STUDY OF ALLOYS MODIFICATION BY NANOMATERIALS

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Abstract. In last years, improvement of metals mechanical properties and performance comes to be one of the main challenges in materials science and particularly in metallurgical manufacturing. Generally, an alloying process is traditionally applied to reach metals enhanced properties and performance. Recently, nanotechnology approach is also applied, usually to produce composite materials with improved performance. This work, however, describes a different technique, where different nanoparticles are used as modifiers in metal casting process. The influence of these nanomaterials was investigated on a hypoeutectic casting aluminum alloy and on pure copper. Microstructural evaluation of modified Al alloy illustrated that a coarse Al grains were refined. Tensile strength tests revealed that Al ductility improved while the strength remained unchanged. Particularly, results pointed that addition of up to 0.1 wt. % of ceramic nanoparticles enhanced metals elongation at fracture by 20 – 60 %, depending on the mold location. Strengthening mechanism, which took place in the process, was evaluated by applying a high resolution transmission electron microscopy (HR-TEM) studies. HR-TEM investigations, jointly with mechanical properties test results, led to hypothesis that a grain-size strengthening mechanism works in the process. In this mechanism metal strengthening occurs due to a high concentration of grain boundaries which are serving as dislocation movement blockers. Results obtained on copper modification showed the improvement of metal strength simultaneously with its elongation at fracture. This behavior was obtained after addition of multi walled carbon nanotubes (MWCNT) and TiN nanoparticles up to 0.1 wt. %. Further application of the described approach can lead to its implementation into foundry industry turning it to more economically beneficial.

Keywords: nanomaterials, modification, casting alloys, mechanical properties, strengthening mechanism.

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One of the main tasks in current metallurgy processes is materials obtaining with required properties. Typically, advanced mechanical properties can be conventionally reached by alloying process, where some chemical compounds are added to affect the chemical composition of the formed material. Addition of a high concentration of costly materials makes the process economically unfavorable.

Aluminum alloys are a key class of metals which is used often in various industrial applications such as automotive or aerospace. Al alloys have advanced properties, such as good thermal and electrical conductivity and low density which is only one third of steel [1]. Unfortunately, these alloys show relatively low mechanical properties matched to those of steel.

Al–Si cast alloys are of the most interested alloys in aluminum foundry. These alloys have a good castability, and mechanical and physical properties. Generally, Al–Si A356 alloy mechanical properties improves by basic alloying method [2 – 7] using master alloys or by applying ultrasound during solidification [8 – 10]. Other works show the addition of TiB₂ particles, which serve as a solidification nucleates, causes refinement of the metallic grains [11, 12]. Relatively small additions of Sr and Na into Al-Si cast alloys improve the formation of refined eutectic phase [13, 14]. Other works showed A356 alloy modification by rear-earth metals, such as Er, La and Ce [15, 16]. Semi-Solid Metal processing (SSM) is other technology for Al alloys strengthening. Using SSM method, metals strengths as a result of the dispersion of the non-metallic particles into the melt [18, 19].

Nanoscience approach has become a prevalent study topic in last two decades. It would be rational to assume that nanomaterials in the formed metal would cause to different changes in the mechanical properties. Unfortunately, the influence of nanoparticles addition to metallic materials has not been carefully studied yet, but some works described A356 alloy mechanical properties improvement by addition of Al₂O₃ or TiB₂ nanoparticles through the casting process [20, 21].
Copper production as well as aluminum depends on non-ferrous metallurgy. Therefore, their physical behavior is close to each other. In some works it mentioned that copper can be modified by nanomaterials and its strength improves through the grain boundary mechanism [22 – 24].

In current research work we present different nanomaterials influence to the formation of Al–Si alloy as well as copper, and as the result to their mechanical properties.

**Results and Discussion**

*WC nanoparticles application in metallurgical process*

Tungsten carbide (WC) used in the research due to its progressive properties such as superior hardness and modulus of elasticity, high melting point, and outstanding wear and corrosion resistances. Lekatou et.al [25] described that WC nanoparticles can be applied in Al strengthening technique in a relatively small quantity of Al. Unfortunately, WC has low wettability by aluminum alloys. The possible solution to this issue was reported by Chattopadhyay et.al [26]; the researchers solved the problem by various treatment methods. In our work an alternative approach will be suggested; a modification process by hot extrusion method.

The experimental work was conducted using a commercial Al A356 hypoeutectic Al–Si cast alloy. WC nanoparticles with a crystallite size of 40 – 70 nm were mechanochemically treated with aluminum powder in planetary ball mill Retsch GmbH PM 100. The obtained mixture undergoes hot-extrusion special home-made equipment at 350 °C.

During the process the oxide layer on the nanoparticles surface disappeared because of relatively high compressive forces [27]. The final product is a modifier which in a form of rod containing a mixture of Al powder and WC nanoparticles. Electron microscope image of the obtained modifier is presented in Fig. 1.

Industrial experiments were conducted using a 100 kg portion of Al A356 alloy ingots which were melted and overheated up to 760 °C. The melt was treated by typical industrial methods, and then, a modifier was added to the melt and stirred for 10 min using FDU rotor without gas addition. Here 0.03 wt. % of WC nanoparticles out of the total Al mass was added. Then, the melt was poured into a sand mold (Fig. 2). Finally, all specimens were subjected to T6 heat treatment.

The mechanical properties were performed by Instron 3369 testing machine according to ASTM B 108-01. Two specimens of modified and non-modified alloys were cut from the center and two from the perimeter of three different modified parts. Then they were T6 heat treated and subjected to tensile test which are presented in Table 1.

Obtained results indicate that nanoparticles addition into the melt improve metals’ ductility by 30 and 60 % in perimeter and in central part of the mold, respectively. Simultaneously, tensile and yield strengths remained unchanged. These results show an unusual behavior, where the ductility growths while the strength remains unchanged.

The microstructural evaluation of the alloys was analyzed as well. Optical micrographs of the alloys are presented in Fig. 3.

**Fig. 3** micrographs evaluate that the microstructure became finer and the number of pores (black dots on the microstructures) reduces after modification process. Additionally, the coarse elongated α-Al grains were refined into a fine equiaxed grains with eutectic Si network around them.
**Mechanical properties of A356 alloy subjected to modification by WC nanoparticles**

*Table 1. Механические свойства сплава A356, модифицированного наночастицами WC*

|                | Tensile Strength [MPa] | Yield Strength [MPa] | Elongation [%] |
|----------------|------------------------|----------------------|----------------|
| Mold center    |                         |                      |                |
| Before modification | 277.5 ± 1.1          | 226.7 ± 1.8         | 2.8 ± 0.1      |
| After modification    | 284.8 ± 0.9           | 226.7 ± 1.6         | 4.6 ± 0.3      |
| Mold perimeter  |                         |                      |                |
| Before modification | 303.5 ± 13.1          | 231.8 ± 3.6         | 6.5 ± 1.8      |
| After modification    | 307.3 ± 7.6           | 230.3 ± 4.4         | 8.6 ± 0.8      |

![Optical micrographs](image)

Fig. 3. Optical micrographs of (a) non-modified and (b) subjected to modification by WC nanoparticles Al A356 alloy

*TiC nanoparticles application in metallurgical process*

The experimental work performed by preparation and addition of titanium carbide (TiC) nanoparticles was similar to the discussed above (addition of the WC nanoparticles) paragraph. A hot extrusion process of modifier preparation and pouring processes were similar as well.

The experimental work was conducted using the commercial A356 hypoeutectic Al–Si cast alloy. TiC nanoparticles (20 nm) were mechanochemically treated with aluminum powder in planetary ball mill by Retsch GmbH PM 100. The obtained mixture undergoes hot-extrusion special home-made equipment at 350 °C.

The mechanical properties were performed by Instron 3369 testing machine according to ASTM B 108-01. Two specimens of modified and non-modified alloys were cut from the center and two from the perimeter of three different modified parts. Then they were T6 heat treated and subjected to tensile test which are presented in Table 2.

Obtained results indicate that nanoparticles addition into the melt improve metals’ ductility by 20 and 50 % in the mold perimeter and in the central part of the mold, re-

**Mechanical properties of A356 alloy subjected to modification by TiC nanoparticles**

*Table 2. Механические свойства сплава A356, модифицированного наночастицами TiC*

|                | Tensile Strength [MPa] | Yield Strength [MPa] | Elongation [%] |
|----------------|------------------------|----------------------|----------------|
| Mold center    |                         |                      |                |
| Before modification | 268.3                  | 225.0                | 1.9            |
| After modification    | 280.9 ± 1.0            | 221.7 ± 4.0         | 3.8 ± 0.7      |
| Mold perimeter  |                         |                      |                |
| Before modification | 311.0                  | 233.0                | 6.5            |
| After modification    | 310.4 ± 3.1            | 226.9 ± 2.2         | 9.0 ± 1.3      |
spectively. Simultaneously, tensile and yield strengths remained unchanged.

Fractographs evaluation of the alloys was analyzed as well. Electron microstructures of the alloys are presented in Fig. 4.

Modified alloy fractographs demonstrate ductile to brittle fracture. On the modified alloy (Fig. 4, b) more dimples are presented which is an indicator of a ductile fracture. Lee et.al also reported the same behavior where the metals’ elongation improved by the ductile fracture [28].

The strengthening mechanism was studied by HR-TEM technique. In this work HR-TEM JEOL JEM 2010 was applied.

![Fractographs](image)

**Fig. 4.** Scanning electron microscopy fractographs of (a) non-modified and (b) subjected to modification by TiC nanoparticles Al A356 alloy

The obtained images are shown in Fig. 5. Here a high concentration of dislocations found across the grain boundary (Fig. 5, a); simultaneously Ti inclusions which are originated from TiC nanoparticles found into Al grain (Fig. 5, b).

As deriving, a large concentration of dislocations is observed near the grain boundaries in the modified alloy. In addition, ceramic nanoparticles were found into aluminum grains. Obviously that nanoparticles act as nucleation accelerators during solidification process and cause to the formation of a fine-grained microstructure. As the result, the alloys’ mechanical properties are improved. Based on both,

![HR-TEM images](image)

**Fig. 5.** HR-TEM images of modified A356 alloy by TiC nanoparticles: 

- a – grain boundary; b – Al grain

Рис. 4. СЭМ микрофотографии излома алюминиевого сплава A356: 

- a – до модификации, b – модифицированного наночастицами TiC

Рис. 5. Структура сплава A356, модифицированного наночастицами TiC, полученная с помощью HR-TEM: 

- a – граница зерна, b – зерно алюминия
the mechanical properties results and the microstructure investigations, it was assumed that a grain boundary mechanism is responsible for the modification process.

**Copper modification by various nanomaterials**

In this section we show our experimental work obtained on pure copper using various nanomaterials namely, multi walled carbon nanotubes (MWCNT) and TiN nanoparticles.

The experimental work was conducted using pure copper rods CW004A. TiN nanoparticles with a crystal size of 10 – 20 nm and MWCNT with an outer diameter of 30 – 50 nm, length of 10 – 20 µm and purity of >95 wt. % were used in the research. These nanomaterials were mechanochemically treated with aluminum powder in planetary ball mill Retsh GmbH PM 100. The obtained mixture undergoes a cold pressing by a pressure of 18 GPa.

The mechanical properties were performed by Lloyd EZ50 universal testing machine according to ASTM B 108-01. The obtained results are presented in **Table 3**.

As it is seen from the obtained results, mechanical properties of copper can be improved by addition of ceramic TiN nanoparticles as well as MWCNT. Both nanomaterials show improvement of tensile strength around 30 %; the yield strength improved by 13 and 47 % adding MWCNT and TiN, respectively. Ductility of a modified alloys improved by 60 and 35 % after addition of MWCNT and TiN nanoparticles, respectively.

**Summary.** The presented work showed the novel method of nanotechnology application into traditional metallurgical processes. The effect of modification by specially prepared ceramic nanoparticles on Al–Si casting alloy, and ceramic nanoparticles and MWCNTs on copper were described. The following results were obtained:

- Addition of ceramic nanoparticles to the Al–Si casting alloy improved the ductility of the metal by 20 and 60 % in different mold areas while the tensile and the yield strengths of the alloy remained unaffected.

- The strengthening mechanism was studied in the work as well. It was found that ceramic nanoparticles act as nucleates during the crystallization process and do not change phase composition. The grain boundaries stop the dislocation motion and, as a result a grain-size strengthening mechanism works in the process.

- Addition of MWCNT and TiN nanoparticles improved the strength and the ductility of copper by 30 – 40 and 35 – 60 % simultaneously.

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**Mechanical properties of copper subjected to modification by various nanomaterials**

|                        | Tensile Strength [MPa] | Yield Strength [MPa] | Elongation [%] |
|------------------------|------------------------|----------------------|----------------|
| Before modification    | 173.75 ± 5.97          | 58.63 ± 1.39         | 28.36 ± 1.12   |
| After modification by MWCNT | 225.17 ± 6.00          | 66.20 ± 6.48         | 45.36 ± 5.23   |
| After modification by TiN nanoparticles | 220.98 ± 7.25          | 86.43 ± 5.20         | 38.20 ± 5.83   |

**Fig. 6.** Stress-strain graph of pure copper subjected to modification by various nanomaterials: 1 – unmodified; 2 – MWCNT modification; 3 – TiN nanoparticles modification

Рис. 6. Диаграмма растяжения чистой меди, модифицированной различными наночастицами: 1 – без модификации; 2 – модификация многослойными углеродными нанотрубками (MWCNT); 3 – модификация наночастицами TiN

**Table 3.** Механические свойства меди, модифицированной различными наночастицами
ИССЛЕДОВАНИЕ МОДИФИКАЦИИ СПЛАВОВ НАНОМАТЕРИАЛАМИ

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Аннотация. В последние годы улучшение механических свойств и характеристики металлов является одной из основных проблем в материаловедении и, особенно, в металлографическом производстве. Как правило, процесс легирования представляется направленным для улучшения свойств и характеристик металлов. В последнее время для производства композитных материалов с улучшенными свойствами применяется нанотехнологический подход. Однако данная задача описывает другой метод, в котором различные наночастицы используются в качестве модификаторов в процессе лития металла. Влияние этих наноматериалов исследовано на гипофазовом выделении алюминиевого сплава в чистой меди. Испытания на прочность и на растяжение показали, что пластичность алюминия улучшилась, а прочность оставалась неизменной. В частности, добавление до 0,1 % (по массе) керамических наночастиц увеличивает удлинение металлов при разрушении на 20 – 60 %. Механизм упрочнения, предложенный для этого процесса, был оценен путем применения низкой скорости упрочнения над макроскопической дислокацией (HR-TEM). Исследования HR-TEM, вместе с результатами испытаний механизмов и характеристик металлов, привели к гипотезе о том, что в этом процессе работает механизм упрочнения зерна. В этом механизме упрочнение металла происходит из-за высокой концентрации границ зерен, которые блокируют движение дислокаций. Результаты, полученные при модификации меди, показали улучшение прочности металла одновременно с пластичностью. Такое поведение было получено после добавления многослойных углеродных нанотрубок (MCWNT) и наночастиц TiN до 0,1 % (по массе). Дальнейшее применение описанного подхода может привести к его внедрению в литейную промышленность, превратив ее в экономическую выгодную.

Ключевые слова: наноматериалы, модификация, литейные сплавы, механические свойства, механизм упрочнения.

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