MICROSTRUCTURE STUDY OF MIXTURES OF MICROPOWDER Al AND NANO POWDERS TiN, SiC AND Al_2O_3 PRODUSED BY TWO STAGE PROCESS

Veselin Petkov[1], Yana Mourdjeva[1], Bojko Krastev[1], Vitaliy Bliznuk[2], Roumen Petrov[2, 3], Angel Velikov[1], Valentin Manolov[1]

[1]Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre at Bulgarian Academy of Sciences
67 Shipchenski prohod St., Sofia 1574, Bulgaria
veselin.petkov@ims.bas.bg (V.P.); yana@ims.bas.bg (Y.M.);
boikokrastev@gmail.com (B.K.); anmabg@abv.bg (A.V.); v.man.1943@abv.bg (V.M.)
[2]Ghent University, Technologiepark 46, Ghent, B-9052, Belgium
vitaliy.bliznuk@ugent.be (V.B.); roumen.petrov@ugent.be (R.P.)
[3]Delft University of Technology, Mekelweg 2, Delft, 2628 cd, The Netherlands
roumen.petrov@ugent.be (R.P.)

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ABSTRACT

Composite wires obtained from aluminium shell, micron sized aluminium powder and nano - sized TiN, SiC and Al_2O_3 powders were fabricated by a two stage process. The stages included ultrasonic treatment and hot extrusion. TEM and SEM observations were performed to investigate the wires' microstructure. Individual nano powder particles as well as particle agglomerations were observed by two microscopic methods, as well as nanoparticles distribution and localization in the matrix. It was found that the observed nanoparticles and clusters were in the volume of micron-sized Al particles and along the grain boundaries of the matrix. The provided EDX analysis confirms the presence of nanoparticles in the aluminium matrix. From the obtained results, it can be concluded that the two stage fabrication process of nanocomposite wires leads to better wetting of the nano powders from the aluminium melt. Nanocomposites obtained by mixing and extruding TiN, SiC and Al_2O_3 nano powders and Al micro powders can be used as modifiers of aluminium alloys, as the nanoparticles will contribute to grain refinement and will participate as additional crystallization centers.

Keywords: extruded nanocomposites, nanoparticles, nano - scale powders, TEM and SEM study.

INTRODUCTION

Aluminium's light weight and high corrosion resistance make it highly desirable for many applications. Al alloys and Al - based composite materials are widely used in industry due to their excellent mechanical properties and low density. Such materials find application also in advanced fields as aerospace, automotive and military industry, where lower density means significant energy savings [1].

For improving mechanical properties of alloys, different modification and refinement processes are used [2]. These can be divided into three categories: (1) chemical, (2) mechanical and (3) thermal. The essence of the chemical processes lies in the addition of a calculated amount of nucleation agents. In the case of mechanical processes methods like ultrasonic, squeeze, stirring, centrifugal and vibration are used to refine materials structure and enhance materials properties. Thermal processes include super - heating, quenching and cooling [3].

The use of nano - scale powders to improve alloys properties is the topic of many recent studies. Most often nano powders are used in the form of carbides, nitrides and oxides [4-10]. Borodianskiy et al. used TiC powder with particle size of 20 nm mixed with aluminium powder with average particle size of 640 μm [11]. Then the powders were activated in a planetary mill for 5 min at 400 rpm. The resulting mixture was extruded at 350°C and an extrusion degree of 17.4. There is no data on the microstructure of the extruded mixture. The latter was used to modify an aluminium alloy.

A similar approach was used by Mazahery - a mixture of nano - sized SiC particles with an average size of 50 nm and Al particles with an average size of 16 μm were mixed with a ratio of 1:1.67 and processed in a planetary mill in an isopropyl alcohol medium for 20 min [12]. After drying in vacuum samples with dimensions 60 x 60 x 60 mm were pressed at 200 MPa. Although extrusion was not performed here, the paper provides information on the mechanical and chemical processing technologies of the powder mixture used.

In method for obtaining a wire of aluminium mixed with nanoparticles described by Reshetnikov different chemical compositions were presented [13]. The technology includes the following steps: making a thin - walled aluminium vessel (165 mm in diameter), filling the vessel with the prepared mixture of Al and nanoparticles, rotating the closed vessel in a drum with eccentric axes for about 30 min, separating excess nanoparticles from the mixture, heating the vessel to 400 - 420°C and extrusion to a wire with a diameter in the range of 5.0 to 9.5 mm. The microstructure of the resulting wire consists of fibers with an average diameter of 0.11 mm. There is no data on the distribution of nanoparticles in the extruded material.

Lee et al. studied TiC particles with an average size of 10 μm and Cu particles with an average size of 20 - 50 μm were mixed [14]. The planetary mill was equipped with balls 8 mm in diameter. The mass ratio of the balls to the powder mixture was 20:1, at a circular mill speed of 1100 rpm, a grinding time of 6 min and a weight ratio of TiC and Cu powders of 1:1. To increase the wettability of the ceramic particles Sn was used as a surfactant.

An important feature of the modification technology is the method of introduction and preliminary preparation of nanoparticles. It is well known that these particles have poor wettability. Therefore, different methods are used to enhance their wettability, such as: 1) plating by processing in a planetary mill, 2) electro - chemical coating of the particles and 3) extrusion of a mixture of micro - sized Al and nano - sized particles. The resulting particles should be used immediately after the plating process as exposure to the environment reduces their effectiveness as crystallization centers. Limiting exposure to the environment can be achieved by 1) pressing nanocompositions in the form of tablets or 2) extrusion. Extrusion is also a method for obtaining nanocompositions in the form of wire, which can find application in casting and welding.

From this brief overview different technologies are used for treatment of the nanoparticles before introducing them into the melt. These technologies are tailored to the alloy being modified and to the type of nanoparticles. In all cases, however, such preparation must be carried out to ensure the following: 1) good wetting of the particles by the melt, 2) homogeneous distribution of the particles in the melt's volume and 3) subsequent improvement of the mechanical properties of the aluminium alloy.

In the present work the last method is applied, namely extrusion of micro - Al and nano powder mixture. The used nano powders are TiN, SiC and Alumina. The resulting wire containing nanoparticles ensures their reliable introduction into the melt. In addition, this product protects the nanoparticles from environmental influence and prevents the reduction of their effectiveness as centers of crystallization in the melt. These nanomaterials can be used in both: bulk modification of castings and in welding.

EXPERIMNTAL

Al powder is produced by Strem Chemicals Inc., USA and has an average particle size of 31.7 μm according to producer certificate. Statistical distribution of Al powder particle size was performed by us using "Analysette 22 NanoTec plus" by Fritsch. The average size was determined as 31 μm. SEM image of the Al powder is shown in Fig. 1.

The TiN, SiC and Al_2O_3 nano powders produced by Nanomaterials Inc., USA were used as composite constitutes in our study. According given from the manufacturer certificate the average sizes per powders nanoparticles were 20 nm, 45 nm and 80 nm for TiN, SiC and Al_2O_3 respectively.

TEM images of the powders are presented in Fig. 2. In Fig. 2a. TiN particles with an average size of 10 nm are observed. There are also single larger particles with an average size of 25 nm. TEM images of the SiC nanoparticles are shown in Fig. 2b. Their particle size ranges from 20 to 60 nm. TEM images of the Al_2O_3 nanoparticles are shown in Fig. 2c. Their shape is spherical, and it is possible to distinguish three size fractions: 100 nm, 50 nm and 20 nm. From the presented figures it can be seen that the nanoparticles tend to form agglomerates regardless of the ultrasonic pre - treatment, which was performed. It should be noted that this agglomeration is a characteristic feature of all nano powders.

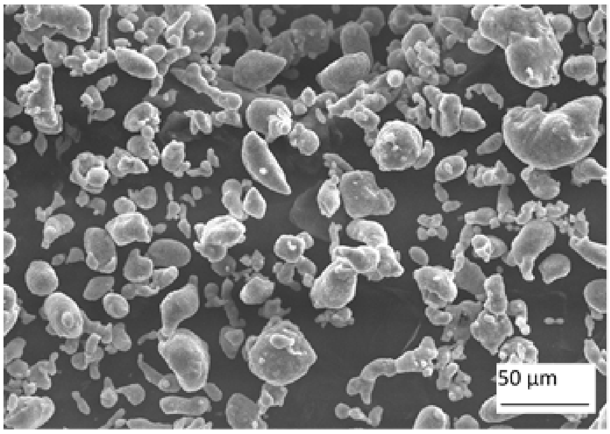
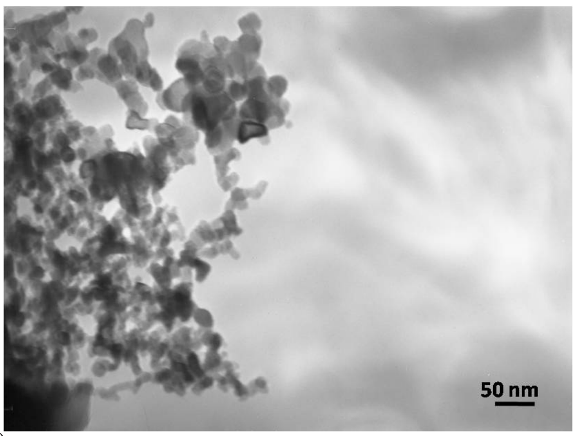


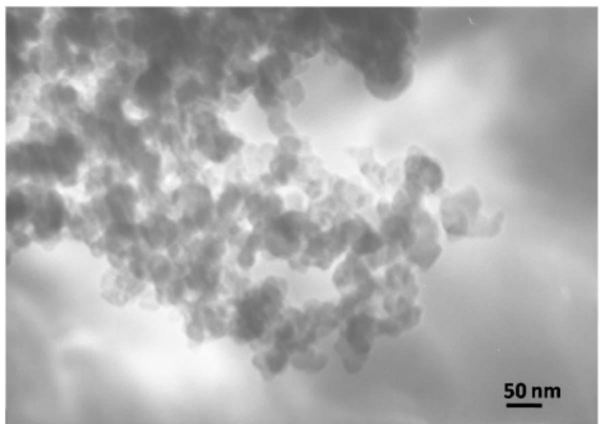
Fig. 1. SEM image of the used Al powder.

Producing a wire of (Al micro powder + nano powders) mixture is two stage process, described in detail in [15]. The process' first stage is ultrasonic dispersion and the second one is hot extrusion. The obtained product from the process is rod (wire) with a diameter of 4.1 mm and a composition: Al + nano SiC, Al + nano TiN and Al + nano Al_2O_3.

For TEM examination of extruded nanocompositions containing TiN, SiC and Al_2O_3 nanoparticles samples were prepared by thinning to residual thickness of 100 µm. The observation plane is parallel to the direction of extrusion. Disks with a diameter of 3 mm were cut from the thinned foils and



a)



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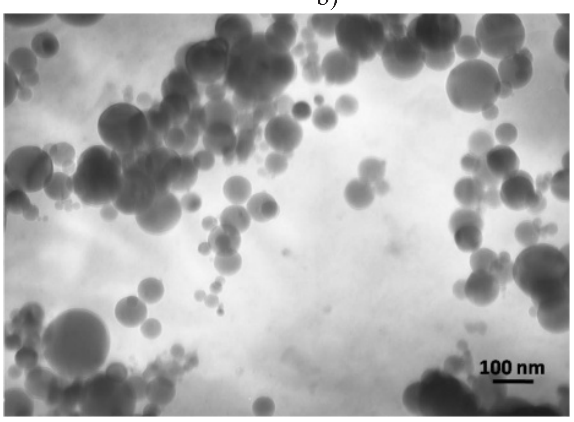

c)

Fig. 2. TEM images of nanopowders (a) TiN; (b) SiC; (c) Al_2O_3.

polished with TENUPOL 3 by Struers GmbH with a standard electrolyte for aluminium alloys. They were subsequently ion - milled for half an hour to obtain a proper sample for TEM observation. The foils were observed by JEM 2200 - FS (JEOL) at accelerating voltage of 200 kV and energy dispersive X - ray (EDX) system by AMETEK.

SEM and EDX analysis of the studied composites are carried out on Quanta 450 FEG (Thermo Fisher Scientific) at accelerating voltage of 20 kV. All studied samples are prepared by standard grinding and polishing procedures.

RESULTS AND DISCUSSION

The microstructural observations of extruded nanocompositions containing TiN nano powder are given below. The weight ratio of nano powder to Al micro-powder for all extruded compositions is 1:3. TEM images reveal agglomeration of TiN particles presumably due to strong Van der Waals forces. Since the particle size of as-delivered TiN powder is in the range 10 - 25 nm (Fig. 2a.), it can be suggested that the dark phase in Fig. 3 represents agglomerations of nanoparticles. This is confirmed by quantitative analysis (Table 1): the higher the number of agglomerated particles the higher is the Ti content. The average size of the small agglomerations is 60 - 80 nm while that of the big agglomerates is 200-300 nm. It is noteworthy that the big clusters tend to form inside Al matrix grains while small ones are frequently found near grain boundaries.

Table 1. Quantitative analysis results of extruded nanocompositions containing TiN nano powder.

The marked phases correspond to the Fig. 3.

Table 1. Quantitative analysis results of extruded nanocompositions containing TiN nano powder.

Phase/Element	Al, at. %	Ti, at. %
009	99.10	0.80
010	94.71	5.06
011	90.14	6.08
012	94.88	1.54
013	95.58	0.89

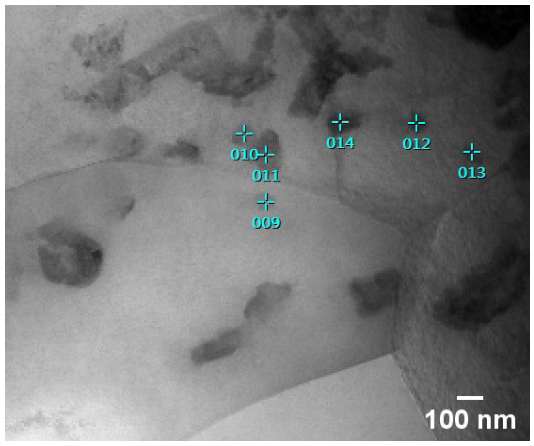

Fig. 3. TEM bright field image of extruded nanocompositions containing TiN nano powder.

Fig. 4 shows the area presented in Fig. 3 with results of performed EDX element mapping. The mapping procedure confirmed that the dark phase represents TiN agglomerates.

Fig. 5 shows SEM micrograph of extruded nanocompositions containing TiN nano powder. Small clusters (3 to 4 nanoparticles) are observed (phase 1) as well as large clusters made of tens of particles (phase 2). EDX analysis results of phase 2 are presented in Table 2.

From the observation on extruded nanocompositions

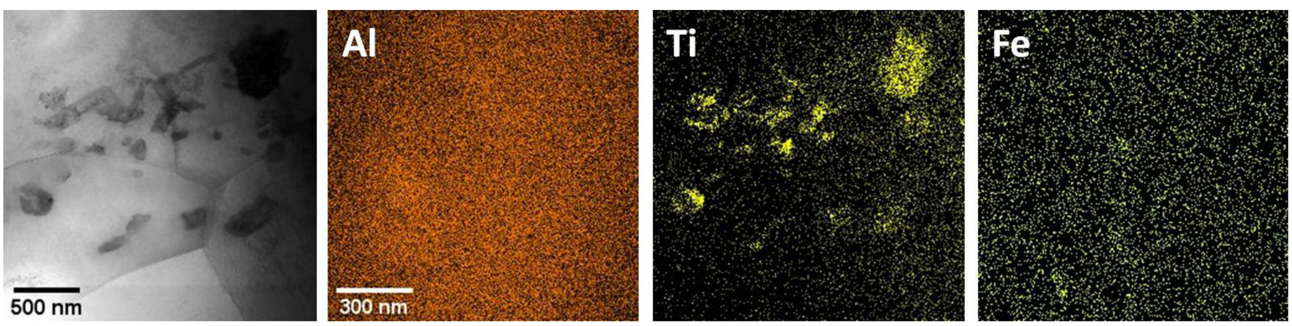

Fig. 4. Results of EDX element mapping of extruded nanocompositions containing TiN nano powder.

containing SiC nano powder can be seen that here, again, agglomeration of the nano powder has occurred, but individual particles are also visible (see TEM image in Fig. 6, individual particles marked with arrows). The reasons for agglomeration are the Van der Waals forces and the high surface activity of nano - sized particles. It is suggested that the dark phase in Fig. 6 represents aggregates of nanoparticles. This is confirmed by quantitative analysis - results are given in Table 3. Results of EDX element mapping show that the SiC nano powder is very unevenly distributed in the sample's volume (Fig. 7). For example, a large aggregate of particles is observed in the bottom part of the imaged area. This cluster of particles has elongated shape, and it is suggested that the direction of elongation coincides with the extrusion direction of the specimen. Most of the observed clusters of particles have sizes in the range from 200 to 500 nm.

The results of SEM analysis are presented in Fig. 8, where even smaller individual particles are shown. EDX analysis results of phase marked as 1 in Fig. 8 of extruded nanocomposition containing SiC nanopowder particles are given in Table 4. This results confirms the nature of the found particles in this nanocomposition.

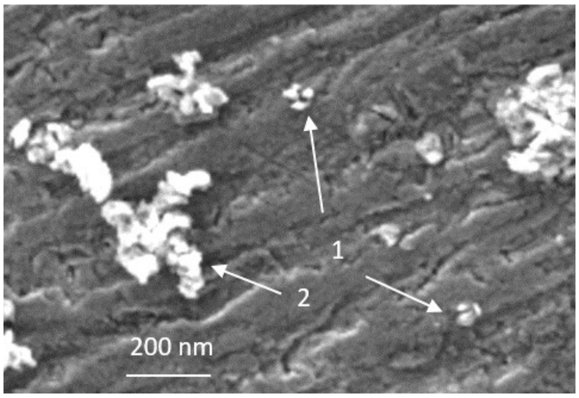

Fig. 5. SEM image of extruded nanocompositions containing TiN nano powder.

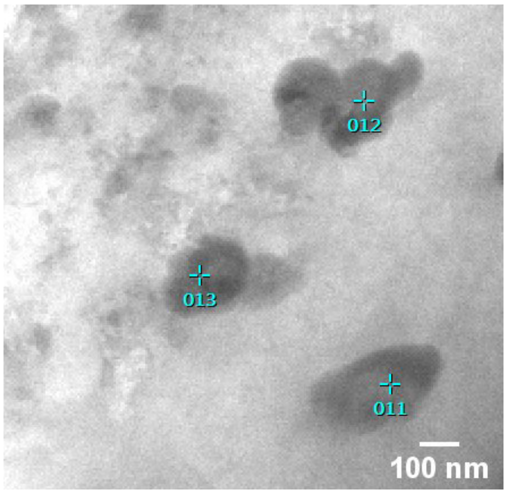

Fig. 6. TEM bright field image of extruded nanocomposition containing SiC nano powder.

Table 2. EDX analysis results of phase 2 marked in Fig. 5 of extruded nanocompositions containing TiN nano powder.

Phase/ Element	Weight %	Atomic %	Relative error, %
Ti	45.84	29.37	2.26
Al	43.13	48.82	2.63

Table 3. Quantitative analysis results of extruded nanocomposition containing SiC nano powder.

Phase/ Element	C, at. %	Si, at. %	Al, at. %
012	10.59	75.77	13.64

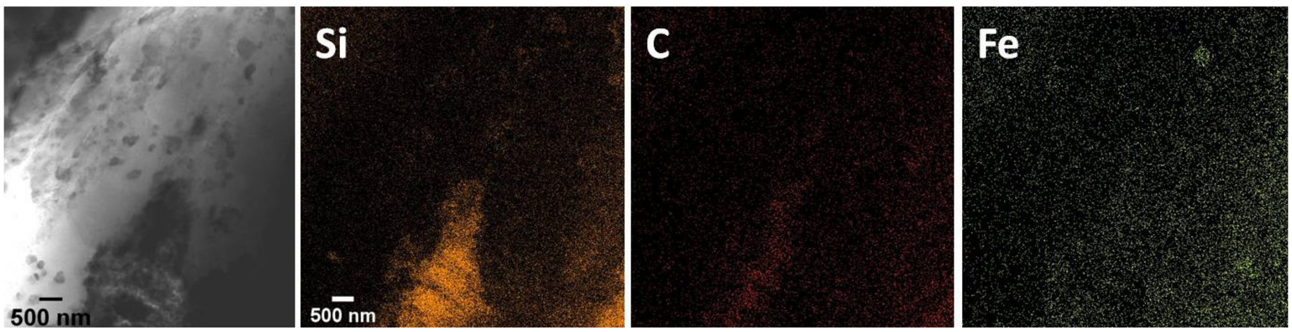

Fig. 7. Results of EDX element mapping of extruded nanocomposition containing SiC nano powder.

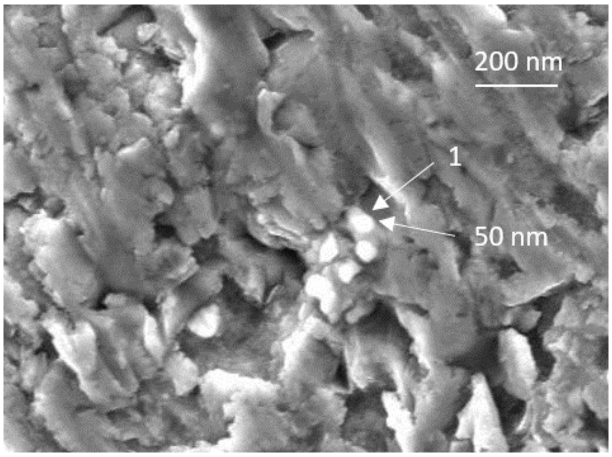

Fig. 8. SEM image of extruded nanocomposition containing SiC nano powder.

Table 4. EDX analysis results of phase 1 (Fig. 8) of extruded nanocomposition containing SiC nano powder.

Phase/ Element	Weight %	Atomic %	Relative error, %
Si	83.91	70.83	1.50
C	13.72	27.09	10.99
Al	2.37	2.08	3.05

At extruded nanocomposition containing Al_2O_3 nano powder it looks that the agglomeration process is less pronounced in this composite material compared with the previous two. This is most probably due to the spherical shape of the nanoparticles. Heterogeneous modifier particles were observed, with measured individual particle sizes ranging from 180 to 40 nm. Several fractions are distinguished: The largest particles are about 12 % and have an average size of 180 nm; the medium ones have an average size of 100 nm and are about 44 % and the rest are the smallest fraction with an average size of 50 nm. Their distribution is relatively even. Around the largest fraction, "halos" can be noticed, which are most likely due to preferential electropolishing or poor incorporation of these particles with the matrix. The nanoparticles are unevenly distributed, as zone location is valid for this type of modification too. Many individual alumina particles with varying dimensions are observed on TEM (Fig. 9) as well as on SEM (Fig. 10) images. EDX analysis results from the place presented on Fig. 9 are given in Table 5. EDX analysis results from place given in Fig.10 are given in Table 6.

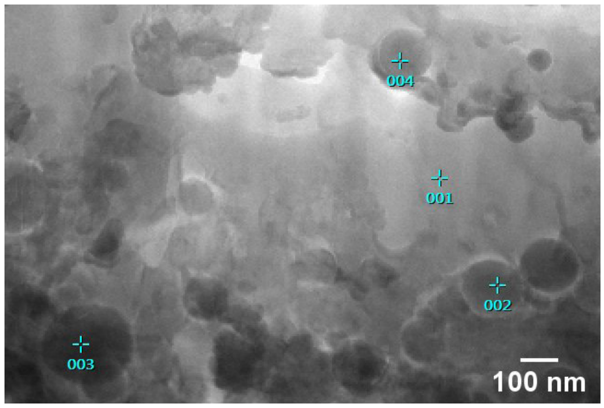

Fig. 9. TEM bright field image of extruded nanocomposition containing Al_2O_3 nano powder.

Table 5. Quantitative analysis results of extruded nanocomposition containing Al_2O_3 nano powder.

Phase/Element	Al, at. %	O, at. %
001	86.90	13.10
004	56.44	43.56

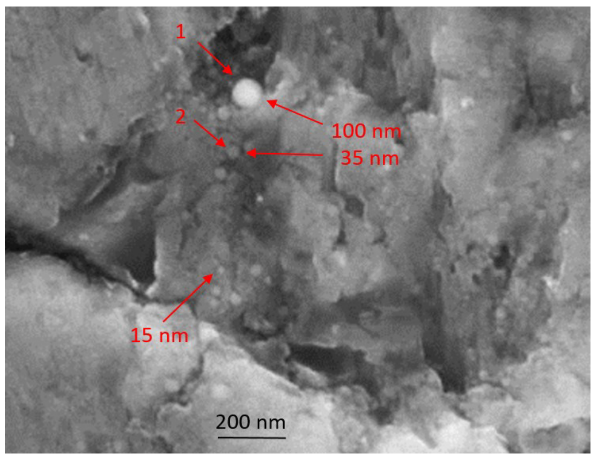

Fig. 10. SEM image of extruded nanocomposition containing Al_2O_3 nanopowder.

Table 6. EDX analysis results of phases marked 1 and 2 in Fig. 10 of extruded nanocomposition containing Al_2O_3 nano powder.

Phase	Element	Weight %	Atomic %	Relative error, %
1	Al	68.62	56.46	1.84
	O	31.38	43.54	4.72
2	Al	65.85	53.35	1.89
	O	34.15	46.65	4.60

Van der Waals forces between two spheres (particles) of constant radius depend on the material properties, particle radius and distance between surfaces. In Van der Waals forces between objects with different geometries were calculated using the Hamaker model [16, 17]. Although the Van der Waals force decreases with decreasing size of the objects, it does not disappear and becomes dominant for very small particles, such as fine-grained dry powder, while the gravity force has a smaller effect for particles of the same substance. As a rule, free flow occurs with particles larger than 250 µm.

The effect of particle agglomeration is observed with all three types of modifiers; however, this effect is less pronounced in the extruded composition containing alumina particles, which is due to their spherical shape. Another observation is that the direction of elongation of the zones rich in particles coincides with the longitudinal section of the sample and with the direction of extrusion. Another observation is that the direction of elongation of the zones rich in particles coincides with the longitudinal section of the sample and with the direction of extrusion. In areas lacking strong agglomeration of modifier particles, small agglomerations or even single particles are observed near the grain boundaries of the matrix while larger agglomerates can be seen in the volume of the matrix grains. The presence of nanoparticles or even agglomerations of particles, but small, close to the grain boundaries can provide a barrier for dislocations and even act as an obstacle for accumulation of dislocations at the boundaries. The entanglement of dislocations by nanoparticles may stop their propagation and, accordingly, is expected to strengthen the material and therefore enhance its mechanical characteristics.

Regarding the modifiers with smaller individual particle sizes (TiN and SiC) no pull out of particles from the matrix is observed. There are no micro-cracks, which indicate good wetting and a good mechanical connection between the modifier and the matrix. However, this is not the case with the alumina modifier especially regarding particle fraction 50 to 100 nm - bad mechanical connection is observed here. Micro - cracks and slits along the contour of the particles are also visible, which indicates poor wetting. With this type of modifier, the particle distribution is not homogeneous. There are places where the particles are predominantly located on the grain boundaries and the grain volume remains free of modifier.

As stated in the introduction, there are only a small number of publications which describe extruded nanocompositions used to modify aluminium alloys [11, 13]. However, they lack micro - structural investigation of the extruded nanocompositions. Thus, our TEM and SEM studies fill this gap and advance the development of technology for obtaining extruded nanocompositions used to modify aluminium alloys.

CONCLUSIONS

- Experimental samples of three nanocompositions were produced by a two-stage technology involving ultrasonic treatment and hot extrusion as follows:

  i) (microparticles of Al + nanoparticles of TiN)

  ii) (microparticles of Al + nanoparticles of SiC)

  iii) (microparticles of Al + nanoparticles of Al_2O_3)

- Microstructural studies were performed using TEM and SEM. Nano - sized particles as well as clusters of different sizes were observed in the nanocompositions. The presence of clusters shows that the duration of ultrasonic treatment applied in our study was not sufficient for clusters destruction.
- The distribution of nanoparticles in the extruded materials is uneven. Individual nanoparticles and clusters are observed, both in the volume of the aluminium micro-particles as well as along their grain boundaries.
- The significance of the conducted research lies in the clarification of the mechanism of extrusion of aluminium - based nanocompositions.

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methodology, investigation; V.M.: Conceptualization, analysis, funding acquisition, project administration.

REFERENCES

1. N.L. Sukiman, X. Zhou, N. Birbilis, A.E. Hughes, J.M.C. Mol, S. Garcia, in: Z. Ahmad (Ed.), Aluminium Alloys - New Trends in Fabrication and Applications. ed Rijeka: In Tech, 2012.
2. K. Borodianskiy, M. Zinigrad, Mechanical Properties and Microstructure Characterization of Al - Si Cast Alloys Formation Using Carbide nanoparticles, J. Mater. Sc. Sc. Applications, 2015, 1, 3, 85-90.
3. W.S. Ebhota, T.C. Jen, Effects of Modification Techniques on Mechanical Properties of Al-Si Cast Alloys. Aluminium Alloys - Recent Trends in Processing, Characterization, Mechanical Behavior and Applications, In Tech, 2017. http://dx.doi.org/10.5772/intechopen.70391.
4. V.P. Saburov, A.N. Cherepanov, M.F. Zhukov, G.V. Galevskiy, G.G. Krushenko, V.T. Borisov, Plasma - chemical synthesis of ultra - disperse powders and their application in metal and alloy modification, Monography, Low - temperature plasma 12, Novosibirsk, Nauka, 1995, (in Russian).
5. K. Borodianskiy, M. Zinigrad, A. Gedanken, Aluminum A356 Reinforcement by Carbide nanoparticles, J. Nano Res., 13, 2011, 41-46.
6. S. Cai, Y. Li, Y. Chen, X. Li, L. Xue, Effect of nano TiN/Ti refiner on as - cast and hot - working microstructure on commercial purity aluminium, Transactions of Non - ferrous Metals Society in China, 23, 2013, 1890-1897.
7. A. Mazahery, M.O. Shabani, Characterization of cast A356 alloy reinforced with nano SiC composites, Transactions of Non - ferrous Metals Society in China, 22, 2012, 275-280.
8. Ch. Yujin, C. Maosheng, X. Qiang, Zh. Jing, Electro less nickel plating on silicon carbide nanoparticles, Surface and Coatings Technology, 172, 2003, 90-94.
9. P. Kuzmanov, A. Velikov, R. Dimitrova, A. Cherepanov, V. Manolov, Study of the influence of modification by nanocompositions both on the process of crystallization and on the structure of aluminium alloy AlSi7Mg, J. Nanomater Mol Nanotechnol 8:3., 4th International Conference on Materials Science & Engineering, June 26 - 27, Paris, France, 2019.
10. P. Kuzmanov, R. Dimitrova, R. Lazarova, A. Cherepanov, S. Popov, R. Petrov, V. Manolov, Investigation of the structure and mechanical properties of castings of alloy AlSi7Mg, cast iron GG15 and GG25 and steel GX120Mn12, modified by nanosizedpowders, Proceedings of the Institution of Mechanical Engineers, Part N: J. Nanoengineering and Nanosystems, 2014.
11. K. Borodianskiy, A. Kossenko and M. Zinigrad, Improvement of the Mechanical Properties of Al - Si Alloys by TiC nanoparticles, J. Metallurgical and Materials Transactions, 44a, 2013, 4948-4953.
12. A. Mazahery, Characterization of cast A356 alloy reinforced with nano SiC composites, Trans. Nonferrous Met. Soc., China, 22, 2012, 275-280.
13. S.N. Reshetnikov, Authoreferat of dissertation thesis “Application of nanopowder chemical compounds to improve the physical and mechanical characteristics of machine - building products”, Krasnoyarsk, 2008, (in Russian).
14. S.- H. Lee, Fabrication of cast carbon steel with ultrafine TiC particles, Trans. Nonferrous Met. Soc., China, 21, 2011, 54-57.
15. V. Petkov, Y. Mourdjeva, B. Krastev, A. Velikov, V. Manolov, Fabrication and micro-structural investigation of (micro - Al + nano - SiC) composition for aluminium alloys modification, Inter. Sci. Conf. “INDUSTRY 4.0”, Borovetz, Bulgaria, 2022.
16. R. Tadmor, The London - Van der Waals interaction energy between objects of various geometries”, Journal of Physics: Condensed Matter., 13, 9, 2001, L195-L202. Bibcode:2001JPCM.13L.195T. doi:10.1088/0953-8984/13/9/101. S2CID 250790137.
17. J. Israelachvili, Intermolecular and Surface Forces. Academic Press. ISBN 978 - 0 - 12 - 375181 - 2, 1985-2004.