

# IMPROVEMENT OF LASER-CLADDED SURFACES WITH ADDED NANOMATERIALS

Cyril Vimalraj, Paul Kah, Belinga Mvola and Pavel Layus

Laboratory of Welding Technology, Lappeenranta University of Technology, P.O. Box 20, FI 53851, Lappeenranta, Finland

Received: November 29, 2016

**Abstract.** Industries like the aerospace, automobile, marine, and other manufacturing sectors require surface modifications on substrates through laser cladding process, because the laser process uses only minimum resources to provide better surface quality compared to conventional processes. As industry's demands have widened, the conventional coating material can no longer satisfy the growing criteria. New technologies have innovated a solution to the coating material through the addition of nanomaterials, which satisfies the growing demands and attains significant improvements in properties. This study reviews the literature about the effects of nanomaterial addition to laser cladding materials. The paper mainly focuses on the effects and factors of nanomaterial addition influencing the microstructure, properties, as well as defect reduction. The review shows that adding nanoparticles to the coating material significantly improves the cladded surface quality and the properties compared to the conventional cladding surface. The cladded surface with nanoparticles has reduced defect formation, increased stable microstructural phase formations and improved mechanical, wear resistance and thermal shock resistance properties. The general factors that influence these improvements are the appropriate selection of nanomaterial addition, uniform dispersion of the nanoparticles, characteristics of the nanoparticles and the quantity of nanoparticles added to the coating material. However, the nanoparticle-added cladding material may also have degraded surface properties. Many studies are investigating various other coating materials using different cladding processes to attain good surface properties and satisfies the demands of industries.

## 1. INTRODUCTION

Laser cladding is an efficient process of depositing materials on substrates compared to other coating processes based on factors, which are detailed in Table 1 [1]. This process provides a protective layer on the substrate, which is mostly used for the reduction of wear and corrosion. For instance, most of the engine parts and tools in the aircraft and automobile industries have been coated; moreover, coatings are also used in repairing turbine blades, buildings and exterior usage applications [2]. Recently, many products only require surface modification with upgraded surface properties rather than

processing the whole components such as metal joining, machining, drilling, forming and rolling. As the surface coatings demands in industries are growing for its high strength, requirements have been rising to improve the cladding materials.

Surface coating requires minimum dilution, in order to improve the mechanical properties and chemical composition between the substrate and the coating material [3]. The minimum dilution between the coating material and the substrate requires the manipulation of the heat input, speed and other processing parameters, which can be efficiently processed by the laser cladding process. Generally, the frequently used cladding or coating

---

Corresponding author: Paul Kah, e-mail: Paul.Kah@lut.fi

**Table 1.** Comparison of laser cladding process with other surface deposition processes, see [1].

FEATURES	Surface deposition processes			
	Laser cladding	Thermal spray	Chemical Vapour Deposition	Physical Vapour Deposition
Bonding strength	High	Moderate	Low	Low
Dilution	High	Nil	Nil	Nil
Coating material	Metals, Ceramics	Metals, Ceramics	Metals, Ceramics	Metals, Ceramics
Coating thickness	50 $\mu\text{m}$ to 2 mm	50 $\mu\text{m}$ to several mm	0.05 $\mu\text{m}$ to 20 $\mu\text{m}$	0.05 $\mu\text{m}$ to 10 $\mu\text{m}$
Repeatability	Moderate to High	Moderate	High	High
Heat-affected zone	Low	High	Very low	Very low
Controllability	Moderate to High	Moderate	Moderate to High	Moderate to High
Cost	High	Moderate	High	High

materials are nickel (Ni)-based, cobalt (Co)-based, and iron (Fe)-based, which show better properties and are used for various applications in the industries.

Studies have shown that the addition of a rare element (RE) to the coating material improves the properties and surface appearance by its unique physical and chemical characteristics [4]. However, adding RE to the coating material has not satisfied the industries demands. Other research showed that the particle size in the cladding coating material has a great influence in the properties and microstructural formation between the substrate and the coating material [1]. For instance, Wellman and Nicholls [5] showed that the size of the carbide in the coating material had a significant influence in the surface property, especially in wear and erosion resistance.

As nanoparticles have unique thermal conducting, mechanical and strengthening properties, due to their size and surface characteristics [6] [6]. Including nanoparticles to the coating materials instead of microparticles will improve the cladded surface with a stable microstructure, thereby generating better surface properties. Research has shown that the nanoparticles reinforces the metal matrix composites through coating, leading to improved properties and surface integrity [7-9]. Studies also show that the amount of nanoparticles added to the coating material have greater influences on the surface microstructures and properties. Therefore, there is need to acknowledge the effect of nanomaterials on the coated surfaces and the factors that influence good surface integrity through the formation of a stable microstructure and improvements in surface properties. The study mainly focuses on microstructural changes and the surface

property improvements through the addition of nanoparticles to the coating materials in Ni-based, Co-based, and Fe-based coating material as well as the factors that influence these improvements.

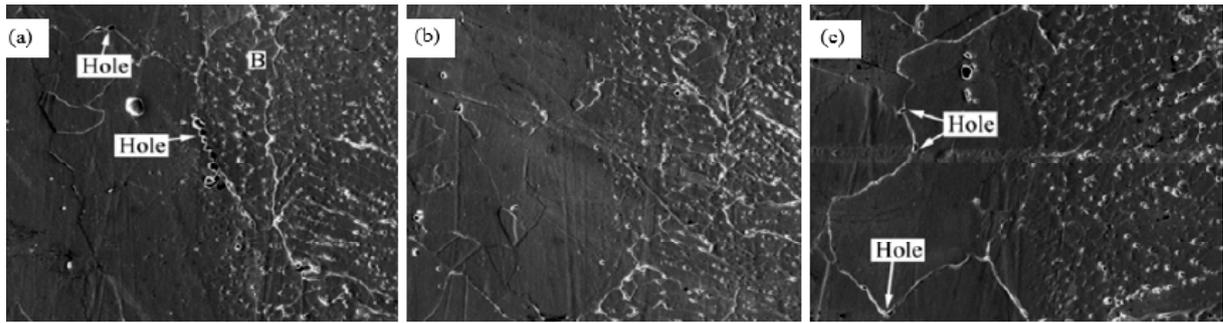
## 2. NICKEL-BASED COATING MATERIAL

Coatings of high-temperature protection have been widely used in the aerospace, thermal power station, chemical and other fields [10,11] for fluctuating service conditions. These high-thermal protection coatings have been most frequently used in gas turbine components [12]. The Ni-based coating is often used and a recommended coating material for thermal protection applications [10]. As there are radical changes in service conditions, improvements to the coating materials prior to the substrates are required. Nanoparticles have been added to the Ni-based coating material to improve properties as well as to attain the microstructural stability at varying climatic and service conditions.

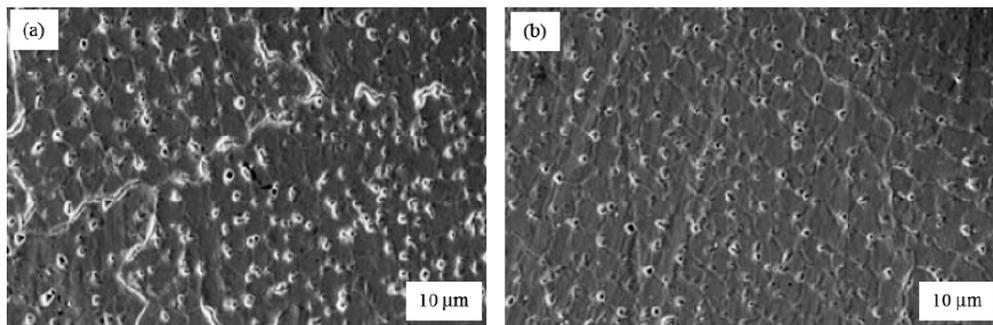
### 2.1. Effect of nanoparticle-added coating material on defects

Defect formations between coated surface and substrate have a significant influence on the properties and strength of the coated surface. The NiCoCrAlY coating material is prone to the pores formation and crack formations by the alloying element in the coating material. The NiCoCrAlY-coated surface shows crack formation in the interfacial region and its propagation from the interfacial cladded region to the cladded surface degrades the strength of the coated surface [13,14].

By the addition of nominal amount (i.e. 2 wt.%) cerium oxide ( $\text{CeO}_2$ ) nanoparticles to the NiCoCrAlY



**Fig. 1.** Defect in interfacial region between the Ni-base super-alloy and Ni-based coating material with addition of (a) low content nanoparticles, (b) nominal content nanoparticles, (c) high content nanoparticles. Reprinted with permission from Wang et al., © 2009 Transactions of Nonferrous Metals Society of China.



**Fig. 2.** Cladding interfacial region between the Ni-base super-alloy and Ni-based coating material formed (a) without nanoparticles (b) with  $\text{CeO}_2$  nanoparticles. Reprinted with permission from Lepski et al., © 2009 Springer Netherlands.

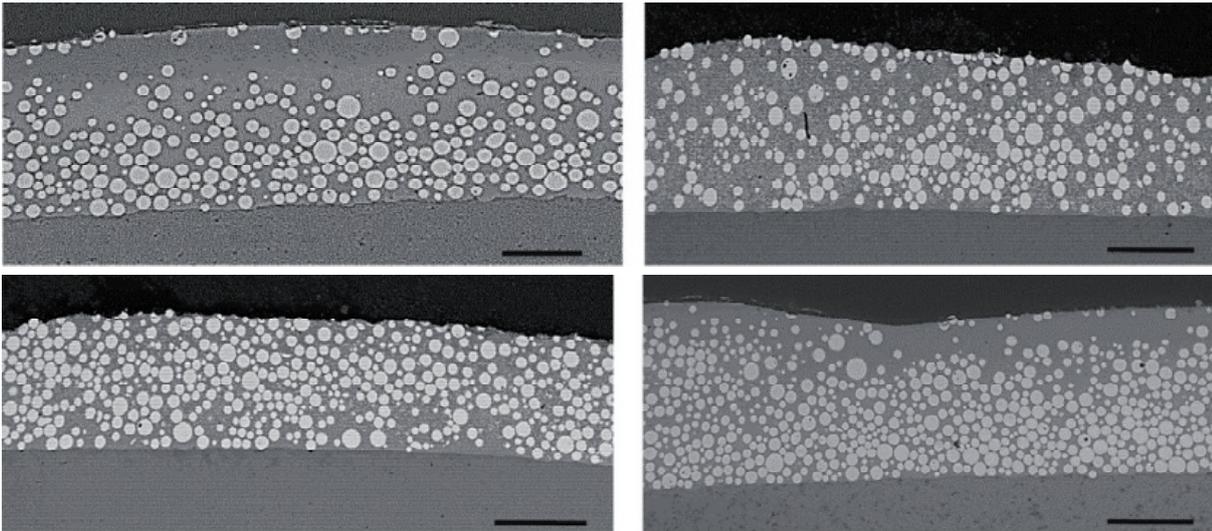
cladding material produced better surface without cracks. However, the high content (3 wt.%) of  $\text{CeO}_2$  nanoparticles to the coating material generated pore formation on the cladded surface [14]. Instead of RE (i.e.  $\text{CeO}_2$ ) as nanomaterial, adding metal oxide nanoparticles (i.e. Aluminium oxide- $\text{Al}_2\text{O}_3$ ) in low amount (i.e. 0.5% mass fraction) to the NiCoCrAlY cladding material also resulted in pores at the interface region. The increased content of  $\text{Al}_2\text{O}_3$  nanoparticles to a nominal level (i.e. 1%) in the coating material decreased pore formation, as shown in Fig. 1 (a and b). The high content (1.5% mass fraction) of  $\text{Al}_2\text{O}_3$  nanoparticles in the cladding again resulted in pores formation as shown in Fig. 1c, [13].

The main cause for the crack and pores formation in cladded surface was because of the difference in the thermal expansion co-efficient between the materials [13]. The nominal quantity of nanoparticles addition to the cladding material decreased the difference in thermal expansion between the coating and the substrate, thereby reducing the formations of pores and crack compared to low and high quantity of nanoparticles. This thermal expansion difference occurred by the segregation of particles in grain boundaries thereby leading to cracks. Thus, either RE nanoparticle or metal oxide

nanoparticles added to the NiCoCrAlY cladding material with a nominal quantity reduces the defect formation by influencing the thermal expansion of materials.

## 2.2. Effect of nanoparticle-added coating material on the microstructure

Grain refinement and grain transformation plays an important role in the formation of stable microstructures on Ni-based cladding surface. Inserting nanoparticles to the surface coating material would aid in grain refinement for the formation of stable microstructures between the surface and substrate. For instance, the experiment by Wang et al. [14] on a Ni-based alloy substrate, with and without the addition of  $\text{CeO}_2$  nanoparticles in the NiCoCrAlY coating showed variation in the microstructures along the interface region and the surface. The cladded surface without added nanoparticles had a microstructure containing equiaxial grains in the clad layer; moreover, the interface region between the substrate and the cladding surface contained a dendrite and epitaxial microstructure with non-uniform distribution, which is shown in Fig. 2a. How-



**Fig. 3.** Uniformity of Ni/WC composite coating (a) without nanoparticles, (b) with 0.5%  $\text{La}_2\text{O}_3$ , (c) with 1%  $\text{La}_2\text{O}_3$  and (d) with 2%  $\text{La}_2\text{O}_3$ . Reprinted with permission from Sun et al., © 2005 Surface and Coatings Technology.

ever, the clad surface with a nominal amount (i.e. 2 wt.%) of  $\text{CeO}_2$  nanoparticles led to fine equiaxial grains in the clad layer and the dendrites structure in the interface region also transformed into equiaxial grains with a uniform distribution, which is shown in Fig. 2b. Thus, only equiaxed microstructure were found in the interface region with a nominal amount of nanoparticles, and other than nominal a content of nanoparticles added to the coating material produced hardly any dendrite microstructures.

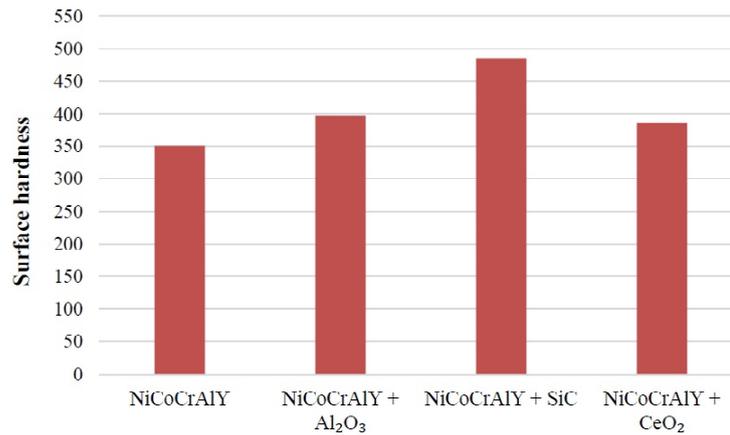
Besides using RE materials as nanoparticles included in Ni-based coatings,  $\text{Al}_2\text{O}_3$  nanoparticles were added to the NiCoCrAlY coating material. Observation showed that the surface coated without  $\text{Al}_2\text{O}_3$  nanoparticles also formed dendrite structures perpendicular to the interface surface; however, a coated surface with  $\text{Al}_2\text{O}_3$  nanoparticle addition had transformed these structures into fine epitaxial structures. This transformation was due to the promotion of heterogeneous nucleation that obstructed the growth of grains. The grain boundaries of the clad region formed without nanoparticles addition were smaller compared to region clad with the nanoparticle [13]. The nanoparticles addition (i.e.  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$ ) in the coating material has led to the segregated into grain boundaries. Moreover, increasing the nano  $\text{Al}_2\text{O}_3$  particle as well as nano  $\text{CeO}_2$  particle content in the Ni-based coating materials increased segregation at boundaries resulting in degradation of properties [13,14].

In both clad regions with additions of RE and  $\text{Al}_2\text{O}_3$  nanoparticles, the clad and the interface

region without added nanomaterial had phases  $\gamma\text{-Ni}$ ,  $\beta\text{-NiAl}$ ,  $\gamma'\text{-Ni}_3\text{Al}$ , and  $\alpha\text{-Cr}$  (Chromium-Cr). However, the phase  $\alpha\text{-Cr}$  was not found in the clad region formed with added nanoparticles in both  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$  surfaces. This disappearance was due to an increase in the solid solubility of the Cr element. As Ce is a RE material, the adhesion of Ce reduces the grain growth and results in the solubility of the Cr element. In the case of  $\text{Al}_2\text{O}_3$  nanoparticle-added coating,  $\text{Al}_2\text{O}_3$  nanoparticles obstructing the dispersion of the element and Cr produced a solid reaction with the Ni substrate [13,14].

As composite materials provide better properties and strength compared to the metal oxide and RE nanoparticles, the composite materials in the coating process produced good properties and strength on the substrate and the surface [9]. In addition, the nanoparticles included in the composite material will provide far better properties compared to the commercial composite coating materials. For instance, Farahmand et al. [15] experimented on laser cladding with coating materials such as the Ni/WC (tungsten carbide) composite on mild steel substrates and found three different microstructure formations: fine bone structure, inter-dendrite structure and equiaxed structure. The dendrite structure initiated growth due to the thermal properties of the WC particles. Moreover, the saturated solid solution present in the microstructure exhibited significant amounts of C (carbon) and W (tungsten).

By the addition of WC nanoparticles to the Ni/WC coating material improved the distribution of WC



**Fig. 4.** Surface hardness of laser cladded Ni-based coating on Ni super-alloy with different nanoparticle addition. Reprinted with permission from Zhong et al., © 2010 Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science.

particles, which resulted in a similar microstructure. Yet, the microstructure was fine compared to the coating without added nanoparticles. However, the significant addition of WC nanoparticles with a low welding temperature resulted in cluster formation, which thereby formed blocky carbide in the coating. Instead of adding WC nanoparticles, the addition of nanoparticle La<sub>2</sub>O<sub>3</sub> (lanthanum oxide) into the Ni/WC coating material showed an improvement in the homogeneity of the cladded surface with an increase in the nanoparticles, which is shown in Fig. 3. The addition of La<sub>2</sub>O<sub>3</sub> resulted in a microstructure with only dendrite and inter-dendrite. The dendrite structure size and inter-dendrite spacing as well as solidified re-melted carbides decreased, due to the La<sub>2</sub>O<sub>3</sub> addition that increased latent heat, thereby reducing the melting temperature and increasing solidification time. Moreover, there were O-rich regions and Cr-rich regions found in the microstructure compared to the Ni/WC coating. The new phase and region formation was due to the RE addition into the Ni/WC composite material [16].

Thus, the addition of nanomaterials in the Ni-based cladding material shows transformation in the transition region microstructure between the substrate and coating. Moreover, phase formation disappeared from the microstructure. The composite material coating with added carbide nanoparticles exhibited a fine microstructure and blocky carbide formation, and added RE nanoparticles showed a homogeneous microstructure and the formation of new phases. Thus, the refinement of the microstructure and microstructural transformation occurred by the nominal content of nanomaterials, uniform dispersion of nanomaterials and appropriate selection of nanomaterials.

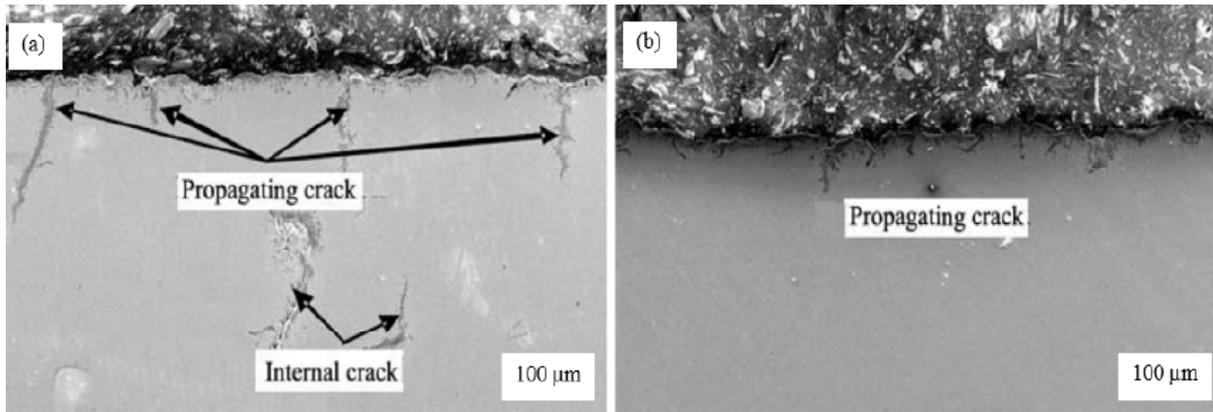
## 2.3. Effect of nanoparticle-added coating material on surface properties

As the Ni-based alloy cladding material provides grain refinement and stable microstructural formations through nanomaterial addition, the nanomaterial will yield high wear and thermal shock resistance for fluctuating service conditions. Besides the wear and thermal shock resistance properties, other properties also influence the service condition.

### 2.3.1. Hardness property

The hardness characteristic of the surface reflects the surface strength and the bonding between the substrate and cladding, and, thus, the nanoparticles added to the cladding surface show improved hardness. For example, Wang et al. [14] observed that adding CeO<sub>2</sub> nanoparticles to the Ni-based coating had uniform hardness distribution on the surface compared to a surface coated with the Ni-based material without nanoparticles. Moreover, the microhardness value increased by the addition of nanoparticles; however, with a medium amount (i.e. 2 wt.%) of CeO<sub>2</sub> nanoparticles, the cladded surface showed the highest hardness value compared to other cladded surfaces.

Previous research has shown that carbide inclusion particles in fabrication processes result in high hardness values compared to other particles [17,18]. Thus, Wang et al. [19] compared Al<sub>2</sub>O<sub>3</sub> nanoparticles, SiC (silicon carbide) nanoparticles, and CeO<sub>2</sub> nanoparticles added to the NiCoCrAlY coating on a Ni alloy surface. The study showed that the highest hardness of the surface was at-



**Fig. 5.** Cracks formation after 100 thermal shock cycles from room temperature to 1050 °C on Ni-based cladded surface (a) without nanoparticles (b) with nanoparticles. Reprinted with permission from Wellman et al., © 2004 Surface and Coatings Technology.

tained by the coating with SiC nanoparticles, followed by the coating with  $\text{Al}_2\text{O}_3$ , and the lowest hardness values were measured by the coating with  $\text{CeO}_2$  particles, which is shown in Fig. 4. This improvement in surface hardness was due to the greater absorption of the laser beam by  $\text{Al}_2\text{O}_3$  and SiC nanoparticles than by  $\text{CeO}_2$  particles. A previous study showed that the hardness depends on the nanoparticle size and the reason for hardness improvement is that the  $\text{Al}_2\text{O}_3$  nanoparticles are in micro-aggregate form and the SiC nanoparticles exist in single particles; however, the  $\text{CeO}_2$  nanoparticles existed in both single particles and micro-aggregates leading to more disintegration of the laser beam [20].

The study shows that apart from the nanoparticles influencing the improvement of hardness, there are also other factors such as microstructures and cladding process parameters that have an effect on the surface properties. For example, cladding with the Ni/WC composite as a coating material on a mild steel substrate showed that the hardness increased by the increasing laser cladding speed, which was due to the fine dendrite structure formation by the high solidification rate. The coating with a nominal amount (i.e. 5 wt.%) of WC nanoparticles produced the highest hardness compared to the coating with the  $\text{La}_2\text{O}_3$  nanoparticle and without nanoparticles. This highest hardness value was the result of the uniform distribution of WC particles and their dissolution impedance. Moreover, adding WC nanoparticles above the nominal level (i.e. 10 wt.%) led to porosity as well as increases in the carbon concentration, thereby showing hardness degradation. The cladding surface with a nominal level (i.e. 1 wt.%) of  $\text{La}_2\text{O}_3$  nanoparticles improved

in hardness but not to the value of the cladding surface with WC nanoparticles. The improvement was due to the grain refinement and new intermetallic compound formations. However, the  $\text{La}_2\text{O}_3$  nanoparticles above the nominal level (i.e. 2 wt.%) produced spongy phases, which decreased the hardness [15].

Therefore, adding a suitable amount of all nanoparticles in the cladding material and dispersing the nanomaterial on the cladded surface with appropriate laser parameters improved the hardness. Above the nominal level, however, nanoparticles degraded the hardness property as well as resulted in the formation of discontinuities.

### 2.3.2. Wear resistance and thermal shock resistance

The general material requirements for industries in service at fluctuating climatic conditions are high wear resistance and thermal shock resistance. As the Ni-based coating materials are best suited for cladding, adding nanoparticles will provide better resistance to the cladding surface. For the case of thermal shock resistance, the cladding surface without nanoparticles exhibited extended spalling; however, with a nanoparticle-added coating only unit spalling was observed with low thermal cycles. Moreover, by increasing thermal cycles, the coating without nanoparticles had large cracks, such as propagating cracks and internal cracks, as shown in Fig. 5a. In the case of a coating with added  $\text{CeO}_2$  nanoparticles, propagating cracks decreased and no formation of internal cracks was observed, as shown in Fig. 5b, [14]. This improvement was due to the fact that the RE increases the anti-spalling capacity of the coating [21].

Wear resistance on a cladding surface without nanoparticles showed deep penetration and a large wear scar. However, a cladded surface with SiC nanoparticles had smaller width compared to the  $\text{Al}_2\text{O}_3$  as well as the  $\text{CeO}_2$  nanoparticle-added surface [19]. The depth wear for the cladded surface with and without nanoparticle addition was similar. The reason for the high wear rate in the coating with  $\text{CeO}_2$  and  $\text{Al}_2\text{O}_3$  nanoparticles compared to the SiC nanoparticle coating was the coating hardness. Moreover, the  $\text{Al}_2\text{O}_3$  nanoparticles produced higher coating hardness compared to the surface with  $\text{CeO}_2$  nanoparticles, which resulted in the greater reduction of the wear rate in the  $\text{Al}_2\text{O}_3$  than the  $\text{CeO}_2$  added surface. Thus, wear resistance and thermal shock resistance were improved by nanoparticle addition compared to the cladded surface with no added nanoparticles.

### 3. COBALT-BASED COATING MATERIAL

Co-based materials have wide usage in various industries such as coating on bearing, tool and die's for its wear resistance and the Co having unique resistance properties even on fluctuating service and climatic conditions [22]. Industrial demands have increased for the improvement of product life by reducing wear rate on various applications. However, the Co-based coatings coating could not satisfy the increasing demands for high properties. In addition, the crack and other defect formations were one of the barriers for attaining the high-level properties [23]. Studies have validated that the addition of appropriate reduced particle size (i.e. nanoparticles or nanocrystalline) to the Co-based cladding material would provide significant improvements in the properties with the stable microstructure along the interface region as well as on the surface [24,25].

#### 3.1. Effects of nanoparticle-added coating material on defects

Defects and the surface appearance have a great influence on the properties prior to the service condition. The Co-based coating resulted in inevitable cracks or discontinuity formations particularly in the case of multi-coatings, which resulted in the degradation of properties [23]. Likewise, Li et al. [26] observed crystallising cracks by the Co surface coating with no added nanoparticles on low-carbon steel, which reduced the coating bonding as well as the properties. This cracking occurred due to the micro-segregation of the dendrite structure and impu-

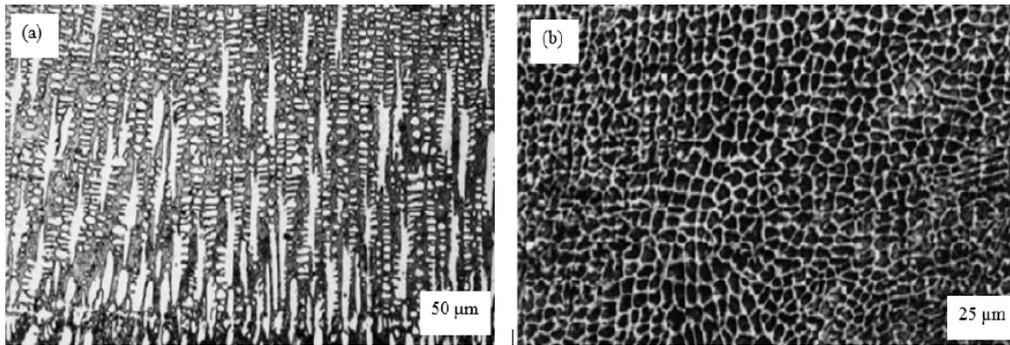
rities leading to thin layer formation, which was torn by thermal stress during solidification [27]. Crack formation decreased, however, in the coated surface with added  $\text{CeO}_2$  nanoparticles in the Co-based alloy, which was due to the Ce in  $\text{CeO}_2$  which reduced dendrite growth and formed into homogeneous fine dendrite [26]. The reduction of cracks was also observed in the Ni-based alloy by the coating of a Co-based alloy with added  $\text{Al}_2\text{O}_3$  nanoparticles [25].

The surface without nanoparticle addition had a coarse surface appearance on low-carbon steel, whereas the coating surface with nanoparticles exhibited a smooth and defect-free surface. The increasing amount of  $\text{CeO}_2$  nanoparticles in the Co-based coating material improved the surface quality [26]. Thus, cracks can be reduced and the surface quality improved by the addition of the rare element oxide and metal oxide nanoparticles to Co-based coating materials.

#### 3.2. Effects of nanoparticle-added coating material on microstructural formation

As the added RE nanoparticles provided a defect-free surface coating, they are expected to have an effect on grain refinement for stable microstructure formations in Co-based surface coating materials. The rare earth element influences the microstructure through new phase formations as well as transformation in crystal structures. For instance, Li et al. [26] examined low-carbon steel with a Co-based alloy cladding surface with no added nanoparticles and found dendrite formation in perpendicular direction to the interface; moreover, the structures were multi-orientated and had only two phases ( $\gamma$ -Co and  $\text{Cr}_{23}\text{C}_6$ ). However, the coating with  $\text{CeO}_2$  nanoparticles produced equiaxed crystal structures, which was due to the  $\text{CeO}_2$  nanoparticles that acted as a nucleation site by their melting temperature. Moreover, the  $\gamma$ -Co and  $\text{Cr}_{23}\text{C}_6$  phases and two other new phases ( $\epsilon$ -Co and  $\text{CeCo}_2$ ) were found in the coating with nanoparticles.  $\text{CeCo}_2$  formed while the decomposition of  $\text{CeO}_2$  nanoparticles and  $\epsilon$ -Co formed due to the low thermal conductivity of  $\text{CeO}_2$ .

No new phases in the microstructure were formed, but instead there were changes in the microstructural phase by the addition of nanoparticles. This was observed in the experiment by Li et al. [28] on coating a Ni-based alloy substrate with  $\text{Y}_2\text{O}_3$  nanoparticles added in the Co coating material, which produced a phase change in the primary phases ( $\gamma$ -Co and  $\epsilon$ -Co) with the addition of



**Fig. 6.** Microstructure of Co-based coating on Ni super alloys (a) without nanoparticles and (b) with 1.0% nano- $Y_2O_3$  particles. Reprinted with permission from Gleiter, © 2000 Acta Materialia.

nanoparticles; however, the original phases i.e. coating with no added nanoparticles were  $\gamma$ -Co and  $Cr_{23}C_6$ . The phase change was due to the low thermal conductivity of  $Y_2O_3$  (yttrium oxide) nanoparticles. The coating formed with no added nanoparticles exhibited a columnar dendrite microstructure while rapid solidification, which is shown in Fig. 6a. However, the coating with the addition of nanoparticles showed a reduced dendritic structure with different orientation and an equiaxed grain structure, which is shown in Fig. 6b. Moreover, the change was more intense, when the amount of nanoparticles was increased. The reduction of the grain size resulted in a change from dendrite to equiaxed structure. This change was due to the  $Cr_{23}C_6$  phase and  $Y_2O_3$  nanoparticles that act as a heterogeneous nucleation site accompanied with dispersion [29].

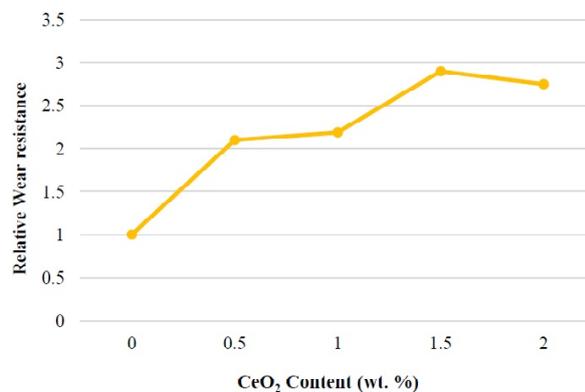
Besides the RE nanoparticle addition to the Co-based coating material, metal oxide (i.e.  $Al_2O_3$ ) nanoparticles were also added to the Co-based coating material on a Ni-based alloy substrate, which resulted in fine microstructure formations. Moreover, increasing the content of  $Al_2O_3$  nanoparticles increased the fine microstructures. Attaining 1% (mass fraction) of  $Al_2O_3$  nanoparticles and an increase in laser power transformed the dendrite microstructure into equiaxed grain structures, which also occurred with  $Y_2O_3$  nanoparticle addition in the Co-based coating material. The reason for the formation of equiaxed grains were the fine grains at the surface while solidification, which settled at the bottom by gravity and resulted in the reduction of dendrite grain growth. In addition, the phases with a high melting temperature and a significant amount of dispersed nanoparticles also resulted in equiaxed grain formations [25].

Thus, grain refinement and transformation in the microstructural phases occurred due to the addition of nanomaterials (i.e.  $CeO_2$ ,  $Y_2O_3$ , and  $Al_2O_3$ ),

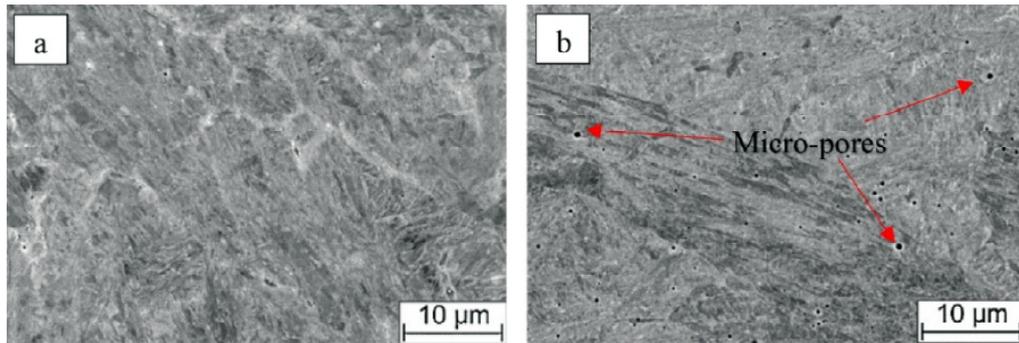
and the nanoparticle size had an influence on the distribution to the grain boundaries. If the particles are aggregated along the grain boundaries, it results in unstable microstructural formation.

### 3.3. Effects of nanoparticle-added coating material on properties

Due to the addition of RE materials, the grains were refined and stable microstructural phases were formed, which provided improvement in the properties. Li et al. [26] observed that the hardness of the coating increased with an increasing content of  $CeO_2$  nanoparticles. However, a nominal content (i.e. 1.5 wt.%) of  $CeO_2$  nanoparticles in the coating showed higher hardness compared to the low (i.e. 0.5 wt.%) and high content (i.e. 2.0 wt.%) of  $CeO_2$  nanoparticles in the coating. This highest hardness was due to the uniform distribution of the nanoparticles. Moreover, wear resistance was also highest in the coating with a nominal content of  $CeO_2$  nanoparticles compared to the other



**Fig. 7.** Wear resistance vs  $CeO_2$  nanoparticle content in the Co-based cladding material. Reprinted with permission from Xu et al., © 2003 Chinese Journal of Mechanical Engineering.



**Fig. 8.** (a) Defect free forging surface without nanoparticle addition to the Fe-based coating material and (b) Micro-pores formation by the  $Y_2O_3$  nanoparticle addition to the Fe-based coating material. Reprinted with permission from Li et al., © 2005 Rare Metal Materials and Engineering.

nanoparticle contents in the coatings, shown in Fig. 7. The decrease in hardness with the high content  $CeO_2$  nanoparticles coating was due to the accumulation of the particles, which led to an increase in wear.

Thus, the Co-based coating material with a nominal content of added nanoparticles showed improvement in properties; moreover, other than the nominal content of nanoparticles added resulted in reduced strength. The degradation of properties was due to the accumulation of nanoparticles, which also led to unstable microstructural formation.

#### 4. IRON-BASED COATING MATERIAL

The coatings in forging dies require high thermal shock and wear resistance due to the forming of shape by hot metal ingots. Coatings are degraded by mechanical fatigue due to high loads and high temperatures [30,31]. Therefore, forging dies require a surface coating with low friction wear and high temperature resistance which has been achieved by the Fe-based coating with added nanoparticles through laser processing. The insertion of nanoparticles in the Fe-based coating alloy material showed improvements in the properties and microstructure [32,33].

##### 4.1. Effects of nanoparticle-added coating on defect formation

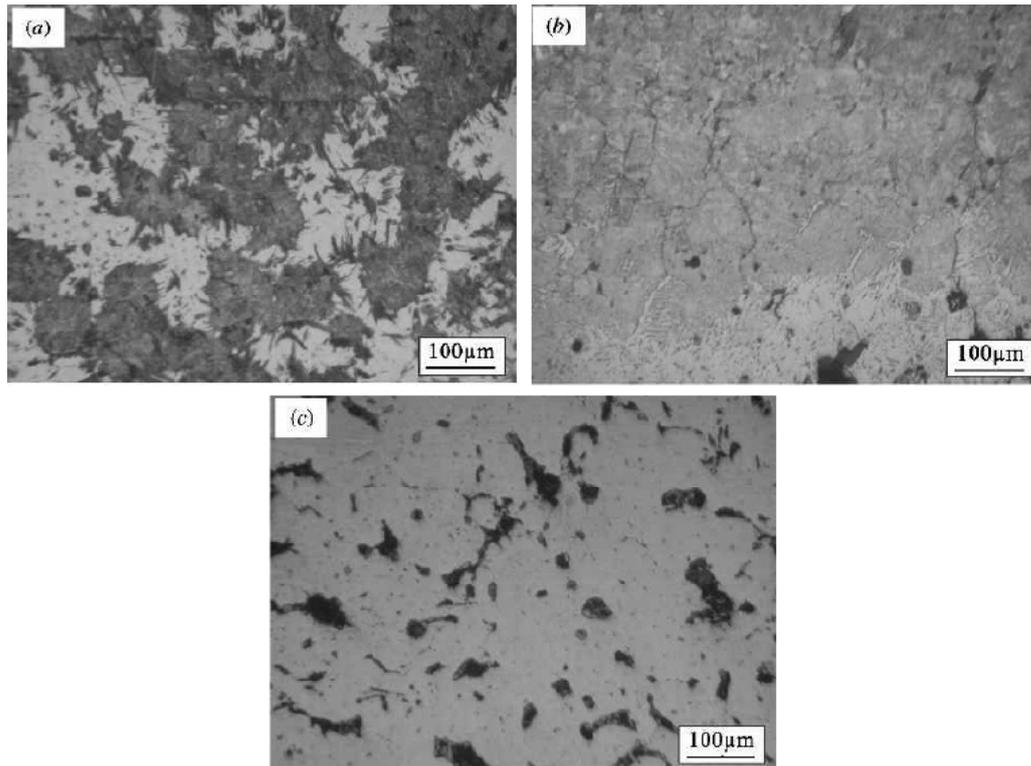
As the forging dies are used in fluctuating temperatures and friction, stable microstructure formation will provide resistance to enhance the properties and reduce defects on the surface. Behrens et al. [33] experimented forging dies as a substrate with the addition of TiC and WC nanoparticles in the tool steel coating material (AISI H10) and showed that a defect-free surface coating was produced by a

nanoparticle coating. The addition of  $Y_2O_3$  nanoparticles to the tool steel coating material, however, resulted in micro-pores, shown in Fig. 8.

Besides the forging surface, the Fe alloy as a substrate coated with the Fe-based alloy coating material with added  $Al_2O_3$  nanoparticles also resulted in micro-pore formation. Even though the amount of  $Al_2O_3$  nanoparticles in the Fe-based coating material was varied, the coating exhibited same micro-porous formation [32]. Hence the studies showed that an appropriate addition of nanoparticles according to the substrate and with proper cladding parameters should produce a defect-free surface coating. Moreover, the quantity of nanoparticles added to the surface coating material does not have an effect on defects.

##### 4.2. Effects of nanoparticle-added coating on microstructural formation

The microstructural phase formation determines the properties of the surface coating. The surface coating used in industry mainly requires wear resistance and thermal resistance with a stable microstructure, which does not lead to the formation of discontinuities while in service. Adding nanoparticles to the coating material improves grain refinement and microstructural change, thereby resulting in the improvement of surface coating properties. For instance, the experiment by Behrens et al. [33] on forging dies as a substrate without any additions to the Fe-based coating material resulted in an interface region with the grain size of  $50 \mu m$  and a pure martensitic microstructure due to the rapid cooling rate of above  $100 K/s$ . The coating material added with WC nanoparticles resulted in a surface with a slightly decreased grain size of  $45 \mu m$  with a



**Fig. 9.** Microstructure of Fe-based alloy coating material with addition of  $\text{Al}_2\text{O}_3$  nanoparticles (a) cladded region, (b) interfacial region and (c) Fe alloy substrate. Reprinted with permission from Zhang et al., © 2006 Journal of Anhuni University of Technology.

martensitic microstructure; in addition, the WC precipitated at the coating microstructure, whereas the surface coating with added TiC nanoparticles reduced the size of grains to the minimum of about  $10\ \mu\text{m}$ . Moreover, precipitation was noted with an addition of TiC nanoparticles at the grain boundaries and the transformation of the microstructure occurred from martensite to austenite. Thus, an appropriate addition of nanoparticles improved stable microstructural formation in accordance with property requirements [33].

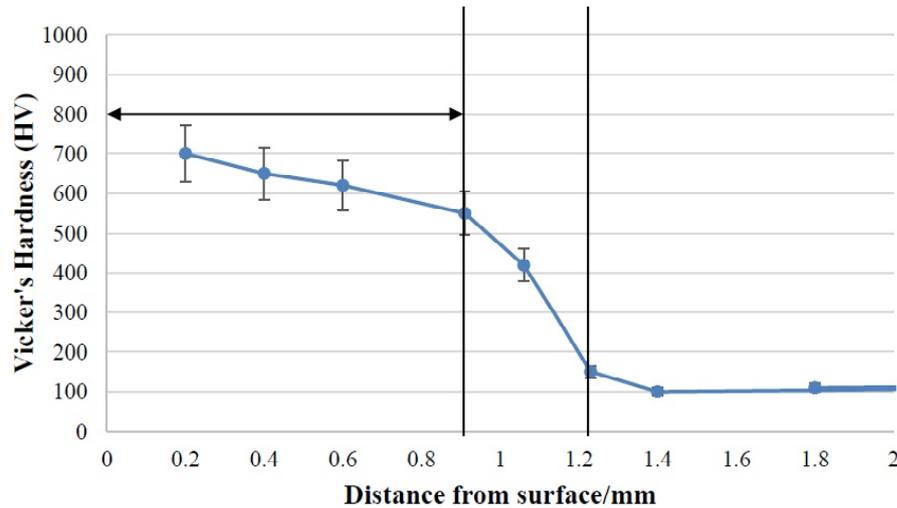
If nanoparticles are inappropriately added to the coating material without considering the substrate material, the surface coating can result in deteriorated properties, unstable microstructural formations and defects. The  $\text{Y}_2\text{O}_3$  nanoparticle coating on the substrate increased the grain size (i.e.  $85\ \mu\text{m}$ ) above that of the coating material with no added nanoparticles. Moreover, adding  $\text{Y}_2\text{O}_3$  to the coating material resulted in defect formations; however, the  $\text{Y}_2\text{O}_3$  nanoparticles melted completely and dispersed compared to other added nanoparticles [33]. Thus, RE nanoparticles (i.e.  $\text{Y}_2\text{O}_3$ ) in the cladding surface have a negative effect on the microstructure and defect formation, whereas adding carbide (i.e.

WC & TiC) in the cladding surface produces grain refinement and a defect-free cladded surface.

The amount of nanoparticles added to Fe-based coating material alloys does not have an impact on microstructural formations. For instance, the study on the Fe-based alloy coating material with an addition of varying amounts (i.e. 4, 8, and 12 wt.%) of  $\text{Al}_2\text{O}_3$  nanoparticles coated on the Fe alloy substrate showed similar microstructural formation on the surface coated, and also there were three different zone formations while cladding. Firstly, the cladded zone contained three microstructural phases, black, grey, and white, shown in Fig. 9a. The uniformly distributed black region is the martensite phase, the grey region is the pearlite phase and the white region is the ferrite phase [32].

Secondly, the interfacial region only contained the pearlite and ferrite phases, when the martensite phases were reduced by low heat, shown in Fig. 9b. Finally, the low heat by the laser had no influence on the Fe alloy substrate, shown in Fig. 9c, [32].

Thus, the study showed that the selection of appropriate nanoparticles to the Fe-based coating material, in accordance with the substrate, had a



**Fig. 10.** Microhardness of the Fe-based alloy cladded surface with  $\text{Al}_2\text{O}_3$  nanoparticle addition. Reprinted with permission from Schulz et al., © 2003 Aerospace Science and Technology.

significant influence in microstructural formations. However, the quantity of the nanoparticles added to the Fe-based coating had only a small effect on the microstructure.

### 4.3. Effects of nanoparticle-added coating material on surface properties

The coating requirement of the wear resistance, hardness and thermal resistance properties necessitates a stable microstructure. The nanoparticle-added coating attains these requirements and has no influence on other properties. Consequently, adding nanoparticles to the coating influences microstructural formation, which fulfils the properties.

#### 4.3.1. Hardness and tensile properties

The martensite phase in the microstructure improves the hardness property of the coating. The forging dies with added WC nanoparticles in the tool steel coating material exhibited increased hardness by the increasing content of WC nanoparticles. The  $\text{Y}_2\text{O}_3$  and TiC nanoparticle content in the cladded surface, however, reduced the hardness properties due to the greater amount of ferritic content in the microstructure. Hence, the proper nanomaterial addition corresponding to the substrate improved the hardness property [33]. Moreover, the quantity of nanoparticles added to the Fe-based coating material had no effect on the hardness property. This was demonstrated by the experiment by Yu et al. [32] on the Fe alloy substrate coated with the  $\text{Al}_2\text{O}_3$  nanoparticle-added Fe-based alloy coating material.

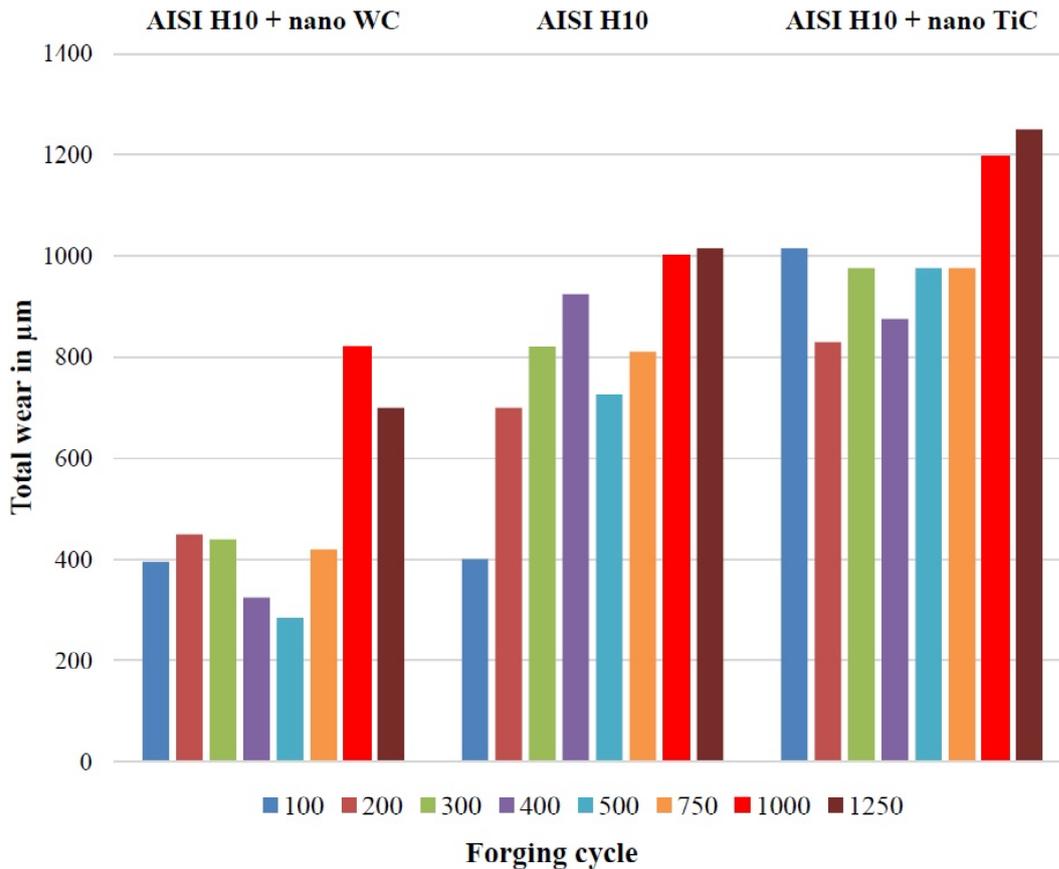
The study showed that the low (i.e. 4 wt.%), medium (i.e. 8 wt.%) and high (i.e. 12 wt.%) amount of  $\text{Al}_2\text{O}_3$  nanoparticles added produced similar hardness properties. Moreover, the hardness value was high in the cladded zone, which was due to the martensite microstructure. Hardness decreased rapidly at the interfacial region by the pearlite microstructure formation; in addition, the hardness value had no effect on the substrate, which was due to the low heat input by the laser. The hardness range is shown in Fig. 10, [32].

In the case of tensile property, the addition of WC nanoparticles to the Fe-based coating material on the forging die resulted in improvement in tensile strength; however, elongation was reduced. The tensile strength and elongation decreased by the  $\text{Y}_2\text{O}_3$  nanoparticle-added coating as well as the TiC nanoparticle-added coating, which was also due to the ferritic content.

The studies thus revealed that the appropriate selection of nanoparticles considering the Fe-coating material and the substrate improves the hardness and tensile properties by influencing the microstructures. Moreover, the amount of nanoparticles added to the coating material had little effect on the properties.

#### 4.3.2. Wear resistance

The cladded surface with the WC nanoparticles showed the lowest wear rate compared to surfaces with TiC nanoparticles and without nanoparticles in thermal fluctuating conditions, shown in Fig. 11. The cladded surface with TiC nanoparticles had a higher wear rate than the surface without nanoparticles.



**Fig. 11.** Total wear vs forging cycle for different nanoparticle addition in the Fe-based coating surface. Reprinted with permission from Liu et al., © 2003 Chinese Journal of Nonferrous Metals.

When increasing the thermal cycles, the wear rate of the clad surface with WC nanoparticles lowered, whereas that of the surface with TiC nanoparticles increased [33]. This degradation in the properties could be due to microstructural formations by the high ferrite content.

Thus, an inappropriate selection of nanoparticles in the cladding material will result in the degradation of properties due to undesirable microstructure formation. In addition, carbide in the nanoparticles provided defect-free microstructures and surfaces.

## 5. FACTORS AND EFFECTS BY NANOMATERIAL ADDITION TO COATING MATERIALS ON THE SURFACE

The overview effect and factor of nanoparticle addition to various coating material are shown in Table 2.

## 6. DISCUSSION AND CONCLUSIONS

In the competitive world, the manufacturing industries are focusing on more and more efficient and

economical practices of production both qualitatively and quantitatively. This has led them to improve their processes and the materials used. Various products processed in industry only require surface modifications with high properties produced through cladding. Laser cladding is one of the best processes for coating substrates due to the minimum dilution between the substrate and the coating material, as well as the better manipulation of process parameters. The products processed through laser coating cannot, however, satisfy the increasing demands. This issue has been solved by the addition of nanomaterials to the coating material, which fulfills the demands and improves the material strength and properties.

Adding nanoparticles to the cladding material reduces weld defects, such as crystallisation cracks and micro-pores caused by the heterogeneous microstructure and non-uniform thermal expansion. The addition of appropriate nanoparticles in proper amounts to the coating not only reduces defects, but also improves the properties.

Nanoparticles in the cladding material also improve the microstructure by reducing brittle phase

**Table 2.** Overview of effects and factors by nanoparticles insertion in different coating materials.

Coating material	Microstructure Factors	Effects	Defects Factors	Effects	Properties Factors	Effects
Ni-based coating material	<ul style="list-style-type: none"> <li>Nominal amount of nanoparticle addition leads to uniform distribution of microstructural grain.</li> <li>Nucleation of nanoparticle at boundaries and appropriate addition of nanoparticles.</li> </ul>	<ul style="list-style-type: none"> <li>Grain transformation</li> <li>Grain refinement and new microstructural phase formation.</li> </ul>	<ul style="list-style-type: none"> <li>Appropriate quantity of nanoparticle addition influencing thermal expansion of materials.</li> </ul>	<ul style="list-style-type: none"> <li>Reduction of crack and pores formation.</li> </ul>	<ul style="list-style-type: none"> <li>Appropriate nanoparticle addition with suitable amount.</li> <li>Uniform distribution of nanoparticles.</li> </ul>	<ul style="list-style-type: none"> <li>Uniform high hardness.</li> <li>Reduces spalling and defects leading to improvement of thermal shock resistance and wear resistance.</li> </ul>
Co-based coating material	<ul style="list-style-type: none"> <li>Thermal characteristics of nanoparticles and nanoparticles acting as nucleation site.</li> <li>Increasing nanoparticle addition with uniform distribution.</li> </ul>	<ul style="list-style-type: none"> <li>Homogeneous microstructural transformation and new microstructural phase formation.</li> <li>Grain refinement.</li> </ul>	<ul style="list-style-type: none"> <li>Homogeneous microstructure by nanoparticle addition.</li> <li>Increasing the nanoparticle addition.</li> </ul>	<ul style="list-style-type: none"> <li>Reduced the crystallization cracking.</li> <li>Improved surface appearance.</li> </ul>	<ul style="list-style-type: none"> <li>Nanoparticle addition to nominal level.</li> <li>Uniform distribution of nanoparticles.</li> </ul>	<ul style="list-style-type: none"> <li>High and uniform hardness on the surface.</li> <li>Increased the wear resistance.</li> </ul>
Fe-based coating material	<ul style="list-style-type: none"> <li>Appropriate nanoparticle addition, which is selected according to substrate and coating material</li> <li>Variation in the quantity of nanoparticle addition to the coating material</li> </ul>	<ul style="list-style-type: none"> <li>Reduced the grain size and changed the microstructures.</li> <li>No impact on microstructural formation and the cladded surface had similar microstructures.</li> </ul>	<ul style="list-style-type: none"> <li>Appropriate nanoparticle addition (i.e. selected considering the substrate and coating material).</li> <li>Quantity of nanoparticle addition to coating material.</li> </ul>	<ul style="list-style-type: none"> <li>Reduced the defect formation on the coated surface.</li> <li>No effect on defects reduction.</li> </ul>	<ul style="list-style-type: none"> <li>Increase in proper nanoparticle to the coating material.</li> <li>Varying the nanoparticle addition to the coating material.</li> </ul>	<ul style="list-style-type: none"> <li>Increased the tensile strength, reduced the wear rate, and increased the hardness through increasing the Martensite.</li> <li>No effect on hardness property.</li> </ul>

formation and by producing uniform stable microstructures and grain refinement. Furthermore, the formation of new phases increases.

Adding nanoparticles also improves the mechanical properties: the hardness and tensile properties improve mainly due to the quantity of nanoparticles added and their dispersion.

Nanoparticles moreover improve wear resistance and thermal shock resistance: the wear rate is reduced through an increase in the nanoparticles added and their uniform dispersion.

These improvements are mostly influenced by the appropriate selection of nanomaterial added in accordance with the coating material and substrate, the uniform dispersion of the nanoparticles to the grain boundaries, the characteristics of the nanoparticles and the quantity of nanoparticles added to the coating material. By considering these factors, the nanoparticle coating material can provide high surface properties. Moreover, the nanoparticle added cladding material can be used in industry for the mass production of products, which requires economical surface enhancement technologies. Still, research is being conducted to achieve high surface properties with other coating materials using various cladding processes.

## REFERENCES

- [1] E. Toyserkani, A. Khajepour and S. Corbin, *Laser Cladding* (CRC Press, London, New York, 2004).
- [2] D. Lepski and F. Brückner, In: *The Theory of Laser Materials Processing*, ed. by J. Dowden (Springer, Netherlands, 2009), p. 235.
- [3] S. Sun, Y. C. Durandet and M. Brandt // *Surface and Coatings Technology* **194** (2005) 225.
- [4] M. Zhong and W. Liu // *Journal of Mechanical Engineering Science* **224** (2010) 1041.
- [5] R. G. Wellman and J. R. Nicholls // *Surface and Coatings Technology* **177-178** (2004) 80.
- [6] H. Gleiter // *Acta Materialia* **48** (2000) 1.
- [7] B. Xu, S. Liu and X. Liang // *Chinese Journal of Mechanical Engineering* **39** (2003) 21.
- [8] M. Li, Y. He and G. Sun // *Rare Metal Materials and Engineering* **34** (2005) 248.
- [9] H. Zhang and Y. He // *Journal of Anhui University of Technology* **23** (2006) 21.
- [10] U. Schulz, C. Leyens, K. Fritscher, M. Peters, B. Saruhan-Brings, O. Lavigne, J. M. Dorvaux, M. Poulain, R. Mévrel and M. Caliez // *Aerospace Science and Technology* **7** (2003) 73.
- [11] C. Liu, F. Lin and X. Jiang // *Chinese Journal of Nonferrous Metals* **17** (2007) 1.
- [12] I. Gurrappa and A. Sambasiva Rao // *Surface and Coatings Technology* **201** (2006) 3016.
- [13] H.-Y. Wang, D.-w. Zuo, Y.-I. Sun, F. Xu and D. Zhang // *Transactions of Nonferrous Metals Society of China* **19** (2009) 586.
- [14] H. Wang, D. Zuo, X. Li, K. Chen and H. Mingmin // *Journal of Rare Earths* **28** (2010) 246.
- [15] P. Farahmand, S. Liu, Z. Zhang and R. Kovacevic // *Ceramics International* **40** (2014) 15421.
- [16] K. Wang, Q. Zhang, M. Sun and X. Wei // *Journal of Materials Processing Technology* **139** (2003) 448.
- [17] . Asadi, M. K. B. Besharati Givi, K. Abrinia, M. Taherishargh and R. Salekrostam // *Journal of Materials Engineering and Performance* **20** (2011) 1554.
- [18] M. Fattahi, M. Mohammady, N. Sajjadi, M. Honarmand, Y. Fattahi and S. Akhavan // *Journal of Materials Processing Technology* **217** (2015) 21.
- [19] H. Wang, D. Zuo, M. Wang, G. Sun, H. Miao and Y. Sun // *Transactions of Nonferrous Metals Society of China (English Edition)* **21** (2011) 1322.
- [20] H. Wang, D. Zuo, X. Chen, S. Yu and Y. Gu // *Chinese Journal of Mechanical Engineering (English Edition)* **23** (2010) 297.
- [21] B. Ruiliang, Y. Huijun, C. Chen and Q. Dong // *Surface Review and Letters* **13** (2006) 509.
- [22] G. Freeman, In: *ASM Handbook: Powder Metal Technologies and Applications- Volume 7*, ed. by A. I. H. Committee (ASM International, 1998), p. 179.
- [23] M. L. Hu, C. S. Xie, B. L. Zu and A. H. Wang // *Transactions of Materials and Heat Treatment* **22** (2001) 23.
- [24] X. Li, M. L. Curry, G. Wei, J. Zhang, J. A. Barnard, S. C. Street and M. L. Weaver // *Surface and Coatings Technology* **177-178** (2004) 504.
- [25] M. Li, Y. He, X. Yuan and S. Zhang // *Materials and Design* **27** (2006) 1114.
- [26] M. Li, S. Zhang, H. Li, Y. He, J. Yoon and T. Cho // *Journal of Materials Processing Technology* **202** (2008) 107.
- [27] Y. He, Z. Huang, H. Qi, D. Wang, Z. Li and W. Gao // *Materials Letters* **45** (2000) 79.
- [28] M. Li, Y. He and X. Yuan // *Applied Surface Science* **252** (2006) 2882.

- [29] Y. Zhou, Z. Hu and W. Jie, *Solidification Technology* (Mechanical Industry Press, Beijing, 1998).
- [30] J. Sjöström and J. B. Bergström // *Scandinavian Journal of Metallurgy* **34** (2005) 221.
- [31] H. Paschke, M. Weber, G. Braeuer, T. Yilikiran, B.-A. Behrens and H. Brand // *Archives of Civil and Mechanical Engineering* **12** (2012) 407.
- [32] S. Yu, Y. Liu, L. Ren and W. Li // *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science* **37** (2006) 3639.
- [33] B. A. Behrens, T. Yilikiran, S. Ocylok, A. Weisheit and I. Kelbassa // *Production Engineering* **8** (2014) 645.