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Performance evaluation of laser surface alloyed hard nanostructured Al_2O_3–TiB_2–TiN composite coatings with *in-situ* and *ex-situ* reinforcements

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ABSTRACT

Hard and wear resistant Al_2O_3–TiB_2–TiN composite coatings have been developed on low carbon steel (AISI 1025) substrate by following two different routes involving laser surface treatment. In the first (termed '*in-situ*' process), reinforcing phases TiB_2 and TiN, as well as the matrix Al_2O_3 of the composite are synthesized *in-situ* by laser-triggered self-propagating high temperature synthesis (SHS) from a mixture of Al, TiO_2 and h-BN and coated onto the substrate surface by laser surface alloying (LSA). In the second (termed '*ex-situ*' process), the constituents Al_2O_3, TiB_2 and TiN of the coating are provided directly as a pre-placed precursor powder mix and laser surface alloyed onto the substrate. Of these two laser assisted manufacturing procedures, it is of interest to determine the one that is more appropriate for the development of a hard, wear resistant coating. In the present work, investigation of the comparative merits and demerits of Al_2O_3–TiB_2–TiN coatings produced by *in-situ* and *ex-situ* processes is attempted through analysis of microstructure and evaluation of mechanical and tribological properties.

1. Introduction

A composite is comprised of two or more distinct materials existing in a mixed or bonded manner with recognizable interface between them. Composites consist of a reinforcing phase in the form of particles, flakes, fibers and/or fillers embedded in a matrix of metal, ceramic or polymer. The matrix holds the reinforcements while the reinforcements influence the mechanical properties of the matrix. Composites are designed and developed as single, homogeneous structural material with all of the desired characteristics for some specific applications.

Development of such new materials with improved properties is the need of the hour of the present engineering world. New composites may play significant role in innovations, particularly in the fields of aerospace engineering, high temperature applications etc. Ceramic matrix composites (CMCs) combine ceramic reinforcements with a ceramic matrix to create materials with superior properties. For CMCs, the main challenge is to provide toughness to a hard but brittle monolithic ceramic matrix. Combination of some desirable characteristics envisaged is high hardness, good electrical and thermal properties, high thermal stability, high wear and corrosion resistance. CMCs provide attractive alternatives to traditionally processed materials such as high alloy steels and refractory materials. Ceramic matrix composites may be used as protective coating materials applied on engineering surfaces due to their high hardness and wear resistance [1–8]. Self-propagating high temperature synthesis (SHS) combined with laser surface alloying (LSA) can be a very appropriate process combination for producing coatings of particulate reinforced CMCs.

The term "*in-situ* composite" is applied to those where the reinforcements of a composite are synthesized from their respective precursors or parent phases during composite fabrication by controlled melt growth, chemical reaction, transformation and deformation [9]. This is in contrast with the formation of with *ex-situ* composites where the reinforcement(s) are synthesized separately and then inserted into the matrix through a secondary process such as infiltration or powder processing. *In-situ* composites have a number of advantages over conventional (*ex-situ*) composites as they avoid complicated additional steps in the process such as sorting, alignment, infiltration and sintering. These make the *in-situ* composites more cost-effective with better controllability and reproducibility. The interfaces produced between reinforcement and matrix is defect-free with relatively better stability and strength and more significantly, free of impurities. Zuhailawati and Yong observed significant differences in the distribution and particle sizes of *ex-situ* and *in-situ* composites [10]. *In-situ* composites have much finer particulates with

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better homogeneity in distribution than *ex-situ* composites that exhibit poor coating integrity with gaps and porosity suggesting poor adhesion between matrix and particulate interfaces. Tjong et al. showed the agglomeration of ceramic particulates during processing of *ex-situ* composites, leading to the formation of composites with poor mechanical strength and toughness [11].

There has been significant utilization of the *in-situ* route in the development of composite coatings for the associated mechanical and metallurgical advantages. However, substantial amount of investigation has also been carried out in developing CMC coatings with *ex-situ* reinforcements [12,13]. Over the years, laser and plasma technologies have been two very popular routes of producing thick coatings. The process of coating by laser surface alloying (LSA) especially by powder pre-placement method can be employed to produce desired compositions. The use of LSA can afford interesting properties to materials exposed to aggressive environments [14]. In this process a mixture of the reactant powders is pre-placed as a thin layer coating on the surface of a substrate and irradiated with a high power laser to form an alloy.

Self-propagating high temperature synthesis (SHS), carried out alone or as part of a manufacturing route, has become an innovative technique to produce metal, ceramic and intermetallics composites. Conversion of chemical energy to thermal energy is the key principle of the process. Once triggered, the reaction does not require any further externally applied energy for its sustenance. The large enthalpy release at the reaction front causes the reaction to become self sustaining. SHS is a rapid process and results in the formation of substances with high purity, often in the form of fine powders [15–20].

Previously the authors have reported successful synthesis of hard, nanostructured coatings by combining SHS and LSA. A mixture of Aluminum (Al), Titania (TiO_2) and h-BN powders was pre-placed on steel substrate and subsequently irradiated by laser to produce the coating by SHS and LSA. The percentage composition of the constituent materials of the precursor powder was as per Eq. (1). Authors' previous publication on the same type of coating has already shown that the product of the aforesaid SHS reaction also follows Eq. (1) [7,8].

$$\begin{array}{llllll} 4Al + & 3TiO_2 + & 2BN = & 2Al_2O_3 + & TiB_2 + & 2TiN \\ 10 & 22.39 & 4.638 & 19.05 & 6.49 & 11.56 \\ \multicolumn{6}{l}{-(\text{stoichiometric proportion})} \end{array} \qquad (1)$$

The two phenomena, SHS and LSA, on combination, form hard substances (Al_2O_3, TiB_2 and TiN) *in-situ* through SHS — where one phase acts as the matrix (Al_2O_3) with the other two (TiB_2 and TiN) present in the form of fine and pure particulate reinforcements. SHS products come with high levels of porosity (~50%), which is undoubtedly a serious drawback. However, the association of LSA with SHS compensates for this drawback. It may be observed in this respect that the role of LSA is similar to that of post-laser treatment of pre-applied coatings. SHS products get thoroughly mixed in molten condition together with part of substrate material to produce nanostructured coating with desired properties.

In the present work, authors aim to investigate the comparative merits and demerits of the synthesis of Al_2O_3–TiB_2–TiN coatings produced by *in-situ* and *ex-situ* processes in terms of microstructural characterization and mechanical performance.

In order to carry out this comparative investigation, the authors aim to carry out experiments of the synthesis of coatings with *in-situ* and *ex-situ* coatings respectively, followed by their microstructural and mechanical characterization.

2. Experimental details

Al_2O_3–TiB_2–TiN based composite coating is produced by two different processing techniques viz., (a) by combining SHS and LSA [Coating *s*] and (b) by LSA alone [Coating *p*], on AISI 1025 steel [size: $100 \times 50 \times 8$ mm^3] substrate. The nomenclature used for two types of coatings (*s* and *p*) are based on the idea that *s* stands for SHS while *p* stands for products of SHS. *In-situ* coatings are essentially carried out with SHS so that they are referred to as *s* coatings. The corresponding *ex-situ* coatings in this investigation are carried out with products of SHS and hence are referred as *p* coatings. Precursor powder mixtures (to be applied on sample surfaces and lased) were different for different processes as listed in Tables 1 and 2. The precursor powder mixture used for SHS + LSA coating (coating *s*) comprised of reactants of the SHS reaction (Eq. (1)) to produce *in-situ* reinforcements. The precursor powder mixture used in other type of coating (coating *p*) comprised of products of the reaction (Eq. (1)) with LSA alone to produce *ex-situ* reinforcements.

Table 1
Specifications of powders used for pre-placement in SHS + LSA experiments.

Powder name	Size	Purity	Make
TiO_2	1.0–2.0 μm	99.5%	*Alfa Aesar*
h-BN	~40 μm (−325 mesh)	99.5%	*Alfa Aesar*
Al	~10 μm	99.7%	*Loba Chemie*

Measured quantities of these powders along with small amount of a poly-urethane based adhesive (*Dendrite*, PU-201) are mixed in acetone (Supplied by *Merck*, water content ≤ 0.3%) by alternate cycles of mechanical stirring (by a magnetic stirrer, *Remi Equipments*, 1 MLH) and ultrasonic vibration (ultrasonic vibrator, *Systronics*, Model : 1201) for 20 min. After mixing, the powder–acetone blend is applied manually on the steel substrate surfaces with a smooth paintbrush. After allowing the coating to dry thoroughly, the samples are baked in furnace at a temperature of 100 °C for a period of 5 min in argon atmosphere for setting the adhesive and for the complete removal of moisture.

LSA was carried out with a CW diode laser system (Model: *LDF 6000, Laserline, Germany*, power range: 200 W–6000 W, wavelength: 915–980 nm) integrated with an 8-axis robot (Make: *Reis Robotics, Germany*), special beam delivery system and computer-controlled process controller. A multi-mode rectangular beam of 17 mm × 2 mm size with homogenous energy distribution is utilized for irradiating the surface. A specially designed nozzle with rectangular orifice equivalent to that of laser beam is used to shield the irradiating area with argon shroud (pressure: 1 bar), covering entire scan area, during processing to avoid atmospheric contamination. Table 3 presents the

Table 2
Specifications of powders used for pre-placement in LSA experiments.

Powder name	Size	Purity	Make
TiB_2	~40 μm (−325 mesh)	–	*Alfa Aesar*
TiN	< 1.0 μm	99.7%	*Alfa Aesar*
Al_2O_3	0.35–0.49 μm	–	*Alfa Aesar*

Table 3
Laser treatment parameters for different samples and initial visual observations of coatings.

Laser power_ speed (kW_mm/s)	Coating developed by LSA (*ex-situ*)		Coating developed by SHS + LSA (*in-situ*)	
	Sample name	Visible quality of coating	Sample name	Visible quality of coating
3.5_20	*p*4	Coating not formed (laser energy density too low)	*s*2	Coating formed
3.5_10	*p*3	Coating formed (poor adhesion)	*s*1	Coating formed
3.5_5	*p*2	Coating formed	*s*4	Coating not formed (Laser energy density too high)
4.5_20	*p*1	Coating formed	*s*3	Coating formed