# Effect of Annealing on Tribo-Mechanical Properties of Plasma Sprayed Alumina-Chromia Coatings

**M.Tech.** Thesis

By Akshay Namdeo



### **DISCIPLINE OF MECHANICAL ENGINEERING**

## INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2016

# Effect of Annealing on Tribo-Mechanical Properties of Plasma Sprayed Alumina-Chromia Coatings

### A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

Master of Technology in Mechanical Engineering With specialization in Production and Industrial Engineering by Akshay Namdeo



# DISCIPLINE OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE



## INDIAN INSTITUTE OF TECHNOLOGY INDORE

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **Effect of Annealing on Tribo-Mechanical Properties of Plasma Sprayed Alumina-Chromia Coatings** in the partial fulfillment of the requirements for the award of the degree of **Master of Technology** and submitted in the **Discipline of Mechanical Engineering, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2014 to July 2016. Thesis submission under the supervision of Dr. Kazi Sabiruddin, assistant professor, Discipline of Mechanical Engineering.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

# Signature of the student with date Akshay Namdeo

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Signature of PSPC Member 2 Date:

#### ACKNOWLEDGMENT

I would like to thank all those people who made this thesis possible and an unforgettable experience for me. This work is a result of the efforts of many individuals, who helped me mentally or physically or both to successfully complete it.

First of all, I would like to express my deepest sense of gratitude to my supervisor Dr. Kazi Sabiruddin, who offered his continued advice and encouragement throughout the course of this thesis. I thank him for the systematic guidance and great effort he put in. I feel greatly privileged to be one of his students.

I am immensely grateful to Dr. Satyajeet Chatterjee, for his ever-ready support throughout the work. Discussions with him have been extremely knowledgeable and have significantly shaped this thesis. I acknowledge my gratitude towards Dr. I. A. Palani and Dr. Abhinav Kranti, my PSPC members for their kind suggestions and support during the various presentations of this work.

I am grateful to Sophisticated Instrumentation Centre (SIC), IIT Indore for providing the P-XRD and FESEM facility equipped there. I am thankful to IIT Indore for giving me an opportunity to carry out the research work and providing all the facilities.

I would like to express my very sincere gratitude to Mr. Balmukund Dhakar for the technical assistance to my project to make this thesis possible. His involvement in the work from the first day I joined to the last is highly acknowledged. I would also like to express my thanks to all members of Metallography and Tribology lab for their moral support and the friendly atmosphere they have created in the lab.

I also would like to give my gratitude to the entire batch of M. Tech 2016. Dherendra Jay Pant, who helped me to explore the new place Indore and his kind suggestion during the preparation of the thesis, is highly acknowledged. I extend my thanks to my lovely roommates Jitesh V. Bhoyar and Jitendra Kumar. I also thank Swagat Dwibedi for the care and motivation he expressed to me.

I express my gratitude to Muneer Alam and Vinayak Yadav, for the time with laughter, mutual encouragement and love we shared, and of course the time spent dining with you both will be missed always. I am also indebted to Ms Priya Chouhan for her sister like care given to me. Her generous care and support, inside and outside the institute campus is highly acknowledged. Special thanks to Mr. Saurabh Agarwal for the inspiration he brings in my life whenever I feel low and his continuous concern and encouragement despite our locations. A heart-felt thanks to Ms. Aakanksha Tripathi for the moral support she showed towards me. I like to thank her for being with me in every situation and expressing herself.

Finally, I take this opportunity to express the profound gratitude from my deep heart to my beloved parents and my family for their love and continuous support - both spiritually and materially. The support and love they provide to chase my dream is unmatched.

### ABSTRACT

Plasma sprayed  $Al_2O_3$  (alumina) is used as a heat resistant, corrosion resistant and hard coating. While spraying the  $Al_2O_3$  feedstock powder of  $\alpha$ -phase it forms different phases in the coatings. Considering the mechanical properties stable  $\alpha$ - $Al_2O_3$  is desirable in coating. However the other metastable phases formed due to the complexity of the spraying process and rate of solidification. It is expected that the prevention of these phases in the coatings will significantly improve the mechanical, electrical, and other properties of  $Al_2O_3$  coatings. The result regarding the possibility of stabilization of  $Al_2O_3$  through addition of  $Cr_2O_3$  (chromia) has been already reported. When  $Cr_2O_3$  is added in the feedstock of  $Al_2O_3$ , a solid solution ( $Al_xCr_{1-x})_2O_3$  forms in the deposit which is superior to other phases of  $Al_2O_3$ . Annealing of  $Al_2O_3$  deposit at the temperature higher than its recrystallization temperature also improves the quantity of  $\alpha$ - $Al_2O_3$ content.

This work is carried out on plasma sprayed  $Al_2O_3$ - $Cr_2O_3$  coatings to study the effect of annealing temperature on the phase transformation and other properties with different compositions. Plasma sprayed  $Al_2O_3$  coatings with 1 to 6 wt.%  $Cr_2O_3$  content is annealed at different temperature from 900 °C to 1200 °C and then characterized along with as-sprayed coatings. Analysis of phase formation of the coatings is studied with X-ray diffraction patterns. SEM micrographs are used to study the microstructure of the coatings. The effect of annealing on the coating properties is investigated in terms of vickers microhardness, wear resistance and coefficient of friction.

 $Cr_2O_3$  addition influences the phase formation, and maximum solid solubility of  $Al_2O_3$ - $Cr_2O_3$  is found at  $Al_2O_3$ -4wt.%  $Cr_2O_3$ . It is observed with the XRD patterns that complete transformation in to stable  $\alpha$ - $Al_2O_3$  phase obtain at 1200 °C and it has the maximum hardness among coatings annealed at lower temperatures. Annealing at 1200 °C leads to formation and propagation of cracks at very large extent which decreases its wear resistance. Hence the maximum hardness is observed for  $Al_2O_3$ -4wt.%  $Cr_2O_3$  coating annealed at 1200 °C and maximum wear resistance for  $Al_2O_3$ -4wt.%  $Cr_2O_3$  coating annealed at 1100 °C among all the coatings.

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### ACRONYMS

APS	:	Atmospheric plasma spray
CMAD	:	Cathodic micro-arc deposition
CVD	:	Chemical Vapor deposition
FE-SEM	:	Field-Emission Scanning Electron Microscope
HVOF	:	High velocity oxy-fuel
HVSFS	:	High-velocity suspension flame spray
PVD	:	Physical vapor deposition
VPS	:	Vacuum plasma spray
WSP	:	Water stabilized plasma
XRD	:	X-ray Diffraction

#### **1.1 Surface Engineering**

Surface engineering is a multidisciplinary activity intended to tailor the properties of the surfaces of engineering components so that their function and serviceability can be improved. Surface engineering can be defined as "the branch of science that deals with methods for achieving the desired surface requirements and their behavior in service for engineering components." Engineering environments are normally complex, combining loading with chemical and physical degradation to the surface of the component. Surface wear damage is a phenomenon which effects how a component will last in service [1]. An example of a component working in an aggressive environment is a cutting tool used in machining processes. The tool experiences high loads, high speeds and friction and, as a consequence, high temperatures. These factors lead to surface wear of the component. Lubrication in tribological applications reduces friction and wear, however conventional liquid lubricants fail under extreme conditions, namely low pressure, oxidative or corrosive environments, high speeds and high loads. Surface coatings can help deal with these circumstances. Improving the tool surface, not only improves the life of the tool, but also improves the surface finish of the machined part. Obviously it is important to understand the physical and chemical makeup of the applied surfaces, in order to design quality components which, yield high service lives [1]. The desired properties or characteristics of surface-engineered components include [2]:

- Improved corrosion resistance through barrier or sacrificial protection
- Improved oxidation resistance
- Improved wear resistance
- Reduced frictional energy losses
- Improved mechanical properties, for example, enhanced fatigue or toughness
- Improved electronic or electrical properties

- Improved thermal insulation
- Improved aesthetic appearance.

The surface shape or topology depends upon the process used for forming, be it moulding, casting, or cutting and abrading. As shown in Fig. 1.1 Surface asperities of a nominal smooth surface. This is often seen microscopically as a series of asperities rather than the flat surface seen macroscopically.



#### Fig. 1.1 Surface asperities of a nominal smooth surface [1]

The geometrical texture may be characterized by its surface profile as shown in Fig 1.2, and results from three different components of surface texture (roughness, waviness and error of form).

Roughness	······		
Waviness			
Error of Form			
Profile	man		
= Sum of abov	e 3 components		

Fig 1.2 Components of surface texture [1]

#### **1.2 Surface Modification Techniques**

The selection of technology to engineer the surface is an integral part of an engineering component design. The first step in surface modification technique to determine the surface and substrate engineering requirements which involves one or more of the properties like wear resistance, corrosion anderosion resistance and thermal resistance, fatigue, creep strength, pittingresistance etc. The various surface treatments generally used in engineering practice are namely [1]: 1. PVD process, 2. CVD process, 3. Electoless Ni-deposition, 4. Composite, 5. Thermal spraying, 6. Surface welding, 7. Ion Implantation, 8. Anodizing, 9. Nitriding, 10. Carbonitriding, 11. Carburizing, 12. Nitrocarburising, 13. Surface alloying and 14. Thermal hardening.

#### **1.3 Friction and Wear**

Friction and wear occur where two surfaces undergo sliding or rolling under load. Friction is a serious cause of energy dissipation, where wear is the main cause of material wastage. Friction is the resistance to relative motion of contacting bodies. Two modes of friction may occur; sliding or rolling friction. The friction between sliding surfaces (sliding friction) is due to the combined effects of adhesion between flat surfaces, ploughing by wear particles and hard asperities, and asperity deformation. Rolling friction is a complex phenomenon because of its dependency on so many factors, including in consistent sliding (called slip) during rolling, and energy losses during mixed elastic and plastic deformations.

Wear is a process of removal of material from one or both of two solid surfaces in solid state contact, occurring when two solid surfaces are in sliding or rolling motion together. The rate of removal is generally low, but steady and continuous. The fig 1.3 indicates the various wear mechanisms [1].



#### Fig. 1.3 Flow chart of various wear mechanisms [1]

#### **1.4 Thermal Spray Coating**

#### **1.4.1 Thermal Spraying**

Thermal spray is a generic term for a group of coating processes used to apply metallic or nonmetallic coatings. These processes are grouped into three major categories: flame spray, electric arc spray, and plasma arc spray. These energy sources are used to heat the coating material (in powder, wire or rod form) to a molten or semi molten state. The resultant heated particles are accelerated and propelled toward a prepared surface by either process gases or atomization jets. Upon impact, a bond forms with the surface, with subsequent particles causing thickness buildup and forming a lamellar structure as shown in Fig. 1.4. The thin "splats" undergo very high cooling rates, typically in excess of 10<sup>6</sup> K s<sup>-1</sup> for metals. A major advantage of thermal spray processes is the extremely wide variety of materials that can be used to produce coatings. Virtually any material that melts without decomposing can be used. A second major advantage is the ability of most thermal spray processes to apply coatings to substrates without significant heat input. Thus, materials with very high melting points, such as tungsten, can be applied to finely machined, fully heat-treated parts without changing the properties of the part and without excessive thermal distortion of the part. A third advantage is the ability, in most cases, to strip off and recoat worn or damaged coatings without changing part properties or dimensions. A disadvantage is the line-of-sight nature of these deposition processes. They can

only coat what the torch or gun can "see." It is impossible to coat small, deep cavities into which a torch or gun will not fit [2].



Fig. 1.4 Basics mechanism of thermally sprayed coating [2]

Thermal spraying can provide thick coatings (approx. thickness range is 20 micrometers to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating, physical and chemical vapor deposition. Coating materials available for thermal spraying include metals, alloys, ceramics, plastics and composites. They are fed in powder or wire form, heated to a molten or semi molten state and accelerated towards substrates in the form of micrometer-size particles. Combustion or electrical arc discharge is usually used as the source of energy for thermal spraying. Resulting coatings are made by the accumulation of numerous sprayed particles. The surface may not heat up significantly, allowing the coating of flammable substances [2].

#### **1.4.2 Substrate Preparation**

The adhesion of the coating to the substrate predominantly consists of mechanical bonding, careful cleaning and pretreatment of the surface to be coated is extremely important. After the removal of surface impurities by chemical or mechanical methods, the surface is usually roughened using a blasting procedure. The liquid or molten coating particles impact the surfaceat high speed. Heat from

the hot particles is transferred to the cooler base material. As the particles shrink and solidify, they bond to the roughened base material. Adhesion of the coating is therefore based on mechanical "locking". The amount of metallurgical bond caused by diffusion between the coating particles and base material is small and can be neglected for discussions about bonding mechanisms. Surface roughening usually takes place via grit blasting with dry corundum. In addition, other media, such as chilled iron, steel grit or SiC are used for some applications. Besides the type of grit, other important factors include particle size, particle shape, blast angle, pressure and purity of the grit media [2].

#### **1.4.3 Coating Material**

In principle, any material that does not decompose as it is melted can be used as a thermal spray coating material. Depending on the thermal spray process, the coating material can be in wire or powder form. Choosing a coating material that is suitable for a specific application requires special knowledge about the service environment as well as knowledge about the materials. Apart from the physical characteristics, such as coefficient of expansion, density, heat conductivity and melting point, additional factors, such as particle shape, particle size distribution and manufacturing process of powder material (i.e., agglomerated, sintered, composited) will influence coating performance [2].

#### **1.4.4 Techniques of Thermal Spray**

There are several different processes used to apply a thermal sprayed coating. They are:

- a) Conventional flame spray
- b) Electric arc wire spray
- c) Plasma spray
- d) High velocity oxy-fuel spray (HVOF)

#### a) Conventional flame spray

Wire Flame Spray

With the wire flame spray process, the wire spray material is melted in a gaseous oxygen-fuel flame. The fuel gas can be acetylene, propane or hydrogen. The wire is fed concentrically into the flame, where it is melted and atomized by the addition of compressed air that also directs the melted material towards the substrate surface. Fig. 1.5 shows the technique of wire flame spray [2].



Fig. 1.5 Wire Flame Spray Technique [2]

Powder Flame Spray

This coating process is based on the same operational principle as the wire flame spray process, with the difference that the coating material is a spray powder. Thus, a larger selection of spray materials is available, as not all spray materials can be manufactured in wire form [2]. Figure 1.6 shows the process of powder flame spray.

#### b) Electric Arc Wire Spray

With electric arc wire spray, an arc is formed by contact of two oppositely charged metallic wires, usually of the same composition. This leads to melting at the tip of the wire material. Air atomizes the melted spray material and accelerates onto the substrate. The rate of spray is adjusted by appropriate regulation of the wire feed as it is melted, so a constant arc can be maintained [2]. Figure 1.7 indicates the electric arc wire spray techniques.



Fig. 1.6 Powder flame Spray Technique [2]



Fig. 1.7 Electric Arc Wire Spray Technique [2]

#### c) Plasma Spray

The principle of plasma spraying is shown schematically in the fig. 1.8. High frequency arc is ignited between an anode and a tungsten cathode. The gas flowing through between the electrodes (i.e., He, H<sub>2</sub>, N<sub>2</sub> or mixtures) is ionized such that a plasma plume several centimeters in length develops. The temperature within the plume can reach as high as 16000 °K. The spray material is injected as a powder outside of the gun nozzle into the plasma plume, where it is melted, and propelled toward the substrate surface by the gas [2].

For specialized applications, a variant of the process is to plasma spray in a controlled, low pressure atmosphere. In contrast to coating in air (atmospheric





Fig. 1.8 Plasma Spraying Technique [2]

Plasma spraying is a technology that can be applied in many industrial fields. Plasma spraying can be used for production of various protective coatings of ceramics or composites which are difficult to prepare by other techniques. During the process, powder injected into the plasma jet undergoes at least two and often more phase transformations, including melting, solidification and solid-state transformations. Both, the dynamic loading accompanying impact of the molten droplets onto the substrate, and the cooling rates of the order of  $10^6$  K s-1, may affect the final structure and properties. Deposited structures are mostly in non-equilibrium and non-stoichiometric states rather different from the original state and properties of the feedstock [2].

#### d) High Velocity Oxy-Fuel Spray (HVOF)

The high velocity oxy-fuel spray (HVOF) process is a relatively recent addition to the family of thermal spray processes. As it uses a supersonic jet, setting it apart from conventional flame spray, the speed of particle impact on the substrate is much higher, resulting in improved coating characteristics. The mechanism differs from flame spraying by an expansion of the jet at the exit of the gun. Fuel gases of propane, propylene, acetylene, hydrogen and natural gas can be used, as well as liquid fuels such as kerosene [2]. Figure 1.9 shows the process of high velocity oxy fuel technique.



Fig. 1.9 High Velocity Oxy Fuel Technique [2]

### Chapter 2 Literature Review

#### 2.1 Mechanical and Tribological Properties of Alumina based coatings

**Fervel et al.** [3] studied the tribological behavior of plasma sprayed  $Al_2O_3$ ,  $Al_2O_3/TiO_2$  and  $Al_2O_3/TiO_2/Copper$  in dry condition. The effect of  $TiO_2$  and copper additions on the properties of coatings was investigated in terms of microhardness and fracture toughness, and was related to the friction behavior and wear resistance. It was found that  $TiO_2$  improves the fracture toughness of coatings and copper reduces friction and wear. It has been confirmed that  $TiO_2$  additions to an  $Al_2O_3$  plasma sprayed  $Al_2O_3$  base allows, in spite of a hardness reduction, to improve its wear resistance by increasing its toughness. A copper addition leads to a further hardness reduction but has little effect on the toughness value. With such an addition, a cermet coating with an improved friction behavior against ceramic was obtained.

**Ouyang and Sasaki [4]** studied the microstructure and high-temperature tribological properties of low-pressure plasma-sprayed  $Cr_2O_3$  ceramic coatings undoped or doped with different additives, such as  $CaF_2$ ,  $Ag_2O$  and  $ZrO_2$ . Under the identical plasma-spray condition, the composite coatings doped with additives exhibited a larger thickness and distinctly lower hardness than pure  $Cr_2O_3$  coating. At room temperature, the friction coefficients of the composite coatings doped with additives were quite high. With the increase of temperature, the friction coefficients of the composite coatings gradually decreased. The situation was reversed for the pure  $Cr_2O_3$  coating.

Ahn et al. [5] investigated the correlation of microstructure and wear resistance of  $Al_2O_3$ -TiO<sub>2</sub> coatings plasma sprayed with nanopowders. The nanostructured coatings showed microstructure composed of fully melted regions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and partially melted regions, while the conventional coating mostly consisted of fully melted  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, together with some TiO<sub>2</sub>-rich regions and unmelted Al<sub>2</sub>O<sub>3</sub> powders. The wear test results revealed that the wear resistance

of the nanostructured coatings was 3 or 4 times better than that of the conventional coating, because the preferential delamination seriously occurred along  $TiO_2$ -rich regions in the conventional coating. In the nanostructured coatings,  $TiO_2$  was homogeneously dispersed inside splats and around, thereby leading to higher splat bonding strength and to better wear resistance over the conventional coating.

**Bolelli et al.** [6] prepared  $Al_2O_3$  coatings by the high-velocity suspension flame spraying (HVSFS) technique using a nanopowder suspension. Their structural and microstructural characteristics, micromechanical behavior, and tribological properties were studied and compared to conventional atmospheric plasma sprayed and high-velocity oxygen-fuel-sprayed  $Al_2O_3$  coatings manufactured using commercially available feedstock. The HVSFS process enables near full melting of the nanopowder particles, resulting invery small and well flattened lamellae (thickness range 100 nm to 1 lm), almost free of transverse microcracking, with very few unmelted inclusions. Thus, porosity is much lower and pores are smaller than that in conventional coatings.

**Tao et al.** [7] deposited  $Al_2O_3$  and  $Cr_2O_3$  coatings deposited by atmospheric plasma spraying and their tribological properties against copper alloy were evaluated using a block-on-ring configuration at room temperature. It was found that the wear resistance of  $Al_2O_3$  coating was superior to that of the  $Cr_2O_3$ coating under the conditions used in the study. This mainly attributed to its better thermal conductivity of  $Al_2O_3$  coating, which was considered to effectively facilitate the dissipation of tribological heat and alleviate the reduction of hardness due to the accumulated tribological heat. As for the  $Al_2O_3$  coating, the wear mechanism was plastic deformation along with some micro-abrasion and fatigue-induced brittle fracture, while the failure of  $Cr_2O_3$  coating was predominantly the crack propagation-induced detachment of transferred films and splats spallation.

**Yang et al. [8-9]** studied the microstructural and mechanical properties of plasma sprayed coatings of Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>. Mechanical properties including microhardness and fracture toughness were evaluated. The results

indicate that the addition of  $Cr_2O_3$  is conducive to the stabilization of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Compared with the pure Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> coatings, Al<sub>2</sub>O<sub>3</sub>--Cr<sub>2</sub>O<sub>3</sub> composite coatings show lower porosities and denser structures. Heterogeneous nucleation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> occurs over the iso-structural Cr<sub>2</sub>O<sub>3</sub> lamellae and partial solid solution of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> might be occurring as well. Furthermore, grain refining and solid solution strengthening facilitate the mechanical property enhancement of Al<sub>2</sub>O<sub>3</sub>--Cr<sub>2</sub>O<sub>3</sub> composite coatings.

#### 2.2 Phase Formation and Stabilization of Coatings

**McPherson [10-11]** suggested that the solidification of liquid droplets at considerable undercooling results in the formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> rather than  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> because of its lower critical free energy for nucleation. He studied the stabilization of Al<sub>2</sub>O<sub>3</sub> and showed that when  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles are only partially melted, their unmelted cores can act as nuclei for  $\alpha$  formation and, consequently, the volume of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> after plasma spraying can be substantially increased. This means that the cooling rate of the particles is relatively unimportant and under the conditions existing in flames and plasmas, metastable Al<sub>2</sub>O<sub>3</sub> will be formed on solidification.

**Chraska et. al [12]** studied the thermal stability of various Al<sub>2</sub>O<sub>3</sub> phases. Phase change routes of heating for different starting Al<sub>2</sub>O<sub>3</sub> modifications were discussed in the study, and a case study of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> was analyzed. Both types of as-sprayed structures, a mixture of  $\alpha$ ,  $\delta$  and  $\gamma$  phases were annealed up to 1300 °C and the phase composition checked. At lower temperatures and shorter holding times, the amount of  $\alpha$  phase decreases while another metastable  $\theta$  phase appears, and the fraction of  $\gamma+\delta$ , if present, increases. At temperature above 1100 °C the amount of  $\alpha$  phase increases again.

**Ilavsky et.al [13]** suggested  $Al_2O_3$  deposits consist of a number of metastable crystallographic modifications, which at elevated temperatures, transform to the stable  $\alpha$  phase. It was shown that additions of various oxides changed the phase composition and shift phase transformation temperatures. The variation of phase compositions and temperatures of the phase changes for

plasma-sprayed  $Al_2O_3$  deposits manufactured with  $Al_2O_3$ -base materials containing  $Cr_2O_3$  and  $TiO_2$  was also addressed. The phase compositions and phase transformation temperatures in plasma-sprayed  $Al_2O_3$  samples were varied widely by changing the chemical composition of the feedstock material. The addition of  $Cr_2O_3$  increased the  $\alpha$ -phase formation temperature, while the addition of  $TiO_2$ caused a temperature decrease. The range within which the  $\alpha$ -phase formation temperature was varied was about 200 °C.

Kear et. al [14] studied the phase formation of deposits with nanostructured Al<sub>2</sub>O<sub>3</sub>-13%TiO<sub>2</sub> powder feed and found metastable *x*-Al2O3·TiO2 phase in the coating, when the molten droplets are quenched on a chilled substrate. The metastable phase has a defect spinel structure and a nanocrystalline grain size. When heated, it decomposes into equilibrium twophase structure, consisting of  $\alpha$ -Al2O3 and  $\beta$ -Al2O3·TiO2. Both types of ceramic materials have potential as hard, wear-resistant coatings.

**Cava et. al [15]** studied on nanocrystalline  $Al_2O_3$  powders synthesized by the polymeric precursor method. The single-phase  $\alpha$ - $Al_2O_3$  powder was obtained after heat-treatment at 1050°C for 2 hours. A study of the morphology of the particles was accomplished through measures of crystallite size, specific surface area and transmission electronic microscopy and suggested that particle size is closely related to  $\gamma$ - $Al_2O_3$  to  $\alpha$ - $Al_2O_3$  phase transition.

Stahr et.al [16] studied the dependency of the phase content of  $Al_2O_3$  on the spray process. It is found that the phase content of the coatings depends both on the spray process and on the powder composition. For both WSP and APS process, the positive effect of an increase in the  $\alpha$  phase with increasing Cr<sub>2</sub>O<sub>3</sub> content in the coating was observed. In the APS process starting from mechanical mixtures, no stabilization effect was found when mechanically mixed powders are sprayed.

Sabiruddin et. al [17] found that the retained  $\alpha$  phase content in the plasma sprayed coating has a strong relationship with coating process parameters like primary gas flow rate, secondary gas flow rate, standoff distance and nozzle diameter. The retention of the  $\alpha$  phase in the coating is attributed to the presence

of an unmelted core in the particles. The weight fraction of metastable phases has been found to be near 100% for those parametric combinations where particle melting is good.

**Dubsky et. al [18]** studied the phase transition of Al<sub>2</sub>O<sub>3</sub> by spraying two types of Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub> powder feedstock: fused materials and mixtures of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> powders. It was stated that the presence of Cr<sub>2</sub>O<sub>3</sub> definitely facilitates formation of  $\alpha$  phase in plasma-sprayed Al<sub>2</sub>O<sub>3</sub> coatings. When fused feedstock is used then the complex  $\alpha$ -(Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> phase will form, regardless of the plasma system used. When the feedstock is made of a mechanical mixture of powders, only WSP spraying will bring in increased formation of the corundum  $\alpha$  phase in coatings APS technology will not yield the needed results i. e.  $\alpha$  phase formation. Practically no  $\delta$ -phase has been observed in APS coatings where  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is predominant where as in WSP, besides  $\alpha$ -type phase both  $\gamma$  and  $\delta$ -phases has been found.

**Jamnapara et. al [19]** in order to generate  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, aluminized P91 steel samples were subjected to normalizing and tempering treatments at 980°C and 750°C respectively and then compared. It has been found that the thermally tempered samples had  $\theta$ -Al<sub>2</sub>O<sub>3</sub> coating while the plasma tempered samples had  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coating after heat treatment. Such transformation of Al<sub>2</sub>O<sub>3</sub> phase was not visible without plasma.

**Zeng et. al [20]** studied Cr doped  $Al_2O_3$  ceramic coating fabricated on 316L stainless steel by cathodic micro-arc deposition (CMAD) technique. The study of effect of chromium on the phase transition of  $Al_2O_3$  from  $\gamma$  to  $\alpha$  suggested that the ceramic coatings have a porous microstructure and was mainly composed of Cr doped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It is stated that the introduction of Cr in the electrolyte solution can promote the nucleation and growth of the corundum phase of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

**Jung et. al [21]** stated that crystalline phase of  $Al_2O_3$  is obtained and/or their portion was increased as the oxides were additionally heat-treated at 950°C. In the case of ZrO<sub>2</sub>, a desirable oxide phase was formed when the samples were cured at 750°C during the coating process. In addition to the heat-treatment after

the coating, the coatings were effective in crystallizing the coated layers and forming proper oxides.

**Shao et. al [22]** fabricated  $Cr_2O_3$ - $Al_2O_3$  composite coatings by APS technique. The fused  $Cr_2O_3$ - $Al_2O_3$  feedstock leads to the complex  $(Al_xCr_{1-x})_2O_3$  phase coating.  $\alpha$ - $Al_2O_3$  is fully stabilized, which is the result of plenty  $Cr_2O_3$  in the fused feedstock.

**Dhakar et. al [23]** studied the phase stabilization of atmospheric plasma sprayed Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> coatings. By Rietveld analyses it was found that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> content in Al<sub>2</sub>O<sub>3</sub> coatings maximum with 4wt.% Cr<sub>2</sub>O<sub>3</sub> content. The 4wt.% Cr<sub>2</sub>O<sub>3</sub> shows full solubility with maximum  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> content in Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> coating. This is supported by the improved hardness and wear resistant properties of the Al<sub>2</sub>O<sub>3</sub> coatings containing 4wt.% Cr<sub>2</sub>O<sub>3</sub> in it. The formation of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> solid solution and solidification of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are found to be the reasons behind the enhancement in mechanical properties of the coating.

### **Chapter 3**

#### **Experimental Procedure**

#### **3.1 Coating Preparation**

The details of the process parameters used while processing atmospheric plasma sprayed coating of pure  $Al_2O_3$  and  $Al_2O_3$ - $Cr_2O_3$  powders on low carbon steel (AISI1020) are shown in Table 1.

**Parameters** Value Nozzle diameter (mm) 7 500 Current (A) Voltage (V) 80 Plasma Gas (N<sub>2</sub>) flow rate (SCFH) 50 Secondary Gas (H<sub>2</sub>) flow rate (SCFH) 5 Powder feed rate (kg/h) 4.5 - 4.8 Preheating temperature (°C) 200 Standoff distance (mm) 125 Robot scanning velocity (mm/s) 40

Table 1 Used parameters of plasma sprayed

A plasma spray gun (3MB II, SulzerMetco, USA) mounted on a CNC X-Y manipulator is used for this purpose. The substrates are grit blasted ( $R_a$ = 4.05±0.65 µm) prior to the application of plasma sprayed layer of Ni-5wt.%Al (Metco 450NS) bond coat (thickness: 70-90 µm). Agglomerated Al<sub>2</sub>O<sub>3</sub> (Hindalco, India, Indalcalcined HI grade, purity: 99.6%) and crushed Cr<sub>2</sub>O<sub>3</sub> (Saint Gobain #2020, purity: 99.05%) powders are used as feedstock materials. Cr<sub>2</sub>O<sub>3</sub> is blended with Al<sub>2</sub>O<sub>3</sub> in six different proportions (as shown in Table 2) by using ball milling equipment (Fritsch Pulverisette 6) operated at 120 rpm for 4 hours (clockwise and counter clockwise rotation are applied repetitively for a cycle time of 15 min) in air without using the balls in the vial. The average particle sizes of Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> feedstock powders selected are of 65 µm and 30 µm respectively. The same set up is used for the application of top coating of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> on the previously applied bond coat. The average thickness of the top coating kept around 300 µm.

The substrates are preheated to 200 °C using plasma torch prior to the deposition of the coating materials.

Designation of Coatings	Corresponding Coating Powders
А	Pure Alumina
A1C	Alumina– 1wt.% Chromia
A2C	Alumina- 2wt.% Chromia
A3C	Alumina- 3wt.% Chromia
A4C	Alumina- 4wt.% Chromia
A5C	Alumina– 5wt.% Chromia
A6C	Alumina- 6wt.% Chromia

**Table 2 Composition and Nomenclature of the coatings** 

#### **3.2 Annealing of Coatings**

The coating prepared is then annealed at different temperatures. The heat treatment of coated samples was carried out in tube furnace (Nobertherm GmbH, Germany). The inert environment inside the furnace is maintained by continuous flow of Argon. The rate of heating is 5°C per minute throughout the heating and then the coatings is kept at the maximum temperature for 2 hours. The coatings were annealed at temperatures 900 °C, 1000 °C, 1100 °C and 1200 °C. The rate of cooling is also same as that of heating till 500 °C then it is left inside the furnace for several hours to reach upto the room temperature. Table 3 indicates the different annealing temperatures and coating compositions.

#### **3.3 X-ray Diffraction**

X-ray diffraction (XRD) analyses of the coated and annealed surfaces are done by using an X-ray diffractometer (Rigaku Smart Lab 3 kW) with nickelfiltered Cu K $\alpha$  radiation ( $\lambda$ =0.15406 nm) operating at 30 kV and 40 mA. X-Ray diffraction data is analyzed for all the coatings using the X'PertHighscore Plus<sup>®</sup> analysis package.

#### 3.4 Microstructure Study

Field emission scanning electron microscope (FESEM, Zeiss Supra-55) used to characterize microstructure of the coatings. The coated samples are cut and its cross-section is polished in order to attain the microstructure of the

coatings. The polishing is carried out in the proper metallographic manner i.e. starting from the sand paper of grit size 220 to sand paper of grit size 2500, and then polished on selvyt polishing cloth of  $1\mu m$  size diamond paste on it. The cross sectional images of different coatings are then analysed visually.

#### 3.5 Vickers Microhardness

The microhardness of the coatings is measured by indenting the cross sections of the coatings using a Vickers microhardness testing machine (UHL-002). The indentation load taken is 200 gf and dwell time is 15 seconds. The microhardness taken is the average of more than 10 indentations on each coating.

#### 3.6 Linear Reciprocating Wear Study

In order to assess the tribological properties of the coatings, sliding wear tests are performed with Ducom CM-9104 linear reciprocating tribometer against WC–6wt.%Co balls (5 mm diameter). Test is carried out under 10 N load, sliding amplitude 2 mm and 12 Hz frequency for 15 minutes on the top surface of the coating. Volume loss is calculated by measuring depth and width of the wear track by Taylor-Hobson, Surtronic 50 contact type stylus profilometer. The wear results are calculate by 3 experiments for each set of parameters and track depth.

As-sprayed	900 <sup>°</sup> C	1000 °C	1100 °C	1200 °C
$Al_2O_3$	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	$Al_2O_3$
$Al_2O_3-1wt.\%Cr_2O_3$	$Al_2O_3-1wt.\%Cr_2O_3$	Al <sub>2</sub> O <sub>3</sub> - 1wt.%Cr <sub>2</sub> O <sub>3</sub>	$Al_2O_3-1wt.\%Cr_2O_3$	$Al_2O_3-1wt.\%Cr_2O_3$
$\begin{array}{c} Al_2O_3-\\ 2wt.\%Cr_2O_3\end{array}$	$Al_2O_3-2wt.\%Cr_2O_3$	$Al_2O_3-2wt.\%Cr_2O_3$	$\begin{array}{c} Al_2O_3\text{-}\\ 2wt.\%Cr_2O_3\end{array}$	$\begin{array}{c} Al_2O_3-\\ 2wt.\%Cr_2O_3\end{array}$
$Al_2O_3-3wt.\%Cr_2O_3$	$Al_2O_3-3wt.\%Cr_2O_3$	$\begin{array}{c} Al_2O_3-\\ 3wt.\%Cr_2O_3 \end{array}$	$\begin{array}{c} Al_2O_3-\\ 3wt.\%Cr_2O_3\end{array}$	$Al_2O_3-3wt.\%Cr_2O_3$
$\begin{array}{c} Al_2O_3-\\ 4wt.\%Cr_2O_3\end{array}$	$Al_2O_3-4wt.\%Cr_2O_3$	$\begin{array}{c} Al_2O_3-\\ 4wt.\%Cr_2O_3\end{array}$	$\begin{array}{c} Al_2O_3-\\ 4wt.\%Cr_2O_3\end{array}$	$\begin{array}{c} Al_2O_3-\\ 4wt.\%Cr_2O_3\end{array}$
$Al_2O_3-5wt.\%Cr_2O_3$	$Al_2O_3-5wt.\%Cr_2O_3$	$Al_2O_3-5wt.\%Cr_2O_3$	$\begin{array}{c} Al_2O_3\text{-}\\ 5\text{wt.}\%\ Cr_2O_3\end{array}$	$Al_2O_3-5wt.\%Cr_2O_3$
$\begin{array}{c} Al_2O_3-\\ 6wt.\%Cr_2O_3\end{array}$	$Al_2O_3-$ $6wt.\%Cr_2O_3$	$Al_2O_3-$ 6wt.%Cr <sub>2</sub> O <sub>3</sub>	$Al_2O_3- \\ 6wt.\%Cr_2O_3$	$Al_2O_3- \\ 6wt.\%Cr_2O_3$

Table 3 Annealing temperature and coating compositions

#### Chapter 4

#### **Results and Discussion**

#### **4.1 X-ray Diffraction Analysis**

Figures 4.1 to Fig. 4.7 shows x-ray diffraction pattern of as-sprayed and annealed coatings of different compositions i.e. Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-1wt.% Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-2wt.% Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-3wt.% Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-4wt.% Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-5wt.% Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-6wt.% Cr<sub>2</sub>O<sub>3</sub> respectively. The x-ray diffraction pattern of pure Al<sub>2</sub>O<sub>3</sub> powder reveals the presence of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase only. However as-sprayed and annealed Al<sub>2</sub>O<sub>3</sub> coatings contain  $\alpha$ ,  $\gamma$  and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase. The x-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> powder mixture shows the presence of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase along with Cr<sub>2</sub>O<sub>3</sub> in the feedstock. However as-sprayed and annealed Al<sub>2</sub>O<sub>3</sub>- $Cr_2O_3$  coating contains metastable  $\theta$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase and stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase along with  $(Al_xCr_{1-x})_2O_3$  and  $Cr_2O_3$  phase. Traces of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase found after annealing of coatings at 1000 °C and 1100 °C temperature, which shows the transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase undergo to formation of intermediate  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase as the quantity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase is not altered much. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase can be present in the as sprayed coating either due to the presence of unmelted core of Al<sub>2</sub>O<sub>3</sub> feedstock incorporated into the lamella, or due to slow cooling rate of the fully molten Al<sub>2</sub>O<sub>3</sub> splat. The preferential formations of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> may be due to the nucleation energy of it is lower than that of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [10, 17]. The effect of annealing temperature can be identified as the annealing at 900 °C does not have much effect on the transformation of phases, whereas at annealing at 1000 °C and 1100 °C introduces the formation of intermediate  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase. Annealing of the coatings at 1200 °C results in transformation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phaseas it does not contain any peak of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Significant peaks of (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> phase indicate formation of Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> solid solution in different Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> coatings. Positions of a number of peaks identified as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the x-ray diffraction data, coincide with those of (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solution. In APS process, before reaching the substrate, both partially melted Al<sub>2</sub>O<sub>3</sub> and fullymelted  $Cr_2O_3$  start transferring heat to the surrounding atmosphere. The fully

melted  $Cr_2O_3$  splats deposit along with partially melted  $Al_2O_3$  splats. At elevated temperature having higher thermal conductivity, while solidifying; these  $Cr_2O_3$ splats start transferring heat in a rapid manner to the surrounding air and to already deposited  $Al_2O_3$  splats. Simultaneously, at high temperature having comparatively lower thermal conductivity, form the solid solution,  $Al_2O_3$  and  $Cr_2O_3$  should mix in the liquid state and solidify together in right proportion at a suitable temperature [23].



Fig. 4.1 X-ray diffraction pattern of pure Al<sub>2</sub>O<sub>3</sub>



Fig. 4.2 X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-1wt.% Cr<sub>2</sub>O<sub>3</sub>



Fig. 4.3 X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-2wt.% Cr<sub>2</sub>O<sub>3</sub>



Fig. 4.4 X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-3wt.% Cr<sub>2</sub>O<sub>3</sub>



Fig. 4.5 X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-4wt.%Cr<sub>2</sub>O<sub>3</sub>



Fig. 4.6 X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-5wt.% Cr<sub>2</sub>O<sub>3</sub>



Fig. 4.7 X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-6wt.% Cr<sub>2</sub>O<sub>3</sub>

#### 4.2 Microstructure Study

Scanning electron micrograph (SEM) of Al<sub>2</sub>O<sub>3</sub>-4wt.% Cr<sub>2</sub>O<sub>3</sub> coating cross section with different annealing temperatures is shown in Fig. 4.8 (a-d). It shows layered microstructure of splats with very rough surface due to the cracks formed during annealing. The crater marks are produced possibly due to the removal of loosely adhered unmelted core of agglomerated Al<sub>2</sub>O<sub>3</sub> powders during polishing operation of the coating cross section. In addition to that non uniform distribution of pores, fractured surface is present. Chraska et. al [12] reported that transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by annealing resulting formation of microcracks due to significant change in volume.





Fig 4.8 SEM micrograph of Al<sub>2</sub>O<sub>3</sub>-4wt.% Cr<sub>2</sub>O<sub>3</sub> (a) annealed at 900 °C, (b) annealed at 1000 °C, (c) annealed at 1100 °C and (d) annealed at 1200 °C

The SEM micrographs of coatings annealed at 1100 °C with different composition are shown in the Fig. 4.9 (a-g). These Cr rich white zones increase with increasing  $Cr_2O_3$  content up to 4wt.% in coatings as Cr has higher atomic number than Al and it appears brighter. This is visible at all over the microstructural cross section of the coatings with up to 4wt.%  $Cr_2O_3$  content. It suggests well spreading of the splats containing Cr. It is also observed that unlike pure Al<sub>2</sub>O<sub>3</sub> coatings, no distinct boundary lines exist between splats at these white zones. The Cr rich area appears to have lesser cracks and discontinuities as compared to the zones with pure Al<sub>2</sub>O<sub>3</sub> splats. However, thin micro-cracks across the white Cr rich zones are visible.







Fig 4.9 SEM micrograph of coatings annealed at 1100 °C (a) Al<sub>2</sub>O<sub>3</sub>, (b) Al<sub>2</sub>O<sub>3</sub>-1wt.% Cr<sub>2</sub>O<sub>3</sub>, (c) Al<sub>2</sub>O<sub>3</sub>-2wt.% Cr<sub>2</sub>O<sub>3</sub>, (d) Al<sub>2</sub>O<sub>3</sub>-3wt.% Cr<sub>2</sub>O<sub>3</sub>, (e) Al<sub>2</sub>O<sub>3</sub>-4wt.% Cr<sub>2</sub>O<sub>3</sub>, (f) Al<sub>2</sub>O<sub>3</sub>-5wt.% Cr<sub>2</sub>O<sub>3</sub>, (g) Al<sub>2</sub>O<sub>3</sub>-6wt.% Cr<sub>2</sub>O<sub>3</sub>,

#### **4.3 Vickers Microhardness**

The average microhardness of  $Al_2O_3$  coatings prepared with variable  $Cr_2O_3$ content and variable annealing temperatures are shown in Fig. 4.10. It is noticed that initially the hardness of the coating increases with increasing Cr<sub>2</sub>O<sub>3</sub> content up to 4wt.% and with further increase in  $Cr_2O_3$  contentup to 6wt.% the hardness decreases. Similar trend is followed by all the coatings prepared at different annealing temperatures. Hardness of the coating is also determined by the amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> present in it, it is found that the microhardness varies according to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase content of the coatings. Mechanical properties of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase are superior among all the phases. For instance, as the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase content of as-sprayed  $Al_2O_3$  coating is the lowest, the microhardness of such coating also shows the minimum value as compared to that of others [23]. The hardness of coatings increases with increase in the annealing temperature. Among different coatings maximum hardness found in coatings with 4wt.%Cr<sub>2</sub>O<sub>3</sub> content at each annealing temperature. The coatings annealed at 1200 °C, shows the maximum hardness for each composition of coating when compared with the different annealing temperature.

The average value of hardness of as-sprayed pure  $Al_2O_3$  coating is found to be 885.16 HV<sub>0.2</sub> whereas that for as-sprayed  $Al_2O_3$ -4wt.% Cr<sub>2</sub>O<sub>3</sub> coating is 1494.2

 $HV_{0.2}$ . The maximum hardness among all the compositions and different annealing temperature is observed to be 1607.4  $HV_{0.2}$  i.e. for  $Al_2O_3$ -4wt.%  $Cr_2O_3$ coating annealed at 1200 °C. This huge difference in hardness values between pure  $Al_2O_3$  coatings and  $Al_2O_3$ - $Cr_2O_3$  coatings annealed at 1200 °C suggests formation of solid solution. Low quantity of  $Cr_2O_3$  addition to  $Al_2O_3$  forms  $(Al_xCr_{1-x})_2O_3$  solid solution. Formation of  $(Al_xCr_{1-x})_2O_3$  is maximum for coatings with 4wt.%  $Cr_2O_3$  content in it. The mechanical properties of this solid solution are superior to  $\alpha$ - $Al_2O_3$ .



Fig 4.10 Variation of microhardness with respect to Cr<sub>2</sub>O<sub>3</sub> content at different annealing temperature and as-sprayed coatings

#### 4.4 Linear Reciprocating Wear Study

The specific wear rate of the coating is calculated by calculating the volume loss of the coating per unit of load and sliding distance. The response of the coatings against wear with respect to variation of  $Cr_2O_3$  content at different annealing temperature is shown in the Fig. 4.10. As  $Cr_2O_3$  content increases, first the specific wear rate decreases up to 4wt.%  $Cr_2O_3$  content and then increases. This trend of specific wear rate is result of the amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> along with (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> which are found maximum with Al<sub>2</sub>O<sub>3</sub>-4wt.% Cr<sub>2</sub>O<sub>3</sub> [23].





The wear rate with different annealing temperatures follows the similar trend when compared with the content of  $Cr_2O_3$ . The wear rate decreases with increase in annealing temperature which is because of higher quantity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation. But annealing at temperature 1200 °C has very high wear rate when compared with the other lower annealing temperatures. The high wear rate of coatings annealed at 1200 °C is attributed because of the crack formation in the

coatings. The surface is hard enough at micron scale but at the same time for a macroscopic test of wear the cracks formed plays very crucial role, and lowers the wear resistance. The lowest specific wear rate is observed at 1100 °C annealing temperature and 4wt.%  $Cr_2O_3$  content. Such high resistance of wear may be attributed to the considerable improvement in hardness taking place with the rise in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and (Al<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> content.

Figure 4.12 indicates the variation of depth of wear track with respect to  $Cr_2O_3$  content at different annealing temperature and as-sprayed coatings. It is the depth of wear track, which is used to calculate the volume loss in the estimation of specific wear rate. Thus shows the similar variation among all compositions and different annealing temperatures.



Fig. 4.12 Variation of depth of wear track with respect to Cr<sub>2</sub>O<sub>3</sub> content at different annealing temperature and as-sprayed coatings

For the assessment of coefficient of friction fig. 4.13 and 4.14 shows the variation of coefficient of friction with different annealing temperature and different compositions respectively. The variation of coefficient of friction resembles the same variation as that of for specific wear rate. This supports the calculation of specific wear rate and suggests that lower the friction coefficient results lower wear. The decrease in the friction coefficient of the corresponding coating was attributed to a decrease in the shearing force which increases the wear resistance [3].



Fig. 4.13 Variation of coefficient of friction with respect to sliding distance of Al<sub>2</sub>O<sub>3</sub>-4wt.% Cr<sub>2</sub>O<sub>3</sub> coating at different annealing temperature and assprayed coatings



Fig. 4.14 Variation of coefficient of friction with respect to sliding distance with different coating compositions at annealing temperature 1100 °C

Chapter 5 Conclusion

The effect of gradual changes in the annealing temperature, on the phase formation of plasma sprayed Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> is judged in this study. Besides, the effect of the Cr<sub>2</sub>O<sub>3</sub> on the formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase in Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> coatings is investigated as well. This work is evident that the addition of Cr<sub>2</sub>O<sub>3</sub> and heat treatment play a very crucial role on the formation of phases. Even with a little change in Cr<sub>2</sub>O<sub>3</sub> content influences the phase content significantly. The annealing temperature also has its importance for the transformation of phases. The content of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> increases with increase in annealing temperature. The annealing temperature does not affect much on the transformation with the Cr<sub>2</sub>O<sub>3</sub> content but both have its individual effect. The coatings annealed at 1200 °C temperature contain maximum  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> where as coatings annealed at 900 °C and 1000 °C temperature contains both  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Annealed coatings at 1000 °C and 1100 °C, have  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, which forms during the transformation of  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

The hardness of the coating increases with increase in  $Cr_2O_3$  content up to 4wt.% and then decreases with further increase in  $Cr_2O_3$  content, the hardness increases with increase in annealing temperature also. The increase in hardness of the coating is due to increase of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase content in coating. The effect of  $Cr_2O_3$  and annealing on the wear resistance is similar to that in the hardness of the coatings, except for coatings annealed at 1200 °C. The coatings annealed at 1200 °C have very low wear resistance property, which is the result of cracks formed and propagated in the coatings during annealing.

### **Future Scope**

Few meta-stable phases ( $\theta$ ) found when annealed at 1100 °C. Further increment of annealing temperature to 1200 °C proves to be the best for hardness where complete conversion of meta-stable phases occurs. But because of poor wear properties 1200 °C cannot be accepted as a suitable annealing temperature. To find the suitable temperature for both wear as well as hardness property more experiments are required. It can be suggested that the temperature is somewhat close to 1100 °C and less than 1200 °C.

The work can be extended to study the effect of annealing on other properties of the coatings like fracture toughness, adhesion strength, corrosion resistance etc.

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