

# Microstructure and Wear Resistance of *In situ* TiCp Composite Coating by Laser Cladding

Xiaolei WU<sup>†</sup> and Guangnan CHEN

Materials Research Center, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China

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A new *in situ* method was realized by one step laser cladding to produce Ni-base alloy composite coating reinforced by *in situ* reacted and gradiently distributed TiCp particles. The submicron TiCp particles were formed and uniformly distributed because of the *in situ* reaction and trapping effect under the rapid solidification condition. And, TiCp particles were of gradient distribution on a macro scale and their volume fraction increased from 1.86% at the layer/substrate interface to a maximum 38.4% at the surface of the layer. Furthermore, the *in situ* generated TiCp/ $\gamma$ -Ni interfaces were free from deleterious surface reactions. Additionally, the clad coating also revealed a high microhardness of gradient variation with the layer depth and the superior abrasive wear resistance.

## 1. Introduction

The simple and economical way to realize a multiphase microstructure containing the tough matrix with a finely dispersed inert hard phase, which meets the requirement for high wear resistance at room and especially elevated temperatures, is of great importance in material science.

Ceramic particulate-incorporation to provide a metal matrix composites (MMCs) layer on various substrates by laser cladding is a relatively newly developed technique, in which the powders of an alloy with a desirable composition and a thin surface layer of the substrate materials are simultaneously melted and then rapidly solidified to form a dense coating perfectly bonded to the base materials. The ceramic particles are pre-placed onto the substrate surface or directly blown into the laser molten pool. Various ceramic-alloy systems, such as SiC/Co-Cr-W, Cr<sub>2</sub>O<sub>3</sub>/Ni-Cr-Mo, WC/Ni-Cr-Si-B and TiC(TiN,TiB)/Ni-base alloys *et al.*, synthesized on traditional substrate materials have been studied<sup>[1~5]</sup>.

The interaction between ceramic particulates and the alloy matrix especially at ceramic/matrix interface has an important influence upon properties. Poor wettability, gas entrapment and deleterious interface reactions are major problems. For particulate-reinforced MMCs, the main strengthening mechanism is transfer of stress from the matrix to the reinforcement phase through a shear mechanism. A weak interface bond restricts the effective stress transfer, and

the scope of application is reduced.

At present, two fabrication methods of bulk particulate-reinforced MMCs have generated considerable interest. One is the *in situ* reaction method, such as XD<sup>TM</sup><sup>[6,7]</sup>. In this method, reinforced phases are introduced into the metal matrix by the direct reaction among the added particles. Therefore, the reinforced phases *in situ* reacted, such as TiB<sub>2</sub><sup>[8]</sup>, TiC<sup>[9]</sup> and Al<sub>4</sub>C<sub>3</sub><sup>[10]</sup> *et al.*, may be more compatible with the matrix and the phase interfaces may be cleaner as compared with the composites produced conventionally. Meanwhile, because the *in situ* formed precipitates are often ultra-fine and thermally stable, the composite matrix has sufficient strength to transfer stress. The *in situ* MMCs exhibit improved strength retention, and useful improvement in wear and fatigue resistance<sup>[6,9,10]</sup>. The other is rapid solidification processing<sup>[11~13]</sup>. Because of the high solidification rate and the cooling rate as well, the interface reaction between the particle and the molten alloy is restrained to a large extent. And, the rapid movement of the solid/liquid interface limits the particle pushing effect and brings about a uniform distribution. Additionally, rapid solidification can also decrease effectively coarsening of particles that is detrimental for the structure-sensitive properties of composites.

As is well known, the clad layer is often different from the substrate in microstructural, physical and mechanical characteristics and as a result, the layer/substrate interface becomes possible failure mode because of large stress concentration *et al.* The functionally gradient materials (FGMs), in which composition, structure and property vary progressively as a function of position, is pursued in ma-

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: xlwu@cc5.imech.ac.cn

materials development in order to avoid the problem due to interface. Recently high power CO<sub>2</sub> lasers have been used to produce functionally gradient coatings (FGCs) by the successive deposition of several alloyed/cladded layers superimposed in a direction normal to the substrate. Jasim *et al.*<sup>[14]</sup> obtained a FGC by three vertically overlapping laser-processed tracks, in which the proportion of SiC reinforcement increased in steps from 10 to 50 vol. pct. Abboud *et al.*<sup>[15]</sup> also produced FGCs on Ti-Al and Ni-Al substrates by deposition of superimposed layers with different feed rates. However, the above multilayer coating consists of essentially discrete layers rather than a smooth gradient of composition and structure. And, there exist sharp demarcations between the layers, which create sudden changes in mechanical properties across the whole coating.

The aim of the present investigation is to synthesize *in situ* TiCp dispersoid in Ni-base alloy laser cladding coating on a 5CrMnMo steel substrate. A new original method, *in situ* formation of TiCp with a gradient distribution by one step laser cladding of rapid solidification, is proposed. TiCp particles are introduced by an *in situ* reaction of titanium and graphite during laser cladding process, rather than TiCp particles being directly added into the laser molten pool. The experimental results reveal that the optimum way to obtain submicron TiCp particles with uniform distribution is to induce their *in situ* formation in the macrohomogeneous molten pool during rapid solidification. The exploratory study here deals only with the microstructural characteristics of *in situ* laser synthesized TiCp reinforcement and tests an alternative approach, which is different from the conventional fabrication of ceramic-alloy laser cladded coating and the above FGC.

## 2. Experimental

A powder mixture of a Ni-base alloy, Ti (99.7 pct purity) and crystalline graphite (99.5 pct purity) was used as the coating alloy. The titanium-graphite powder was 30 vol. pct. The ratio of Ti to carbon powders corresponded to that of stoichiometric TiC. The average size of Ti and graphite powders were 2 and 4 μm respectively. A self-melted Ni-base alloy was selected as the matrix of the composite layer because of its good resistance against corrosion and erosion as well as its fine compatibility with TiCp. The Ni-base alloy powder possessed an average size of 20 μm and its chemical composition (wt pct) was 16Cr, 3.5B, 4.5Si, 0.8C, balanced by Ni. The substrate material was 5CrMnMo steel in a quenched and tempered condition.

Laser cladding was carried out with a 3 kW continuous wave CO<sub>2</sub> laser to produce a series of single clad tracks without overlapping. The processing conditions were 4 ~ 15 mm/s scanning speed, 3 mm beam

diameter and 2 kW laser power. Surface oxidation was prevented by using two argon jets, one coaxial with the laser beam and the other lateral to it, making an angle of 30 deg. with the surface. The mixed powders were pre-coated on the surface at a thickness of about 0.8 mm.

The microstructure, composition and interface structure were observed by using Neophot-21 optical microscopy (OM), KYKY2800 scanning electron microscopy (SEM), CM12 transmission electron microscopy (TEM) and H9000 high resolution electron microscopy (HREM) equipped with EDAX. The size distribution and volume fraction of TiCp particles in the MMCs layer were measured by a computerized image analysis method.

Apart from above microstructural analyses, mechanical experiments were performed on the layer, including a Vickers hardness measurements and wear tests. The pin-on-disc abrasive wear was carried out by using FALEX friction and wear test machine. The specimens for the test were small pins of φ3 mm×6 mm. Flint paper having Al<sub>2</sub>O<sub>3</sub> particle of -380 mesh size was used as an abrasive. The specimen rotated at a speed of 100 r/min with a load of 2 pounds at room temperature. Each test involved a sliding distance of 14.5 m. The experiment was lasted for 10 min, then the wear loss was measured. The surface was smoothed before tests because after laser clad processing all specimens had surface roughness of at least a few tens of micrometers.

## 3. Results and Discussion

### 3.1 Microstructural analysis

Basically, a solidification microstructure is characterized by its phase and growth morphology. The growth morphology of the rapidly solidified coating depends mainly upon the temperature gradient and the solidification rate as well<sup>[16]</sup>. From the coating/substrate interface to the top surface of the coating, the morphology was observed to consist of the planar front, cell and dendrite successively, consistent with the decreased temperature gradient and increased solidification rate. The planar, cellular and dendritic phases were fcc γ-Ni austenite. The interdendritic eutectic consisted of γ-Ni and (Fe,Cr)<sub>7</sub>C<sub>3</sub> carbides. X-ray diffraction showed that phases of the layer consisted of γ-Ni, TiCp, Cr<sub>7</sub>(C,B)<sub>3</sub>, Ni<sub>5</sub>Si<sub>2</sub> and Cr<sub>2</sub>B, without the existence of Ni-Ti binary system intermetallic phases. The detailed microstructural analyses of the Ni-base alloy matrix by TEM and X-ray diffraction were reported elsewhere<sup>[17,18]</sup>. The results were in agreement with those of other studies in similar Ni-alloy coatings<sup>[3,4]</sup>.

Figure 1 shown the OM and SEM micrographs of a cross-section of the laser-clad composite coating and the distribution of TiCp particles *in situ* formed during laser clad on a micro scale, relevant to various

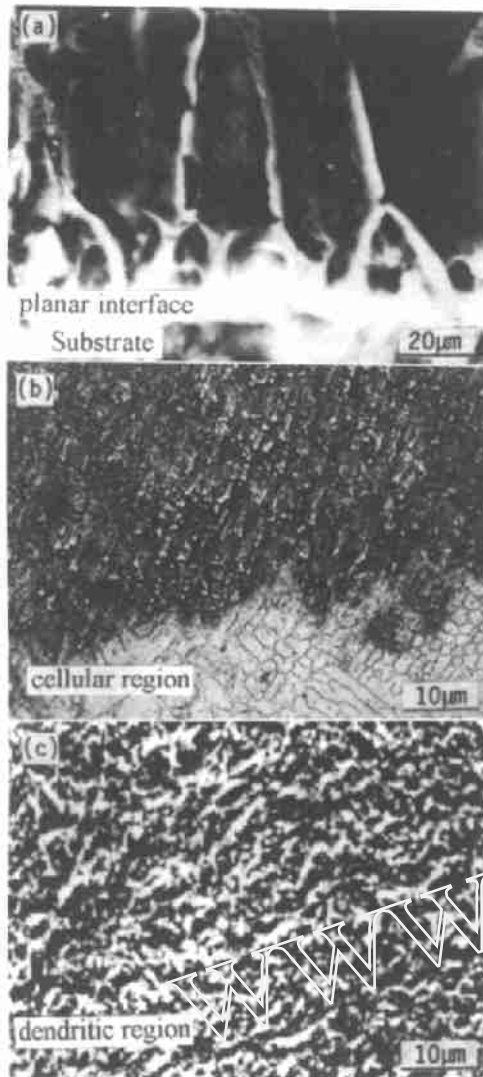


Fig.1 Distribution of *in situ* formed TiCp particles in planar front (a), cellular (b) and dendritic (c) growth zone respectively at 15 mm/s beam scanning speed

growth morphologies of Ni-base alloy. The bond area between the clad layer and the substrate was a 8  $\mu\text{m}$  thin band of planar growth, as shown in Fig.1(a), and free from pore and crack, which meant an excellent metallurgical bond between the coating and the substrate. No TiCp particles were observed in this region. In the optical micrograph of Fig.1(b), the specimen was etched with different etching reagents for the purpose of evidently revealing the cellular growth morphology of the Ni-base alloy and *in situ* formed TiCp particles respectively. It was observed that TiCp particles were dispersely distributed. Figure 1(c) shows the SEM micrograph of TiCp particles with deep etching in dendrite growth zone, where the solidification rate of the advancing solid/liquid interface increased. It can be seen that a large amount of TiCp particles were dispersely and uniformly distributed in interdendritic regions, which means that TiCp particles were

trapped by rapidly moved solid/liquid interface. And, most of TiCp particles was of the size distribution of orders of hundreds nanometer. A small amount of even finer TiCp with orders of tens nanometer were considered to precipitate from  $\gamma$ -Ni solid solution during rapid solid-state cooling after solidification. Additionally, the volume fraction of TiCp particles in dendritic zone was clearly enhanced, as compared with that in cellular zone. The clad layer was about 820  $\mu\text{m}$  in maximum thickness.

Figure 2(a) is the bright-field TEM micrograph showing *in situ* formed TiCp particles in eutectic structure. Figure 2(b) is the SADP of TiCp. Most TiCp particles uniformly distributed were found with hexahedral geometry, which should be formed by a lateral spreading mechanism and finally surrounded with the low index faces of TiC cubic crystals. The present observation is well consistent with the previous study by Flemings<sup>[19]</sup>.

Figure 3 is a HREM image illustrating the phase interface between TiCp and  $\gamma$ -Ni austenite. It can be noted that the interface was clean and free from gas absorption, oxidation or other deleterious surface reactions. This is considered to be one of main advantages of *in situ* generated interfaces. This clean interface structure is consistent with that obtained by other *in situ* process<sup>[4]</sup>. Thus, the matrix-TiC bond may be stronger.

The beam scanning speed had a key effect on the micro-distribution of TiCp particles, as shown in Fig.4. It can be seen that most of TiCp particles segregated at dendrite arms because of the solute pushing effect at a 4 mm/s beam scanning speed. Furthermore, it is important to note that in the experimental range investigated, there existed a critical beam scanning speed, 8 mm/s, corresponding to the transition of trapping to pushing of TiCp particles by advancing solid/liquid interface.

The micro-distribution of particles depended mainly upon the interaction between particles and the advancing solid/liquid interface. This interaction might lead to trapping or pushing of particles by solid/liquid interface. Trapping might bring about a uniform distribution of particles within interdendritic regions whereas pushing resulted in segregation at regions finally solidified. The interaction between particles and advancing solid/liquid interface was studied under the condition of equilibrium thermodynamics, i.e., at a very low crystal growth speed<sup>[20,21]</sup>. And, it is widely accepted that there exists a critical speed which corresponds to a transition of pushing to trapping.

Unfortunately, a quantitative or qualitative criterion on such an interaction under the rapidly solidified condition has not been built up because of the complexity of thermal physics in laser molten pool. And, the size, morphology, volume fraction, thermal conductivity of particles and flow, stickability of the

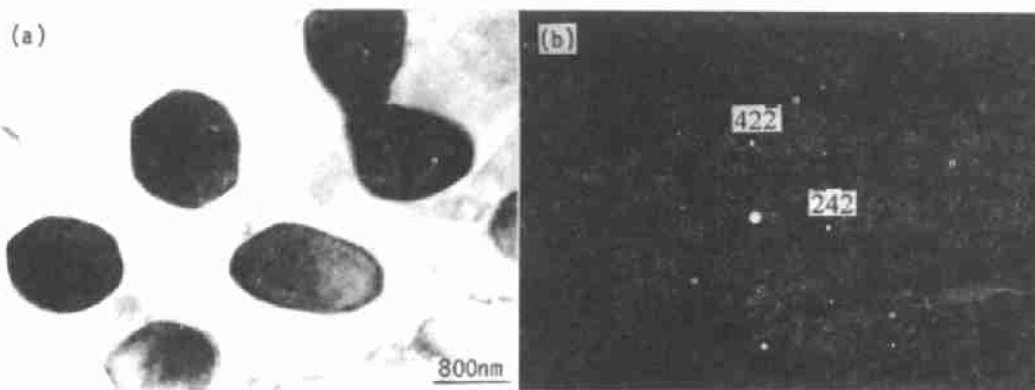


Fig.2 Bright-field TEM micrograph showing micro-morphology of TiCp in eutectic structure (a) and SADP of TiCp (b) at 15 mm/s beam scanning speed

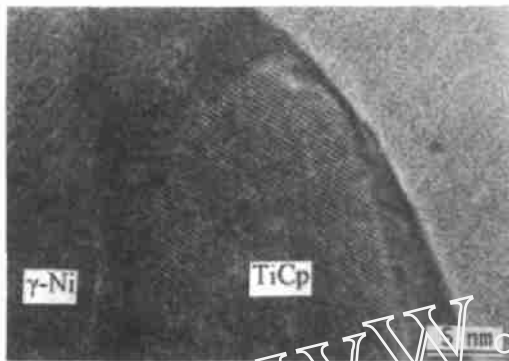


Fig.3 HREM image showing TiCp/ $\gamma$ -Ni interface



Fig.4 Segregation of TiCp particles in dendritic zone at 4 mm/s beam scanning speed

matrix have an influence upon particle pushing effects. However, to increase the local interface solidification rate, which is relevant to the beam scanning speed, is considered to have an important effect to realize particle trapping. Ehrstrom et al.<sup>[11]</sup> and Li<sup>[12]</sup> pointed out that increasing the solidification rate and the cooling rate might weaken or even suppress the particle pushing effect in rapid solidification processing of MMCs. Fulcunaga et al.<sup>[13]</sup>

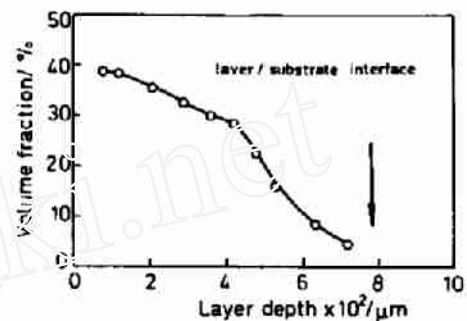


Fig.5 Gradient distribution of TiCp particles with the layer depth

confirmed that under rapid solidification there existed a critical rate, at which the transition of pushing to trapping occurred. From Figs.2 and 5, it can be seen that to increase the beam scanning speed has a key effect to restrain the solute pushing effect.

It was further observed that the volume fraction of TiCp particles possessed a smooth gradient distribution as a function of the layer depth based upon image analyses, as shown in Fig.5. The volume fraction of TiCp particles changed from 1.86% at the bottom to 38.4% at the top surface of the layer. The average volume fraction of TiCp in the whole layer was approximately 22.6%, which was smaller than that of the original content in the mixture powder.

The relative lower density of TiCp compared with that of Ni-base alloy will cause a gradient distribution on a macro scale. The differential-density-driven particle movement was also found in the previous studies<sup>[22,23]</sup>, where the particles tended to segregate to the upper region in the particle reinforced MMCs layer. Hu et al.<sup>[22]</sup> pointed out that whenever the liquid viscosity and the time allow, there would be ceramic particulate movement due to the relative densities of the components. Additionally, the convective flow in the liquid would have its effect on the movement of the ceramic particulate. The forces and flow

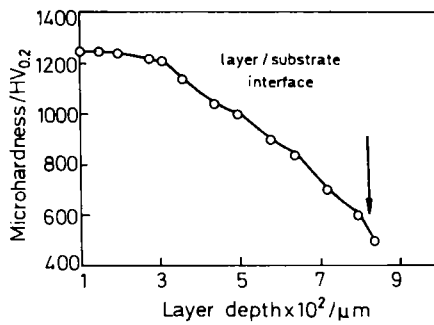


Fig.6 Microhardness variation with the layer depth

patterns resulted from surface tension gradients, undoubtedly, would influence strongly the distribution of *in situ* formed ultra-fine ceramic reinforcements.

### 3.2 Microhardness

Figure 6 illustrates the hardness variation of a crosssection as a function of the layer depth, without a sudden change across the whole coating. The result shows that the highest hardness, 1250 HV<sub>0.2</sub>, was at the layer surface, consistent with the volume distribution of TiCp particles. The hardness decreased gradually with the depth of molten pool away from the surface.

### 3.3 Wear properties

Figure 7 shows the wear volume, wear rate and friction coefficient of the TiCp MMCs layer, as compared with laser clad Ni-base alloy layer and the substrate. It can be seen that TiCp particulate-reinforced MMCs layer had the smallest wear volume and lowest wear rate. It is noted that the friction coefficients of TiCp MMCs layer were only a little higher than that of the Ni-base alloy layer. Therefore, TiCp reinforced composite layer may enhance the hardness and wear resistance without evidently increasing the friction coefficient of the layer. The present result is well consistent with the previous studies<sup>[24,25]</sup>. The abrasive wear resistance of particle reinforced MMCs layer is proportional to the size, distribution, kind, volume fraction and hardness of the hard phase. Cerri<sup>[24]</sup> studied the abrasive wear behavior of laser clad-layer of WC/Ni-Si-B and TiC/Fe-Cr-Al-Y ceramic-alloy system and concluded that the rate at which the matrix material removed was determined by the removal rate of TiCp particles. The finer, more disperse and well-distributed the ceramic reinforced particles, the higher the wear resistance of the layer. Boas<sup>[25]</sup> proposed another abrasive wear mechanism in that the nucleation, propagation, and link of the crack at the phase interface between the ceramic particle and the matrix might bring about the removal of the reinforced particles. Therefore, under the present wear condition, it is expected that a

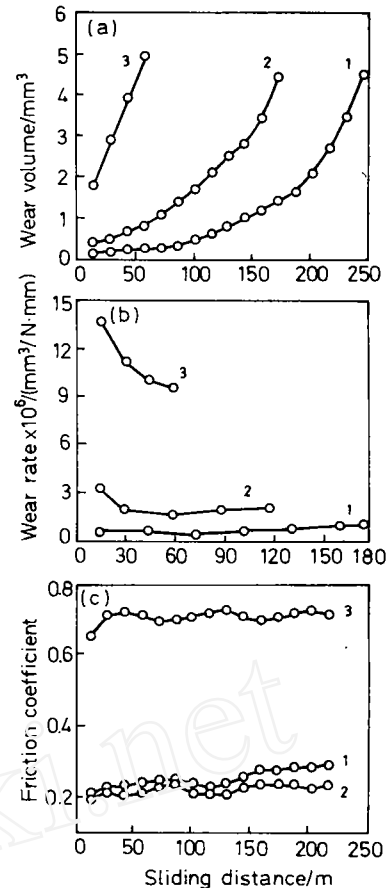


Fig.7 Variation of wear volume (a), wear rate (b) friction coefficient (c) of the layer with the sliding distance  
Curve 1 to 3 correspond to TiC/Ni-alloy layer, Ni-alloy layer, and the substrate, respectively

large amount of fine, disperse and well-distributed *in situ* TiCp particles with a strong interface bond will be sure to enhance the wear properties of the layer effectively.

## 4. Conclusions

(1) An *in situ* method was realized to produce Ni-base alloy composite coating reinforced by *in situ* reacted and gradiently distributed TiCp particles.

(2) The disperse and ultra-fine TiCp particles were *in situ* formed. The TiCp particles were mainly uniformly distributed because of solute trapping effect. There existed a critical beam scanning speed which corresponded to the transition of pushing to trapping of particles by advancing solid/liquid interface. And, TiCp particles were of gradient distribution on a macro scale as a result of the differential-density-driven and the convective flow. The TiCp/ $\gamma$ -Ni interfaces were found to keep clean and free from gas absorption, oxidation or other deleterious surface reactions, which led to a stronger interface bond.

(3) The microhardness of the layer also revealed

a gradient variation and the highest value was 1250 HV<sub>0.2</sub> at the surface of the coating. The wear property of the coating was significantly enhanced.

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