

# Physical and wear properties of laser melting deposited composites on a TA1 alloy

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## Abstract

This work is based on the Stellite SF12-NB-Sn composites deposited on a TA1 titanium alloy using a laser melting deposition (LMD) technique, the parameters of which are such as to provide almost crack-free composites with very low porosity. To our knowledge, it is the first time that the Stellite SF12-NB-Sn mixed powders are deposited as the hard composites by a LMD technique. The test results indicated that the heteromorphy  $Ti_3Sn$  phases were produced through the in situ metallurgical reactions, which grew along (101), (110) and (200), and a lot of the amorphous phases were also produced. Scanning electron microscope images indicated that the nanoscale particles and nanorods were produced in such composites. Compared with a TA1 alloy, an increase of the micro-hardness and wear resistance is obtained for such composites.

**Key words:** amorphous materials, coating materials, nanofabrications, lasers

## 1. Introduction

Laser processing technology, such as LMD, is a new production route, which can be used as a surface modification technique for improving the surface related properties of bulk component, in which coating having excellent resistance to wear is deposited onto a surface of a substrate [1, 2]. Titanium (Ti) and its alloys have been widely utilized in the aeronautical, chemical and the defense industrial sectors, because of the high specific strength, sufficient stiffness and outstanding corrosion resistance. Nevertheless, the limited wear resistance of Ti and its alloys is regarded as a significant disadvantage for the application environments involving abrasive and erosive phenomena [3, 4]. Stellite represents cobalt-base alloys typically used in applications that require high resistance to wear in aggressive environments. As the most promising method, nanoparticles are expected to play an important role in strengthening the light metal surface [5]. Nanocomposites reinforced with hard and stiffer ceramics are accordingly developed to strengthen the wear resistance of titanium alloys. LMD has created the new technological opportunities

for producing composites parts with tailored structures.

The conventional Co-based wrought alloys can be categorized into three types, namely, wear resistance alloys, high temperature alloys and corrosion resistance alloys. The wear resistance alloys, such as Stellite SF12, are essentially Co-Cr-W-C quaternaries, with Cr providing strength and wear resistance to the Co-rich solid solution, as well as functioning as the chief carbide former during alloy solidifications [6, 7]. The strengthening of Stellite alloys benefits from the refractory elements (tungsten or molybdenum) solid solution hardening and carbide precipitation. Through the experiments, it is noted that LMD of the Stellite SF12-NB-Sn mixed powders on a TA1 titanium alloys can form the composites. In this study, the physical/wear properties of the nanocrystals-reinforced LMD composites were investigated in detail.

## 2. Experimental

Metallographic samples and wear testing specimens were machined by the electric discharging cut-

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ting. The materials used in this experiment: TA1 titanium alloy samples ( $8\text{ mm} \times 8\text{ mm} \times 35\text{ mm}$ ) for the wear test or ( $10\text{ mm} \times 10\text{ mm} \times 9\text{ mm}$ ) for the microstructure analysis, which were polished with SiC grit paper prior to the coating operation, and chemical compositions (wt.%) of the TA1 alloy in this study: 0.2 Fe, 0.08 C, 0.03 N, 0.18 O, 0.015 H and balance Ti. The powders of Stellite SF12 ( $\geq 99.5\%$  purity,  $45.5\text{ }\mu\text{m}$ ), NB ( $\geq 99.5\%$  purity,  $50\text{--}200\text{ }\mu\text{m}$ ), and Sn ( $\geq 99.5\%$  purity,  $50\text{--}250\text{ }\mu\text{m}$ ) were used for the LMD technique, chemical compositions (wt.%) of Stellite SF12: 1.00 C, 19.00 Cr, 2.80 Si, 9.00 W, 3.00 Fe, 13.00 Ni, and balance Co. Mechanical mixing device was used to mix all of the powders. Compositions (wt.%) of the powders used in this experiment: 85Stellite SF12-10NB-5Sn. LMD was conducted on a 5 kW transverse-flow continuous-wave  $\text{CO}_2$  laser materials processing system equipped with four-axis computer numerically controlled (CNC) laser materials processing machine under an ambient atmospheric environment, and coaxial powder feeding device (DPSF-3) was employed to melt the surface of the samples at the same time

during LMD process. Four-track lap composite coating was formed on the TA1 substrate, and the lap rate was approximately 30 % in order to uniformly cover a large area. The parameters of LMD process: laser power = 0.80 kW, scanning speed =  $2\text{--}11\text{ mm s}^{-1}$ , the powder feed rate =  $15\text{ g min}^{-1}$  and the laser beam = 4.5 mm.

After the LMD process, the metallographic sections were prepared using standard mechanical polishing procedures and wear etched in aqua regia ( $\text{HCl}:\text{HNO}_3 = 3:1$ , in volume ratio). Wear resistance of such LMD composites was tested by WMM-W1 disc wear tester. The wear volume loss was measured after 60 min. The rotational speed of the wear tester was  $415\text{ r min}^{-1}$ . Linear velocity of friction surface was  $0.98\text{ m s}^{-1}$ . Microstructural morphologies of the composites were analyzed by means of a LEO 1525 scanning electron microscope (SEM) and a Hitachi transmission electron microscopy (TEM). A HV-1000 microscloerometer was used to test the micro-hardness distribution of the composites.

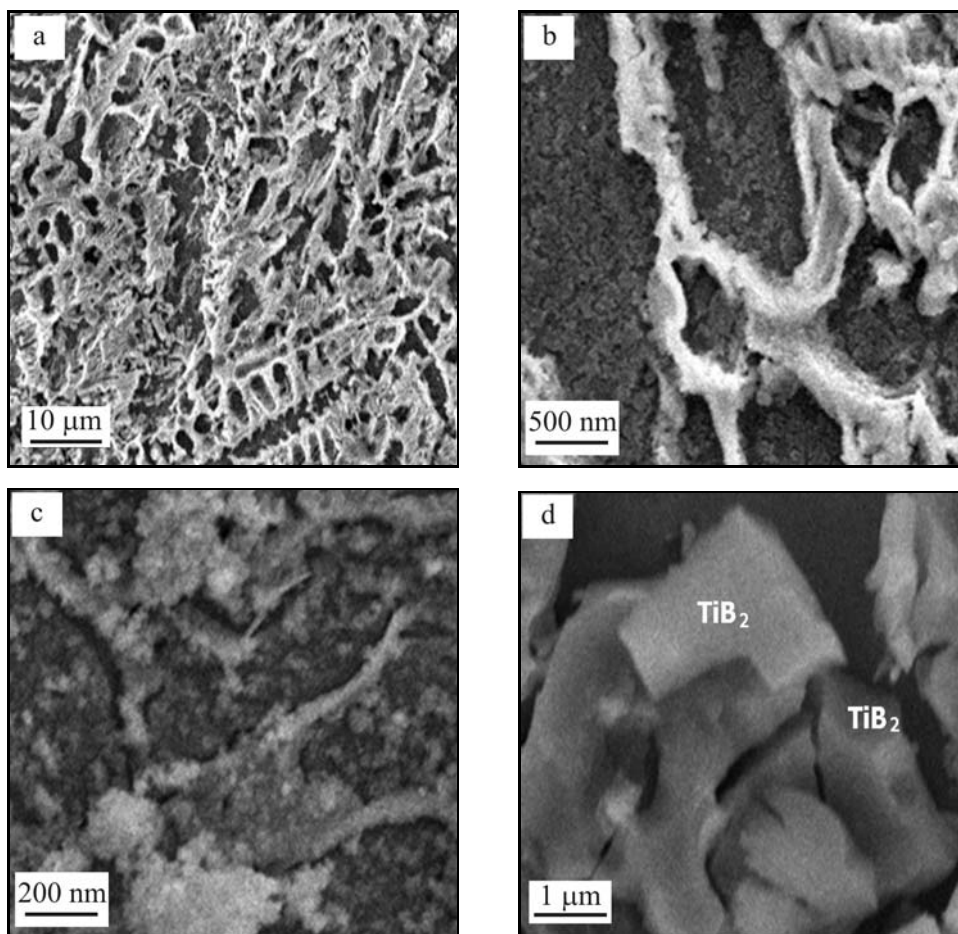


Fig. 1. SEM images of the LMD composites: middle-coating (a), nanoscale precipitates (b, c), and  $\text{TiB}_2$  block shape precipitates (d).

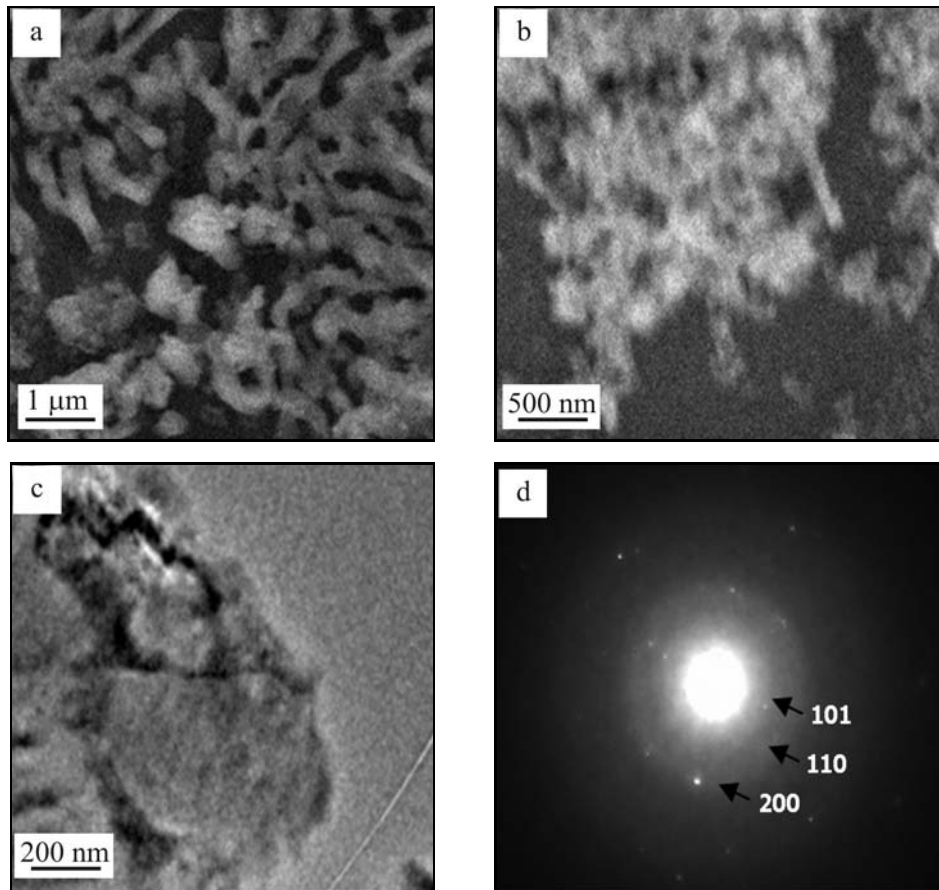


Fig. 2. The SEM images of the composites: eutectics (a) and agglomeration of nanoscale particles (b), the TEM image of selected location (c), and the corresponding electron diffraction pattern (d).

### 3. Results and analysis

#### 3.1. Microstructure analysis

It was noted that the interdendritic lamellar eutectic phases were produced in the middle-composites (Fig. 1a), which were made up mainly of Co, Ni and small amounts of Si, Cr, also other chemical elements. The matrix phase is a solid solution of Co and Ni with some B, N, Cr, Fe, Si, and the other chemical elements, providing the dendritic structures. As shown in Fig. 1b, a lot of nanoscale particles were produced in the coating matrix. The fact that due to the sufficiently rapid heating and cooling rates of the laser cladding technique, the ceramics, such as TiN or TiB<sub>2</sub>, did not have enough time to grow up, forming the nanoscale particles; moreover, the Sn addition was beneficial in producing the nanoscale particles [8, 9]. The SEM image revealed that the stick/block-shape precipitates gathered together in some location of the coating (Fig. 1c), which retarded their growth in a certain extent, favoring the formation of a fine microstructure.

The fact that LMD occurs via a mechanism involving complete metallurgical melting, indicating

that even the high melting-point ceramic phase tends to be fully molten during LMD process. The used powders demonstrate a high tendency to melt completely due to: (i) the application of a CO<sub>2</sub> laser having high energy density and resultant elevated LMD temperature; (ii) the significantly elevated activity of fine pre-placed fine powders induced by the extremely large surface area to volume ratio. As shown in Fig. 1d, the TiB<sub>2</sub> block shape precipitates were produced in such coating. The fact that hexagonal TiB<sub>2</sub> crystal structure is the alternating series of the hexagonal symmetrical titanium and boride layers, and its cylinder index is {1010}. (0001) plane is vertical to cylindrical surface, and its growth direction is along the (1010) lateral plane [1]. It was known that TiB<sub>2</sub> did not include the crystal plane and the direction of obvious growth advantage, favoring the formation of the block-shape precipitates [10].

Figure 2a shows the SEM image of the eutectic structure in the crystal boundaries of the coating matrix. In fact, the eutectics, such as the Co-Ti or Ti-Si binary intermetallic alloy, has a uniform and dense microstructure consisting of predominantly the primary dendrites and minor amount of interdendritic eutectics. The glass forming alloy compositions are

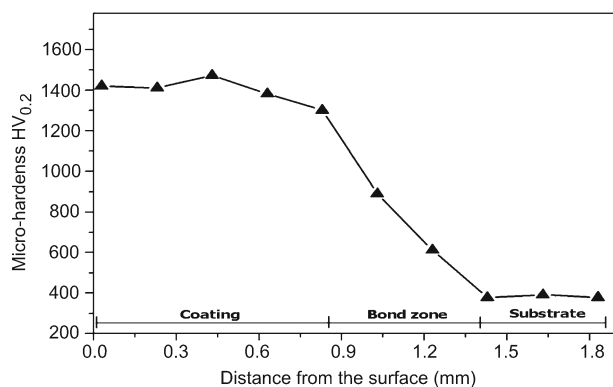


Fig. 3. Micro-hardness distribution of the LMD composites.

close to eutectics, which implies a (relative) low melting point, i.e., the production of the eutectics greatly promotes formation of the amorphous phases [11].

It is known that the nanoscale particles own the large specific surface, such particles usually gather together, forming the secondary particles in order to decrease the interface energy of the system. Thus, an agglomeration of nanoscale particles is produced (Fig. 2b). It is considered that the production of agglomeration of nanoscale particles may retard growth of the ceramics in a certain extent, forming a fine microstructure.

Figures 2c,d show the test location and its corresponding electron diffraction pattern, respectively. The corresponding Selected Area (Electron) Diffraction (SAED) pattern clearly revealed that the heteromorphous  $Ti_3Sn$  phase grew along (101), (110) and (200). It was located that  $Ti_3Sn$  were produced through the in situ metallurgical reaction during the LMD process. Moreover, the obvious diffraction rings were present in SAED pattern, which proved the production of the amorphous phases. The production of the amorphous phases in such coating is mainly ascribed to the sufficiently rapid heating and cooling rates of an LMD technique [12].

### 3.2. Wear properties

As shown in Fig. 3, the micro-hardness distribution of such LMD composites is in a range of 1300–1500  $HV_{0.2}$ , which is significantly higher than that of the substrate (355  $HV_{0.2}$ ). The phase constituent, fine grain/nanocrystals strengthening and the amorphous glassy phases all played important role in increasing the micro-hardness and wear resistance of such LMD composites [13, 14].

When the load was 55 N, the wear test results indicated that the wear volume loss of the LMD composites was about 1/12 of pure TA1 due to the action of many factors, such as the nanocrystalline-

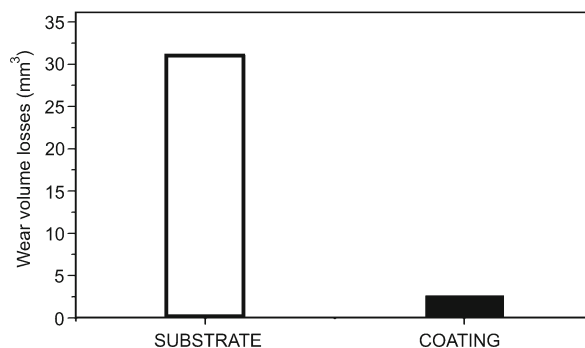


Fig. 4. Wear volume losses of the substrate and the composites.

-amorphous phases, hard phases, fine grain strengthening of the titanium borides, and the solution strengthening (Fig. 4). Owing to a rapid cooling rate of the molten pool, a small amount of the elements, such as Cr, W and Si, etc., had no time to precipitate from the liquid and solution in  $\gamma-Co/Ni$  to form a super-solution, which caused the solution strengthening.

Combined with an effect of micro-hardness enhancement, the strain-hardened tribolayer tends to form on the worn surface, acting as a protective layer to improve the wear resistance of such composites. Moreover, under the action of Sn, a lot of the nanoscale particles, such as the  $Ti_3Sn$  nanoscale particles were produced, which also greatly increased the wear resistance of such composites [9]. According to the previous microstructure analysis, many hard phases and different kinds of amorphous phases were dispersed in such composites, which decreased the wear volume loss [15].

SEM images showed that the worn surface of TA1 was very rough after 60 min wear time. The deep plowing grooves were present in the worn surface of the TA1 substrate. Since the micro-hardness of TA1 was significantly lower than that of the counterpart, the hard asperities on the surface of the counterpart can easily penetrate into the sliding surface of the substrate, forming an un-smooth surface (Fig. 5a). As shown in Fig. 5b, a smooth worn surface of the LMD composites was obtained. According to the previous microstructure analysis, many hard phases, such as the  $Ti_3Sn$  nanocrystalline phases and different kinds of amorphous phases were dispersed uniformly in such composites, which prevented the stretching of the wear grooves in a certain extent [9]. As shown in Fig. 5b, a fine microstructure of composites was obtained, which also showed excellent properties of the plasticity and toughness, favoring the formation of a smooth worn surface [16]. It should be mentioned that a lot of the brittleness phases existed in some location of the composites, which can be easily peeled off due to the ac-

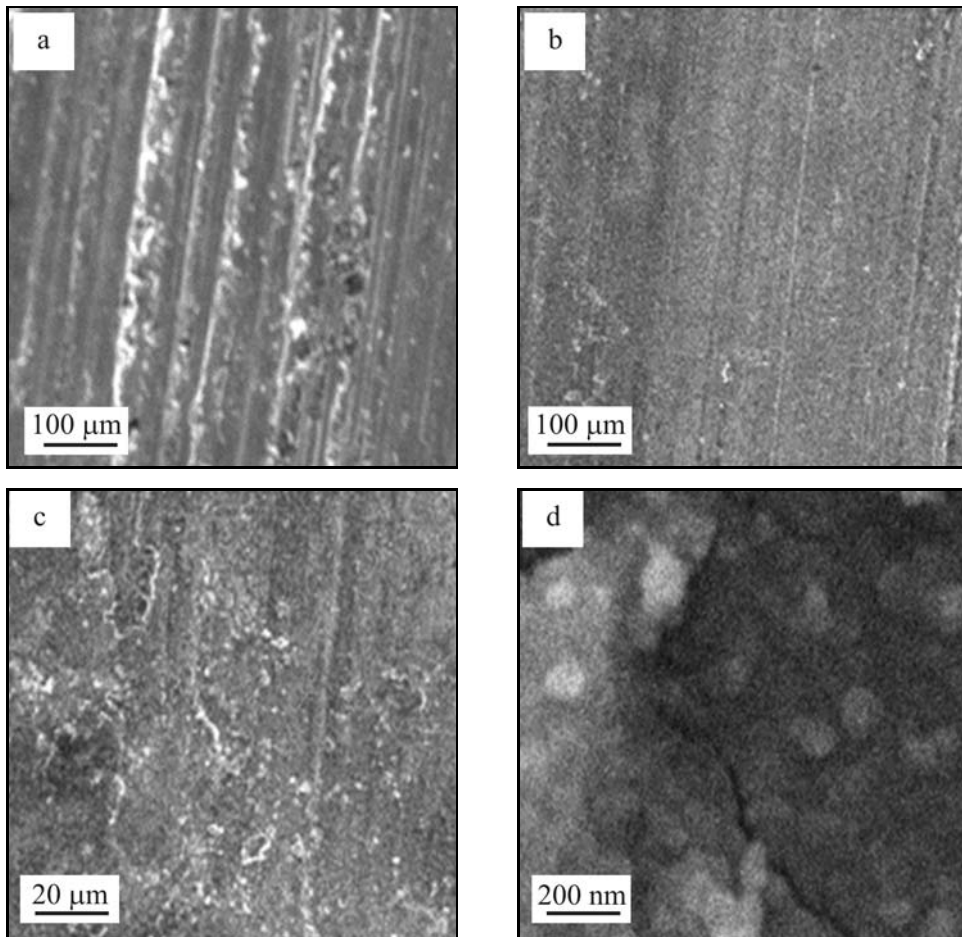


Fig. 5. Worn surface of the TA1 substrate (a), LMD composites (b, c), and etched composites (d).

tion of the brittleness phases. So the peeled large hole was present in the worn surface (Fig. 5c). As shown in Fig. 5d, the nanoscale particles were present in the etched worn surface of laser-treated sample. It should be mentioned that the production of a lot of the nanocrystalline phases is also beneficial in improving the worn surface of such LMD composites.

#### 4. Conclusions

Stellite SF12-NB-Sn hard composites can be deposited on a TA1 titanium alloy by a LMD technique. The correct choice of the laser parameters provides the LMD composites on a TA1 titanium alloy with the micro-hardness distribution in a range of 1300–1500 HV<sub>0.2</sub>, which is approximately 4 times higher than that of TA1 alloy substrate (about 350 HV<sub>0.2</sub>). There is an interdendritic lamellar eutectic phase made up mainly of Co, Ni and a small amount of Si, Cr and other chemical elements. The matrix phase is a solid solution of Co and Ni with some W, Cr, Fe, Si and other chemical elements, providing a dendritic structure. The heteromorphous Ti<sub>3</sub>Sn phases

are produced through the in situ metallurgical reaction in such composites, which grew along (101), (110) and (200), and a lot of the amorphous phases were also produced. Scanning electron microscope images indicate that nanoscale particles and nanorods are produced in such composites. Under the actions of the hard phases, fine grain strengthening of many compounds, the solution strengthening, and also the amorphous/nanocrystalline phases, the wear volume loss of such composites is 1/12 of a TA1 alloy.

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