade (the charge included copper, tin of the O1 grade, and phosphorous copper of the MF 10 grade). The melt was overheated by 2500 s above the melting point of copper. Within no more than 30 seconds from the moment of readiness, the melt entered the metal receiver and then into the nozzle, which was simultaneously supplied with compressed air. The dispersed powder particles were cooled in water located in the lower part of the apparatus housing. Then the powder was dried in an oven for 2.5 hours at a temperature of 110–120°C, its granulometric composition was determined by sieve analysis, and the shape factor was studied according to the method [3] using the Mini-Magisk automatic image analyzer by Joyce Loeb. The appearance of the powder is shown in Figure 3, the granulometric composition (averaged data for four experimental batches of powder are given) - in Figure 4. The shape factor was in the range of 0.95–0.97.

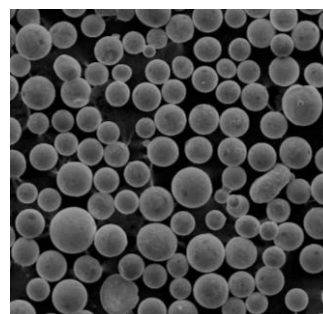


Fig. 3. Appearance of the manufactured powder

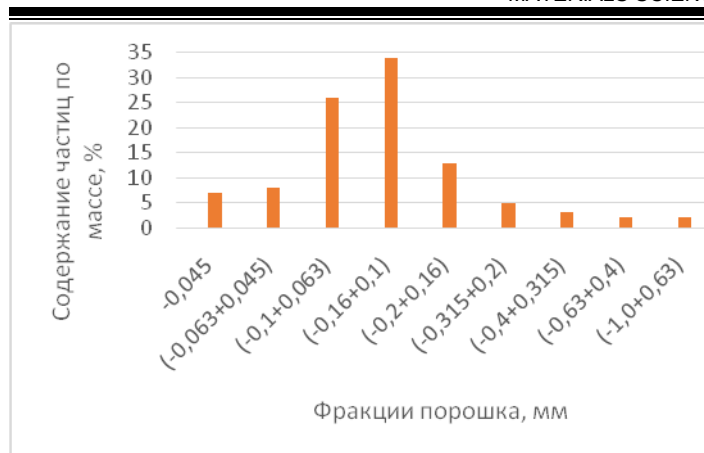


Fig. 4. Particle size distribution histogram of manufactured powder

In the experiments course, 40 kg of powder was produced, after which it became necessary to replace the nozzle for the outflow of the melt jet, that is, in comparison with the previous design, the service life was increased by more than 6 times. However, despite the fact that the yield of fine fractions is quite high (at the level of 75% of particles with sizes less than 160 μm), it decreased by 5–10% [4] (depending on the particle size (up to 160 or 100 μm)). On the whole, it can be concluded that it is expedient to use the proposed nozzle design.

Conclusion. The results of testing a nozzle with a zero angle of attack for obtaining atomized metal powders are presented, which indicate its increased overhaul life, a satisfactory yield of fine fraction powders with a good spherical shape of the powder. It has been established that, compared with the previous design, the service life can be increased by more than 6 times. At the same time, the yield of fine fractions is quite high (at the level of 75% of particles with sizes less than 160 μm), although it decreased by 5–10%. In general, it can be concluded that it's expedient to use the proposed nozzle design.

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Nanomaterials: Properties and Applications in Structural engineering

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Abstract: Nanotechnology has grown in popularity due to the enormous potential for producing materials and products with diverse properties, allowing significant advancement of existing technology and the development of new innovative technologies. Nanomaterials behave differently at the nanoscale than their conventional counterparts, opening exciting new possibilities in a wide range of construction applications. Nonetheless, the lack of information on nanomaterials' suitability, high costs, and health risks limits their use in construction and structural engineering. As a result, research must be conducted to provide accurate information and facts about the properties and performance of nanomaterials under various load conditions, as well as information on the advantages of using nanomaterials over other construction materials. This paper provides information on nanomaterial properties and how they affect structural materials' microstructure and mechanical properties. It also demonstrates the benefits of using nanotechnology and suggests new possibilities.

Keywords: NANOMATERIALS, NANOPARTICLES, PROPERTIES, CONSTRUCTION, COATING

1. Introduction

The rapid development of nanoscience and nanotechnology in recent years is due to nanomaterials' enormous potential in terms of material and product production. The primary distinction between nanoscience and nanotechnology is that nanoscience provides knowledge of the fundamental properties and arrangements of atoms, whereas nanotechnology uses matter to create new materials with advanced properties [1]. Nanotechnology is the understanding, fabrication, and application of small-scale structures and materials (nanostructures and nanoparticles). It is gaining popularity in almost all engineering branches because it is regarded as an interdisciplinary advanced technology that creates nanomaterials composed of ultra-small particles with properties and behaviors distinct from the larger building blocks of the substances [1],[2]. The independence of electrostatic and quantum forces from gravity at the nanoscale suggests new effects on properties, making nanotechnology more powerful than the traditional practice of manipulating materials on a macro-scale [3]. When obtaining nanoparticles from one matter, surface atoms are much more likely to improve the material's properties than those in the interior [4]. The new properties result from the fact that a small particle has a limited number of molecules and thus interacts differently with the surrounding area [2].

Nanomaterials have at least one nanoscale dimension, and depending on the number of nanoscale dimensions, they can be classified as zero, one, two, or three-dimensional. They are classified based on their morphology (spherical, flat, needle, or random orientations with various shapes such as quantum dots, nanowires, nanotubes, nanofluids, nanobelts, nanosheets, nano-springs, nano-capsules) and composition (monometallic, bimetallic, trimetallic, metal oxide, magnetic, hybrid) [5]. According to their design, nanomaterials can be classified as carbon-based, metal-based, dendrimers, and composites [2]. They can occur naturally as a byproduct of biological systems, accidentally as a byproduct of an industrial process, or deliberately manufactured through some engineering process to obtain materials with specific properties [6].

The use of nanomaterials is appropriate for technological advancement because modifications to the shape, size and internal order of the nanostructures can improve a variety of chemical and physical properties such as melting point, conductivity, absorption, and light dispersion [2]. It's already utilized in numerous engineering disciplines and research areas, but there are still possibilities that are yet to be discovered for further developments. Fig. 1 depicts the interests and role of nanoscience and nanotechnology in science and engineering [1].

Although public awareness of the advantages of using nanotechnology in structural engineering has grown in recent years, there is still a scarcity of information on the subject. This article outlines the most recent achievements in structural engineering of nanotechnology, with an emphasis on properties, the benefits of

their application, and their potential for further development and use in construction.

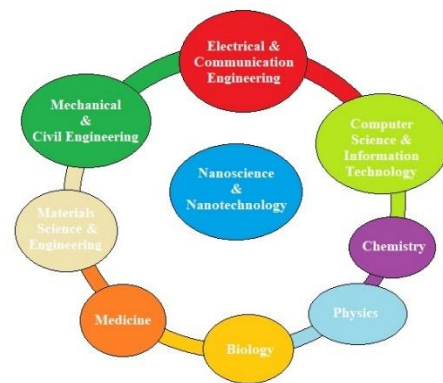


Fig. 1 Nanotechnology and nanoscience in relation to other sciences and engineering disciplines [1]

2. Application and properties of nanomaterials in structural engineering

The development of new concepts and understanding of the use of nanoparticles in construction materials is important in structural engineering. Materials can be made stronger, more durable, and tougher using nanotechnology. Furthermore, self-cleaning, insulating, and water resistance properties can be introduced to new structures on their glass surfaces or applied by paint, making these buildings modern and self-sustaining. These materials are used to create stronger and lighter structural composites, low-maintenance coatings, water repellents, UV light protection, and nano-sensors for structural health monitoring [4].

Carbon nanotubes (CNT) are the most commonly used nanomaterials in construction, used for concrete strengthening and monitoring. These nanotubes are made up of graphene-embedded sheets that are rolled into tubes [1]. CNTs are classified into two types: single-wall CNTs and multi-wall CNTs. The single-walled (SW) CNT is made up of one cylindrical shape with various atom arrangements, whereas the multi-walled (MW) CNT is made up of two or more cylindrical shapes packed layer by layer, as shown in Fig.2 [8]. They have significantly higher mechanical properties than steel, such as young's modulus and strength, as well as exceptionally high thermal conductivity along their axis. These carbon-based nanomaterials have good electrical properties and have a growing potential for smart materials and self-monitoring structures [7]. Nanotubes are used in concrete to increase strength and durability, as well as to prevent cracks. They are used in ceramics to improve mechanical and thermal properties, as well as in structures for health assessments [4]. Fullerenes, which have a hollow cage structure of particles with sixty or more carbon atoms and exhibit good electrical conductivity, electron affinity, and high strength [1], are another carbon-based nanomaterial. Carbon

nanomaterials may also be used in automobiles as batteries, engine oils, self-lubricating materials, nano-lubricants, and coatings to improve surface wear and antifriction [5]. The molecular structure of carbon can be changed using nanotechnology to a spherical geodesic form, making it more fluid, resulting in the development of nanotubes with an extremely high elastic modulus of 1 TPa, yield strength of 60 GPa, and yield strain of the order of 6% [8]. The CNT can be used to reinforce polymers, glass, composites, and metals in addition to ceramics and cement-based matrix. Materials with a great deal of potential for use in structural engineering include cutting tools, springs, wear-resistant, impact, and earthquake-resistant structures, ductile cement, and glass. In cementitious composites, graphene oxide and graphene nanoparticles are used to enhance the material's mechanical qualities. They are somewhat investigated for application in reinforcing cement composites due to their exceptional elastic characteristics and tensile strength. The structure of graphene and graphene oxide is depicted in Fig.3 [8].

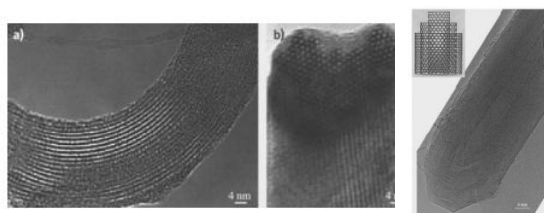


Fig. 2 Images made of high-resolution transmission electron microscope: a) SWCNT rope – longitudinal view, b) SWCNT rope – cross-sectional view, c) MWCNT with a representation of the layers in the left top corner [8]

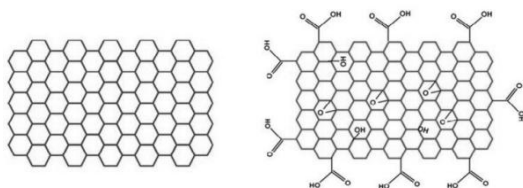


Fig. 3 Structure of graphene (left) and graphene oxide (right)[8]

Metal nanoparticles, also known as quantum dots, monometallic oxides (zinc oxide, titanium dioxide, iron oxide), nano-gold, and nano-silver can be used to create nanomaterials [2]. Metal nanoparticles with a high surface area and good absorption of small molecules are formed by reducing divalent and trivalent metal ions with agents [1]. Titanium dioxide (TiO_2) is a two nano-sized particle used as a white pigment in paints, cement, windows, and tiles for sterilizing, deodorizing, and anti-fouling properties, and it reduces airborne pollutants through a photocatalytic process. When exposed to UV light, it becomes water-repellent and can be used for anti-fogging or self-cleaning. Furthermore, TiO_2 nanoparticles can be used in concrete as a partial replacement for cement because they increase compressive, flexural, durability, and split tensile strength [10]. Similarly, Fe_2O_3 and CuO nanoparticles are used to improve the mechanical properties of cement and concrete, but they can reduce setting time, workability, and mechanical properties by 3–4%. For denser cement with improved porosity, nanoparticles of silicious dioxide SiO_2 (nano-silica) are used in cement composites. Al_2O_3 nanoparticle use offers comparable advantages when added in small amounts to cement and concrete with an average particle size of 15 nm or less, but it also reduces workability and setting time due to the nanoparticles' quick reactivity with $\text{Ca}(\text{OH})_2$ [10]. With the addition of ZrO_2 , the concrete's compressive, flexural, and tensile strength can also be increased. However, because of the quick reaction between ZrO_2 and calcium hydroxide, this also affects the workability and setting time, hence superplasticizer is recommended [10]. Nano ZnO_2 particles can help concrete's pore structure and its recovery from polycarboxylate's harmful impacts.

The application of CaO_3 nanoparticles provides enhancing characteristics of cement and concrete and increases hydration, setting time, and compressive properties. The silver nanoparticles are used in paints for antibacterial properties on surfaces, this is usually applied to the walls of hospitals to lower the growth of infectious viruses and bacteria [10]. There are also bimetallic nanoparticles (Fe/Pd , Fe/Ag , or Zn/Pd), they can serve as catalysts and reductants [9]. Semiconductor nanomaterials contain metallic and nonmetallic properties. They are used in photocatalysts, electron devices, solar cells, nanoscale electronic devices, light-emitting nanodevices, laser technology, waveguide, chemicals, and biosensors. This type of nanomaterials are made of different compounds and are referred to as II-VI, III-V or IV-VI semiconductor nanocrystals [1]. They have interesting attractive physical and chemical properties, narrow and intensive emission spectra, continuous absorption bands, high chemical and photobleaching stability, processability, and surface functionality [11]. These nanomaterials are advanced materials intended for various applications like new emerging technologies, nanoelectronics, nanophotonic, energy conservation, non-linear optics, miniaturized sensors and imaging devices, solar cells, detectors, and biomedicine [12].

There has been significant progress in exploring a wide range of materials such as nanocomposites and nanohybrids [2]. Nanocomposites are materials with more than one phase where one of the phases has at least one dimension that is less than 100nm, whereas nanohybrids are a combination of 2 or more nanomaterials for satisfying a different function. Compared to the traditional composites, these materials have a high surface volume ratio, and based on their size, shape, or properties they can be different types like ceramic matrix nanocomposites, metal matrix, and polymer matrix nanocomposites [1]. Nano-clay particles are already being added to different products from auto parts to packaging materials as reinforcement in high-performance composites. Nanocomposites with incorporated nanotubes are popular because nanotubes show outstanding properties that in the composite mixture improve the overall properties of the materials. For example, alumino-silicates and nanotubes mixture produces strong and durable films and by further reducing the size of alumino-silicates to 5 to 10 nm more advancement in properties can be achieved [11]. Wrapping existing concrete structures with a fiber sheet matrix of nano-silica show excellent results for strengthening [11].

Steel is extensively used as a construction material in structures that are subjected to cycling loading which can lead to fatigue failure. It is a durable material that holds a high-strength-to-weight ratio in comparison to other construction materials. By adding copper nanoparticles, the surface unevenness can be reduced, and this will limit the stress concentrations and lower fatigue crack initiation [12]. Vanadium and molybdenum nanoparticles can lower fractures in bolts. Stronger steel can be produced by adding nanoparticles in paints and coatings when used as reinforcement bars in concrete [13]. These are known as micro-composite multi-structural formable (MMFX) that are corrosion resistant and have durable properties. The effect of hydrogen embrittlement and their inter-granular cementite phase are reduced through the improvement of steel microstructure [13]. With nanoparticles, steel can become corrosion resistant which is a challenging matter with the traditionally used steel and by adding nanoparticles like calcium and magnesium finer grains in the microstructure of the weld and heat-affected zone can be achieved [14]. Nanotechnology in the metallurgy of steel is used for the reduction of ural steel where microalloying steel with nitride phases is combined with plastic-deformation nanotechnology make the steel stronger [14]. Table 1 contains information on the application of nanoparticles added to traditional materials and summarizes the benefits of their use.

Table 1: Summarized data on nanomaterials used in traditional construction materials for enhanced properties

Category	Nanomaterial		Application/Base material	Nanoparticle
Carbon-based nanomaterials	Carbon Nanotube		Cement/Concrete	Improved durability, compressive and flexural strength, self-sensing, and self-cleaning properties,
			Ceramics	Enhancement in thermal and mechanical properties, reduced shrinkage, antibacterial
			Nano electrical mechanical systems	Real-time health assessment of structures
			Solar cell	Effective electron mediation
	Graphene and graphene oxide		Cement/Concrete	improved microstructure, mechanical properties, and durability. improved microstructure, mechanical properties, low cost, accelerated hydration, enhanced corrosion resistance
\Metal- based nanomaterial	Semiconductor	Silicon dioxide	Cement and concrete	Enhancement in mechanical strengths and durability, denser cement paste, improved porosity, corrosion reduction, insulating properties
			Glass	Enhancement in mechanical Strengths and durability, nonreflective, fire and heat protection, easy-to-clean properties
			Coatings	Antibacterial, photocatalytic, self-cleaning, hydrophobic, scratch resistance, fire retardant
			Ceramics	Coolant; light transmission; fire resistant
		Titanium dioxide	Solar cell	Producing non-utility power
			Glass	Antifogging, hydrophilicity, fouling resistance, IR reflection, photocatalytic self-cleaning
			Cement and concrete	Self-cleaning, rapid hydration and improvement in mechanical strengths, increased flexibility, pore structure improvement, improved performance at elevated temperatures
			Coatings/Paints	Antibacterial, photocatalytic, self-cleaning, hydrophobic properties, UV protection on wood, active air pollution reduction on asphalt, road pavement blocks, sound barriers, and tunnels
			Solar cell	Non-utility electricity generation
		Ferric oxide	Cement and concrete	Improvement in strength, durability, compression, and abrasion resistance, hydration of cement is increased
		Copper oxide	Cement and concrete	Improved mechanical strengths and durability, reduced the porosity
			Steel	Improved weldability, formability, and corrosion resistance
		Calcium carbonate	Cement and concrete	Improve rheological properties of concrete, increased rate of hydration, setting time, and improve compressive strength
		Chromium Oxide	Cement and concrete	Improves properties of concrete, higher mechanical strength, and durability properties
		Aluminium oxide	Cement and concrete	Compacted microstructure, decreased porosity, enhanced compressive strength, frost resistance, accelerated hydration, reduced water absorption
			Coatings	Scratch resistance
		Zirconium oxide	Cement and concrete	Enhancement in mechanical strengths
		Zinc dioxide	Cement and concrete	Advancement in mechanical strengths, antibacterial properties
			Coatings/Paints	Antimicrobial activity, UV protection
		Silver (Ag)	Paints	Antimicrobial properties, reduce the growth and multiplication of fungi, viruses and bacteria

3. Conclusion

The interest in nanomaterials and their application is constantly growing in many industries. It opens a variety of new possibilities in structural engineering for implementing novel innovative technologies and solutions through improving the properties of the available traditional materials and obtaining and with that obtaining a wider spectrum of new materials. The basic properties of the materials on the nanoscale level bring up significant changes in the mechanical, physical, and thermal properties. The research and applications of nanomaterials are mainly focused on the understanding of the nanostructure of materials and their modification, functional films and coatings, smart structures and devices, and their effect on the environment and health [5]. In structural engineering, there are carbon-based, metal-based nanomaterials, semiconductors, dendrites, nanocomposites, and nanohybrids that can improve the construction materials and bring them completely new capabilities. Table 1 summarizes all of the benefits that nanoparticles bring to materials like cement, concrete, glass, coatings, composites, and steel. It is evident that nano-alumina, nano-titania, nano-silica, nano-magnesium oxide, nano-zinc oxide, silver nanoparticles, carbon nanotubes, or graphene derivatives may have enhanced hydration, microstructure, porosity, and thus mechanical properties and transport-related properties of cementitious composites and introduce new properties such as self-cleaning, self-sensing and antimicrobial properties. There are most recent advancements in applications of nanomaterials in cement composites and structural health monitoring, but the industrial-scale application and toxicity remain a challenge for further development of nanomaterials. Also, lowering the already high energy consumption in buildings and structures is the possible direction of future investigations. A broader perspective should be considered when investigating the possibilities of nanomaterials for enhancing sustainability. Improving the properties of materials, and conserving energy and toxicity are important and should be a high priority for further investigations. Advanced analytical techniques are required for the detection and characterization of nanomaterials realization or incorporation in construction materials [8]. This paper presents a review of the achievements in structural engineering with an emphasis on properties and applications. Further investigation should be done on the sustainability possibilities of incorporating nanotechnology in the construction industry.

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