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# INFLUENCE OF CARBON NANOPARTICLE INOCULATION ON THE STRUCTURE OF ML5 CASTING MAGNESIUM ALLOY

*The object of this study is to investigate the structure of cast magnesium alloy (Mg-Al-Zn) inoculated with nano particles of different allotropic forms of carbon. The aim of this study is to improve the processability and quality of critical load bearing magnesium alloy part castings. The tasks of the study are: attainment of efficient control of the alloy structural features by introduction of incremental additions of carbon nano particles; determination of the relationship between the quantity of the added inoculating carbon agent and α - solid solution grain size; determination of the influence of allotropic forms of carbon on the morphologic characteristics of the intergranular borders and the eutectoid (a+$Mg_{17}Al_{12}$); and comparative analysis of the phase composition of the standard ML5 alloy and the experimental alloy ML5 inoculated with carbon black, nanographite, and single-wall carbon nanotubes. The phase composition was determined by X-ray diffraction analysis using copper radiation. Micro X-ray spectral analysis was performed. The following findings were obtained. Using an optical microscope α – solid solution grain size was measured in the standard and inoculated alloy. In the samples of the alloy variants inoculated with 0.1 % wt. of carbon black, nanographite, and single-wall carbon nanotubes, the grain size was reduced by appox. 50 % compared with the standard alloy. In the samples of the alloy inoculated with 0.1 % wt. of nanographite and single wall carbon nanotubes, eutectoid (a+$Mg_{17}Al_{12}$) precipitates along the grain boundaries were thinner than those in the standard alloy samples and those inoculated with carbon black. X-ray diffraction analysis revealed no new phase formation. The X-ray diffraction patterns of the alloy samples with nanographite and nanotubes display weak peaks of free carbon, which may indicate the presence of free carbon in small quantities in the structure. The scientific and practical originality of the obtained results consists of the following: a technology of inoculation with incremental additions of allotropic forms of nano carbon, namely carbon black, nanographite, and single-wall carbon nanotubes, has been tested on a standard cast magnesium alloy (Mg-Al-Zn system) in an environment similar to the industrial production of critical magnesium cast components. It has been shown that the introduction of nanocarbon in a quantity of 0.1 % wt. can have a beneficial effect on the structural characteristics of ML5 cast magnesium alloy with no change in its phase composition. Nanographite and single wall carbon nanotubes with a regular structure contribute to the formation of thinner intergranular boundaries than amorphous carbon black.*

***Keywords**: cast magnesium alloy; inoculation; grain size; intermetallic phase $Mg_{17}Al_{12}$; carbon nanoparticles; nanographite; single wall carbon nanotubes.*

## Introduction

At the present stage of development of the aeronautical industry much efforts is focused on enhancement of the aircraft performance characteristics through more extensive utilization of light alloys [1]. In this regard it is worthwhile to note that Motor Sich JSC medium-term foundry development program envisions development of a magnesium casting technology, which guarantees production of magnesium castings having high quality sound wall with the thickness of 3 mm and an overall size of up to 1000 mm, which should decrease the weight of the cast components by 10%.

Cast magnesium alloys of Mg-Al-Zn system are widely used for production of structural parts of aero engines and rotorcraft transmission thanks to its low specific weight $\rho = 1.8\text{-}1.9$ g/cm$^3$, high specific strength and good cast ability. However, this group of magnesium alloys has a number of drawbacks, such as low temperature capability (up to 150°C) and susceptibility to formation of shrinking micro porosity that compromise the mechanical properties [2, 3]. Therefore, at present there is a pressing need in aeronautical engineering for development of new generation light structural magnesium materials offering increased mechanical properties and temperature capability via a controllable structure.

## Selection of inoculating agent type and inoculation method

One of the promising techniques of improving the physical and mechanical properties of the cast high strength magnesium alloys of Mg-Al-Zn system is carbon inoculation. Over the last decade much efforts have been undertaken to develop commercially reliable carbon-based grain refiner for aluminum bearing magnesium alloys [4].

Among the advantages of using the carbon materials as the grain refinement agent is the absence of contamination of the liquid metal with oxide inclusions and reaction products as a result of contacting with the liquid metal, high grain refinement potential, as well as low waste of metal, reduced energy consumption and melting crucible wear as compared with the grain refinement by overheating [5, 6]. Besides, when inoculating with carbon a very slow grain refinement fading out is observed as the melt is held for a prolonged period of time before pouring [7, 8]. The inoculation of aluminum - bearing alloys might also be potentially a highly cost-effective process, because carbon grain refiners are added in quite small quantities (up to 0.1 wt.% of the liquid metal weight) and belong to a category of inexpensive materials available on the commercial market (e.g.: carbon black and various graphite modifications).

However, inoculation of the magnesium alloys with carbon grain refiners presents certain challenges associated with the intrinsic poor wettability of carbon and susceptibility of superfine carbon powders and nano powders for formation of carbon particle agglomerates, which leads to non-homogeneous distribution of the grain refiner in the melt with the resulting unsatisfactory grain refinement effect [9]. Therefore, the papers published in the recent years, are focused predominantly on a search for an optimal way to introduce the carbon inoculants in the Al - containing magnesium alloys as well as on gaining a better understanding of the grain refinement mechanism with carbon [10].

## Experimental procedure

The grain refiners were prepared by mixing pre-weighted portions of carbon black, nanographite and single wall carbon nanotubes (SWCNT) with a superfine high purity aluminum powder in ethyl alcohol. A mean aluminum particle size measured with magnification of x500 using Karl Zeiss Axio Observer. Dlm optical microscope is 3.3 micrometers. Upon complete ethyl alcohol evaporation the prepared mixtures were uniaxially pressed into pellets sized dia.30 mm x height 6 mm on a hydraulic press Q = 40 tons. The SWCNT/Al powder mix was not subjected to pressing and was introduced into the melt in bulk wrapped with aluminum foil.

ML5 cast magnesium alloy (Al 7,5-9,0%; Mn 0,15-0,5%; Zn 0,2-0,8%) was melted in an induction crucible furnace according to a serial production process using VI-2 flux ($MgCl_2$38...46% KCl 32...40% $BaCl_2$ 5...8% $CaF_2$ 3...5%). The alloy melting procedure included a standard inoculation step using magnesite in a quantity of 0.3 - 0.4 wt.% of the charge weight carried out in a holding furnace at 740°C followed by a refinement step with VI-2 flux.

The preheated inoculants with incremental additions of carbon black, nano graphite and SWCNT (0 %; 0.030 %; 0.10 wt.%) were introduced into the melt at 760°C. After 5 minutes hold the melt was poured into sand molds at 720°C with standard tensile test specimens, gauge Ø 12 mm. The cast specimens were subjected to T6 standard heat treatment. The microstructure was examined on the prepared sections etched in the following etching agent: 5.2 ml of acetic acid, 100 ml of ethyl alcohol [11].

In order to define specifics concerning influence of the inoculation with carbon nanomaterials the samples of the inoculated ML5 alloy were subjected to an X-ray diffraction analysis (XRD) in copper emission. Also, X-ray spectroscopic analysis of the samples was carried out using JEOL IT-300 scanning microscope fitted with an energy dispersion spectrometer.

## The experiment results

The microstructure represents$\alpha$-solid solution of aluminum and zinc in magnesium and $\alpha+Mg_{17}Al_{12}$ eutectoid. Manganese is present in the structure in a form of small particles of bluish color.

It is worthwhile to note that the precipitates of $\alpha$+Mg17Al12 eutectoid at the grain boundaries in the specimens inoculated with the nanographite and SWCNT in a quantity of 0.10 wt.% are found to be finer as compared with the samples cast in standard ML5 alloy and those inoculated with the carbon black (Figure 2).

The mean grain size was defined based on results of minimum five measurements in the field of view made using Carl Zeiss Observer D1m microscope software. The grain size measurements are presented in Table 1

**Note**: the numerator indicates the grain size range in micrometers, the denominator - arithmetical mean value of the grain size in micrometers.

The X-ray diffraction patterns of the standard ML5 alloy and the inoculated ML5 alloy samples were found, in general, similar, with no detected new phases.On the X-ray diffraction patterns of ML5 samples inoculated with thenanographite and SWCNTweak lines of pure carbon were observed, which suggests that small quantities of free carbonmay be present in the alloy structure.The inoculation of the alloy with nanographite and SWCNT resulted in some phase quantitative redistribution (Fig.3 and 4).

The X-ray spectroscopic analysis results are found to be coherent with the XRD analysis (Fig.5 and Fig. 6).

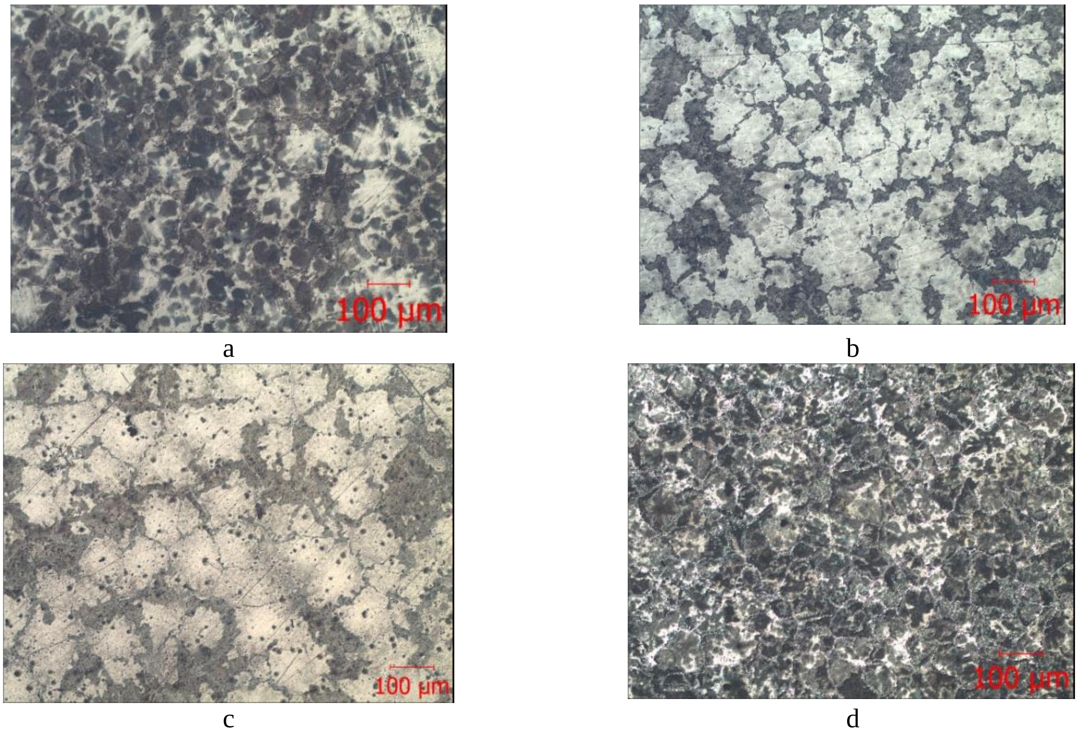


Fig. 1. The microstructure of ML5 alloy inoculated
with the carbon nanoparticles (0.01 wt.%) at magnification x100:
a – standard ML5 alloy; b – ML5 alloy inoculated with carbon black;
c – ML5 alloy inoculated with nanographite; d – ML5 alloy inoculated with SWCNT

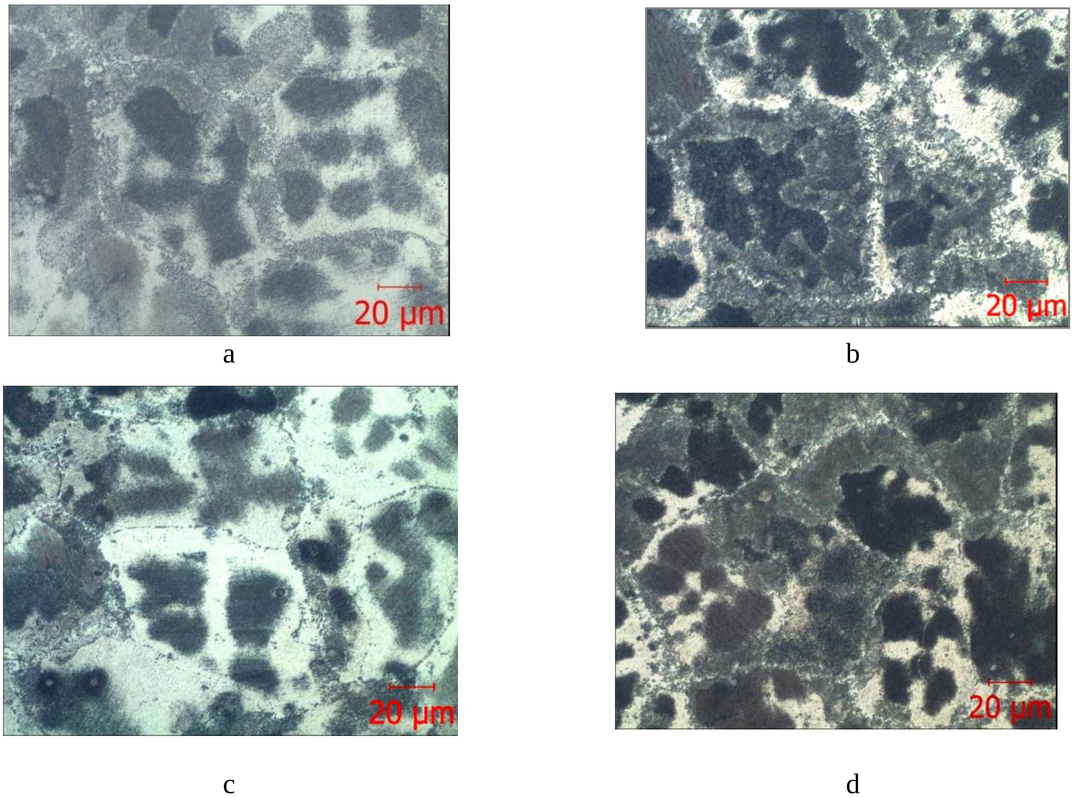


Fig. 2. The microstructure of ML5 alloy inoculated
with carbon nanoparticles (0.01 wt.%) at magnification x500:
a – standard ML5 alloy; b – ML5 alloy inoculated with carbon black;
c – ML5 alloy inoculated with nanographite; d – ML5 alloy inoculated with SWCNT

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Table 1

Comparative data on the grain size in ML5 alloy

| Grain refiner | Mean grain size, μm | | | |
|---|---|---|---|---|
| | No inoculation | Carbon black | Nanographite | SWCNT |
| 0.03% | 126...181<br>142 | 131...142<br>137 | 127...179<br>149 | 95...135<br>115 |
| 0.10% | 120...155<br>135 | 45...93<br>56 | 72...92<br>80 | 52...60<br>56 |

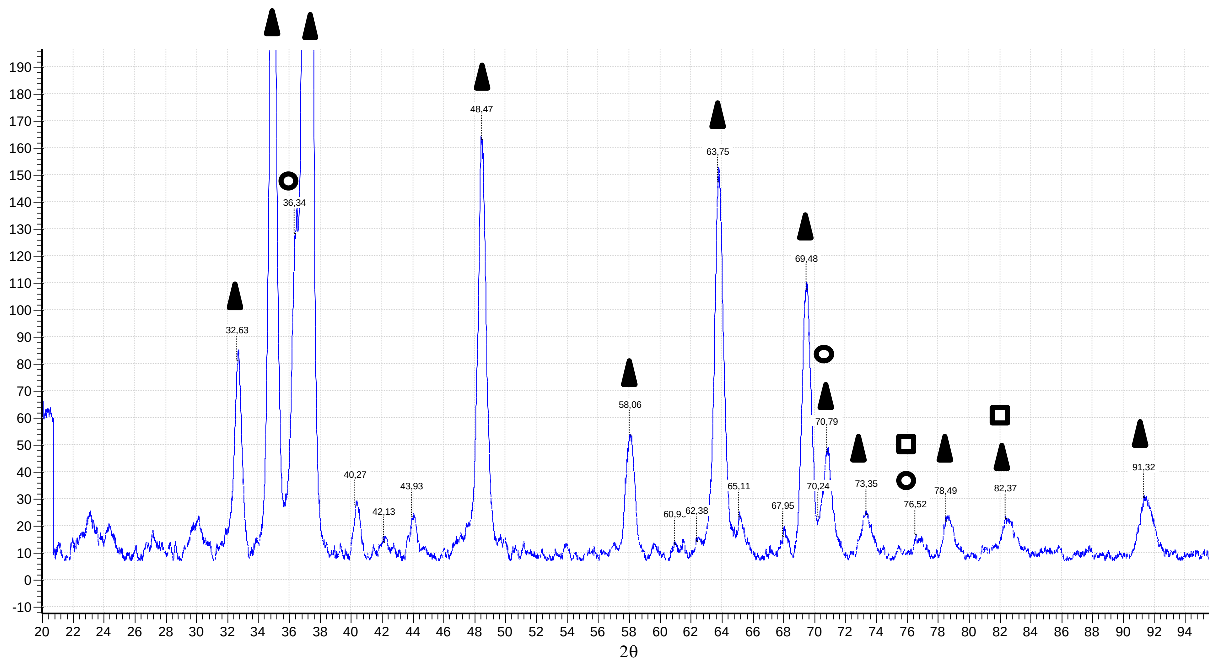


Fig. 3.X-ray diffraction pattern of ML5 alloy inoculated with nanographite (▲- α-Mg, **o** - γ- $Mg_{17}Al_{12}$, □ - C

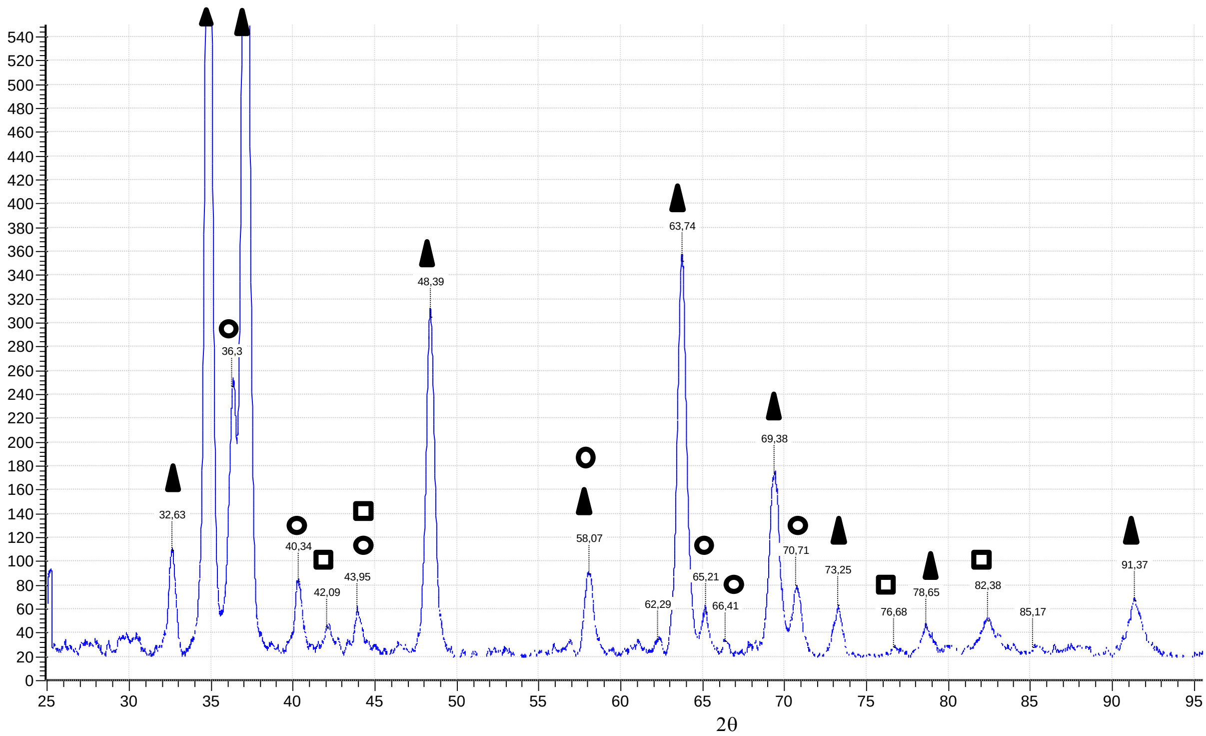


Fig. 4. X-ray diffraction pattern of ML5 alloy inoculated with SWCNT (▲- α-Mg, **o** - γ- $Mg_{17}Al_{12}$, □ - C)

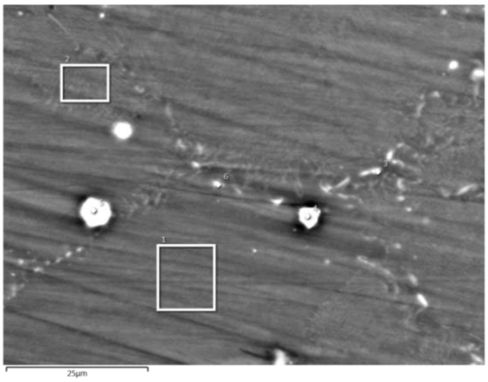

Fig. 5. Electron micrograph of ML5 sample section inoculated with 0.10% SWCNT
with indicated X-ray spectroscopic analysis areas

Table 2

Element content, wt.% according to X-ray spectroscopic analysis

| Spectrum name | Spectrum 1 | Spectrum 2 | Spectrum 3 | Spectrum 4 | Spectrum 5 | Spectrum 6 |
|---|---|---|---|---|---|---|
| Mg | 90.82 | 91.37 | 89.96 | 80.39 | 41.51 | 91.55 |
| Al | 8.70 | 8.63 | 9.49 | 17.30 | 34.21 | 8.44 |
| Si | | | | | 0.20 | 0.02 |
| Mn | | | 0.11 | 1.75 | 22.98 | |
| Ni | | | | | 1.09 | |
| Zn | 0.48 | | 0.44 | 0.56 | | |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

## Conclusion

Using inoculation of ML5 cast magnesium alloy with carbon nanoparticles in a quantity of up to 0.1 wt.% twofold grain size reduction may be achievable.

Inoculation with the carbon nanoparticles, in general, leads to no change in a phase composition of ML5 alloy. Inoculation with nanographite and single wall carbon nanotubes, however, has resulted in some quantitative phase proportion change.

The inoculation with the powdered carbon nanomaterials is a promising cost-efficient way to improve mechanical properties of ML5 cast magnesium alloy, which is attained by controlling the alloy structure. It is suggested that a series of extended experimental melts of the alloy be necessary in order to reveal in full the potential of the technique, which will help mastering the process on a commercial scale and collect a comprehensive statistical data base.

## Acknowledgment

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**Contribution of the authors:** definition of the problem – **Kostyantyn Balushok**, **Viktor Greshta**, **Spartak Makovskyi**; review and analysis of the information sources – **Kyryl Obnosov**; development of the carbon inoculating additive production process – **Spartak Makovskyi**; development of the grain refinement technique by carbon inoculation – **Vadym Shalomeyev**, **Spartak Makovskyi**; X-ray diffraction analysis – **Daria Tkach;** processing of the obtained research results on influence of the carbon nano particle inoculation on the structure of magnesium alloys – **Spartak Makovskyi, Daria Tkach**.

All the authors have read and agreed the published version of the manuscript.

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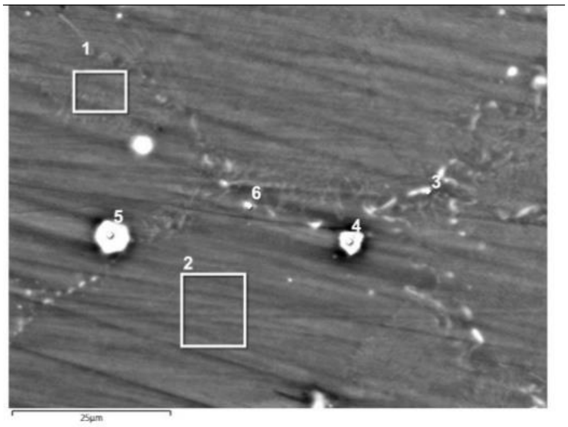


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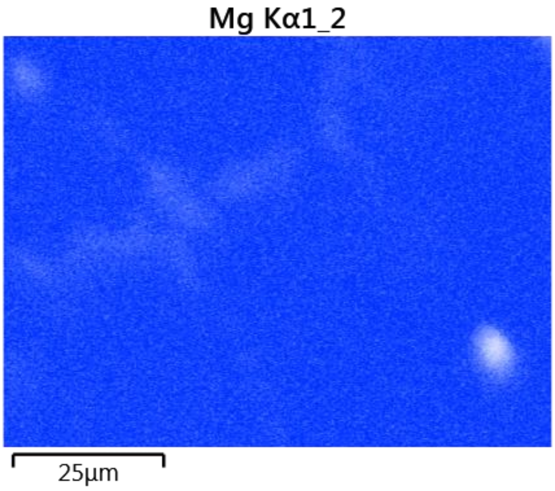


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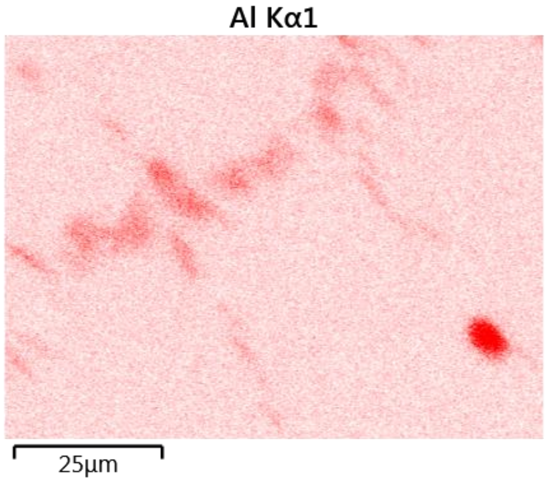


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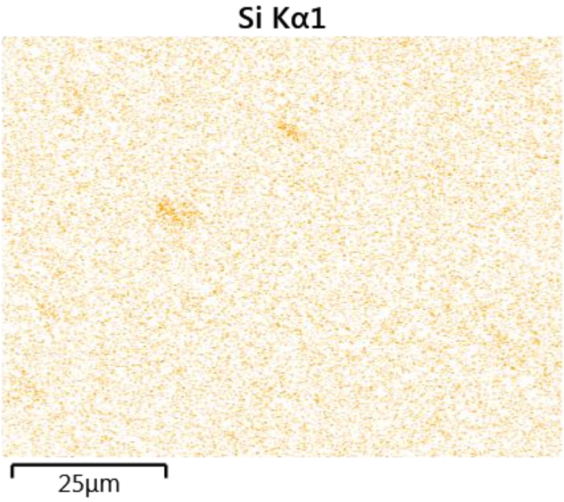
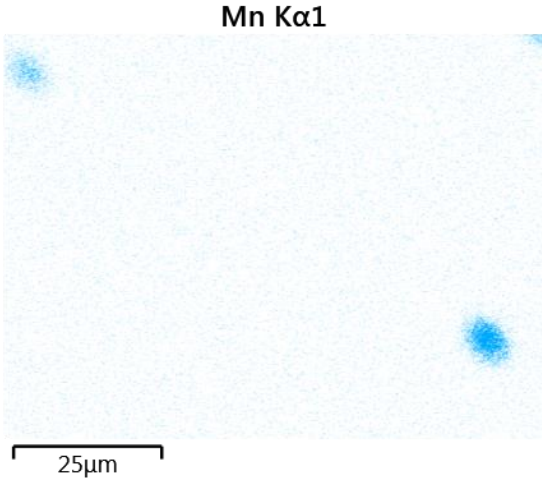



d




e

Fig. 6. X-ray spectroscopic analysis results of ML5 alloy sample inoculated with SWCNT, 0.1 wt.%.
a – electron micrograph (in a back scattered electron mode);
b...e – X-ray spectroscopic analysis results in a mapping mode.
More intense color corresponds to higher element concentration

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## ВПЛИВ МОДИФІКУВАННЯ ВУГЛЕЦЕВИМИ НАНОЧАСТКАМИ НА СТРУКТУРУ ЛИВАРНОГО МАГНІЄВОГО СПЛАВУ ML5

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Предметом дослідження у статті є структура ливарного магнієвого сплаву системи Mg-Al-Zn, модифікованого наночастками різних алотропних форм вуглецю. Метою є підвищення технологічності і якості магнієвих відливків навантажених авіаційних деталей відповідального призначення. Задачі: досягнення ефективного управління структурними характеристиками сплаву за рахунок введення домішок наночасток вуглецю; визначення залежності між кількістю доданого вуглецевого модифікатора та розміром зерна α – твердого раствору; дослідження впливу алотропних форм вуглецю на морфологичні хараткеристики міжзеренних меж і евтектоіду ($\alpha$+$Mg_{17}Al_{12}$); порівнювальне дослідження фазового складу серійного сплаву ML5 і сплаву ML5, модифікованого технічним вуглецем, нанографитом та одностінними вуглецевими нанотрубками. Фазовий состав визначали рентгеноструктурним методом у мідному випромінюванні. Також використовували мікрорентгеноспектральний аналіз (РСМА). Отримані наступні результати: за допомогою оптичного мікроскопу визначені розміри зерна α – твердий розчин у первинному та модифікованому станах. У зразках сплаву, модифікованого 0,1% технічного вуглецю, нанографіту та одностінних вуглецевих нанотрубок розмір зерна зменшено приблизно на 50 % в порівнянні з первинним варіантом. У зразках, модифікованих нанографітом і одностінними вуглецевими нанотрубками у кількості 0,10 % за вагою виділення структурної складової – евтектоїду ($\alpha$+$Mg_{17}Al_{12}$) вздовж меж зерен більш тонкі в порівнянні зі зразками серійного сплаву ML5 і зразками, модифікованими технічним вуглецем. Рентгеноструктурним аналізом створення нових фаз не виявлено. На діфрактограмах зразків спалаву ML5 з нанографітом і нанотрубками присутні слабкі лінії чистого вуглецю, що може вказувати на його присутність у незначній кількості у структурі. Наукова і практична новизна отриманих результатів міститься у наступному: випробувана технологія модифікування зростаючими домішками алотропних форм нановуглецю - технічним вуглецем, нанографитом і одностінними вуглецевими нанотрубками ливарного магнієвого сплаву системи Mg-Al-Zn у середовищі, наближеному до промислового виготовлення манієвого литва відповідального призначення. Показано, що додавання нановуглецю у кількості до

0,1% здатно позитивно впливати на структурні характеристики ливарного магнієвого сплаву ML5 при цьому не приводе до змінення його фазового складу. Нанографіт та одностінні вуглецеві нанотрубки, які мають впорядковану структуру, сприяють формуванню більш тонких межзеренних меж у порівнянні з аморфним технічним вуглецем.

**Ключові слова:** ливарний магнієвий сплав; модифікування; розмір зерна; інтерметалидна фаза $Mg_{17}Al_{12}$; вуглецеві наночастки; нанографіт; одностінні вуглецеві нанотрубки.

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