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ALUMINIUM METAL MATRIX COMPOSITE SINTERING WITH ELECTROLESS METALLIZED COMPONENTS

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Abstract: *In this work was studied the creation possibilities of Aluminium Metal Matrix Composite (AlMMC) with joint electroless co-metallized matrix and non-metallic components. The metal matrix is aluminium alloy (AlSi9Cu3) turnings preliminary Ni-Cu-P coated at the same time as the reinforcing phase thereafter mixed and sintered together. Different types of non-metallic reinforcement and un-reinforcement phases are used to create the sintered composites with aluminium powder, silicon carbide microparticles and carbon nanotubes (CNTs). A comparative analysis of the morphology, hardness and the elemental composition of the obtained composite materials were presented; also tribological research was performed.*

Keywords *aluminium metal matrix composites, electroless metallization, tribology, wear resistance, sintering.*

1. INTRODUCTION

Aluminium Metal Matrix Composites (AlMMC) offer significant potential for use in the automotive and aviation engineering due to their light weight and good mechanical properties coupled with improved wear resistance [1, 2]. Compared to casting, powder metallurgy has the advantage of being able to produce hypereutectic Al-Si alloys with a high percentage reinforcing phase, which enhances the wear resistance of the produced materials and significantly alters their mechanical properties [3, 4].

The aluminium matrix of most of the structural composites is based on wrought or cast alloy composition containing Cu, Si and / or Mg, and relatively rarely Zn [5, 6]. When composing AlMMC, hard ceramic particles with sharp edges of Al_2O_3, SiC or $ZrSiO_4$ spherical particles and some industrial waste such as fly ash with non-sharp morphology are traditionally used as a reinforcing phase [7]. Carbon nanotubes (CNTs) are a suitable material for the production of Aluminium Metal Matrix Composites by powder metallurgy [8]. Sometimes the carbon nanotubes perform the function of the un-reinforcing phase. To improve the wetting of the non-metallic components of the composite materials (especially in the presence of a liquid phase) and to create better adhesion bonds with the aluminium matrix, electroless metallization of the reinforcing phase is often applied [9-12].

The purpose of the work is to investigate the possibility of creation of Aluminium Metal Matrix Composites based on aluminium turnings and both electroless metsllization (Ni-Cu-P) of the Aluminium Alloy Metal Matrix and reinforcing / un-reinforcing components.

Aluminium alloy turnings (AlSi8Cu3) and three different types of neutral, reinforcing and un-reinforcing material are used to create a co-metallized sintered composite. The three types used materials are as follows: aluminium powder, silicon carbide microparticles and carbon nanotubes (CNTs).

2. MATERIALS AND METHODS

A cast aluminium alloy (EN AB-AlSi8Cu3) is used to produce the aluminium turnings with cross-sectional dimensions of about 0.1 mm x 0.05 mm. The mechanical properties of the basic aluminium alloy EN AB-46200 (DIN 226) are as follows: Brinell hardness 82; yield strength $Rp_{0.2}$ = 130 MPa; ultimate tensile strength R_m = 210 Mpa; with density 2.8 g/cm^3, melting onset (Solidus) 540^{O}C, melting completion (Liquidus) 620^{O}C.

The aluminium powder's size is max. 100 μm, stabilized with 2% fat, 90% base substance. The Silicon carbide is 7-10 μm fraction and it is mixed with aluminium powder in a 1: 1 ratio.

The carbon nanotubes (CNTs) had an average diameter of 10-40 nm and a length of 1.0 - 25 μm, a purity by weight 93% and a specific surface area 150 – 250 m^2/g.

2.1 Electroless Ni-Cu-P of the Components

All components for sintered composite material, after appropriate surface preparation, are chemically nickel-copper plated / coated.

The solution for electroless ultrasonic treatment for realization of the Ni–Cu-P coating procedure [13, 14] contains, as follows: nickel chloride ($NiCl_2.6H_2O$) - 25-40 g/l; copper sulphate ($NiSO_4.6H_2O$) – 10-25 g/l; ammonium citrate $(NH_4)_2C_6H_6O_7.H_2O$ - 50-80 g/l; sodium citrate ($Na_3C_6H_5O_7..2H_2O$) - 30-50 g/l; and sodium hypophosphate ($NaH_2PO_2.H_2O$) - 10-20 g/l.

The preparation of CNTs includes surface cleaning in acetone (CH_3COCH_3) and surface modification containing the following stages: oxidization in concentrated nitric acid (HNO_3); sensibilization and chemical activation in solution, containing $PdCl_2$ and $SnCl_2$ dissolved in 3M hydrochloric acid (HCl).

The result from the fiber modification and the removal of the oxide layer from the aluminium powder is the creation of a low pH at the dispersion phase surface and accordingly the reduction of the total pH of the metallization suspension.

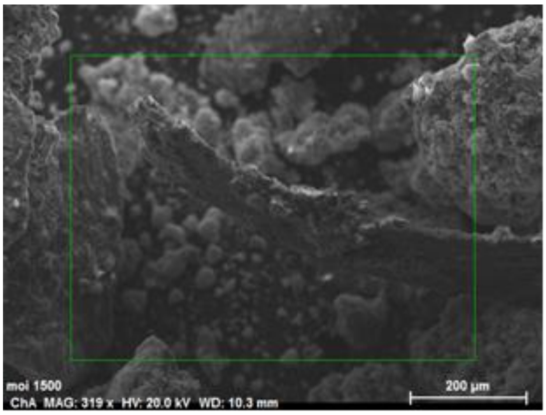
After electromagnetic stirring the suspension for the plating, along with the activated aluminium powder / SiC / CNTs has a pH value of 5.

The suspension is alkalized with ammonia to pH 9-10 under ultrasonic treatment. The alkalysis of the suspension with ammonia results in a gradual initiation of an exothermic reaction at room temperature resulting in an intense release of hydrogen in the form of bubbles. This reaction is maintained by the treatment in an ultrasonic bath without the need for further heating of the suspension.

The degreased aluminium turnings (AlSi8Cu3) are added to the carbon nanotubes or aluminium powder suspension with a started release of hydrogen, and is waited until the ultrasonic bath reaction is complete. The dense suspension containing the aluminium turnings is transferred from the bath for ultrasonic treatment to electromagnetic stirring.

The suspension is diluted with a new solution and stirred intensive at 1800 rpm. The reaction may be accelerated and the metallization re-started by further heating to 70-80^{O}C. The color of the suspension with light aluminium alloy turns gradually darkens. After the completion of the metallization, the suspension is colored in black due to the deposited nickel-copper-phosphor coating and the surface of the aluminium turnings.

After the completion of the co-nickel-copper metallization of the disperse phase and the aluminium turnings, they are filtered through a filter paper ("blue strip"). After an air drying, the metallized components of the composite material are pulverized to a powder state.



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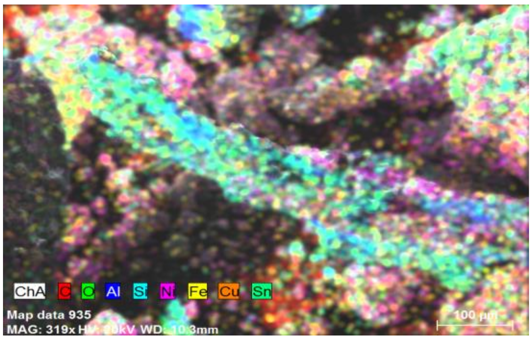

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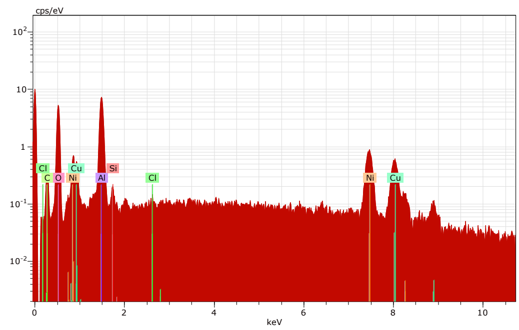

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Figure 1. Co-metallized (NI-Cu-P) aluminium alloy (AlSi8Cu3) turnings and CNTs: (a) Scanning electron microscopy; (b) EDX mapping; (c) EDX spectrum

From the Energy Dispersive X-ray EDX analysis (EDX) shown in Figure 1c it can be seen that when co-metallization with the described ultrasonic treatment solution, the nickel and copper peaks are almost equal, which implies the coating of all sintering components with a copper-nickel-based alloy.

2.2 Sintering of Aluminium Metal Matrix Composites

The production of samples for hardness and wear resistance testing from the co-metallized dispersed phase and aluminium alloy turnings involves several major steps: blending, cold compaction at 300 MPa, and sintering at 540 °C for 4 hours in an argon atmosphere. This heating results in a swelling effect and the emergence of fine drops of molten metal on the surface of the samples due to the formation of small amounts of the supersolidus liquid phase from the basic metal alloy matrix (Fig. 2a).

After the sintering, cooling of air and age hardening is also performed on the produced composites, carried out at a temperature of 140-170^{O}C for 10-14 hours.

The sintering material is a matrix of an aluminium alloy turnings of 8% and up to 18% by weight of a reinforcing / un-reinforcing phase. Before the cold compaction, about 1% lubricant Zn stearate is added to the metallized mixture and homogenized by an intensive agitation. No lubricant is added to the CNTs sintering mixtures, because they themselves act as a lubricant.

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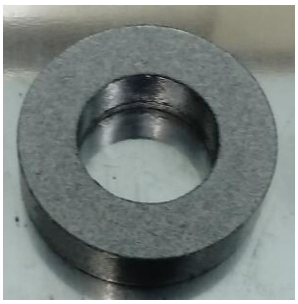

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Figure 2. Sintered co-metallized AlMMC with: (a) aluminium powder; (b) silicon carbide microparticles; (c) carbon nanotubes (CNTs)

The samples for wear resistance and hardness testing are rings with an inside diameter of 23 mm, an outer diameter of 42 mm and a height of 10 mm. Due to the high reinforcing / un-reinforcing components strength, the sintered composites have a different color (Fig. 2) and different densities.

Because of its different density, the Brinell hardness is conducted according to ISO 6506-1: 2014 with two load types 24.52 N and 49.03 N at a 1 mm diameter steel ball on the Zwick 4350, Germany.

The tests of the co-metallized AlMMC tribological parameters were performed on the tribometer with a "disc-roll" contact geometry (Fig. 3).

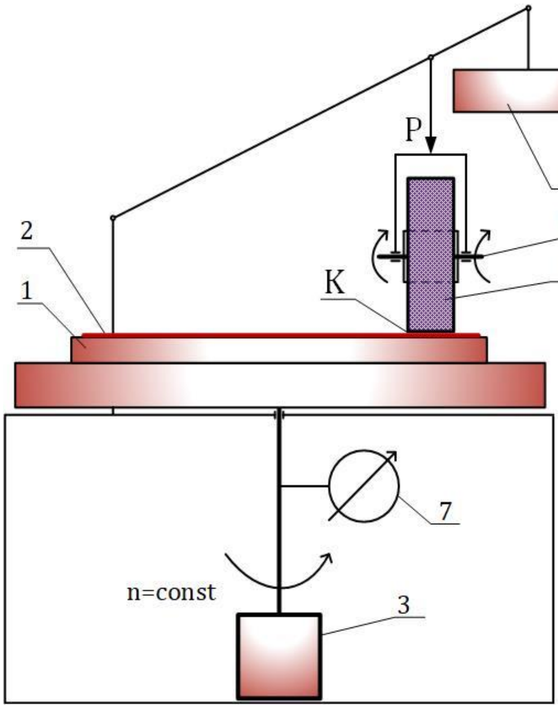


Figure 3. The scheme of "disc-roll" tribometer

The test specimen 4 forms a contact (*K*) with an abrasive surface 2, which is disposed on a horizontal disk 1. The disc 1 rotates around its central vertical axis with a constant frequency ***n***, which is supplied by an electric motor 3. The number of revolutions (*N*) is measured by cyclometer 7.

The test specimen 4 is a disc that rotates freely about a horizontal axis 5. The axes of rotation of the disk 1 and of the sample 4 are two cross axes. An abrasive wear on the cylindrical surface of the specimen occurs in the contact surface (*K*). The contact load (*P*) is provided by weight 6 on the axis 5. The test specimen 4 has the following dimensions: outer diameter Ø 43 mm inside diameter Ø 23.5 mm and contact width 10 mm. The nominal contact area between the abrasive surface and the sample is about 10 mm^2. The linear sliding speed of the center of gravity of the contact surface is 0.239 m/s.

Abrasive wear is calculated as a mass loss, i.e. as a difference between the initial mass of the sample and its mass after given number of abrasion cycles (*N*), counted by the cyclometer. Before and after testing, the mass of co-metallized AlMMC disc is measured by the electronic balance with accuracy of 0.1 mg. Normal contact load of 250 g (2.45 N) is constant for all tests and co-metallized AlMMC. The sliding distance (***S***) is calculated from the following equation

$$S = 2\pi N \quad (1)$$

where: ***r*** = 35 mm is the distance between the rotational axis of disc sample and mass centre of the contact area, and *N* is the number of abrasion cycles.

The wear resistance I is calculated according to the formula

$$I = \rho . A_a S / m \quad (2)$$

where: ρ is the density of the composite material, A_a - the nominal contact surface, and *m* - the measured mass wear.

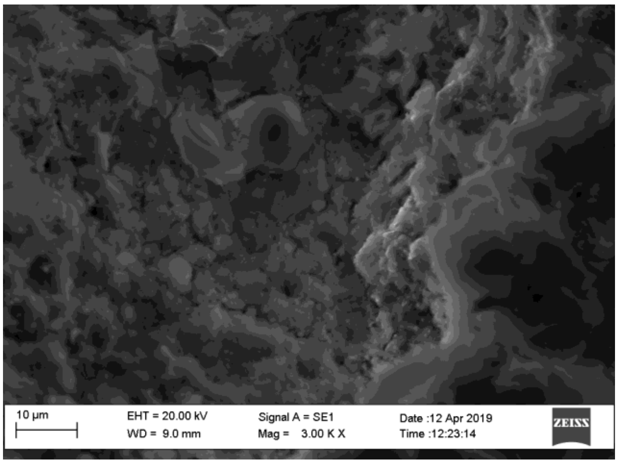
3. TESTING AND RESULTS

3.1 Morphology and Structure of the AlMM Composites

Results from Scanning Electron Microscopy of fracture of sintered co-metallized AlMMC with 18% by weight of aluminium powder are shown in Fig. 4. The photos are show globalized during the sintering aluminium powder (with a melting point of 660^{O}C) between regions with a locally crystallized supersolidus liquid phase (Fig. 4a).

The EDX microanalysis show the presence of the elements Ni and Cu (Fig. 4b, c), which prove the committed nickel-copper coating.

Results from Scanning Electron Microscopy of fracture of sintered co-metallized AlMMC with 18 % silicon carbide and aluminium powder in a ratio of (1:1) are shown in Fig. 5. The silicon carbide particles with their typical sharp edges located in the aluminium alloy matrix are clearly shown on the photos (Fig. 5a).



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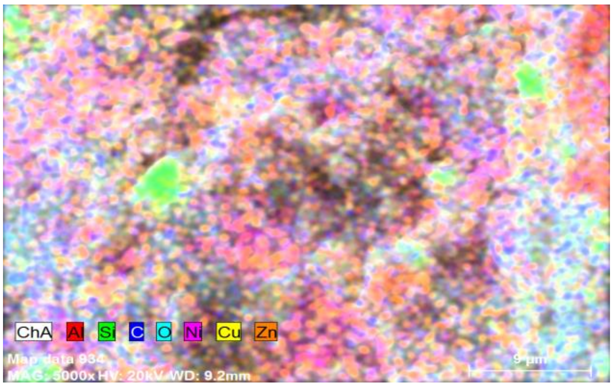

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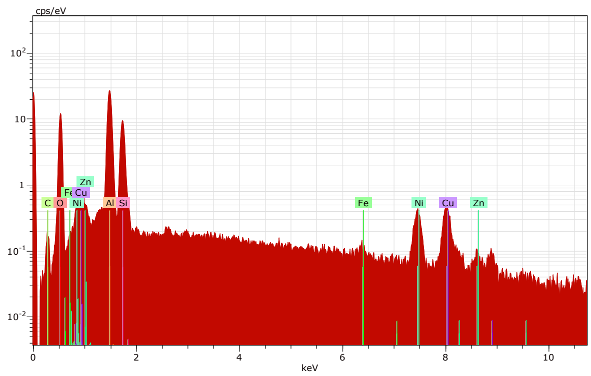

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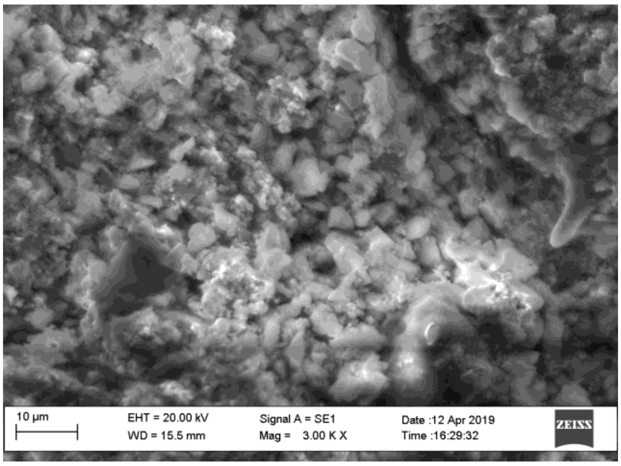
Figure 4. Sintered co-metallized (NI-Cu-P) AlMMC with 18% aluminium powder: (a) SEM magnification 3 000; (b) EDX mapping; (c) EDX spectrum

The EDX microanalysis shows the presence of the elements Ni and Cu (Fig. 5b, c), which prove the committed nickel-copper coating.

Results from Scanning Electron Microscopy of fracture of sintered co-metallized AlMMC with 8 % carbon nanotubes are shown in Fig. 6.

The metallized carbon nanotubes in the aluminium matrix can be distinguished only at large magnitudes from 30 000 to 50 000 times. Distinct CNTs can be distinguished in the cluster beads formed shown In the Figure 6a. Those clusters are seen as separate balls with a scratchy surface at smaller magnitude (Fig. 6b).



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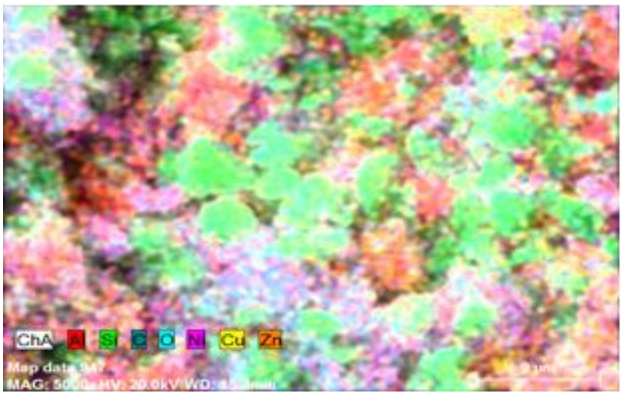

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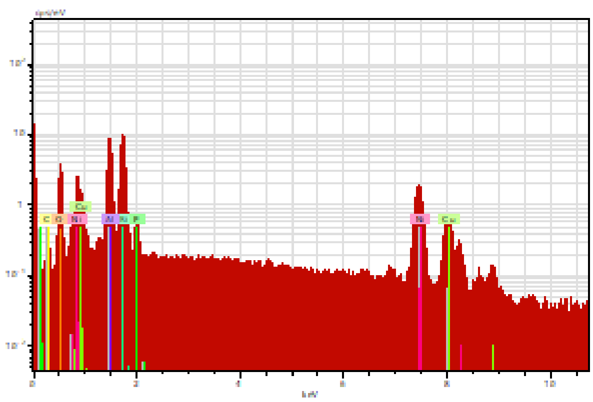

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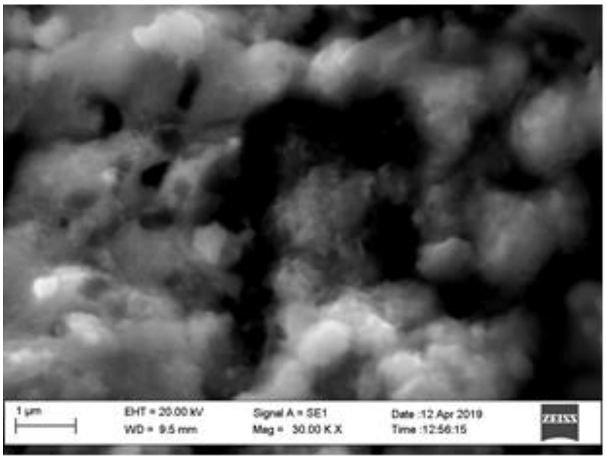
Figure 5. Sintered co-metallized (NI-Cu-P) AlMMC with 18% SiC and Al powder: (a) SEM magnification 3 000; (b) EDX mapping; (c) EDX spectrum



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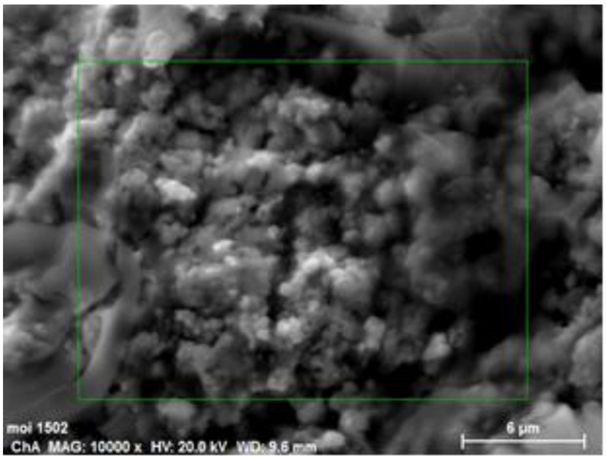

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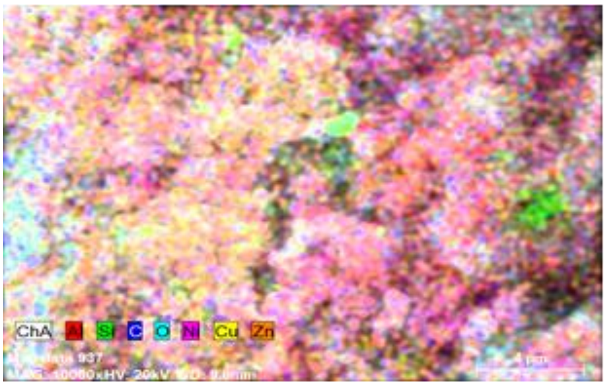

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Figure 6. Sintered co-metallized (NI-Cu-P) AlMMC with 18% CNTs: (a) SEM magnification 30 000; (b) EDX magnification 10 000; (c) EDX mapping

3.2 Results from AlMM Composites Hardness

Table 1 shows the results from the density determination and the hardness testing (mean values and standard deviation S_{HB}) of the sintered co-metallized AlMMC composites with different type and quantity of neutral, reinforced and un-reinforced components.

Table 1. Results of the hardness testing and density of sintered co-metallized AlMMC

Sintered material	Density, g/cm^3	Hardness HBS	
		Mean value	S_{HB}
Al turnings only (№1)	1.76	$25.6^{+1.86}_{-1.94}$	0.40
Al turnings only Ni-Cu (№2)	2.29	$30.7^{+3.90}_{-4.80}$	1.22
Al +8% powder Ni-Cu (№3)	2.50	$46.3^{+3.99}_{-5.01}$	1.20
Al +18% powder Ni-Cu (№4)	2.54	$43.7^{+3.82}_{-4.58}$	1.19
Al + 8% SiC Ni-Cu (№5)	2.22	$53.4^{+8.30}_{-1.60}$	1.49
Al + 18% SiC Ni-Cu (№6)	2.26	$51.0^{+4.10}_{-3.50}$	0.88
Al + 4% CNTs Ni-Cu (№10)	1.87	$19.7^{+5.48}_{-4.82}$	1.05
Al + 8% CNTs Ni-Cu (№8)	1.77	$11.0^{+2.84}_{-1.46}$	0.49
8% CNTs temp. Ni-Cu (№13)	1.78	$18.1^{+5.59}_{-3.21}$	1.10

The density and the hardness of sintered co-metallized AlMMC composites depends on the type and the percentage of the metallised dispersed phase (Table 1). The Ni-Cu coating of aluminium turnings leads to a 20% increase in the hardness, but also to an increase in the non-uniformity of the composite structure.

Insertting the neutral aluminium powder to the aluminium turnings increases the hardness with 70-80% and improves the interfacial bonding in the sintered composite.

Highest hardness values have related to ceramic reinforcement composites (silicon carbide and aluminium powder SiC and Al powder) in which a double increase was observed. The excessive increase in the percentage of the reinforcement phase from 8 % to 18 % leads not only to a slight decrease in the hardness and the density, but also to a degradation of the turnings' interfacial bonding into the common aluminium alloy matrix.

Lowest values of the mechanical parameters and the density is accounted in the sintered co-metallized AlMMC with CNTs. Their comparison with other composites and their behavior during the wear resistance and hardness test shows that the CNTs to a large extent preserved their original structure in the aluminium alloy matrix and they did not break into soot during the compaction at 300 MPa.

The evaluation of this behavior, determination of their friction coefficient and finding more suitable sintering modes are a subject to future research on improving the mechanical behavior of those AlMMC.

3.3 Results from AlMM Composites Tribological Properties

For a reference sample is selected a sintered material only from aluminium turnings.

On the graphs of Figure 7 and Figure 8 there are shown the results from the determination of the mass wear rate and wear resistance of sintered co-metallized AlMMC composites with neutral and reinforcing components.

The lowest wear rate (Fig. 7) and highest wear resistance (Fig. 8) was demonstrated by the sintered co-metallized AlMMC with 8 % Al powder. They are with increased wear resistance by about 50% compared to the reference sample of aluminium turnings.

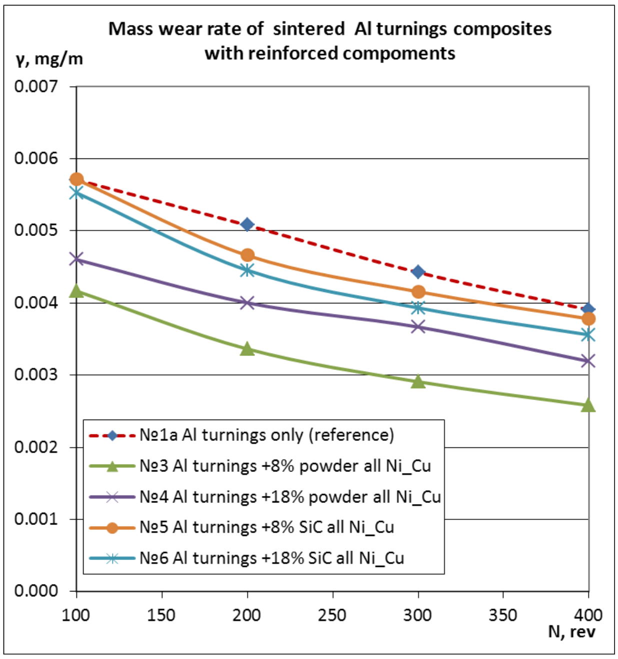

Figure 7. Variation of mass wear rate with the number of friction cycles for AlMMC specimens with reinforcing components

On the graphs of Figure 9 and Figure 10 there are shown the results from the determination of the mass wear rate and the wear resistance of sintered co-metallized AlMMC composites with CNTs.

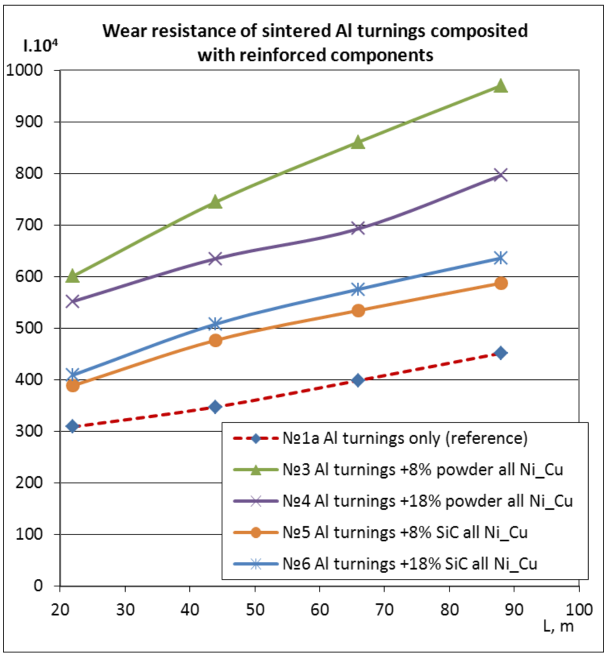

Figure 8. Variations of abrasive wear resistance of AlMMC specimens with reinforcing components

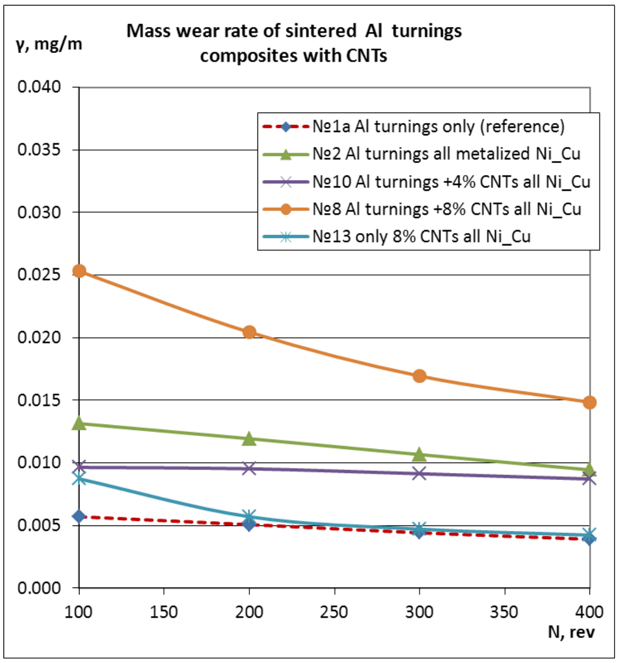

Figure 9. Variation of mass wear rate with the number of friction cycles for AlMMC specimens with CNTs

The highest wear rate is related to AlMMC composites with 8 % CNTs (Fig. 9). The next increase in their percentage ratio results in an instability and a disintegration of the sintered under the specified parameters composite.

The behavior of the sintered co-metallized AlMMC un-reinforced with CNTs shows, that due to the metallization, they have retained their structure and they did not decay to soot during the compaction. However, this results in an instability of the composite material and it does not allow the integration of a higher percentage of CNTs into the aluminium alloy matrix.

The metal-metal composite of metallized (Ni-Cu) aluminium turnings without an additional phase also increases the wear rate and decrease the wear resistance compared to the reference sample (Figs. 9 and 10).

Best performance demonstrates the specimen of Ni-Cu metallized carbon fiber CNTs (without aluminium turnings) (Fig. 10), obtained by additional heating during the electroless metallization. It has a wear resistance commensurate with that of the reference sample, but probably it has a very different coefficient of contact friction.

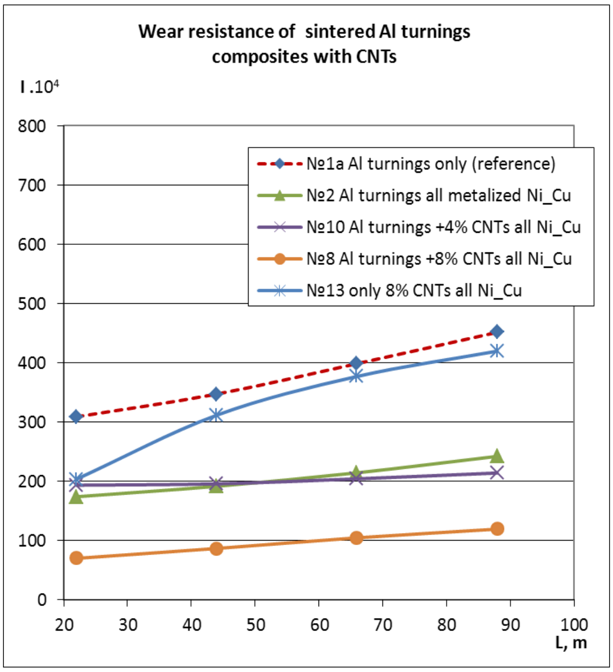

Figure 10. Variations of abrasive wear resistance of AlMMC specimens with with CNTs

On Figure 11 the sintered co-metallized AlMMC composites are compared to the reference sample in regard to their relative abrasion wear resistance.

The AlMMC with reinforcing components have 100-120% increase in wear resistance compared to the reference sample. The AlMMC with neutral components have only 20-40% increase in their wear resistance.

The AlMMC with CNTs have 40-50% decrease in their wear resistance. The specimen from only metallized 8% CNTs without aluminium turnings has a wear resistance commensurate with that of the reference sample.

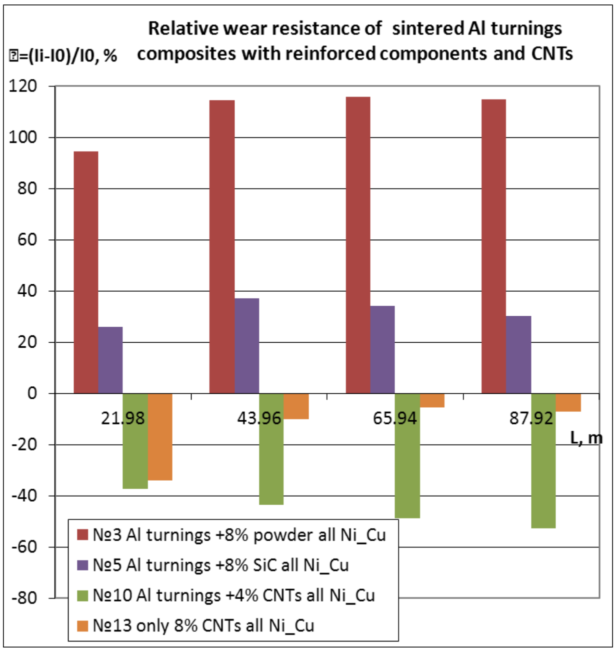

Figure 11. Relative wear resistance change of co-metallized AlMMC specimens with reinforcing components and with CNTs

4. CONCLUSIONS

1. It has been found that the addition of a neutral phase with another fractional composition to the aluminium turnings (in this case aluminium powder) significantly improves the interfacial bonding, the hardness and the wear resistance of the sintered co-metallized AlMMC composites.

2. Co-metallized ceramic reinforced AlMMC demonstrate a double increase in hardness, but the excessive increase in the percentage of the ceramic reinforcement results in a deterioration of the turnings bonding into the common aluminium alloy matrix.

3. Sintered co-metallized AlMMC composites un-reinforced with CNTs demonstrate the lowest density, mechanical and tribological performance. Their behavior during the test and scanning electron microscopy shows that through to the metallization CNTs have retained their fibrous structure after the cold compaction.

4. It has been proven that it is possible to sinter composite material only from

electroless metallized CNTs obtained by further heating of the solution described in the work. The specimen from metallized CNTs has a wear resistance commensurate with that of the reference sample, but is likely to have a very different coefficient of contact friction.

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