MECHANICAL PROPERTIES OF NC-TiB_2 /STEEL AND NC-TiC/STEEL COMPOSITE SYNTHESIZED BY SELECTIVE LASER MELTING

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Abstract (Times New Roman 12 pt, bold, single-line spacing, left-aligned text)
The innovative method of the nanocomposite materials manufacturing has been developed, in which the SLM (Selective Laser Melting) technique is used. Nanocrystalline TiC and TiB_2 powder, obtained in non-hydrolytical sol-gel synthesis and 316L stainless steel have been applied in SLM process. In present work, the composition, structure of obtained composites, along with the results of morphology, hardness measurements and oxidation resistance have been presented. During investigation the following analytical techniques have been applied: XRD, TEM, TG-DSC-MS, SEM and nanoindentation. In addition nanoindentation results has been compared with FEM model.

1 Introduction

Selective Laser Melting is one of the additive manufacturing methods, in which metallic powder is used as a raw material. It is an advanced method of single parts manufacturing by adding pulverized material layer by layer and melting it in specified places resulting from part geometry of the actual layer. This technology was developed for work with one type of the powder at the same time and to use the full melting joint effect. However, due to some device modification, process parameters changes and different powders use, it becomes possible to gain other joint effects [1]:

- SSS – Solid State Sintering – thermal process whose the most important effect is the diffusion causing the "neck" formation between particles
- LPS – Liquid Phase Sintering/Partial Melting – common feature of this group is using particles, which are melted and particles, which are not melted at the same process

Metal matrix composites (MMC) are the focus of intense research and development. In many applications, where reduction of products weight along with the improvement of specific modulus, strength, thermal stability, wear resistance and service life are required MMCs can be the best solution [2-5].

These kind of materials are mainly used in aerospace, automotive and defence technologies, and everywhere the main criterion is the strength and lifetime. The most widely matrix materials used in MMCs are stainless steels and alloys of magnesium, aluminium, copper or titanium [6]. As a reinforced phase carbides (SiC, TiC, WC), nitrides (TaN, TiN), borides (TiB, TiB_2, WB), metal oxides (Al_2O_3) and carbon fibres are mainly applied [6, 7, 8, 9, 10].

Depending on the composites application, strengthening phase can be introduced as dispersed particles, platelets and short or long fibres. It is also possible to use various strengthening phases in single composite. There are three main technologies for MMCs manufacturing: high-pressure diffusion bonding, casting and powder metallurgy [6, 11, 12, 13].
In presented work the SLM technique was used to ncMMCs preparation.

2 Materials and testing methods

In this studies 316L stainless steel was used as a matrix. Powders containing nanocrystalline TiC and TiB_2 (with small amount of TiC, B_4C and amorphous carbon) were synthesised by non-hydrolytical sol-gel method [14, 15]. The average size of particles was in the range of 40 – 100 nm and 60 – 120 nm in case of TiC and TiB_2 respectively. Stainless steel together with nanocrystalline powders (5 – 50 vol.%) was homogenized in "Pulverisette 4" planetary mill (Fritsch GmbH) using WC/Co milling balls in the weight ratio 10:1 (balls to powder) during 5 minutes with rotation speed 300 rpm. Such obtained powders were then used in composites manufacturing processes by SLM/S technique.
Nanocomposite structure was manufactured with MCP REALIZER II device with 250mmx250mmx200mm process chamber and 100W maximum laser power. The process parameters differing from typical SLM were: exposition time, laser lines spacing, laser power and number of laser passing on single layer. The series of samples have been prepared with different filler amount (5 – 50% of nc-TiC and 5 – 40% of nc-TiB_2 with small amounts of TiC and B_4C) and with different layer thickness (50 and 75µm).
Nanoparticles size, chemical and phase composition were determined with XRD (PANalytical PW3040/60 X'Pert Pro), TEM (JEOL JEM 1200EX) and SEM (Hitachi SU-70) techniques. Hardness measurement on polished surfaces was performed by LM 247 AT (LECO) microhardness tester equipped with Vickers indenter using 50g load. Hardness and modulus measurements were performed on MTS Nano Indenter XP using Brekovich tip.
The investigations on the oxidation process were carried out by thermoanalytical method using TG-DSC (SDT Q600, TA) coupled with MS (Thermostar GDS 301 Pfeiffer Vacuum) for gaseous products identification. Measurements were performed under non - isothermal (β = 10 Kmin-1) conditions, in temperature range from 298 to 1473 K.

3 Results

X-Ray diffraction pattern of the steel/nc-TiC nanocomposite is presented on fig.1.

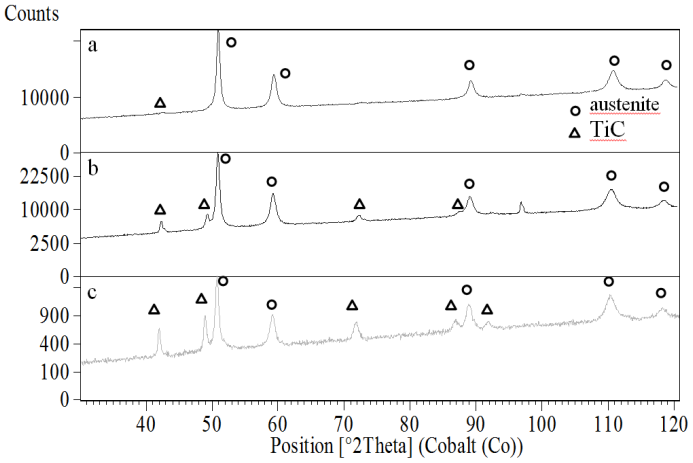

Fig.1. XRD pattern of SLM/S composites a) 5% vol. nc-TiC, b) 20% vol. nc-TiC, c) 40% vol nc-TiC.

A strong peak of these spectra belong to the phase of austenitic stainless steel (JCPDS card no. 00-033-0397). With the increasing volume fraction of the strengthening phase, also the presence of nanocrystalline TiC (JCPDS card no. 00-001-1222) was identified.
The composite material, containing nc-TiC and nc-TiB_2, obtained by SLM technique was characterized by satisfying dispersion of particles in steel matrix. The exemplary picture of such nanocomposite structure is given on fig. 2.

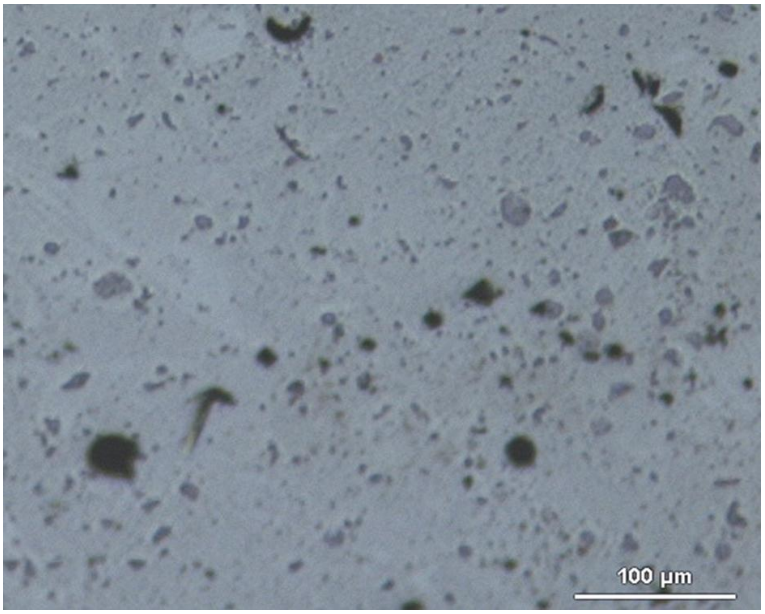

Fig. 2. Optical microscope images of composite with 20 % vol. nc-TiC.

The dark places on the picture are assigned to the pores in the structure. In case of nc-TiB_2 composite high magnification SEM pictures have revealed strong particles agglomeration of strengthening phases what was not observed in nc-TiC composites (fig. 3).

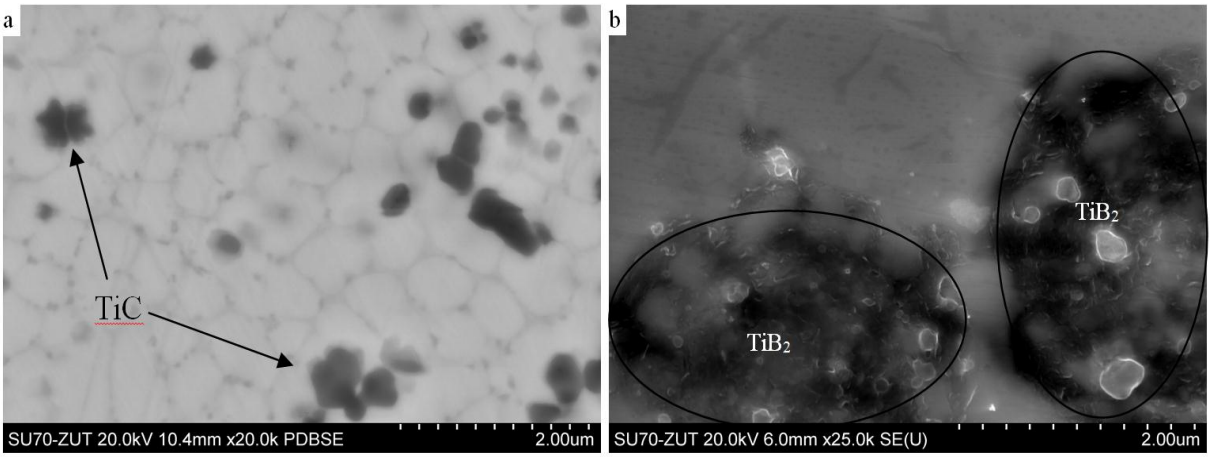

Fig. 3. SEM images of composite a) 20 % vol. nc-TiC b) 40% vol. TiB_2 in steel matrix.

Elemental analysis obtained by EDS technique, confirmed nanocrystalline strengthening phase occurrence (fig. 4). Carbide, boron and titanium formed agglomerates with the size up to 3µm.

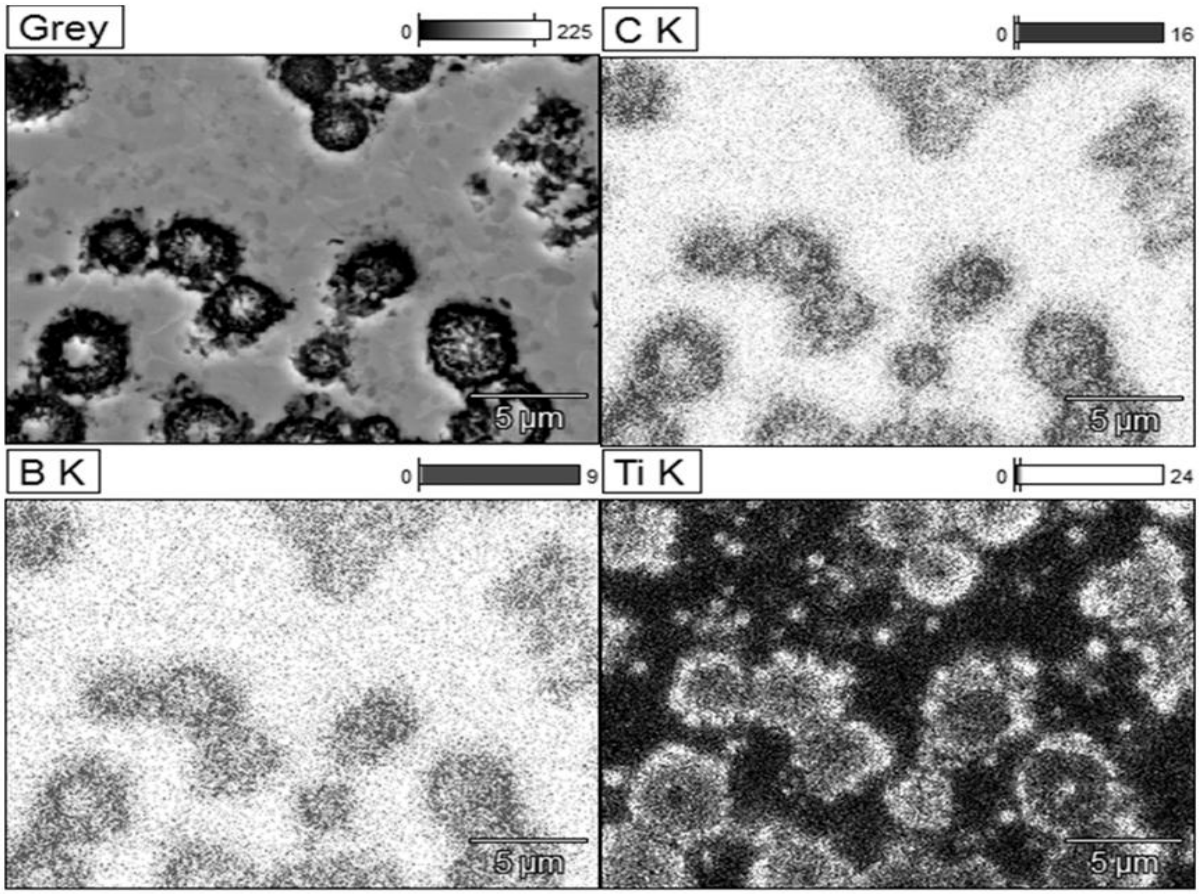

Fig.4.Elemental analysis by EDS of steel/nc-Ti-B-C composite

The Vickers hardness measurement results are depicted on fig. 5. For the steel/nc-TiC system, gradual hardness increase along with increasing volume fraction of TiC from 300 HV to 1000 HV was observed. In the case of nc-TiB_2 powders, significant, fourfold hardness growth was observed when the amount of hardening phase was increased from 5 to 20 vol.%. It is probably related with creation of hard FeB_2 phase in the steel/agglomerates interphase boundary.

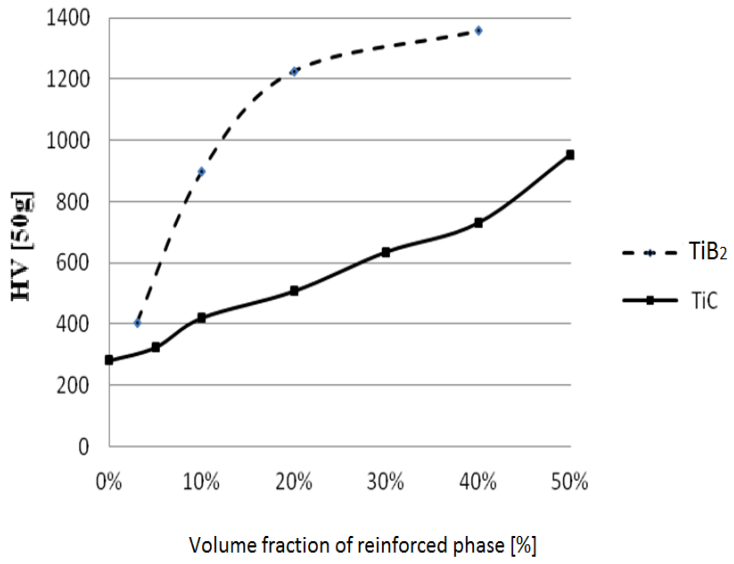

Fig.5. Graph of hardness vs volume fraction of reinforced phase of SLM/S composites

In fig.6a plots of TGu function in time and in fig.6b plots of DTG function in temperature for sintered sample (ball shape) composed of 10 vol.% nc-TiC particles in steel matrix and for the reference sample made of pure steel powder, both heated in synthetic air, are compared.

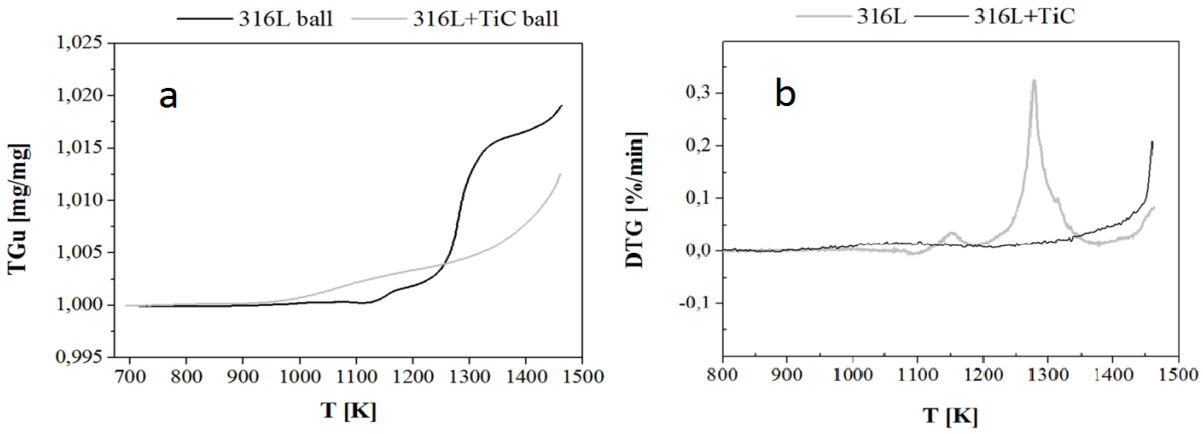

Fig.6. Comparison of the TGu (a) and DTG (b) curves for oxidation processes of the sintered 316L steel and the 316L steel/TiC (10 vol.%) nanocomposite.

Process of nanocomposite oxidation was started at temperature of 936 K. In this process, two stages have been distinguished. In temperature range of 930-1200K the first stage was finished and the second stage was started.
It was stated, that the nanocomposite material was characterized by better resistance to oxidation in air at high temperatures comparing to sintered 316L steel. After heating in dry air up to temperature of 1473 K at heating rate of 10 Kmin-1 on the surface of 316L steel/nc-TiC nanocomposite the thin passive layer was formed. In this layer, besides Fe_2O_3 and Ni_xFe_3-xO_4, Cr_2O_3 was identified by XRD method [16]. Among the oxidation products of sintered steel two phases were identified: Fe_2O_3 and Ni_xFe_3-xO_4. Products of sintered steel oxidation formed thicker, loose layer of rust. Among the oxidation products of the mixed powder containing 10 vol.% of nc-TiC and 90 vol.% of 316L steel no Cr_2O_3 was found, whereas TiO_2 (rutile) was identified. The process started at the temperature about 240 degrees lower in comparison to the sinter of the same composition.

4 FEM modeling

Chosen samples was used as the reference for finite element method (FEM) modeling. Virtual sample has been modeled as quarter of the cylinder with symmetry boundary conditions applied on the walls resulting from cutting the whole cylinder. To obtain the reaction between the indenter and the sample, “interaction” function has been used with the following parameters: “surface to surface contact” type of interaction, “surface to surface” discretization method, “finite sliding” sliding formulation. As the contact interaction properties, the “contact” type has been taken with the following parameters: “penalty” friction formulation type for tangential behavior, “hard” contact pressure-overclosure type for normal behavior.
Elastic-Plastic material model has been taken for analysis. Young modulus was received from the real measurements. Kinematic hardening model has been applied for plasticity definition.
The resulting “Force-Indentation depth” curves for nanocomposite containing 50vol.% of nc-TiC and nanocomposite containing 20vol.% of nc-TiB_2 are shown in figure 7. They were compared with the curves obtained by real nanoindentation process.

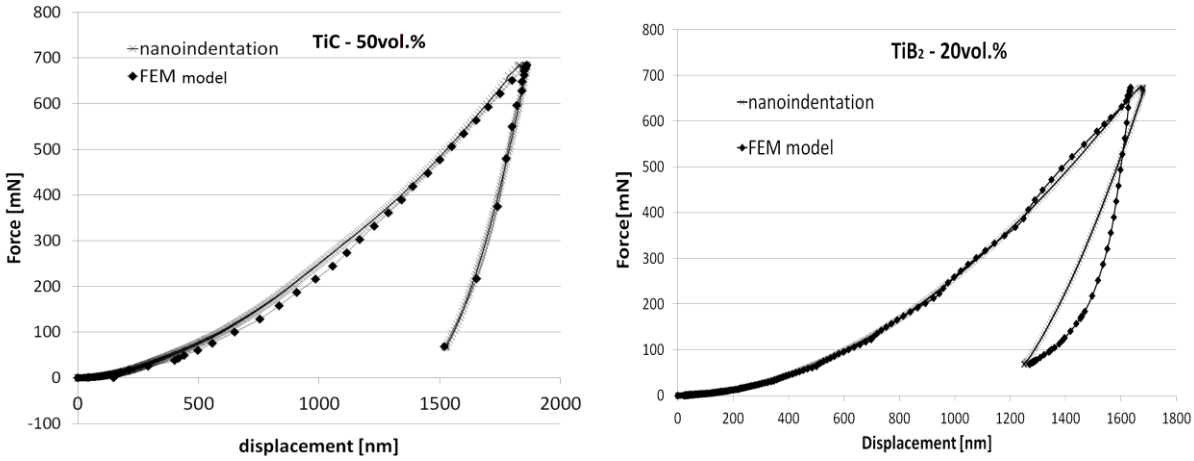

Fig.7. Comparison of nanoindentation curves for 50vol.% nc-TiC and 20vol.% nc-TiB2 nanocomposites with FEM models.

In the case of steel/nc-TiC composites better correlation between nanoindentation and FEM model was achieved in comparison with steel/nc-TiB_2 system.

5 Conclusion

Selective Laser Melting is useful tool for preparation of nanocomposite materials, especially with complex geometry. High hardness of such prepared parts often makes problem with postprocessing them, especially by standard cutting processes. Specific character of additive manufacturing allows preparing the final products with no additional processing needed. The analysis of nanocomposites manufactured by SLM technology shows, that they have good mechanical properties, and better resistance to oxidation in air at high temperature, what allows expecting successful with its development.

Good dispersion of nanocrystalline particles in steel matrix was stated. In the case of TiB_2 nanopowders, particles agglomerates with size up to 3μm was observed. Microhardness measurements results for steel/nc-TiC have shown up to threefold increase of hardness along with volume fraction growth from 0 to 50%. For steel/nc-TiB_2 system significant, fourfold hardness increase along with volume fraction from 0 to 20% was observed.

Presented FEM model have shown quite good adjustment to the real nanocomposites structures, which was confirmed by the nanoindentation process simulation. Because such prepared (SLM) nanocomposite have no equivalent, predicting of the well-fitted material model for the FEM applications is very important for further analysis of produced parts. It will also allow optimizing the amount of nanocrystalline filler for different applications and to analyze alternative filler and matrix materials combinations.

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