# Nano Indentation Studies on Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20nicr) Based Coatings Developed using Mechanical Alloying and HVOF Technique

Nagaraja C Reddy<sup>1</sup>, <sup>1</sup> Research Scholar, Dept of Mechanical Engg, Bangalore Institute of Technology, Karnataka, India

H N Reddappa<sup>3</sup>, <sup>3</sup> Associate Professor, Dept of Mechanical Engg, Bangalore Institute of Technology, Karnataka, India

*Abstract* - The new intermetallic coating materials based on the nickel and titanium alloy were developed using mechanical alloying technique. The Ni<sub>3</sub>Ti intermetallic compound was obtained after mechanical alloying of Ni and Ti for about 11 hours after. Along with this another coating material was obtained my blending Ni<sub>3</sub>Ti with (Cr<sub>3</sub>C<sub>2</sub>+20NiCr). These coating materials were deposited on two industrial gas turbine grade substrate materials for surface protection using HVOF technique. The cross section view of the coated substrates was analysed using scanning electron microscopy for studying the microstructure and coating thickness. Finally nano indentation technique was used to obtain mechanical properties like elastic modulus and nano hardness of the developed coatings.

# Keywords: Intermetallics, Nano Indentation, Mechanical Alloying, HVOF.

## INTRODUCTION

For petrochemical applications the gas turbines need to be heavy duty, highly reliable and should have higher operational efficiency. The efficiency of gas turbine used in commercial airliners or any other industry depends on many factors and engine related materials are one of the most important one. As said earlier gas turbine plays a key role in deciding the efficiency as it is working in the most demanding environment like high temperatures and stresses. Degradation of main components of gas turbines by high temperature oxidation and corrosion is major problem for many of the manufactures as these components define the efficiency of a gas turbine. The hot sections of industrial gas turbines meant for power generation are often subjected to corrosion and oxidation mainly because hot of contamination due to usage of different composition of fuels. The fuel gas produced after gasification of biomass and coal can have different composition which can later combine with moisture and SO<sub>x</sub> produced in the gas turbines to form harmful compounds like Na<sub>2</sub>SO<sub>4</sub> and V<sub>2</sub>O<sub>5</sub>. When the working temperature of the turbine exceeds the melting of these compounds which is 600°C can lead to deposition

Babu E R<sup>2</sup>, <sup>2</sup> Assistant Professor, Dept of Mechanical Engg, Bangalore Institute of Technology, Karnataka, India

Ajay Kumar B S<sup>4</sup> <sup>4</sup> Professor, Dept of Mechanical Engg, Bangalore Institute of Technology, Karnataka, India

of these compounds on turbine blades. Once these compounds deposit on blade they can lead to corrosion which can cause failure of these blades [1-4].

Coating materials in gas turbines are used for many applications, whether in jet engines, marine or land based power generation turbines. The primary function of coatings is to help the gas turbine to operate at high temperatures by providing protection against degradation by hot corrosion and high temperature oxidation. This is one of the most interesting intermetallic as it has two different crystal structures, one is B2 (CsCl) structure i.e. high temperature austenitic phase while another is monoclinic B-19' structure that is low temperature martensite. This type of crystal structure gives this intermetallic excellent high temperature mechanical property such as oxidation resistance up to 900°C and good creep resistance up to a temperature of 1000°C. Out of these intermetallic compounds, Ni<sub>3</sub>Ti has been tried and used in high temperature applications mainly because of its high melting point of 1380°C which has a topologically close packed structure. Due to its tetragonal structure it displays high thermal stabilities which is due to its microstructure stability. So when compared to existing nickel intermetallic phase like Ni<sub>3</sub>Al, Ni<sub>3</sub>Ti has higher stability and have the ability to retain strength at higher temperatures. This intermetallic can be obtained by mechanical alloying of pure Ni and Ti powders in 50:50 or 40:60 at.% [5-8].

Mechanical alloying is a technique developed almost 4 decades back and was used for synthesis of oxide dispersion strengthened superalloys. From past few decades days it is used to produce powders with unique microstructures. It can be used to produce virtually any composition by mixing with elemental and master alloy powders. In this regard development of intermetallic compounds using mechanical alloying has received tremendous interest from researchers owing to versatility. Elemental powders are subjected to

high energy ball milling process leading to fracture and welding of the powder particles repeatedly. The process in which particulate deposition in the form of molten droplets of coating species are deposited on substrate is generally known as thermal spraying. In this method hot carrier gas is used to carry the coating material and sprayed on the target with a spraying gun. The microstructure of the coating depends upon the precursor material and it particle size. The various process parameters like gas composition, temperature, pressure, flow rate and stand-off distance between gun and substrate material. There are various types of thermal spray techniques like flame spray, plasma spray, high velocity oxy-fuel (HVOF) and detonation spray. Out of these mentioned coating techniques. HVOF is the one which is capable of producing coatings with low porosity, high hardness and excellent bond strength. In addition to this lower decarburization and lower surface oxidation due to very short exposure time of particles with air are other advantages of HVOF. Using this method one can obtain coating thickness close to 300 µm on the surface of engineering parts [9-11].

In this work, we have developed  $Ni_3Ti$  and  $Ni_3Ti+(Cr_3C_2+20NiCr)$  surface coatings on two substrates namely AISI 420 stainless steel and titanium ASTM B265 which are materials used in industrial gas turbine applications. The coated substrates were characterized using scanning electron microscope and the mechanical properties like elastic modulus and nano hardness was evaluated using nano indentation.

#### **EXPERIMENTATION**

Starting powders of Ni (size: 45 µm) and Ti (size: 40 µm) each were used for mechanical alloying in the proportion of Ni75:Ti25 (wt.%) for synthesis of Ni<sub>3</sub>Ti. About 75 g of nickel and 25 g of titanium were loaded in tungsten carbide container and balls. The powders were subjected to mechanical alloying process using Planetary ball mill (Make: Insmart Systems, Hyderabad, India) under a protective argon atmosphere. Addition of toluene as a process control agent was done in order to reduce the cold welding of both the metallic particles during milling process. The alloying was conducted for about 11 hours by utilizing a ball to powder weight ratio of 10:1 and running at a speed of 300 rpm. A special industrial gas turbine grade steel MDN-420 (Cr - 13.79, Si - 0.47, Mn - 0.71, C - 0.19, and Fe - Bal) and titanium Ti-15 (Fe - 0.25, O2 - 0.2, Ti -Bal) were procured from Mishra Dhatu Nigam Limited, Hyderabad, India for using as substrate materials. Both mechanical alloyed powder Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) powders were sprayed on both the substrates having a size of  $25 \times 25 \times 5$  mm<sup>3</sup>. The HVOF process parameters used for deposition of both the coating materials on the aforementioned substrate materials are listed in Table 1. The scanning electron microscope was used to check the coatings microstructure at the cross section as well as the coating thickness. The nanoindentation studies conducted on the both Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coatings at 145 mN load to obtain

mechanical properties like elastic modulus and nanohardness.



Fig.1. Optical micrographs of substrates, (a) MDN-420 and (b) Ti-15

Table.1. HVOF process parameters		
Oxygen flow rate	250 LPM	
Fuel flow rate	60-70 LPM	
Air flow rate	700 LPM	
Stand-off distance	0.20 - 0.25 m	
Powder feed rate	0.30 - 0.50 N/min	

### **RESULTS AND DISCUSSION**

The optical micrographs of the two substrate materials used for the current study were stainless steel MDN-420 and titanium Ti-15 are shown in Fig. 1. Fig 2 and 3 shows the top surface of uncoated, Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coated Ti-15 and MDN-420 substrate materials. It can be observed from Fig. 2 a and b, that the uncoated Ti-15 substrate is light brown in colour while that of Ni<sub>3</sub>Ti coated Ti-15 is dark grey in colour. In case of Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coated Ti-15 substrate shows quite dark grey colour when compared to that of bare Ti-15 and Ni<sub>3</sub>Ti coated Ti-15 substrate. While in case of uncoated MDN-420, the uncoated surface is dark brown in colour while that of Ni<sub>3</sub>Ti coated MDN-420 colour changes to grey in colour as shown in Fig. 3 a and b. The Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coated MDN-420 substrate is having light brown coloured appearance when compared to that of other substrate surface after coating process. So in both cases the coated substrates had significant colour change and surface appearances. The coating thickness of the both Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coated on MDN substrates is shown in Fig. 4 and 5. It can be seen that the average thickness of the Ni<sub>3</sub>Ti coating is about 277  $\mu$ m and whereas the thickness of Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) is about 280  $\mu$ m. if we observe the coatings carefully we can see that the microstructure doesn't have any visible porosity and the structure is quite dense.

The nanoindentation studies conducted on the both  $Ni_3Ti$  and  $Ni_3Ti+(Cr_3C_2+20NiCr)$  coatings at 145 mN load gave mechanical properties like elastic modulus and nanohardness. The nanohardness values for both the coatings were obtained on the polished cross sections of the coatings and is deduced from the below equation.

Ianohardness (H) = 
$$\frac{P(h_{max})}{A_c(h_{max})}$$

Where P is applied load in mN and  $A_c(h_{max})$  is the area of contact between specimen and indenter. On the other hand elastic modulus (E) was calculated from the reduced elastic modulus ( $E_r$ ) which is obtained from nanoindentation test [12].

$$\frac{1}{E_r} = \frac{(1 - v_s^2)}{E} + \frac{(1 - v_i^2)}{E_i}$$

Where  $E_r$  is the reduced young's modulus,  $v_s$  is the Poisson ratio of specimen,  $v_i$  is the Poisson ratio of indenter ( $v_s$ =0.07) and  $E_i$  is the young's modulus of indenter ( $E_i$ =1140 GPa). Both the elastic modulus and nano hardness for both the coating materials are listed in Table.2. It can be observed that both elastic modulus and nano hardness of Ni<sub>3</sub>Ti were higher than that of Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coating. So we can conclude that Ni<sub>3</sub>Ti coated substrates had higher nano hardness than that of Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coating. The high hardness in case of Ni<sub>3</sub>Ti coating can be attributed to good cohesive strength between the individual splats without having any kind of porosity as seen from the microstructure.



Fig.2. Macrographs of (a) Uncoated, (b)  $Ni_3 Ti$  coated and (c)  $Ni_3 Ti + (Cr_3 C_2 + 20 Ni Cr)$  coated Ti-15 substrate.



Fig.3. Macrographs of (a) Uncoated, (b)  $Ni_3Ti$  coated and (c)  $Ni_3Ti+(Cr_3C_2+20NiCr)$  coated MDN-420 substrate.



Fig.4. SEM micrograph of Ni<sub>3</sub>Ti coated MDN-420 substrate depicting coating thickness.



Fig.4. SEM micrograph of  $Ni_3Ti+(Cr_3C_2+20NiCr)$  coated MDN-420 substrate depicting coating thickness.

Table.2. Elastic modulus and nano hardness of coatings		
Coating material	Elastic	Nano hardness GPa
	modulus GPa	
Ni <sub>3</sub> Ti	64.55	0.48
Ni <sub>3</sub> Ti+(Cr <sub>3</sub> C <sub>2</sub> +20NiC	51.54	0.43
r)		
CONCLUSIONS		

The following conclusions were drawn from the present study

- The Ni<sub>3</sub>Ti and Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coatings were successfully developed on the two industrial gas turbine grade substrate materials
- The microstructure studied using scanning electron microscope showed no porosity and an average coating thickness of close to 280 μm.
- Both the elastic modulus and nano hardness of Ni<sub>3</sub>Ti coating was found to be higher than that of Ni<sub>3</sub>Ti+(Cr<sub>3</sub>C<sub>2</sub>+20NiCr) coating.

#### REFERENCES

- R. Kurz, Gas turbine performance, Proceedings of Thirty-fourth turbomachinery symposium, Texas September 12-15, 131-146, 2005.
- [2] M. Konter, M. Thumann, Materials and manufacturing of advanced industrial gas turbine components, J. Mater. Process. Technol. 117, 386-390, 2001.
- [3] H. Oguma, K. Tsukimoto, S. Goya, Y. Okajima, K. Ishizaka, E. Ito, Development of advanced materials and manufacturing technologies for high-efficiency gas turbines, Mitsubishi Heavy Industries Technical Review 52, 5-14, 2015.
- [4] N. Eliaz, G. Shemesh, R.M. Latanision, Hot corrosion in gas turbine components, Engineering Failure Analysis 9, 31-43, 2002.
- [5] Z. Mutasim, W. Brentnall, Thermal barrier coatings for industrial gas turbine applications: An industrial note, Journal of Thermal Spray Technology, 6, 105-108, 1997.
- [6] D. Fan, Y. Sun, M. Zheng, J. Zhang, Y. Zheng, Intermetallic Alloys Ni<sub>3</sub>Si and Ni<sub>3</sub>(Si,Ti): microstructures and properties, Key Engineering Materials, 368-372, 2008.
- [7] C.L. Yeh, W.Y. Sung, Synthesis of NiTi intermetallics by selfpropagating combustion, Journal of Alloys and Compounds, 79-88, 2004.
- [8] N. Cinca, C.R.C. Lim, J.M. Guilemany, An overview of intermetallics research and application: Status of thermal spray coatings, Journal of Materials Research Technology 2, 75-86, 2013.
- [9] R. Sundaresan, F.H. Froes, Mechanical alloying, Journal of Metals 39, 22-27, 1987.
- [10] C.C. Koch, J.D. Whittenberger, Mechanical milling/alloying of intermetallics, Intermetallics 4, 339-355, 1996.
- [11] T.S Sidhu. S. Prakash, R.D. Agrawal, Studies on the properties of high-velocity oxy-fuel thermal spray coatings for higher temperature applications, Materials Science 41, 805-823, 2005.
- [12] B. Bhushan, Handbook-of-Nanotechnology, Springer, 2004.