Pulsed laser irradiation of plasma sprayed alumina-zirconia coatings

Hala Mohamed Omar

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Pulsed Laser Irradiation of Plasma Sprayed Alumina-Zirconia Coatings

By
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B.Sc. in Mechanical Engineering, 2011
The American University in Cairo

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science in Engineering
With specialization in
Materials Science and Manufacturing

Under the supervision of

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May 7th, 2013
The American University in Cairo
School of Sciences and Engineering
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ABSTRACT

Plasma sprayed alumina and zirconia coatings are widely used coatings for many industrial applications. One of the most important applications is the production of thermal barrier coatings (TBCs). As sprayed alumina-zirconia coatings have relatively high degree of porosity and the properties of these coatings, such as high temperature, corrosion resistance, toughness and abrasion resistance may thereby be reduced. Laser surface treatment is one novel method that has potential for eliminating porosity and producing a homogeneous surface layer.

In this research work the effect of excimer laser annealing on the surface of alumina-zirconia coatings was investigated. Alumina-40% zirconia (AZ-40) coatings were sprayed with a water-stabilized plasma spray gun. The coated surface was treated by excimer laser having a wavelength of 248 nm and pulse duration of 24 ns. In the first phase of the work an analytical model was developed in COMSOL Multiphysics 4.2 in order to investigate the effect of the defects on the heat distribution at the surface of samples irradiated by KrF beam. The model revealed that much higher temperatures were localized at areas having defects than at continuous surfaces. A detailed parametric study was carried out to investigate the effects of different laser surface treatment parameters including laser energy density (fluence), pulse repetition rate (PRR), and number of pulses on the microstructure, surface morphology, and mechanical properties of the coatings. The surface structure of the treated coating was examined by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). Treating the surface with low laser energy of 200mJ/cm² etched a very thin layer from the coating, which helped
revealing the microstructures initially present but hidden on the surface of as sprayed coatings. High laser energy of 800mJ/cm$^2$ resulted in significant changes in the coat surface morphology where eutectic colonies growing in a pool of zirconia matrix were identified on the surface. The surface of untreated coating was continuously alternating up and down; it had a zigzag nature. After irradiating the surface with high laser fluence of 800mJ/cm$^2$ the zigzag nature of roughness profile of untreated coating disappeared. Also irradiating the surface with high pulse repetition rate exhibited ‘dome-like’ structures on the surface, which were associated with an increase in surface hardness.
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Finally, I would like to thank my family for their constant support throughout everything. They were and always will be my everlasting source of love and inspiration.
DEDICATION

I dedicate this work to my family and husband...
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>AZ-40</td>
<td>Alumina-40%zirconia</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat (J/kg.K)</td>
</tr>
<tr>
<td>$da$</td>
<td>Absorption length (m)</td>
</tr>
<tr>
<td>$E$</td>
<td>Laser fluence (mJ/cm²)</td>
</tr>
<tr>
<td>$F$</td>
<td>Force exerted by electromagnetic radiation</td>
</tr>
<tr>
<td>$H$</td>
<td>Heat transfer coefficient (W/m².K)</td>
</tr>
<tr>
<td>$HS_{laser}$</td>
<td>Heat source of laser</td>
</tr>
<tr>
<td>$HS_{Hm}$</td>
<td>Heat source for latent heat</td>
</tr>
<tr>
<td>$I$</td>
<td>Laser intensity</td>
</tr>
<tr>
<td>$KrF$</td>
<td>Krypton Florid</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity (W/m.K)</td>
</tr>
<tr>
<td>$L$</td>
<td>Latent heat</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index</td>
</tr>
<tr>
<td>$Pin$</td>
<td>Laser input power (W/m²)</td>
</tr>
<tr>
<td>$R$</td>
<td>Reflectivity</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (kg/m³)</td>
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CHAPTER 1: INTRODUCTION

1.1. Background and motivation

The incessant increase in demand for products to work in severe environment has developed a whole field of surface modification. Surface modification is defined as "the design of substrate and surface together, as a system, to give a cost effective performance enhancement, of which neither is capable on its own"[1]. Many research efforts have focused on development of new materials; however, significant advancement in material properties and durability through development of new alloys was found to be difficult. Thus, research moved towards enhancing the performance of different components by modifying their surface. This would allow producing surfaces capable of combating degradation phenomena such as corrosion, wear, fatigue and improving components' performance, reliability and durability. Depositing a protective coating on the surface of a component to act as a barrier between the surface of the product and the aggressive environment that it is exposed to during operation is globally acknowledged. It was found to be an attractive way to reduce components' damage. Although there are many methods to deposit coatings on the surface of a substrate, thermal spraying is widely used for applying thick coatings for various industrial applications [2]. Thermal spray is popular because it provides coatings well adhered to the substrate and, durable. It is a process in which powder particles are injected in a plasma flame where it melts and accelerates to impact the surface of the substrate where it solidifies. The jet is produced either using combustion gases or electrical power such as plasma as the heat source. The important advantage of plasma over other thermal spray sources is its high operating
temperatures which allow using any high melting temperature material such as ceramics [3].

There has been a growth in the number of applications of thermally sprayed coatings. Availability of hardware and adaptability of the technique are the most important factors for this advancement. Plasma spraying has been successfully applied to a wide range of industrial technologies. The aerospace industry was the first manufacturing sector responsible for driving the development of thermal spray process. Coating of aircraft engines had a great influence on the growth of this industry, thermal spray coatings are used for advanced gas turbine components such as compressor blades, compressor stator vanes, etc… [2, 3].

Plasma spraying technique is widely used because material in the form of powder is melted, quenched, and solidified in a single step. It allows the formation of corrosion, wear and temperature resistant coatings. Also, it is an attractive way to coat components with complicated shapes and different sizes and to produce high quality coatings from metals, ceramics and polymeric materials [2-5]

Plasma sprayed alumina is one of the most widely used coatings for many applications. Alumina is a ceramic material characterized by its low density, chemical inertness, high hardness, high wear, corrosion, and oxidation resistance, which makes it suitable to make wear resistant coatings, electric insulators, thermal barriers, etc...[6, 7]. Also zirconia ceramics present a combination of properties including high chemical resistance, high wear resistance, high toughness, and low thermal conductivity, which make it attractive for components operating in harsh environment.

One of the primary disadvantages of ceramic materials is their brittle nature characterized by low fracture toughness, which limits their use. One of the
promising means used to solve this problem is developing ceramic composites. Pure alumina provides high hardness and strength but poor toughness, while zirconia has high strength and toughness and low thermal conductivity. Therefore, alumina-zirconia composites can give a compromise among these properties [8, 9]. Zirconia based plasma sprayed ceramic coatings are widely used as thermal barrier coatings (TBCs). TBCs are extensively utilized in aerospace and land base gas turbines and diesel engines [3, 10]. Research showed that adding 10 to 40% of zirconia to alumina matrix can be used for high wear and thermal resistance insulation [9, 11-13]. This study focuses on plasma sprayed alumina-40% zirconia coatings (AZ-40).

The main problem with plasma spray coatings including alumina and zirconia is the tendency toward brittle behavior. This is generally attributed to porosity and the lack of a uniform structure within the material. The pores and other flaws can act as crack initiation sites thus forming microcracks. Once these cracks form, they often cause failure of the ceramic material.

Several methods have been proposed to improve the surface properties including impregnation with polymers or ceramics, seal sintering with liquid alloys and post-laser irradiation [10, 14]. Laser irradiation has attracted the attention of researchers as it allows accurately delivering large amount of energy into confined regions on surface of the coatings. This energy is absorbed near the surface and modifies surface chemistry, crystal structure, morphology and mechanical properties without altering the bulk or substrate. This study investigates the influence of employing pulsed excimer laser on the properties of plasma sprayed alumina-zirconia coatings. Earlier studies with pulsed ruby lasers showed that laser material interaction might result into permanent changes in the material's properties, which is not easily achievable via other means. The advantage of nano-
second pulsed lasers is the ability to precisely deposit large amount of energy into a material over a short time scale in a very shallow depth. This allows control of local surface properties relative to the bulk and relative to other regions on the surface [15].

Over the last decades excimer laser has been widely used in various sectors of micromachining. It belongs to gas lasers and stands for "excited dimer". It uses a mixture of reactive gases (i.e. chlorine or fluorine) and inert gas (i.e. argon, krypton or xenon) that produce a dimer (a pseudo molecule) once electrically simulated [16, 17].

Excimer laser operates in the ultra-violet (UV) range (wavelengths from 190-310nm) and is characterized by a short pulse duration (24 ns) [16]. The main motivation for using excimer laser is localized thermal effect, which is attractive for low thermal budget applications where the substrate is not allowed to exceed certain limit [18]. Hence, today excimer laser is widely used for micromachining of different materials as polymers, ceramics and glasses [19], modifying the properties and structure of bulk materials and thin films [20], fabricating high performance thin film transistors [21], improving the efficiency of solar cells [22] and adjusting the mechanical properties of MEMS structures [23], (4) medical use in refractive laser surgery (i.e. by means of intense excimer pulses the surface of the human cornea is reshaped to change its refractive power and thus correct for short or long sightedness) [24]. The wide spread use of excimer laser in micromachining and medicine has led to the discovery of ablation of materials under intense illumination with ultraviolet laser pulses [16, 17]. Excimer laser is used for thermal treatment of ceramic materials because of its short wavelength where the reflectivity of most ceramics is low and absorptivity is high [25].
In excimer laser treatment there are three laser parameters that need to be controlled; energy density, frequency and number of pulses. Using optimal combinations of these parameters allows the realization of high quality surface coatings. Unfortunately, limited research activity focused on the effect of excimer laser on the morphology and microstructure of the ceramic coatings' surface.

1.2. Objectives

The main aim of this work is to study the effect of different excimer laser (248nm, 24ns) parameters on surface morphology and properties of plasma sprayed alumina-40%zirconia (AZ-40) coatings used for high temperature and wear resistance applications. The interaction between the laser and the coating was modeled using COMSOL Multiphysics 4.2. to understand the heat distribution caused by laser pulse across the surface of the plasma sprayed alumina-40% zirconia (AZ-40) coatings. The simulation is also used for predicting the influence of surface defects and material composition on temperature change across surface of the coating. A parametric study of the laser annealed surface will be carried to specify the effect of varying the laser fluence, number of pulses and pulse repetition rate on the morphology and mechanical properties of surface and hence determine the threshold value.
CHAPTER 2: LITERATURE REVIEW

Plasma sprayed alumina and zirconia coatings are one of the most important coatings used in many applications requiring electrical insulation, wear resistance and thermal barrier [6, 8, 13]. This is due to their high corrosion, wear, insulation and oxidation resistance. Many papers reported that plasma spray coatings are characterized by high density of defects such as pores and inclusions, porosities, thermally induced micro-cracks, and phase variation [25-28]. In order to understand the structure of plasma sprayed coatings it is essential to review the process technique.

2.1. Thermal spraying techniques

Thermal spray is a process used to deposit metallic and non-metallic thick coatings. In plasma spraying the gases mix with energy, in the form of heat, to provide kinetic and thermal energies required to coat the substrate. This process is used to enhance properties of components requiring high thermal, wear, conduction, and corrosion resistance.

There are three methods to heat the material: (1) flame spray, (2) electric arc spray, and (3) plasma arc spray. In the case of plasma spraying, plasma flame heat sources are either direct current arc or radio frequency discharge and at atmospheric pressure, the flame temperature can reach up to 8000K, which allows the melting of any material. [3, 4].

2.2. Plasma spraying setup

The plasma spray gun is made of water-cooled copper anode and tungsten cathode as shown in Figure 2.1. Plasma gases (like argon, nitrogen, hydrogen, helium,
or a combination of them) flow from the cathode through the anode. The plasma can be initiated by voltage discharges or RF discharges.

- In case of voltage discharge a DC arc is formed between the cathode and anode. This arc will heat the gas until it ionizes to form plasma flame. Powder is fed into the plasma flame through an inert carrier gas where it is heated and accelerated [2, 5].
- In the case of RF plasma, energy is generated by induction from a coil around the plasma jet through which alternating, radiofrequency current passes [2].

![Figure 2.1. Schematic diagram of plasma spray process [29]](image)

Another way to categorize plasma spraying is through the plasma-forming medium: (1) Gas stabilized plasma (GSP) where the plasma is formed by ionizing gas, (2) water stabilized plasma (WSP) where plasma is formed from water.

Plasma spraying processes can also be divided according to the spraying environment into the following two categories: (1) air plasma spraying (APS) performed in the ambient air, (2) controlled atmosphere spraying occurs in a chamber either with inert gas (high or low pressure) or under vacuum.
2.2.1. Air and vacuum Plasma Spraying

In air plasma spraying the heating temperature ranges between 6000°C and 15000°C [2, 3]. Powder feed stock is accelerated towards the surface of the substrate to form the coating. Sometimes the substrate is heated to temperatures of 95°C to 205°C. Vacuum plasma spraying process takes place in a chamber of 10 to 50kPa (0.1 to 0.5 bar), this low pressure allow to obtain dense and highly bonded coatings [2].

2.2.2. Water Stabilized Plasma Spraying

Higher plasma temperatures can be reached by creating the walls by liquid and an arc is stabilized by wall evaporation. In this case, plasma is also created between a graphite cathode and external rotating anode around this chamber water vortex is created. Water stabilized plasma spray is used to coat large areas because of its high through put rate (several tens of kilogram per hour) [5, 30].

2.3. Structure of plasma sprayed coatings

Many research efforts were conducted to understand the structure and properties of plasma spayed coatings. In 1989 McPherson presented a comprehensive review of plasma spray ceramic coatings formation and discussed the development of porosity, and the very fine voids that formed by incomplete inter-splats contact [31]. He also discussed the strong relation between porosity and mechanical and thermal properties of ceramic coatings. Some of the controlling factors for the grain size and crystal structure within the deposited splats are also discussed, particularly in reference to zirconia coatings [31]. In 2004, P. Fauchais presented an excellent review that summarized the plasma torches with the resulting plasma jets and their
interactions with the surrounding environment [4]. He also presented the powder injection with the heat, momentum and the mass transfers between particles and first plasma jets and then plasma plumes; the particles flattening and solidification, forming splats [4].

In plasma spray processing, material, usually in the form of powder, is heated and propelled as small droplets onto a substrate surface to produce coatings. Particles are accelerated to speeds of 50 to >1000 m/sec [2, 3]. Once these molten particles hit the surface of the substrate, they flatten to form disc shapes called "splats" that adhere to the irregularities of the prepared substrate and to each other. By depositing splats on top of each other and building up layers, a lamellar structure coating is formed. Each splat has a thickness ranging from 1 to 20 μm and cools rapidly (10^6-10^8 K/s) to form uniform and very fine grained polycrystalline coatings [3]. The microstructure of the coating depends upon the temperature, velocity and size of incident particles. Ideally, all the particles should be fully melted; however, some particles do not melt but rather bounce of the surface reducing the deposition efficiency. Partially melted particles are amalgamated within the coating, which modifies the microstructure and properties of the coating [25, 28]. The substrate is well below melting temperature of the sprayed material, thus once the molten droplets of material hit the surface of the substrate the heat transfer is so rapid that spreading and breaking up is stopped by the solidification process. McPherson described that as splat quenching of material with a cooling rate of 10^6 K.s⁻¹ [31].

Figure 2.2 illustrates the structure of thermally sprayed coating. The coating contains porosity due to incomplete contact between lamellae during coating formation process. According to R. McPherson, there are narrow pores of 0.1μm
between lamellae [31]. Also, it was reported that thermal contraction of lamellae
during the cooling process causes thermal stresses resulting in the formation of fine
cracks perpendicular to the lamellar plane [31].

![Diagram](image)

**Figure 2.2. Schematic diagram of the structure of thermally sprayed coating [31]**

Generally, presence of porosity reduces the properties of materials. For
instance, electrical and thermal conductivity and elastic modulus are reduced. However, this depends on the size and distribution of defects. It was reported that finely distributed porosity can increase the thermal shock resistance of ceramic material. A study on ZrO\textsubscript{2} based coatings showed an increase in number of failure cycles with increase of porosity [31].

Plasma spraying experienced a significant development over the past years to produce highly reliable coatings with superior properties for wide range of applications. The utility and importance of this process was first recognized by the aerospace industry. Some estimates claim that up to 75% of the components in modern aircraft engines are coated and most of them are coated using plasma spraying process [3]. Thermal spraying of many materials applied as coatings have grown to include many applications requiring coatings for wear resistance, thermal insulation, corrosion resistance, oxidation resistance, and biomedical compatibility [3, 13].
Ceramic coatings are usually used to produce thermal barrier coatings (TBCs) in aerospace to produce vane bases, burner cans, afterburners and also in automotive industry to produce TBCs on exhausts and brake parts [3]. Woof thermal management technology company, one of the widely known companies that provides specialist coatings and engineering services to industry and end users reported in 2010 that plasma spraying produces ceramic TBCs that reduce temperature by up to 160°C and can withstand temperature by up to 1400°C compared to traditionally used paints containing ceramic, which can only reduce surface temperature by 9% [32]. Thus the number of research studying the morphology and properties of plasma sprayed ceramic coatings and techniques to improve these properties increased.

Several studies reported on the defects and morphology of plasma sprayed coatings. In 2003, Z. Wang et al. [33] studied the effect of pores and interfaces on the properties of plasma sprayed zirconia coatings. They analyzed the SEM images showing microstructure of plasma sprayed coatings. Figure 2.3 reveals different features of plasma sprayed zirconia coating at high magnification. The image shows splat-splat interaction where columnar grains are observed. Interlamellar pores, cracks and globular pores are also identified in Figure 2.3.

![Figure 2.3. SEM image showing detailed micro-structural features of partially stabilized zirconia coating observed by Wang et al. [33]](image)

Venkataraman et al. [34] studied the microstructure of as plasma sprayed alumina-13% titania coatings using SEM and optical microscope. They described these imaging techniques as the most common and reliable ways to determine all
detailed features of material. The SEM images reported in this paper show similar microstructure of plasma sprayed coatings as reported before.

Ibrahim et al. [25] presented SEM images of as plasma sprayed alumina-13% titania (AT-13) coatings very similar to the ones present in previous publications. Figure 2.4a shows the typical surface morphology of plasma sprayed coatings containing high density of defects including pores, cracks and inclusions. Figure 2.4b illustrates the structure lamination. Lamellas are parallel to the substrate, cracks are formed between splats also interlamellar cracks are present.

![Figure 2.4](image)

**Figure 2.4. SEM Image of as sprayed AT-13 coating observed by Ibrahim et al. (a) surface of the coating and (b) cross section of the coating [25]**

Guanhong et al. [35] studied the effect of different spraying parameters (current and spray distance) on the morphology of plasma sprayed Al₂O₃ coating on polymer substrate. Figure 2.5 shows the morphology of Al₂O₃ observed by Guanhong et al. at different spraying parameters. Even at the best current condition proposed by Guanhong et al. shown in Figure 2.5b, the surface contains splats, pores, cracks and partially melted regions [35].
The presence of these defects in ceramic material is generally detrimental and results in material property degradation especially at high temperature. Therefore, many research focused on improving properties of the coating. This dissertation focuses on plasma spraying of alumina and zirconia ceramic materials. In order to understand the structure and properties of plasma sprayed alumina and zirconia it is essential to review properties of these ceramic materials.

2.4. **Overview of ceramic materials**

Ceramic materials are usually defined as solids whose essential components are metallic and non-metallic materials. A more comprehensive definition of ceramic is proposed by Boch et al. and add to the previous definition that ceramic materials are generally in the form of powder and are then consolidated by the sintering at high temperatures into the desired shape [36]. In general, ceramics are oxides, nitrides, and carbides. They are composed of covalent bonds, ionic bonds or a combination of both [36].

**Figure 2.5.** *SEM images of as sprayed Al₂O₃ observed by Guanhong et al. at (a) 300Å and (b) 360Å [35]*
Metallic elements are electropositive (i.e. they tend to lose electrons to produce cations) while non-metallic elements are electronegative and tend to capture electrons. Thus an ionic bond is formed between the cation and anion. Ceramic materials tend to be very strong but brittle because of this ionic bonding. If the ceramic material is subjected to an external force it tends to deform bringing two cations or anions close to each other, so they will repel each other resulting in a brittle fracture. Brittleness causes limitations in the uses of ceramics and induces restrictions in the manufacturing techniques applicable to ceramics.

Ceramic materials provide a combination of properties that make them very attractive as coatings especially as TBCs. This dissertation focuses on two important oxide ceramics: alumina and zirconia. Aluminum oxide (Al₂O₃), commonly referred to as alumina, is one of the cheapest ceramic materials [36]. Al₂O₃ has an excellent combination of properties, which makes it used in a wide range of applications including wear resistance and refractory high temperature applications. Zirconium oxide (ZrO₂) or Zirconia exhibits high hardness, corrosion and erosion resistance. ZrO₂ is also known for its low thermal conductivity, which makes it widely used for TBCs.

2.4.1. Zirconia

Zirconia is an oxide ceramic usually prepared by chemical and heat treatment of zirconium silicate (ZrSiO₄) also known as zircon to eliminate the silicate content. Zirconia is characterized by its high melting temperature (2,880°C), high ductile to brittle transition temperature and it is an electrical insulator. It is colorless and has high refractive index. This combination of properties makes zirconia used in a wide
range of applications including refractory, medical implants, toughening nano-
composites...[36, 37]

2.4.2. Phase transformation of Zirconia

Zirconia exists in three crystalline forms: monoclinic, tetragonal and cubic
structures at room temperature. Zirconia is stable in the monoclinic (m) structure.
When heated it changes to tetragonal (t) structure at around 1,100°C, followed by a
third transformation to cubical structure at 2,300°C. This phase transformation
process is reversible upon cooling [36].

Cubic phase (c)

The cubic phase is stable at 2370°C up to the melting temperature. Each
Zirconium atom is attached to eight oxygen atoms as shown in Figure 2.6a [38].

Tetragonal phase (t)

The tetragonal phase is stable from 1100° to 2370°C. It is very similar to the
cubic structure but with slight elongation in c-axis as indicated in Table 2.1 [38].

Monoclinic phase (m)

The monoclinic phase is thermodynamically stable below 1100°C. It has a
distorted cubic unit cell as shown in Figure 2.6c. In this structure each Zirconium
atom is attached to seven oxygen atoms [38].
Figure 2.6. Three different phases of Zirconia: (a) cubic, (2) tetragonal and (c) monolithic. The blue circles are Oxygen atoms and red ones are Zr atoms [38]

Table 2.1: Properties of Zirconia phases [39]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice parameters</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>0.51454</td>
<td>0.52075</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>0.5094</td>
<td>0.512</td>
</tr>
<tr>
<td>Cubic</td>
<td>0.512</td>
<td>0.512</td>
</tr>
</tbody>
</table>

These transformations were thoroughly studied and it was reported that they are accompanied by volume changes on cooling. The (c) to (t) transformation causes a volume increase of approximately 2.31% and the (t) to (m) around 4 to 5%. This volume expansion and shear strain of around 0.16, resulted in the instability of zirconia for application requiring integral solid structures; while it was mainly used in refractory applications only. Despite that, for researchers zirconia was a very attractive engineering material because of its high properties including high hardness, wear resistance, high friction coefficient, strength, high melting temperature, low thermal conductivity, high electrical properties and chemical inertness. In the late 1970s, researchers started vigorously evaluating and studying the properties of zirconia. The discovery that (t)-(m) transformation can be controlled to enhance the
properties in 1975 marked a turning point in the development of improved engineering ceramic materials and toughening of ceramics [38].

The transformation toughening of zirconia was first reported by Garvie, Hannink, and Pascoe in their paper entitled "Ceramic steels?" [40]. In this paper an analogy was drawn between steel alloys and ZrO$_2$. They described the ZrO$_2$ lattice transformations as martensitic because they are (1) diffusionless they only involve shifts in lattice position rather than transport of atoms, (2) occur athermally in a range of temperature not at a specific one, (3) exhibit deformation of shape. Similar to the martensite formation, the t-m transformation of ZrO$_2$ can be controlled and used to ameliorate the strength and toughness of the material [38, 39, 41, 42].

In order to stabilize the (c) and (t) structures zirconia is alloyed with lower valence oxides, such as MgO, CaO, CeO$_2$ or Y$_2$O$_3$. The cubic and tetragonal phases are similar to the ones in pure zirconia except that doping ions substitute Zr$^{4+}$ sites and fraction of oxygen sites are vacant to maintain neutrality. It was found that adding 3% of Yttria was sufficient to reduce the (t) to (m) transformation temperature from 1,100°C to 550°C. This temperature is very low and does not allow enough energy for the (t) to (m) transformation to occur. That's why this technique allows the retention of (t) structure at room temperature [38, 39, 41, 42]. The material of interest in this study is pure zirconia added to alumina.

2.4.3. Alumina

Aluminum oxide (Al$_2$O$_3$), known as alumina, is one of the cheaper and commonly used ceramic materials. Alumina has an excellent combination of properties that makes it used in a wide range of applications. The principle sources of Al$_2$O$_3$ are bauxites and corundum [43-45]. The principal method for preparing
aluminum oxide from these two sources is calcinations. The aluminum hydroxide found in nature are heated to 500-800°C to give $\gamma$-$\text{Al}_2\text{O}_3$ and up to 1100°C-1200°C to form $\alpha$-$\text{Al}_2\text{O}_3$. During the heat treatment of aluminum hydroxides many forms of aluminum oxides are form: $\alpha$, $\gamma$, $\delta$, $\rho$, $\vartheta$, $\chi$, $\eta$, $\beta$. The most stable form is $\alpha$-$\text{Al}_2\text{O}_3$.

**Alpha and gamma aluminum oxides**

$\alpha$-$\text{Al}_2\text{O}_3$ is the most stable form having a Rhombohedral crystal structure. While $\gamma$-$\text{Al}_2\text{O}_3$ is a metastable form of alumina and has a cubic crystal structure. $\gamma$-$\text{Al}_2\text{O}_3$ has high elastic modulus and hardness, and high thermal and chemical stability, and has a nanocrystalline nature, which makes it very attractive for a wide variety of advanced applications [43].

### 2.4.4. Ceramic Composites

The major disadvantage of pure ceramic materials is their brittle nature. They are characterized by low fracture toughness. This brittleness limits the use of ceramic materials. Many research efforts focused on increasing the fracture toughness of ceramic materials. One of the promising ways to overcome this problem is the use of ceramic composites. Pure alumina has high hardness and good strength properties but poor toughness, while zirconia has high strength and toughness but low hardness. Zirconia also has low thermal conductivity. Alumina-Zirconia composite can then give a combination of these mechanical properties and offer high level of strength, toughness, hardness and thermal resistance [8, 9]. Research work showed that adding
10 to 40% zirconia to alumina matrix could be used for high wear and thermal resistance insulation [9, 11-13]. This study focuses on plasma sprayed alumina-40% zirconia coatings (AZ-40).

In order to understand the phase transformations of the alumina-zirconia system, it is beneficial to understand the alumina-zirconia phase diagram presented in Figure 2.7. Alumina-Zirconia system contains a eutectic point at 1860°C with a composition of about 58% alumina. The transformation of cubic zirconia solid into tetragonal phase completes at temperature of 2260°C and its transformation into monoclinic phase in the presence of alumina occurs at 1150°C. Figure 2.7 shows that alumina and zirconia have a complete miscibility in the liquid state. The solubility of alumina into solid zirconia is very low (less than 2%), while the solubility of zirconia into solid alumina is almost zero. Some other references reported that the solubility of the zirconia into solid alumina may extend to about 5% [46]. In this work segregated zirconia will be observed. The current work deals with thermally sprayed alumina-40% zirconia coatings, which is the eutectic composition. It has m-ZrO$_2$+Al$_2$O$_3$ at room temperature and transforms to t-ZrO$_2$+Al$_2$O$_3$ at 1150°C to 1860°C at which the ceramic start melting.
2.5. Plasma sprayed alumina-zirconia coatings

As mentioned previously, zirconia is widely used as TBC because of its high melting point, high thermal, wear and oxidation resistance, as well as high hardness and fracture toughness associated with relatively low density. However, the (t) to (m) phase transformation causes cracking and deterioration of the coating limited its use. Thus Yttria Stabilized Zirconia (YSZ) was used instead of pure zirconia. However, YSZ still have some drawbacks. It was found that low thermal conductivity can be achieved only at high porosity content, which in turn reduces the mechanical properties such as hardness, wear and elastic modulus. The other problem is that yttrium has lower capacity for oxygen bonding than zirconium so substitution of yttrium atoms in the zirconium oxide will leave some oxygen vacancies within the unit cell. This can result into oxidation of interface between the coating and the substrate causing failure of the coating [47, 48]. An important composite under investigation for replacing the present YSZ TBC is its combination with alumina. It
was found that alumina-zirconia possesses lower residual stress, higher hardness, lower porosity, and improved adhesion compared to YSZ [47, 49]. Other studies showed that alumina-zirconia has high fracture toughness and can be an alternative material to produce cutting tools [8] and for structural applications such as in motor, aerospace and biomedical field [9]. Also alumina has higher resistance to oxygen diffusion than zirconia. Hence, it controls the growth of oxides at the coating/substrate interface [47, 49].

However, plasma sprayed alumina-zirconia coatings are characterized by high density of defects similar to other plasma sprayed ceramic coatings. It was also reported that plasma sprayed alumina-zirconia is characterized by formation of non-crystalline phases. This is because of high cooling and solidification rates of splats formed during plasma spraying, which prevent atoms to order themselves in crystalline manner. Also metastable crystalline phases are observed in plasma sprayed materials. For instance, thermally sprayed alumina mostly consists of γ-Al₂O₃ rather than α-Al₂O₃. This is because metastable phases require low energy to nucleate. Yet traces of α-Al₂O₃ are present in plasma spraying because of partially melted particles. Figure 2.8 illustrates some of the possible metastable phases that can be found in alumina-zirconia system such as γ,α, θ alumina and/or tetragonal and cubic zirconia. Also at higher cooling rates glassy or amorphous structure is formed.
Figure 2.8. Critical cooling curves superimposed on binary equilibrium phase diagram of alumina–zirconia system [47]

Kim et al. [50] studied the structure plasma sprayed Al₂O₃–ZrO₂ thick coatings of thickness 2mm with near eutectic compositions. They sprayed the coating using atmospheric plasma spraying (APS) and micron size powder and reported that the structure of as sprayed coating is mostly amorphous. Sodeoka et al. [51] also reported the presence of amorphous phase in 50/50 volume ratio of alumina/3YSTZ (zirconia stabilized with 3mol% yttria) using APS. Vasiliev and Padture reported similar structure while studying plasma sprayed composite coatings of alumina-zirconia and alumina-YSZ. They were able to identify the amorphous phase through X-ray diffraction and transmission electron microscope studies.

To have control over the coatings properties, it is important to understand their structure and mechanism of formation of the amorphous and crystalline phases in the coatings. In 2011, Tarasi et al. [28] studied the amorphous and crystalline phase formation in plasma sprayed alumina-yttria stabilized zirconia coatings (YSZ). They studied two types of powders, powder (1) initially containing tetragonal YSZ and γ-alumina and powder (2) containing monoclinic and tetragonal zirconia and γ and α
alumina. In their work, they went through a long process and collect in ‘flight particles’ to further understand the formation of crystalline and amorphous phases of plasma sprayed alumina-zirconia composites. They showed that some plasma sprayed particles are fully mixed, while other particles are partially mixed as shown in Figure 2.9. They observed that in-flight particles the unmixed components show dendritic solidification and in the partially mixed particles only grains of unmixed portions are dendritic. However, no grains can be seen in the mixed areas. This amorphous structure of mixed areas can only occur after complete melting because of the low solid solubility of alumina and zirconia.

![Figure 2.9. Fully and partly molten particles of powder 1 [28]](image)

Some in-flight collected particles showed typical eutectic crystallite. Figure 2.10 shows fine eutectic structure with about 10nm alumina and 20nm zirconia lamella. Also equiaxed cellular grains with small pore at the center were observed.
This eutectic structure was previously studied in bulk alumina-zirconia system at eutectic composition [52, 53]. Eutectic colonies formed of ZrO₂ fibers in Al₂O₃ matrix were observed. Ando et al. [54] examined the growth of these eutectic colonies at different cooling rates. They observed lamellar structure at low cooling rate and as the cooling rate increases the spacing between lamellas decreases. At the highest cooling rate the eutectic structure is replaced by fully amorphous structure. Bourban et al. [55] studied the solidification microstructure of laser treated Al₂O₃-ZrO₂ eutectic (36.8% ZrO₂) using high power CO₂-laser. They used electron microscope to observe the orientation of microstructure to measure the growth rate and they noted that structure was essentially a lamellar structure. As shown in Figure 2.11 the grains are formed of eutectic colonies and the white regions are zirconia and dark ones are alumina [55].
Figure 2.11. *Scanning electron micrograph of a longitudinal section of Al₂O₃-ZrO₂ eutectic microstructure* [55]

The observation of eutectic structure on surface of plasma sprayed Al₂O₃-ZrO₂ after laser treatment is reported in this work.

2.6. **Proposed methods to improve plasma sprayed coatings**

A great amount of work has been done to improve the properties of sprayed coatings as described by P. Fauchais [56]. Many researchers studied the effect of changing spraying parameters on the properties of the coating. Yet, plasma sprayed coatings present defects including pores, holes between splats corresponding to lack of filling, unmolten and partially melted particles. Also micro and macro-cracks are created within cracks due to different stresses generated during coating, the density of these cracks depends on the coating temperature during the deposition process [57]. In order to reduce some of these defects plasma spraying was conducted in controlled atmosphere, which is more expensive in regard to conventional
atmospheric plasma spraying. Vacuum plasma spraying (VPS) is preferred to atmospheric plasma spraying (APS) for oxidation sensitive materials and where improved adhesion and density is required. The low oxidation associated with VPS allows very dense coatings to be deposited [10, 57].

Other methods were proposed to improve the coating properties including sealing the pores by impregnation of ceramic compound [10, 14, 58]. Another method used is altering the material composition of the coating by adding other species to improve phase stability [14]. For instance, Lee et al. added CeO₂ to ZrO₂-Y₂O₃ to improve phase stability [59]. However, these techniques remain palliative treatments and require several additional steps in manufacturing process.

Laser surface treatment is one novel and promising method that has potential for eliminating porosity, producing a homogeneous surface layer, and improving its protective efficiency.

2.7. Lasers

Various post-treatment have been tried to improve the properties of sprayed coatings including mechanical, chemical and heat treatment. Heat treatment is the most important property-enhancing operation that involves heating and cooling of a material to improve its properties. Lasers became very attractive tools and are widely used because it allows local treatment, short processing time and simple and precise operation.

The term laser refers to "Light Amplification by Simulated Emission of Radiation". Laser is a transducer that converts electrical energy into highly coherent light beam. A laser light beam is monochromatic, which means that light has a single wavelength and the light rays in the beam are almost perfectly parallel [60].
2.7.1. Working principles of laser

Electrons of atoms can take different energy states $E_1<E_2<E_3\ldots$ Atoms at lower energy level are more stable than ones at higher energy levels. Thus, the atoms are not satisfied at the high energy level so they release energy in the form of photons to go to a lower energy state. This is called spontaneous emission. This energy can be given out as electromagnetic radiation [61]:

$$E_2-E_1=h \nu_o$$

(2.1)

Where $E_2$ is the higher energy level, $E_1$ is the lower energy level, $h$ is Plack's constant and $\nu_o$ frequency.

Radiation is considered as a stream of particles called photons. Released photons have a wavelength that characterizes the energy state of the electrons at the time the photon was emitted.

When external electromagnetic waves of frequency $\nu_o$ near the transition frequency between $E_2$ and $E_1$ are incident on electrons in material, it forces the electrons to undergo transition from $E_2$ to $E_1$ which gives rise to an external electromagnetic wave (a photon), while incident photon still exists [60]. This transition process caused by the external excitation is called stimulated radiation.

In laser, lasing gases are added to excite the atoms, which are called absorption. However, the atoms are not satisfied at the high energy level so they release energy in the form of photons to go back to their initial state. This is called spontaneous emission. Released photons have a wavelength that characterizes the energy state of the electrons at the time the photon was emitted. Excited atoms will interact with non-excited ones creating more photons this is called simulated emission. The emitted photons move in the same direction and are in phase with the
initial ones. When the process takes place in a system composed of mirrors of opposite side of lasing gas, coherent, monochromatic and highly directional oriented beam is generated [16].

There are different types of laser depending on the lasing material employed. The most commonly known are [16]:

- **Solid-state laser**: In solid state laser the medium is a crystalline or amorphous (such as glass) material in which dopant is added (neodymium, chromium, or erbium). The first laser was developed by Theodore Maiman. The most commonly used solid state laser consists of neodymium doped with YAG (yttrium-aluminum garnet) and it is commonly referred to as Nd:YAG laser. It emits infra-red light.

- **Gas laser**: Uses gas like helium or helium-neon (HeNe) and produces light in the visible red region. For example, CO₂ lasers, used to cut stiff materials, release light in the far-infrared region.

### 2.7.2. Laser material interaction

When the laser beam is incident on the surface of a material various phenomena occur. This section briefly explains the laser material interactions as described by Dahotre *et al.* [62].

Once the laser beam of intensity $I_o$ irradiate the surface of the material part of the light is reflected and the rest is transmitted into the material as illustrated in Figure 2.12.
The transmitted light exerts a force causing the motion of electrons. Equation (2.2) describes the force exerted by the electromagnetic radiation of the electrons [62]:

\[
F = eE + e \left[ \frac{\nu}{c} \times H \right]
\]  

(2.2)

where \( \nu \) is the velocity of electron and \( c \) is the speed of light \( E \) and \( H \) are electric and magnetic field vectors respectively. According the equation (2.3), the absorbed radiations result into vibrations inside the material. The absorbed energy is described by Beer-Lambert law as follow:

\[
I(z) = I_0 e^{-\alpha z}
\]  

(2.3)

Where \( I_0 \) is the incident intensity, \( I(z) \) is the intensity at depth \( z \), and \( \alpha \) is the absorption coefficient. The laser beam intensity gets attenuated inside the material and the attenuation length \( L \) is expressed as:

\[
L = \frac{1}{\alpha}
\]  

(2.4)

Absorptivity of the material greatly influences the laser-material interaction process and is described for opaque material as follow:
\[ A = 1 - R \] \hspace{1cm} (2.5)

Where \( R \) is the reflectivity of the material and can be calculated from the complex refractive index \( n_c \):

\[ n_c = n - ik \] \hspace{1cm} (2.6)

where \( n \) is the refractive index and \( k \) is extinction coefficient. The reflectivity at normal incidence is then defined as:

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \] \hspace{1cm} (2.7)

The excitation energy caused by absorbed light converts into heat with a time duration ranging from 10^{-12} to 10^{-6} s in non-metals and 10^{-13} s in metals [62]. The conversion from light into heat causes temperature distribution in the material. Depending on the laser intensity and material properties several phenomena could occur as illustrated in Figure 2.13.

---

**Figure 2.13.** Different effects of laser-material interactions [62]
The dominant phenomenon is the heat conduction into the material. The temperature distribution in the material depends on the properties of the material as well as the laser parameters. At sufficiently high laser intensity (referred to as laser threshold energy) phase transformation could occur like melting and vaporization. A detailed analysis of excimer laser material interaction with AZ-40 coatings is presented in section 6.1.

2.8. Effect of laser treatment on surface of plasma sprayed coatings

Plasma sprayed ceramic coatings sealed by laser have been the subject of several investigations. According to the literature, there are several types of lasers used for post treatment of thermally sprayed coatings. It is reported that Nd: YAG laser is operated at energy densities from 0.2 up to 4kJ/mm² [63]. CO₂ laser is used at lower energies of 5J/mm² [64] to 37J/mm² [65] and 100J/mm² [63]. Excimer laser could be used at very low fluences of 0.002J/mm² or 200mJ/cm² [25] as well as very high power densities up to 1MW/mm² [63]. Considerable research studies were carried out to demonstrate the effect of laser treatment using continuous and long wavelength laser like CO₂ and Nd: YAG lasers on surface of plasma sprayed ceramic coatings.

Laser treatment of ZrSiO₄ coatings was studied by Schelz et al. [66]. ZrSiO₄ is a very important oxide ceramic material known for its high refractoriness and chemical stability. In their study, ZrSiO₄ coating was deposited with the aid of atmospheric plasma spraying. Then laser treatment was carried out using a continuous wave CO₂ laser with a Gaussian shape. During plasma spraying ZrSiO₄ decomposes into SiO₂ and ZrO₂. They showed that setting the laser power density and scanning
speed, SiO$_2$ and ZrO$_2$ phases can recombine into ZrSiO$_4$. This is accompanied by volume contraction.

Pinto et al. [67] investigated laser surface treatment of plasma sprayed yttria stabilized zirconia. They treated the surface of atmospheric plasma sprayed of 8wt.% yttria stabilized zirconia coating with continuous wave CO$_2$ laser. After laser treatment a shiny surface layer of fine cellular structure was observed. The cellular structure grows perpendicular to free surface of the coating. The sealed surface exhibit lower surface roughness, higher hardness and higher corrosion resistance.

According to Citibor et al. [63], laser treatment of plasma sprayed coating results in melting of the surface layer of ceramic material, which re-crystallizes rapidly. The lamellar microstructure disappears and fast nucleation occurs. They also noted that the laser annealing of alumina results in phase transformation from $\gamma$ to $\alpha$. While in the case of zirconia heat removal from melted zones is a very complicated process because of its very low conductivity.

According to Citibor et al. [63], several studies reported that Nd-YAG laser energy of 5J/mm$^2$ penetrates approximately 100$\mu$m and increases the microhardness of alumina by 25% and also diminish the porosity tremendously. For instance Fernandez et al reported that the microhardness of alumina coatings increased from 1161 HV to 1444 HV others noted an increase from 940HV to 1400HV.

Yilbas et al. [68] examined the effect of laser treatment on surface of zirconia. The study revealed that laser treatment depth reached 50$\mu$m in depth and that a dense layer was formed at the surface of the coating accompanied with an increase in surface hardness and a reduction in the fracture toughness.

Chwa and Ohmoriv [69] illustrated on the effect of surface roughness of plasma sprayed zirconia coatings on laser treatment process. They treated the surface
of plasma sprayed 8-wt% Yittria stabilized zirconia using YAG laser. The treated surface mainly contained non-transformable metastable tetragonal (t) phase and (m) phase was not observed. The results revealed that the absorption and reflectance of laser energy decreases as the surface roughness increases. Laser beams are randomly scattered and some light beams re-radiate the hills and valleys present at the surface of samples, as shown in Figure 2.14. Thus, in the current study the surface of the samples were grinded before laser treatment.

Figure 2.14. Schematic diagrams illustrating the transition from specular to diffuse scattering in accordance with the different surface conditions [69]

As illustrated in this section CW–CO₂ and Nd:YAG lasers, with the appropriate parameters can modify the microstructural and morphological characteristics of plasma sprayed ceramic coatings and improve their properties.

Many studies also showed that pulsed laser irradiation can be used to melt or soften very thin surface layer of metal or ceramic that resolidifies, due to the high thermal gradients. Excimer lasers present certain distinct advantages for material processing applications in comparison to the other types of lasers. This is due to the fact that excimer lasers operate in the ultraviolet region of the spectrum at short wavelengths from 190 nm to 310 nm. At these short wavelengths the reflectivity of
most metals and ceramics is lower than at longer wavelengths [25]. The short wavelength corresponds to high photon energies from 3.5 to 6.4 eV, which are efficiently absorbed by most of the ceramic materials [25, 70]. These energies are sufficient to break many ceramic bonds unlike in case of light from longer wavelength lasers such as Nd:YAG and CO$_2$ requires great photon absorption to break down constituent molecules. Long wavelength lasers will then develop high temperature at the surface of the material resulting in undesirable effects including combustion, melting, flow and boiling of the surrounding material. However, pulsed excimer lasers heat the surface of the material to a temperature above the melting temperature for a very short period from 10 to 100ns. Then, the surface rapidly cools through heat transfer into the bulk at a rate of $10^8$-$10^9$ °C/s [71]. Excimer laser treatment of the surface of the material allows very shallow thermal penetration depths in the range of few microns [25, 71, 72]. Studies of material/laser interactions showed that when the surface of material is irradiated with sufficient laser energy, modification in the atomic and microscopic level occurs. The phenomena occurring depend on the laser parameters and conditions as well as the material chemical physical and optical properties. Excimer laser has been proven a low thermal budget technique for sealing pores of silicone membranes of MEMS and NEMS devices [18, 73]. In order to reach the optimum laser treatment conditions it is crucial to understand the phenomena occurring during laser/material interaction. Excimer laser became very attractive tool for surface modification especially that it is rapid enough to be commercially viable.
2.8.1. Excimer laser

Excimer laser belongs to gas lasers. Excimer stands for excited dimer. It uses a mixture of reactive gases and inert gas that produces a dimer once electrically simulated. Excimer laser operates in the ultra-violet (UV) range (wavelengths from 190-310nm).

This dissertation deals with krypon-florid excimer laser (KrF laser). Noble gases like Krypton (Kr) in normal conditions cannot form compounds with other elements. The noble gas is then excited and ionized in the laser cavity. Once ionized, they attract neutral atoms in this case florine (F\textsubscript{2}) to form ionized molecules as shown in equation (2.8). These molecules are called exited complex; that's why the proper name of this type of laser is exiplex since they involve unlike atoms. Yet, the name 'excimer laser' is still commonly used so this is the name that will be used throughout this dissertation.

\[ 2\text{Kr} + \text{F}_2 \rightarrow 2\text{KrF} \]  \hspace{1cm} (2.8)

The bond between the two atoms is very strong but can only last for few nanoseconds. The ionized compound exists only temporally when the Kr is in excited electrical state. Once the noble gas return to its stable form, the molecule dissociate into its elemental components as shown in equation (2.9). This process is accompanied with a release of energy in the form of photons. The laser beam produces is monochromatic, directional with low divergence, coherent and provide an intense high energy.

\[ 2\text{KrF} \rightarrow 2\text{Kr} + \text{F}_2 \]  \hspace{1cm} (2.9)

Excimer laser can be used in many applications one of them is annealing of surface coatings. Excimer laser annealing was showed to be superior to all other techniques [16]. With excimer laser annealing, efficient heating of coatings can be
attained by applying excimer laser radiation of sufficiently high energy. During excimer laser annealing light in the UV range is produced and the pulse duration is very short only allowing treatment of very shallow thickness. This leaves the substrate not affected by heat. However, there are some laser parameters that need to be carefully controlled in order to achieve good treatment.

2.9. Applications of excimer laser for surface treatment

Excimer laser was reported for the first time in 1970 by N. G. Basov et al. They used in their study a high-current electron beam to agitate liquid Xe, and Xe$_2$ was emitted at around 172nm since then excimer lasers started to be used. Many researches were done on this new class of material and in 1975, lasers emitting light at all most UV wavelengths were demonstrated [17].

Lambda Physik, a German company, manufactured the first commercially available excimer laser, known as EMG 500 in 1977. That laser could work at several wavelengths (193nm, 222nm, 248nm, 282nm, 308nm, 337nm, 351nm, 427nm, or 713nm), and frequency of 0.05Hz or 20Hz [17].

Starting 1977 IBM laboratory, the T.J. Watson Research Center in Yorktown Heights, NY a group under R. Srinivasan used a laser having a monochromatic pulse at 193nm. They observed a very interesting phenomenon that they referred to as "ablation photodecomposition (APD)". They proved that the surface of polymer, polyethylene terephthalate, irradiated with laser beam was etched. Since then excimer became widely used as a manufacturing technique. Excimer laser is very attractive because it operates at UV wavelength offering high depth resolution and excellent machining quality. The progress in excimer laser technology made it a reliable and
cost-effective tool for the industrial application. This technology has expanded to the field of medicine [17].

In 1983, Srinivasan and his group were the first to describe APD on polymers and tissue at 193nm. After that, Dyer and his group at the University of Hull, U.K., obtained same results by excimer laser wavelengths at 248nm and 308nm [17].

There have been a number of papers describing the effect of different types of excimer laser on surface of polymers. In 1992 Thomas et al. compared the effect of irradiating different types of polymers with laser of 193nm and 248nm [74]. They observed that excimer laser could be used to create irregular microscopic structure on the surface of polymers. In fact, SEM images of polyvinyl chloride (PVC) irradiated with ArF 193nm excimer laser illustrate the formation of conical like-structure at the surface. This phenomenon occurs on the surface of different types of polymers irradiated by laser of different wavelengths. SEM images of laser treated polyethylenimine and polycarbonate surfaces exhibit the formation of irregular structures at the surface and increasing the wavelength from 193 to 248nm allow the formation of coarser and densely packed conical shapes. This can be useful for improving material properties like adhesive bonding and surface friction [74].

The formation of similar structure was also observed on the surface of laser treated ceramic materials. However, ceramic material required higher laser energies to be modified.

It has been demonstrated that controlling thermal effects during laser-material interaction allows the modification of the composition and microstructure of ceramic surfaces. It has also been proven that irradiating porous surfaces with sufficiently high energy results in sealing surface cracks and pours. Thus modification of ceramic
surfaces became an attractive way to diminish surface defects and improve the mechanical properties of the surface of ceramic coatings [27, 75].

There has been very limited research on the study of excimer laser irradiation of alumina and zirconia coatings. Grossman et al. [76] examined excimer laser induced melting and decomposition of alumina and zirconia. In their study, surface of plasma sprayed alumina and yttria partially stabilized zirconia was irradiated by excimer laser of wavelength 308nm and pulse duration of 55ns. They found that surface roughness of Al₂O₃ decreased after irradiating it with medium energy densities of 20 to 30mJ/mm². Higher energies (40mJ/mm²) and high number of pulses (16-32) increased the surface roughness. The surface defects and cracks disappeared after laser annealing of alumina. In case of zirconia, drastic surface smoothening was observed because the surface layer evaporates once subjected to laser irradiations [76].

Sciti et al. [70] studied the microstructural changed induced by excimer laser treatment of alumina. They treated the surface of alumina using KrF excimer laser having a wavelength of 248nm. SEM images of treated samples revealed that at low laser energy of 1.8J/cm², surface of the material melted. The thickness of melted layer depends on the number of pulses. At higher laser energy of 7.5J/cm² the surface was removed by ablation and the initial morphology of the sample disappeared and microcracks appeared [70].

Z. Liu [77] investigated the effect of excimer laser on surface of 0.25mm thick plasma sprayed yttria stabilizes zirconia coating. Laser treatment was performed using excimer laser having a wavelength of 248nm in air. The study revealed that excimer laser annealing of coating could result into formation of very thin (few micron) crack-
free and crater free layer at the surface of coating, which was not possible to achieve using CO₂ and Nd:YAG lasers.

A. Ibrahim et al. [25] studied the effect of excimer laser parameters; including energy density, number of pulses and pulse repetition rate, on surface of water-stabilized plasma sprayed alumina-13% titania samples. They indicated that the threshold energy density for melting and recrystallization is about 700mJ/cm². A lower laser fluence of 400mJ/cm² was found to be enough to stimulate thermal stresses on the coating surfaces, which led to the propagation of existing cracks and initiation of new cracks. At higher energy density of 800mJ/cm² the surface drastically changed: porosity decreased significantly, the surface melted and re-solidified and 'dome-like' shape columnar grains were formed, and hardness increased. At 800mJ/cm² and by increasing the number of pulses the tightly bonded columnar grains started to flatten out but the porosity increased. At low energy, increasing the number of pulses caused the propagation and initiation of cracks. At 800mJ/cm² and pulse repetition rate of 10Hz the surface of the coating appeared shinny and smooth and self-organized cluster cracks were induced. At higher pulse repetition rate of 50Hz the surface texture completely changed and columnar grains grew vertically. This surface morphology exhibit higher hardness and lower porosity. All the excimer laser annealing were done in air and all the grain boundaries contained impurities. These impurities hindered the movement of grain boundary movement causing a reduction in grain size and the texture sharpness. SEM and XRD observation indicated that treated surfaces contain nanosized γ-Al₂O₃. These preliminary results indicate that excimer laser caused grain size refinement and modification of the microstructure of the coating.
2.10. **Summary of Literature**

Plasma sprayed alumina-zirconia coatings have many potential applications especially in aerospace and automotive industries requiring high thermal and wear resistance. However, they are characterized by high density of defects including pores, cracks and inclusions. Post laser treatment; as argued by many researchers, is a promising method for surfaces sealing of the coatings and for improving materials' properties. Pulse excimer laser has advantage over other types of laser as it operates in the ultra-violet region at short wavelengths where the reflectivity of ceramics is low and absorptivity is high. Also, the process is rapid enough to be commercially viable. Several investigations showed that excimer laser treatment significantly modifies the microstructure of the surface of the material and improves materials' properties. The changes that occur after laser irradiation depend on laser parameters and conditions as well as the material chemical, physical and optical properties. In order to reach the optimum laser treatment conditions it is critical to comprehend the phenomena occurring during laser/material interaction. Yet, very limited research has been conducted to investigate the effect of excimer laser irradiation on surface of plasma sprayed alumina and zirconia coatings. In this work the effect of excimer laser having a wavelength of 248nm and pulse duration of 24ns on the surface morphology and mechanical properties of plasma sprayed alumina-zirconia coatings is studied.
CHAPTER 3: MATERIALS AND EXPERIMENTAL PROCEDURES

3.1. Materials

In the present work, mild steel substrates of 2x1x0.5cm³ are coated with 5mm thick alumina-40% zirconia coating (AZ-40) using water stabilized plasma spraying. Table 3.1 lists the plasma spraying parameters employed in the current research.

Table 3.1: Spray Parameters for water stabilized plasma

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Alumina-40% zirconia (40-80μm)</td>
</tr>
<tr>
<td>WSP power</td>
<td>125kW</td>
</tr>
<tr>
<td>Voltage</td>
<td>300-320V</td>
</tr>
<tr>
<td>Amperage</td>
<td>400A</td>
</tr>
<tr>
<td>Spray distance</td>
<td>330mm</td>
</tr>
<tr>
<td>Rotation Speed</td>
<td>90rpm</td>
</tr>
<tr>
<td>Feed rate</td>
<td>34 kg/h</td>
</tr>
</tbody>
</table>

The initial material is in the form of powder as shown in Figure 3.1 having particle size ranging from 40 to 80μm.

Figure 3.1. Alumina-zirconia powder
Before spraying the coating, the substrates are grit blasted and a thin layer of aluminum is arc sprayed; after spraying the samples were polished. Figure 3.2 shows a photo of as received samples. The samples are placed in a plastic mount to facilitate handling.

Figure 3.2. Photo of sample

SEM image of plasma-sprayed AZ-40 coatings is shown in Figure 3.3. The surface is characterized by high density of defects due to the plasma spray process itself, e.g. partially melted regions (c.f. Figure 3.3b), pores (c.f. Figure 3.3c), cracks (c.f. Figure 3.3d) and surface craters (c.f. Figure 3.3d). This is consistent with the observations made in previous studies on plasma sprayed ceramics [3, 25, 31]. In plasma spraying, materials in the form of powder are melted and propelled against the surface of the substrate forming splats [3]. Rapid solidification of individual splats creates cracks and large pores between splats. Fragmentation of molten droplets at impact creates cracks within splats and surface craters. In addition, molten material entraps gases and inclusions during plasma spraying process. Some particles do not melt completely causing formation of partially melted regions on surface of the coating [2, 3, 31, 78, 79]. Figure 3.3 also shows white regions rich in zirconia at the surface of the coating (c.f. Figure 3.3a), which will be shown later in the displayed
results. This segregation of zirconia is attributed to low solid solubility of alumina and zirconia [28].

Figure 3.3. SEM images of as sprayed alumina-40% zirconia coatings

5.1. Excimer laser heat treatment

Thermal treatment of AZ-40 coatings is performed using Lambda Physik Compex 205 system shown in Figure 3.4. The specifications of the laser are displayed in Table 3.2. A schematic drawing of the system is shown in Figure 3.5 illustrating the arrangement of different components of the laser system. The system is composed of (1) a manual attenuator, (2) beam focusing through telescope located after the attenuator between mirrors M1 and M2 in Figure 3.4 and consists of two cylindrical
lenses and one spherical lens to conserve the long axis of the beam and to expand the short axis, (3) mirrors M1 and M2 are used to guide the beam, (4) homogenizer consisting of two sets of arrays of cylinder lenses and a condenser lens, a field lens and mask holder, (5) a field lens in front of mask holder, and (6) a doublett projection lens composed of two spherical lenses, (7) a chamber containing sample holder. As shown in Figure 3.4 the optical elements are mounted on an aluminum (BOSCH) frame structure and arranged on an optical table. The laser uses krypton fluoride (KrF) as lasing medium and generates a beam characterized by a wavelength of 248nm, a bandwidth of 300pm, and a pulse duration of 24ns. The output beam has a rectangular cross-section of $0.6 \times 2.4 \text{cm}^2$, and a Gaussian distribution in vertical and horizontal directions. The beam is then directed in a guiding system where the pulse is reshaped into a square of $1.6 \times 1.6 \text{cm}^2$ with homogenized beam intensity in the transverse direction, and then it passes via a magnifying lens to reduce the spot size on the target to $0.48 \times 0.48 \text{cm}^2$. At early stages of this work laser parameters were subjected to trial and error due to lack of background information about effect of different excimer laser parameters on AZ-40. The energy density was varied from 200mJ/cm$^2$ to 800mJ/cm$^2$, the number of pulses was changed from 300 to 3000 pulses, and frequencies of 10 and 50Hz were used. The laser treatment was conducted under vacuum to avoid oxidation or contamination of samples. After several trials, a detailed parametric study was performed to investigate the effects of different parameters such as laser energy density (fluence), pulse repetition rate (PRR), and number of pulses on the mechanical properties, surface morphology, and microstructure of the coatings. Based on the results of first set of experiments, focus is given on energies of 200mJ/cm$^2$, 400mJ/cm$^2$ and 800mJ/cm$^2$, frequencies of 10Hz and 50Hz and from 1000 to 3000 pulses.
Figure 3.4. *Lambda Physik Compex 205 excimer laser system*

- A. Laser Chamber and computer controlled stage
- B. Attenuator
- C. Homogenizer lenses
- D. Mask holder on the right hand side followed by double projection lens
- E. Energy controller
- F. Laser controller
Table 3.2: Specifications of Lambda Physik Compex 205 system

<table>
<thead>
<tr>
<th>Laser source</th>
<th>Krypton Florid (KrF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>248nm</td>
</tr>
<tr>
<td>Maximum pulse energy</td>
<td>700mJ</td>
</tr>
<tr>
<td>Average Power</td>
<td>30W</td>
</tr>
<tr>
<td>Maximum Pulse Repetition Rate</td>
<td>50Hz</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>24ns</td>
</tr>
<tr>
<td>Beam Dimensions (VxH)</td>
<td>24x10mm$^2$</td>
</tr>
<tr>
<td>Beam Divergence(VxH)</td>
<td>3x1 mrad$^2$</td>
</tr>
<tr>
<td>Dimensions (LxWxH)</td>
<td>1682x375x793 (mm$^3$)</td>
</tr>
<tr>
<td>Water cooling</td>
<td>2 to 3L/min, 15 to 20C, only for&gt;20Hz</td>
</tr>
</tbody>
</table>
3.2. Characterization and testing techniques

To investigate the effect of laser treatment on properties of the coating, the morphology and microstructure, mechanical and chemical properties of the coatings are studied. The surface structure of the treated coating is examined by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). The mechanical properties are determined by micro-hardness and nanoindentation testing, surface roughness measurements, and percent porosity measurements.

3.2.1. Surface roughness

The surface roughness of treated and untreated samples is measured using Mitutoyo surface roughness tester. A probe traces the surface of the sample then the profile of the surface and the value surface roughness Ra are displayed.

3.2.2. Vickers Micro-hardness testing

The hardness of the surfaces of treated and as sprayed coatings are measured at room temperature using a Mitutoyo MH Series 810-128A, at 300 gf of load and 15 seconds of dwell time. All readings are taken in Vickers Hardness Number (VHN). Three different indentations are made at different sites on each of the samples as and the average is taken as a final result. Not enough samples were provided to repeat conditions on different samples.

The fracture toughness of samples is then computed using Vickers indentation marks. The values of fracture toughness are obtained by using Evans & Charles equations [80] formulated as follows: $K_{IC} = 0.16 (c/a)^{1.5} (H_v a^{1/2})$

Where $K_{IC}$ is the fracture toughness in MPa.m$^{1/2}$, $H_v$ is Vickers hardness in MPa, $c$ the average length of the cracks obtained in the tips of the Vickers marks (in
µm) and \(a\) is Half average length of the diagonal of the Vickers marks (µm). Figure 3.6 indicates \(c\) and \(a\) values on indentation mark.

![Indentation mark](image)

**Figure 3.6. Indentation mark**

### 3.2.3. Nano-Indentation

Nano-Indentation is done using Universal Nanomechanical Tester (UNAT) (Radeberg OT Rossendorf, Germany) using Quasi Continuous Stiffness Measurement (QCSM) module at a maximum force of 100mN. The QCSM module enables measuring the contact stiffness of the sample not only with the help of an unloading curve for one depth, but for many points during the indentation procedure. Thus hardness and indentation modulus can be determined depth-dependent at one and the same position of the sample. A triangular Berkovich indenter is used. The quality of the calibration is checked with fused silica as reference samples. Fused silica has a nominal Young’s modulus of 72GPa and a Poisson’s ratio of 0.17. Fifteen measurements are carried out on each sample on different positions to reduce the measurement error. The distance between adjacent indentations is set to 100µm to avoid the effect of interaction. The test is allowed to start until the thermal drift rate is stabilized below 0.05nm/s. The indentation test begins by loading the indenter into the sample at a constant rate until it reaches the maximum depth of 800nm. The indenter is held for 3 seconds at maximum force. Then the indenter is unloaded at the same
rate to 90% of the indentation load, where it is held for 60 seconds for thermal drift correction. Finally the indenter is fully unloaded out of the sample. The hardness, given in GPa, and the elastic modulus were calculated according to ISO 14577 (modified Oliver & Pharr method) [81].

3.2.4. Surface porosity

The porosity of the as sprayed and laser treated coatings is estimated with quantitative image analysis. Five SEM images of different locations for each sample were analyzed using Image-J software from the National Institute of Health, Bethesda, MD, USA.

3.2.5. X-Ray diffraction

The phase compositions of treated and untreated coatings are determined by X-Ray diffraction using Philips X-pert Pro diffractometer (Cu-Kα radiation, wavelength 1.54 Å). Analysis of the peak intensity and width as a function of the laser energy density or pulse repetition rate can reveal important information about change in the crystallinity of the coatings.

3.2.6. Scanning electron microscopy (SEM)

SEM investigation was essential to study the surface morphology and microstructure of the coating. Hence, the surfaces of the treated and untreated samples are investigated using Field Emission Scanning Electron Microscope (FESEM) analysis using a LEO Supra 55 FESEM. The samples are placed in a high pressure vacuum chamber installed on a damping table and supports allowing high resolutions. The samples are non-conductive so they tend to charge very quickly when scanned by the electron beam causing scanning faults and making it hard to properly visualize the
microstructure at the surface. Hence, the samples are coated prior to imaging with gold to prevent electrostatic charge at the surface.

The SEM is attached to an energy dispersive spectroscope (EDS). The EDS analysis allows identifying the elements present at the surface of the coating and determining their relative proportions.
CHAPTER 4: RESULTS AND DISCUSSION

Laser beam interaction with materials is a very complex process and still not fully understood. The phenomena occurring change depending on the laser beam and material properties. The problem of laser interaction with plasma sprayed coatings presents many difficulties in both modeling and experimental sides. This chapter presents the modeling and experimental results of the excimer laser interaction with the surface of plasma sprayed alumina-40% zirconia (AZ-40) coatings.

4.1. Laser material interaction

As mentioned in previous chapters, plasma sprayed coating is characterized by high density of pores reducing its properties and its uses. This section investigates the possibility of sealing and smoothening the surface of the coating using localized laser pulses. To have an understanding of the heat treatment process, it is useful to start by studying the heat distribution caused by laser pulse across the surface of the coating and study how the defects can influence the temperature profile. This will allow identifying the areas that can be modified by laser treatment.

4.1.1. Important considerations for thermal analysis

There are several parameters that play an important role in laser material interactions and should be taken into consideration during the thermal analysis. The essential consideration is the laser beam shape. The laser used in experimental investigations has a Gaussian distribution. Due to this non-uniform heat intensity distribution a three-dimensional heat transfer is considered. Difference in heat change
on the surface of a sample irradiated with heating source having a continuous input power is also studied.

Another important consideration is the physical and thermal properties of the material including thermal conductivity, thermal diffusivity, absorptivity, etc… (defined in Table 4.1). These material properties have a strong influence on the temporal and spatial evolution of temperature during laser irradiation. The samples produced by plasma spraying are not homogenous; thus temperature change on surface of material with different compositions is studied.

4.1.2. Physics and representation of source terms in the excimer laser annealing process

When laser beam strikes the surface of the material part of the light is reflected due to discontinuity in the real index of refraction and the rest is transmitted into the material [82]. Once inside the material, two distinct heat sources cause temperature change: (1) laser energy, and (2) latent heat of phase change. The change in temperature field inside the material is governed by heat equation derived from the conservation of energy and Fourier's laws of heat conduction. The equation states that the local heat flux is proportional to the negative of the gradient of the temperature and is written as follow [62, 82-84]:

\[ \rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[ k \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial y} \left[ k \frac{\partial T}{\partial y} \right] + \frac{\partial}{\partial z} \left[ k \frac{\partial T}{\partial z} \right] + HS_{laser} + HS_{M/L} \]  

(4.1)

Where \( \rho \) is the density, \( c_p \) is the specific heat, \( k \) is the thermal conductivity, \( T \) is the absolute temperature \( HS_{laser} \) is the source term for the absorbed laser energy and \( HS_{M/L} \) is the source term for the latent heat released and/or absorbed during phase
change. The objective is to calculate $T$ all over the surface. To achieve this aim, the main task of the model is to compute the two heat source terms in equation (4.1) for each time step in the simulated period. The laser radiation has short wavelength and high photon energies so most material absorb the incident radiation in a sub-micron thick surface layer [16]. The laser energy term can be computed by applying Beer-Lambert’s law for energy distribution in the absorbing medium and is expressed as follow:

$$HS_{\text{laser}} = [1 - R(x,t)]I(t)e^{-\alpha x}$$  \hspace{1cm} (4.2)

Equation (4.2) shows that light intensity decays with depth at a rate determined by material absorption coefficient ($\alpha$). $R$ is the reflectivity and $I(t)$ is the time distribution of laser beam intensity [73, 83].

The latent heat term is computed as follow: $HS_{\Delta h} = mL$, where $m$ is mass and $L$ is the latent heat form phase change.

Typically for this type of problem the boundary condition for irradiated area is described as follow [62]:

$$-n(k\nabla T) = q_0 + h(T_{\text{inf}} - T) + \sigma\varepsilon(T_{\text{amb}}^4 - T^4)$$  \hspace{1cm} (4.3)

The first term of the right hand side $q_0$ represents the surface heat flux and was applied to the holes walls and the surface facing the pulse. The second term in the right hand side refers to convective cooling where $h$ is the convective heat transfer coefficient, $T_{\text{inf}}$ is the external temperature and it is applied to the whole irradiated surface. The third term in the right hand side represents the surface to ambient thermal exchange where $\sigma$ is Stefan Boltzmann constant, $\varepsilon$ is emissivity and $T_{\text{amb}}$ is the ambient temperature and is also applied to the whole irradiated surface. As the treatment is conducted under vacuum, all other boundaries are left at insulation.
4.1.3. COMSOL realization

A 3D transient heat conduction model is created in COMSOL Multiphysics 4.2 as a simulation of temperature change in alumina-zirconia irradiated by laser. First, the heat distribution on the surface of plasma sprayed alumina-40% zirconia coatings irradiated by KrF beam having a wavelength of 248nm and pulsed duration of 24ns is investigated. Then the temperature change on surface of materials with different compositions (pure alumina, pure zirconia, alumina-10% zirconia, and zirconia-10% alumina) is studied. Also temperature change caused by heat source having longer pulse duration and continuous input power is studied.

The most challenging part is to find the properties of plasma sprayed coatings. Most thermally sprayed ceramic coatings inherit high porosity and internal defects. Porosity has a great effect on properties of the coating including thermal conductivity and thermal stress behavior [28, 85]. Another critical factor that affects the properties is the spray process parameters. Few changes in the spraying parameters result into different coating properties [86]. Hence, it is a great challenge to determine value for physical, thermal and electrical properties of the coatings. Properties of alumina and zirconia is found in [55]. The absorption length and reflectivity of alumina and zirconia to pulsed laser radiation having a wavelength of 248nm and pulse duration of 24ns are found in [87] and [88] respectively. The rule of mixture is then used to determine the properties of alumina-zirconia having different compositions. Table 4.1 presents the material properties used for the model. Table 4.2 presents the global expressions used for COMSOL simulations.
Table 4.1: Material properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Alumina</th>
<th>Zirconia</th>
<th>Alumina-10%zirconia</th>
<th>Alumina-40%zirconia</th>
<th>Zirconia-10%alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperatures Tm (K)</td>
<td>2320</td>
<td>2963</td>
<td>2273</td>
<td>2133</td>
<td>2500</td>
</tr>
<tr>
<td>Molar mass (g/mol)</td>
<td>101.961</td>
<td>123.219</td>
<td>225.18</td>
<td>225.18</td>
<td>225.18</td>
</tr>
<tr>
<td>Density of solid rhoS (kg/m³)</td>
<td>3970</td>
<td>5560</td>
<td>4129</td>
<td>4924</td>
<td>5401</td>
</tr>
<tr>
<td>Density of liquid rhoL(kg/m³)</td>
<td>3294</td>
<td>4840</td>
<td>3448</td>
<td>3912.4</td>
<td>4685.4</td>
</tr>
<tr>
<td>Thermal conductivity of solid kthS (W/m.K)</td>
<td>30</td>
<td>0.69</td>
<td>27.069</td>
<td>18.276</td>
<td>3.621</td>
</tr>
<tr>
<td>Thermal conductivity of liquid (W/m.K)</td>
<td>5.86</td>
<td>60</td>
<td>11.274</td>
<td>27.516</td>
<td>54.6</td>
</tr>
<tr>
<td>Specific capacity of solid kthL (J/kg.K)</td>
<td>775</td>
<td>400</td>
<td>737.5</td>
<td>625</td>
<td>437.5</td>
</tr>
<tr>
<td>Specific capacity of liquid (J/kg.K)</td>
<td>1308.375</td>
<td>600.6</td>
<td>1237.6</td>
<td>1025.265</td>
<td>671.4</td>
</tr>
<tr>
<td>Reflectivity R</td>
<td>0.65</td>
<td>0.47</td>
<td>0.632</td>
<td>0.578</td>
<td>0.488</td>
</tr>
<tr>
<td>Latent heat of fusion L (J/g)</td>
<td>1067.4</td>
<td>706.06</td>
<td>1031.266</td>
<td>922.864</td>
<td>742.194</td>
</tr>
<tr>
<td>Absorption length da (m)</td>
<td>27x10⁻⁶</td>
<td>8.41x10⁻⁸</td>
<td>2.43x10⁻³</td>
<td>1.96x10⁻³</td>
<td>2.7x10⁻⁶</td>
</tr>
</tbody>
</table>
Table 4.2: Global expressions used in COMSOL Multiphysics simulation

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
<th>Expression [unit]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Heat transfer coefficient</td>
<td>$10 \ [W/m^2\cdot K]$</td>
</tr>
<tr>
<td>S</td>
<td>Laser area</td>
<td>$0.5 \times 0.5 \ [cm^2]$</td>
</tr>
<tr>
<td>Pin</td>
<td>Gaussian input Power</td>
<td>$E/(\tau)<em>exp(-4(t-\tau)</em>(t-\tau)/(\tau*\tau)) \ [W/m^2]$</td>
</tr>
<tr>
<td>Pin2</td>
<td>Gate input Power</td>
<td>$E/(S*\tau)<em>((t&lt;=\tau)</em>(t&gt;=0)) \ [W/m^2]$</td>
</tr>
<tr>
<td>HS1</td>
<td>Laser heat source</td>
<td>$(Pin*(1-R)/(da)*exp(z/da)) \ [W/m^2]$</td>
</tr>
<tr>
<td>HS2</td>
<td>Heat source from latent heat</td>
<td>$((Hm<em>rhoL/\tau)</em>(T&gt;=Tm)) \ [W/m^2]$</td>
</tr>
<tr>
<td>HS</td>
<td>Total heat source</td>
<td>$((HS1-HS2)<em>(HS1&gt;=HS2))</em>(z&lt;=0) \ [W/m^2]$</td>
</tr>
<tr>
<td>Kth</td>
<td>Thermal conductivity</td>
<td>$kthS*(T&lt;Tm)+kthL*(T&gt;=Tm) \ [W/(m*K)]$</td>
</tr>
<tr>
<td>Rho</td>
<td>Density</td>
<td>$rhoS*(T&lt;Tm)+rhoL*(T&gt;=Tm) \ [kg/m^3]$</td>
</tr>
<tr>
<td>Cpp</td>
<td>Specific heat capacity</td>
<td>$CpS*(T&lt;Tm)+CpL*(T&gt;=Tm) \ [J/(kg*K)]$</td>
</tr>
</tbody>
</table>

For the thermal 3D model heat transfer mode and Time dependent analysis in Conduction type of heat is chosen to solve the heat conduction equations previously presented. The sample geometry is simplified to a square with dimensions of $500 \times 500 \mu m^2$ and thickness of $20 \mu m$ as shown in Figure 4.1. Only $20 \mu m$ of the sample are considered as from the literature laser only acts on the first few microns of the samples [25, 70, 71, 76, 77].

![Sample geometry](image)

**Figure 4.1. Sample geometry**

Figure 4.2 presents an SEM image of the as sprayed sample and the schematic view of the sample drawn on COMSOL. From the SEM image shown in Figure 4.2a, the pores are considered to have a cylindrical shape of circular cross-section as...
illustrated in Figure 4.2b. The surface of the sample is drawn with pores of diameters ranging from 1 to 50 µm. From the surface profile shown in Figure 4.3 the depth of the pores is chosen to vary from few nanometers to 10 µm.

Figure 4.2. (a) SEM image of as sprayed AZ-40 coating, (b) geometry drawn on COMSOL

Figure 4.3. Surface profile of as sprayed coating

As mentioned previously, there are variables and constants necessary for modeling laser pulses that are presented in Table 4.1. The mesh elements have maximal size of 100 nm.
4.1.3.1. Simulation results

Analysis is first done at pt1 shown in Figure 4.2b. Pt 1 is at the edge of a hole. Figure 4.4 shows the Gaussian shape of the heat source distributed in time at different laser fluence. For laser fluences lower than 100mJ/cm² the execution time of the simulations is few minutes while for higher laser fluences the melting process increases to hours.

![Figure 4.4. Gaussian shape of the time distribution of the incident heat source at pt 1](image)

Figure 4.5 demonstrates the returned results concerning surface temperature versus time at pt1 at different laser fluences. Figure 4.5 reveals that as laser energy increases the surface temperature also increases. In fact, at 80mJ/cm² the sample is not melted this is consistent with experimental results, as it will be shown later. At 400mJ/cm² the sample melts for a very small period of time (around 100ns) the energy is just enough to initiate thermal stresses inside the material, which allows initiation and propagation of cracks. At higher laser energies the material melts for a longer period of time, which could be enough to seal some holes.
Figure 4.5. Point temperature versus time at pt1 (a) shows time required to reach room temperature and (b) shows melt phase duration.
In spite of the fact that the laser pulse is only 24 ns, the temperature fades on the sample on a longer time span. This is consistent with observations made in previous studies done by Darif et al. [84] and Sedky et al. [18, 73] on silicon films. Figure 4.6 reveals that at 400mJ/cm^2 the maximum power occurs at 24ns, while the maximum temperature is at 40ns. Figure 4.5b also shows that at energies higher than 640mJ/cm^2, the temperature reaches room temperature after 0.08ms. Experimental results show that multiple pulses are required to produce significant surface change that might allow sealing of holes. The time span required between successive pulses should be long enough to guarantee that the surface cools down to room temperature before application of another pulse [73]. From the previous results it is clear that the surface reaches room temperature after 0.08ms. Hence, a pulse rate of 50Hz or lower is enough to melt areas near the pores.

![Figure 4.6. Point temperature and power versus time at 80mJ/cm^2 at pt1](image)

The results of the simulation also show that the temperature around the hole is higher (shown in blue in Figure 4.7) than that of continuous surface exposed to the pulse (shown in blue in Figure 4.7). In fact, temperature distribution with time at Pt2
is shown in Figure 4.8. Pt2 is present on a continuous surface at the middle between two holes having a diameter of 40µm, depth of 5µm and separated by 50µm (c.f. Figure 4.2b). It is clear from Figure 4.7 that temperature at Pt1 (around at edge of hole) is higher than that at Pt2 (on continuous surface). This agrees with the work of Sedky et al. [73] dealing with application of pulsed laser for sealing of holes in silicon.

![Temperature distribution across the surface of sample at different locations irradiated with 200mJ/cm²](image)

**Figure 4.7.** Temperature distribution across the surface of sample at different locations irradiated with 200mJ/cm²

Figure 4.8 shows the temperature at Pt2 after irradiating the surface of AZ-40 with different laser energies.
Figure 4.8. *Point temperature versus time at pt2 at different laser energies*

Figure 4.9a reveals that the surface of plasma sprayed coating contains surface 'craters' indicated by arrows on the figure. This type of defects is formed due to the impact of droplets of molten material during plasma spraying [2, 3, 31, 78, 79]. In as sprayed coatings the 'craters' are light grey in color and have sharp edges. In Figure 4.9a their sizes vary from 4µm to 16µm. After irradiating the surface, the 'craters' appear to have a darker color as shown in Figures 4.9b, c and d, which indicate that these areas are highly affected by laser beam compared to the rest of the surface [25]. The surfaces of samples irradiated with densities of 200 and 400mJ/cm² have high density of surface craters. The craters on surface of sample irradiated with 400mJ/cm² (14.5 to 3.5µm) are around two times smaller than the ones present at the surface of the samples irradiated with 200mJ/cm² (7.5 to 1.5µm). As shown in Figure 4.9d, higher laser fluence of 800mJ/cm² decreases the density and size of the craters. It is
clear from Figure 4.9d that at 800mJ/cm² the surface of the sample and the edges of the craters completely melt and most of the craters are sealed except deep ones are still present but are less deep with smaller diameter and smoother edges.

**Figure 4.9.** SEM images of (a) as sprayed coatings and coating irradiated with (b) 200 mJ/cm², 1000P, 10Hz, (c) 400mJ/cm², 1000P, 10Hz and (d) 800 mJ/cm², 1000P, 10Hz

Further analysis is conducted at 80mJ/cm², in order to specify the areas affected by laser. The effect of spacing between holes, holes depth and the holes diameter are investigated.

It is worth mentioning that some approximations are made including that the laser power is constant on the walls of the pores which is not necessarily true as real pores would have different level of steepness and also the laser beam could be out of
focus at deep pores. It would be very challenging to account for such factors; therefore, the temperature values resulted from simulations are not very accurate. The simulations only permit having an understanding about the temperature distribution across the sample.

Figure 4.10 shows the effect of space between holes on the temperature. The holes diameter is fixed to 10µm and holes depth to 5µm. As the space between the holes decreases, heat starts to be more concentrated around the central area of the holes. The increase in the spacing from zero to 5µm is accompanied by 85% increase in the temperature around the holes. This agrees with simulation results reported by Sedky et al. [73]. They also observed that as the number of holes is increased, the heat starts to be more concentrated around the central area of the holes, which they used to seal holes on surface of silicon membranes.

![Temperature distribution for different spacing between holes](image)

**Figure 4.10.** Temperature distribution for different spacing between holes
Figure 4.11 shows the temperature distribution along holes of different depths. The holes diameter is fixed to 10µm and space between holes to 5µm. The results reveal that laser have an effect on the first micron of the sample, which is consistent with previous studies [25, 70, 71, 76, 77]. After 1 µm the temperature dropped by around 30% and varied slightly till the end of the hole where it went back to room temperature. The nano-indentation results presented in section 4.2.9 also shows that laser affected uniformly the first micron of the surface.

![Figure 4.11. Temperature distribution along holes of different depths](image)

Figure 4.12 illustrates the effect of holes diameter on the temperature. The space between holes is fixed to 5µm and holes depth to 5µm. As the hole diameter increases from 1µm to 10µm, the temperature increases by 10%. Further increase in hole diameter above 10µm causes a decrease in temperature at the hole edge. In fact, decreasing the diameter from 10 to 20 results in 20% decrease in temperature. Figure 4.12 also shows that when two neighboring holes are small (<10µm) the temperatures
concentration is higher than if they are large (>20μm). For example, temperature between a hole of 20μm and a hole of 10μm is 20% higher than that between holes of 20μm and 70μm.

![Figure 4.12. Effect of hole diameter on temperature](image)

It can be inferred from the numerical analysis and investigation of surface craters that edges of the pores and craters are the most affected by heat coming from laser beam. The heat concentration increases as the space between the holes and the holes diameter decreases. In other words, areas containing high density of porosity will be more affected by heat than other areas on the sample.
4.1.4. Experimental investigations

Comprehensive parametric studies is carried out to determine the influence of different laser parameters (laser energy, pulse repetition rate and number of pulses) on the surface of the samples and determine the parameters that are sufficient to modify the AZ-40 surface in such a way to seal most of the pores.

Figure 4.13 illustrates the surface of as sprayed AZ-40 coatings and surface of laser treated samples. Figure 4.13a shows the microstructure of the as sprayed AZ-40 contains high density of pores. The porosity area percent of as sprayed coating is measured on six different samples using imageJ software showing an average of around 16.4% as shown in Figure 4.14. The SEM image shown in Figure 4.13b reveals that 200mJ/cm² is not sufficient to melt the surface of the sample, which agrees with the numerical analysis. Further increase in the number of pulses at low energy resulted into crack initiation and propagation. Hence, lower number of pulses and higher energies and pulse repetition rate are used. Figure 4.13c illustrates the surface of irradiated sample at 640mJ/cm². The surface starts to melt due to the elevated temperature associated with the increase in pulse energy. Figure 4.14 shows that the percent porosity decreases by around 40% compared to as sprayed coating (from 16.4% to 9.5%). At 680mJ/cm², 200P and 50Hz the surface melts further as shown in Figure 4.13d. Most of the pores are sealed; yet deep holes are still present on the surfaces. At this condition the percent porosity (Figure 4.14) and surface roughness (Figure 4.15) are the lowest of 4.5% and 0.57μm respectively. Further increase in the energy even at lower PRR is suggested to have resulted into thermal stresses that led to propagation of existing cracks and initiation of new ones. As seen in Figure 4.13e, high laser fluence (and same PRR and number of pulses) caused
formation of cracks. This is mainly due to high pulse frequency (50Hz) at high energies, which might have caused thermal shocks and stresses, while low number of pulses (200P) does not allow enough time for the surface to melt.

Figure 4.13. SEM images of (a) plasma sprayed alumina-40% zirconia coatings and irradiated surfaces at (b) 200mJ/cm², 3000P and 10Hz, (c) 640mJ/cm², 300P and 50Hz, (d) 680mJ/cm², 200P and 50Hz, (e) 720mJ/cm², 200P and 50Hz, (f) 800mJ/cm², 200P and 50Hz
In addition to surface roughness and porosity measurements, Vickers micro-hardness measurements are carried out for untreated and treated samples. The results show that highest hardness is obtained after irradiating the surface with 800mJ/cm². Further analysis of morphological and microstructural changes at high laser fluence is displayed in section 4.2.
4.1.5. Influence of different alumina-zirconia compositions

The surface of plasma sprayed alumina-zirconia coating is not homogenous as shown in chapter 3. Simulation of temperature change in alumina-zirconia having different compositions is studied. The properties of materials used for the model are presented in Table 4.2 and Table 4.2 presents the global expressions used for COMSOL simulations.

Figure 4.16 shows temperature distribution across surface of material having different compositions irradiated by KrF beam (248nm and 24ns) with energy of 200mJ/cm² obtained from simulations.

Simulation results show that alumina is more affected by laser beam than zirconia, which also observed experimentally. Figure 4.17, shows that zirconia does not melt, while areas containing more alumina melts after irradiating with low laser
energy. This is attributed to high melting temperature and lower thermal conductivity of zirconia compared to alumina [28, 51]. Temperature reached after irradiation with laser beam is not enough to melt the surface rather very thin layer is etched. Further analysis of these regions is presented in section 4.2.

**Figure 4.17.** (a) SEM image of the surface of alumina-40% zirconia irradiated with 200mJ/cm², 200P and 50Hz and composition identified by EDS in (b and c)
4.1.6. Influence of different power input and pulse duration

The model is also used to predict temperature change caused by heat source having longer pulse duration of 60ns. Figure 4.18 shows the power distribution having pulse duration of 60ns.

![Power input having pulse duration of 60ns](image)

Figure 4.18. Power input having pulse duration of 60ns

Figure 4.19 compares the temperature change on surface of sample irradiated by laser having pulse duration of 24ns and 60ns. Simulation results indicate that at small pulse duration temperature reaches maximum at short period of time than with longer pulse duration.

![Comparison of temperature change caused by heat source having different pulse duration](image)

Figure 4.19. Comparison of temperature change caused by heat source having different pulse duration
In some studies it is argued that laser having continuous input power could have higher effect on surface of coatings [84]. Gate power input equation is inserted in the model (as shown in Table 4.2.) to predict the temperature change on surface of material irradiated with laser power having continuous input power. Shape of gate input power with pulse duration of 100ms is illustrated in Figure 4.20. The laser energy used was also 200mJ/cm². The returned results shown in Figure 4.21 indicate that in the case of gate shape melting occurred at lower energy than in case of Gaussian shape. This is consistent with results obtained by Darif et al. [84]. In other words, laser having continuous power input could have lower threshold energies than pulsed laser beams and could penetrate deeper in the coating. This could be beneficial for some applications requiring sealing of pores throughout the whole thickness of the coating. Yet, the objective of this study was to seal a thin layer of the coating and study the pulsed laser-material interaction. Further analysis is presented in section 4.2.

Figure 4.20. Gate input power
4.2. Surface morphology and structure modification of coating induced by laser radiation

It can be deduced from the previous discussion that laser excimer laser irradiation allows melting and sealing of pores and other defects initially present on the surface of as sprayed coatings. While observing the surface of the treated samples, it is noted that the surface morphology drastically changes by irradiating the surface of the coating with different laser parameters. At this point it is essential to evaluate the effect of different laser parameters on the surface of the coating. This section presents the results of a detailed parametric study that is carried out to investigate the effects of different parameters including laser energy density (fluence), pulse repetition rate (PRR), and number of pulses on the microstructure, surface morphology, and mechanical properties of the coatings.
4.2.1. Properties of as sprayed coatings

Figure 4.22a shows the morphology of as sprayed AZ-40 coatings. As explained and illustrated in chapter 3 the surface is characterized by high density of defects e.g. partially melted regions, pores, cracks and surface craters. EDS results shown in Figure 4.22b reveal that the coating is mainly formed of alumina-40% zirconia. Previous studies on alumina and zirconia show that they have very low solid solubility of less than 2% [28]. However, during thermal spraying alumina and zirconia powders are subjected to very high temperatures in the plasma jet ranging from 3000 to 10,000°C. Such high temperatures result into the formation of crystalline solid solution, amorphous structures and metastable structures as explained by Tarasi et al. [28].

The XRD profiles of the as sprayed as well as laser treated coatings are illustrated in Figure 4.23. XRD patterns indicate that the AZ-40 has crystalline structures consisting mainly of tetragonal zirconia and alpha alumina. The tetragonal zirconia has stronger peak intensity than alumina. Irradiating AZ-40 coatings with
800mJ/cm², 1000P, and 50Hz lead to an increase in diffraction peaks intensity of zirconia and alumina. The XRD patterns also show some amorphous phases. The formation of amorphous structure during plasma spraying is attributed to the high cooling rate [50, 51, 89, 90]. XRD of laser treated coating also show broadening of tetragonal zirconia indicating reduction of crystal size. Also monoclinic tetragonal peaks appear after laser treatment, which is illustrated and discussed later.

**Figure 4.23.** XRD patterns for the as sprayed and laser treated alumina-40% zirconia coatings

4.2.2. Effect of laser energy density (Fluence)

The effect of pulse energy is investigated by following a gradual increase in the laser energy and inspecting its impact on the surface of plasma sprayed AZ-40 coatings. Figure 4.24a shows that the surface of AZ-40 plasma sprayed coating
irradiated at 200mJ/cm² is smoother compared to the as sprayed coating (Figure 4.22). The surface contains relatively less defects (pores and cracks) than the untreated coating, and white regions shows zirconia segregation. Coatings irradiated with 200mJ/cm² are mostly composed of solid solution alumina-40%zirconia as shown in Figure 4.24 similar to the untreated coatings. However, at higher magnification (Figure 4.24b and c) a feature (identified by square in Figure 4.24b), which is not observed on the surface of as sprayed samples, is identified after laser treatment at low fluence. These features are composed of white and dark regions as observed in Figures 4.24. They are partially melted regions usually seen in plasma spraying and in these regions alumina and zirconia kept their crystallinity. Figure 4.25 is an SEM image of treated AZ-40 coating with 200mJ/cm², 300P and 50Hz. The EDS analysis shown in Figure 4.25b indicates that dark regions are rich in alumina. EDS results displayed in Figures 4.26 and 4.27 demonstrate that white regions are rich in zirconia. Hence, the feature marked in Figure 4.24b and c is composed of zirconia embedded into alumina matrix. Once melted together at a very high rate of cooling (10⁶ k/s) during plasma spraying, they crystallize to form this eutectic structure. The advantage of excimer laser treatment at low fluences is that it helps revealing the structures that are initially present but hidden at the surface of as sprayed coatings. In other words, excimer laser is a great tool for etching a very thin (smaller than micron) surface from the coating [26]. This eutectic structure was previously observed by Tarasi et al. as mentioned in chapter 2 while studying in flight particles of air plasma sprayed alumina-zirconia [28]. They had to go through a very long process in order to observe and study this eutectic structure.
Figure 4.24. SEM images of the surface of alumina-40% zirconia irradiated with 200mJ/cm², 1500P and 10Hz (a) at low magnification 120X, (b) at 3KX with EDS analysis and (c) at 10K

Figure 4.25. (a) SEM image of surface of alumina-40% zirconia irradiated with 200mJ/cm², 300P and 50Hz and (b) EDS pattern identifying the composition
Even after irradiating the surface with low number of pulses of 200P, the eutectic structure is still clearly identified as shown in Figure 4.26b and d. The EDS results shown in Figure 4.26e are consistent with SEM observations. EDS reveals that these regions are composed of around 60% alumina and 40% zirconia, which is the eutectic composition of alumina-zirconia composite. Figure 4.26b shows different grains next to each other having this eutectic structure but with different orientations. The boundaries of the eutectic grains show a degree of disorder of the lamellar spacing shown in Figure 4.26d, which is a typical behavior at boundaries. On the other hand, there fully melted regions shown in Figure 4.26c are composed of solid solution alumina-40%zirconia as indicated previously.

Figure 4.26. (a-d) SEM images for the surface of alumina-40% zirconia irradiated with 200mJ/cm², 200P and 50Hz at various regions and (e) EDS for eutectic structure
Figure 4.27 illustrates other areas also showing this eutectic structure at the surface of coating irradiated with 200mJ/cm$^2$, 250pulses, and 50Hz. Figures 4.27a and b show lamellar structure similar to the one shown in Figure 4.26. Figure 4.27c and d show another eutectic structure also observed at the surface of the coating irradiated with 200mJ/cm$^2$, 250pulses, and 50Hz. This structure is finer than the previously shown eutectic areas showing a difference in cooling rate. Also Figure 4.28a and b reveals two eutectic structures present at the surface irradiated with 200mJ/cm$^2$, 300pulses, and 50Hz. This suggests that the observed eutectic structures are formed during plasma spraying and are initially present at the surface of as sprayed coatings. It is suggested that the formation of these eutectic colonies is the result of partially melted regions of zirconia in the AZ-40 as was observed by Tarasi et al. [28] and explained in detailed in section 2.5. The differences observed are due to variations in cooling rate and particle velocity during plasma spraying. The eutectic structure shown in Figures 4.27c and d solidifies at a higher rate than the one displayed in Figures a and b after spraying. Laser irradiation with low laser fluence, of 200mJ/cm$^2$, helps revealing these structures.
Figure 4.27. SEM images at different locations on the surface of alumina-40% zirconia irradiated with 200mJ/cm², 250P and 50Hz

Figure 4.28. Different eutectic structures present at surface of AZ-40 coating irradiated with 200mJ/cm², 300 pulses, and 50Hz

The cooling rate for plasma-sprayed particles approaches 10⁶ K/s and this produces a fine-grained microstructure within the splat. This rapid solidification can produce amorphous and metastable phases in some ceramics [3]. Phase composition and stability of stabilized zirconia coatings have been extensively studied. The phase
structure of stabilized zirconia coatings have been shown to consist of non-equilibrium phases. Irrespective of the starting material, the as-sprayed material was found to contain a non-transformable tetragonal [3]. Figure 4.29a shows that the sample contains areas rich in zirconia. Most of the sample is grey and is smoother than as sprayed coating indicating that it is affected by laser radiation. Additionally, the eutectic structure is observed and just next to it there is a white region. EDS analysis shown in Figures 4.29c and d shows that the white area are rich in zirconia. This region has two different compositions. EDS results show that the edge of this region (light grey) contained relatively higher alumina content than at the center (c.f. Fig 4.29c and d). The edge of this region is characterized by a glassy structure; segments are also formed, which reveal that they were highly affected by excimer laser irradiations (these segmentations will be observed at 800mJ/cm²). However, the center of this region does not melt rather it fractured in a brittle manner. There is also a brittle fracture at the interface of the two regions. These fractures most likely resulted from laser thermal shocks of zirconia rich region that was not melted during the spray. The alumina phase (grey area in Figure 4.27) region clearly presents a phase that is fully melted during irradiation. These areas have different compositions that are not affected similarly by laser radiations as studied in section 4.1.5.
Figure 4.29. SEM images for the surfaces of alumina-40% zirconia irradiated with 200\text{mJ/cm}^2, 200P and 50Hz at (a) low and (b) high magnification and composition identified by EDS in (c and d)

Figure 4.30 shows other areas rich in zirconia, which are observed at different locations on the surface of the sample irradiated with 200\text{mJ/cm}^2, 200P and 50Hz. Figure 4.30a demonstrates the morphology of a white area rich in zirconia. The cracks shown in Figure 4.30b resulted from laser thermal shocks of zirconia and alumina regions. Figure 4.30c reveals another white area rich in zirconia. The center has higher zirconia concentration than the edge. Two main reasons are suggested to be the cause of the fracture observed at the center of the area shown in Figure 4.30c: (1) different thermal expansion coefficient of different areas and most probably (2) phase transformation during solidification resulted into volume expansion hence fracture of the surface. The edge of this region, clearly seen in Figure 4.30d, was darker than the center indicating that it had higher alumina content than the center. At these edges recrystallization of alumina is clearly seen. The different zirconia phases observed are
most likely resulted from temperature difference in areas irradiated with laser as previously explained.

Figure 4.30. SEM images for areas rich in zirconia at different locations on the surface of AZ-40 coating irradiated with 200mJ/ cm², 200P and 50Hz

The results previously displayed and discussed infer that irradiating the surface with low fluence of 200mJ/cm² helps in revealing features initially present at the surface of plasma sprayed coatings. This is one of the main findings of this study. This would facilitate the study of such coatings and prevent researchers from going through long processes in order to examine the structure and properties of the coatings as proposed by Tarasi et al. [28].

The surface of AZ-40 coatings is irradiated with higher fluences to examine the effect of laser energy on the surface of the coatings. Figure 4.31 indicates that a
higher laser fluence of 400mJ/cm² modifies the coating’s morphology. The surface is divided into very fine segments, a typical feature of excimer laser treated surfaces [2,14,23,36]. By comparing 200mJ/cm² presented in Figure 4.26a and 400mJ/cm² shown in Figure 4.31, it is clear that defects (cracks and pores) disappear and protrusions (indicated by arrows in Figure 4.31a) appear at the surface of the coating. These protrusions are columnar grains growing perpendicular to the surface. They do not form at 200mJ/cm² even after increasing the number of pulses to 3000P (Figure 4.31b).

Figure 4.31. SEM images for the surface of laser treated plasma sprayed alumina-40% zirconia coating at (a) 400mJ/cm², 500P and 50Hz and (b) 200mJ/cm², 3000P and 50Hz

Figure 4.32 shows that some protrusions are formed of eutectic columnar grains growing perpendicular to the surface. Energy of 400mJ/cm² was sufficient to allow the dark alumina and white zirconia grains to grow vertically and form columnar grains.
Figure 4.32. SEM image of the surface of laser treated plasma sprayed alumina-40% zirconia coating at 400mJ/cm², 2000P and 10Hz at (a) low and (b) high magnifications

The laser energy is further increased to 800mJ/cm². By comparing laser treated surfaces at 800mJ/cm² and 200mJ/cm² in Figure 4.33, it is clear that at 800mJ/cm² the surface drastically changed. As shown in Figure 4.33b, at 800mJ/cm² the surface is divided into clear segments, typical surface morphology of excimer laser treated surface. The segments are not formed at 200mJ/cm², and at 800mJ/cm² they are more pronounced than in case of 400mJ/cm², which is clear by comparing Figure 4.26a, 4.33a and 4.33b. At 800mJ/cm², the melted layer exhibits a smooth and glassy morphology with shiny appearance indicating the presence of solid solution (Figure 4.33c). Additionally, crystalline white areas are present all over the surface (Figure 4.33d). The white color of these regions indicates that they are rich in zirconia. At these locations the morphology of the surface completely change, which indicates a fundamental change in structure and chemistry at these areas.

Comparing the surface morphology of treated samples at 400mJ/cm² (Fig 4.32b) excimer laser and ones treated with 800mJ/cm² (Figure 4.33d), it is clear that the columnar grains identified before disappear, and crystalline white areas appear instead.
Figure 4.33. SEM image of the surface of laser treated plasma sprayed alumina-40% zirconia coating at (a) 200 mJ/cm², 1500 shots, 10 Hz, and (b, c, d) 800 mJ/cm², 1000 shots, 10 Hz

4.2.3. Formation and Growth of Al₂O₃ – ZrO₂ Eutectic Colonies

Eutectic microstructures are of great interest because of their composite nature, microstructural stability, and their anisotropic properties [91]. Extensive research is done on directional solidification of eutectics. Directional solidification of eutectics has been applied to high temperature engine components like gas turbine blades, materials for aviation and space, and other structural materials, where control of the eutectic microstructure is of utmost importance [91]. Directionally solidified eutectic bulk ceramic materials are usually prepared by specialized methods where solidification is forced in a certain direction and cooling rate is controlled [92]. Directionally solidified alumina-zirconia eutectic ceramics show good retention of mechanical properties at high temperatures. It also presents high stability and good
oxidation and corrosion resistance making it intensively studied by many researchers over the last decade [93].

Eutectic system is a uniform microstructure that can act to enhance various anisotropic properties. This fine microstructure might limit the size of the initial flaws and that the uniformity of the structure could act to blunt crack propagation through the medium [91]. As a crack travels through the ceramic, it continuously encounters other phases in the solidified eutectic ceramic. As it meets a new phase the crack may be deflected along the phase boundary. This increases crack length, which increases the fracture toughness of the ceramic [74]. Eutectic structures are also much finer than other microstructures, and finer structures can allow enhancement of mechanical properties.

Eutectic structures form from a coupled growth of two phases from a liquid state. For a particular system at equilibrium, eutectics form at one specific composition and temperature. However, non-equilibrium systems the eutectic microstructure can form under many different conditions. In these real systems, a range of experimental conditions exists where the eutectic can form, and the growth of the eutectic becomes dependent upon undercooling [94]. The range in which the eutectic forms is called the "coupled zone". This zone can either take a regular symmetrical shape below the eutectic point, or it may be skewed to one side of the phase diagram.

As demonstrated in previous section, eutectic systems are observed at the surface of coatings irradiated with 200mJ/cm². Within a eutectic system, it is possible for the two phases to demonstrate different behavior. Faceted systems are seen in Figure 4.34. It is suggested that the observed faceted eutectic systems are formed during plasma spraying and are initially present at the surface of as sprayed coatings
and laser treatment at low laser fluence helps revealing these structures. Facetted eutectic structure is previously observed by Cicka et al., [92] after directionally solidifying alumina-zirconia eutectic composition by Stepanov (EFG) method at high growth rates. They reported that at high cooling rates Al₂O₃ phase tends to facet the crystallization front and facet colonies are formed. In other words, regions showing these faceted eutectic structures solidify at higher cooling rates than the rest of the sample.

The eutectic systems as shown in Figure 4.35 are composed of several grains each having the eutectic structure and separated by disordered boundaries. The eutectic structures observed in Figure 4.35 have different microstructures. Some areas seem to have lamellar structure and Chinese script microstructures, while other areas seem to have rod like structures. These are all commonly observed microstructures of alumina-zirconia system. Other studies observed formation of different microstructure more commonly lamellar, rod, and Chinese script in the material having the eutectic microstructure. Previous research on directional solidification reported these differences in eutectic structures could be formed due to change in percent composition as well as change in cooling rates [51, 92, 93, 95]. According to Hunt et al. [96] rod like structure is formed if the volume fraction of zirconia is below 32%,
while lamellar structure is formed when the volume fraction of zirconia is above 32%.

However, EDS analysis at these different eutectic microstructures indicated that they had similar compositions as shown in Figure 4.35. It is suggested that these difference in eutectic structures is due to difference in cooling rate during plasma spraying, which is previously observed in previous studies.

![Figure 4.35. Eutectic systems: (a) lamellar and Chinese script and (c) rod-like structure](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>Zr</td>
<td><strong>40.977</strong></td>
<td>wt.%</td>
</tr>
<tr>
<td>Al</td>
<td><strong>59.023</strong></td>
<td>wt.%</td>
</tr>
<tr>
<td>100</td>
<td></td>
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</tbody>
</table>

Eutectic two-phase cells most commonly known as eutectic colonies are also frequently observed during the solidification of alloys when the composition is close to a binary eutectic. Colony formation is generated on two steps both solid phases...
reject an impurity into intercolony space where it diffuses in the liquid and then these intercolony spaces solidify [97].

Colonies, or cells, are groupings of collective eutectic microstructural growth regions within a solidifying material. A colony may contain a fine eutectic microstructure, but this structure may not be in conjunction with the neighboring microstructures. In fact, the colonies tend to have curved interfaces, which butt up against one another causing boundary problems [92, 97].

Figure 4.36 shows the formation of eutectic colonies at the surface of coatings irradiated with 800mJ/cm². These eutectic colonies have an average size of 60µm. Such colonies are not observed at the surface of untreated coatings Figure 4.36. It is suggested that the formation of these eutectic colonies is the result of partially melted regions of zirconia in the AZ-40 that starts to melt after laser treatment with sufficiently high laser fluence.

![Figure 4.36](image)

**Figure 4.36. SEM image of untreated coatings and coatings irradiated with 800mJ/cm² showing eutectic colonies**

Figure 4.37 shows that the white colonies observed at the surface of coating irradiated with 800mJ/cm² are composed of dark regions having the eutectic structure
embedded within a pool of white areas. EDS results displayed in Figures 4.37g and h reveal that the white regions are rich in zirconia while the darker regions are richer in alumina and have the eutectic composition. Figure 4.37e demonstrates that the eutectic structure is composed of lamellae having thickness in the nanoscale. SEM images show that the eutectic structure formed is very fine with around 70nm zirconia and 140nm alumina lamella. Tarasi et al. [28] reported that Moreno et al. was studying rapid solidification of alumina-zirconia on copper substrate and found that eutectic lamellae sizes of 50nm for zirconia and 100nm for alumina is formed at a cooling rate of 10K/s. Tarasi et al. also observed eutectic structure while studying plasma sprayed alumina-zirconia in flight particles and used the results of Moreno et al. to roughly estimate the cooling rate of the particles. Comparing the lamellae sizes shown in Figure 4.37e to the ones produced by Moreno et al. and Tarasi et al. and interpolating linearly, the cooling rate for the present sample can roughly be estimated as $2 \times 10^3$ K/s [28]. The cracks observed in Figure 4.37f are due to phase transformation from tetragonal zirconia to monoclinic zirconia causing a volume change as previously discussed in Chapter 2. They could also be a result of different thermal coefficient of expansion of the different regions. It is also important to note that cracks do not propagate through eutectic grains. In other words, the eutectic structures acted as crack arrestors.
Figure 4.37. (a-f) SEM images of eutectic colonies and composition identified by EDS in (g and h)
4.2.4. Effect of laser frequency (Hz)

The effect of laser frequency is determined by fixing the laser energy and number of pulses and gradually varying the frequency and examining the surface of the samples. Figure 4.38 shows the surface morphologies of AZ-40 coatings treated at 400mJ/cm² with two different pulse repetition rates of 10 and 50Hz. The two surfaces are melted and have similar surface morphology. Increasing the frequency from 10Hz to 50Hz resulted in enlarging surface ‘craters’. Comparing the diameter of the surface craters in Figure 4.38a to those observed in Figure 4.38b demonstrates that the surface craters at 50Hz are about three times larger than that at 10Hz. Figure 4.38 also reveals that surface treatment of 50Hz produced smoother surfaces than ones treated at 10Hz.

![Figure 4.38](image)

*Figure 4.38. SEM images of the surface of laser treated plasma sprayed alumina-40% zirconia coating at (a, b) 400mJ/cm², 1000P and 10Hz, (c, d) 200mJ/cm², 1000P and 50Hz*

Figure 4.39 compares the surfaces of AZ-40 coating treated at 800mJ/cm², 1000P and 10 Hz, and 50 Hz. Both are characterized by segmentations, a typical feature of excimer laser annealing reported in previous studies [25]. The surface of sample treated at 10 Hz was glassy, smooth and also self-organized cluster cracks are formed in addition to segments as shown in Figure 4.39c. At 50 Hz small ‘dome-like’
structures grow all over the treated surface (Figure 4.39d), which are not present at 10 Hz. The surface has been completely melted and re-solidified to form ‘dome-like’ columnar grains causing an increase in surface hardness. The formation of dome-like after irradiating the surface with excimer laser treatment was previously reported. Ibrahim et al. [25] observed these dome-like structure after irradiating the surface of alumina-13% titania coatings with high excimer laser energies of 800mJ/cm$^2$, which causes an increase in surface hardness. Also Thomas et al. [74] observed that excimer laser (having wavelength of 193nm and 248nm) could be used to create irregular microscopic structure on the surface of polymers and ceramic materials. They observed the formation of conical shapes at the surface of polycarbonate. They also reported formation of dome-like structure similar to the ones shown in Figure 4.39 at the surface of alumina. They showed that these irregular structures could improve the surface friction and physical properties of the material.
4.2.5. Effect of number of pulses

Figure 4.40 shows the influence of increasing the number of pulses from 1500P to 3000P at 200mJ/cm². It is clear that increasing the number of pulses up to 3000P is not enough to melt the surface and does not cause significant change in the surface morphology.
Figure 4.40. SEM image of the surface of laser treated plasma sprayed alumina-40% zirconia coating at (a) 200mJ/cm², 1500P and 10Hz, (b) 200mJ/cm², 3000P and 10Hz

Figure 4.41a shows that at 400mJ/cm², 1000P and 10Hz 'protrusions' (shown by arrows on Figure 4.41a). It is suggested that these 'protrusions' are partially melted regions created during plasma spraying and heat from laser irradiation allow vertical growth of these regions. However, at 2000 pulses (Figure 4.41b) these protrusions are flattened out unlike at 1000 pulses. High number of pulses does not allow vertical growth of grains. Also, at 2000 pulses the surface melts more than at 1000 pulses; in fact, the segmentation of the surface is less pronounced.

Figure 4.41. SEM image of the surface of laser treated plasma sprayed alumina-40% zirconia at (a) 400mJ/cm², 1000P and 10Hz and (b) 400mJ/cm², 2000P and 10Hz
At 400mJ/cm² and 50Hz increasing the number of pulses from 500 to 1000 pulses does not allow protrusion to grow vertically and also crack density decreases because the surface melts more as illustrated in Figure 4.42.

Figure 4.42. SEM image of the surface of laser treated plasma sprayed alumina-40% zirconia at (a) 400mJ/cm², 500P and 50Hz and (b) 400mJ/cm², 1000P and 50Hz

At 800mJ/cm² eutectic colonies appear at the surface of the coating as mentioned previously. Comparing surface treated with 500 pulses to the one treated with 1000 pulses shows that increasing the number of pulses increases density of these colonies (comparing Figure 4.43a and 4.43b). Also, at 1000 pulse (Figure 4.43b) the segmentation is much more pronounced than at 500 pulses (Figure 4.43a).

Figure 4.43. SEM image of the surface of laser treated plasma sprayed alumina-40% zirconia at (a) 800mJ/cm², 500P and 50Hz, and (b) 800mJ/cm², 1000P, 50Hz
4.2.6. Effect of laser on the surface hardness and fracture toughness

The micro-hardness ($H_v$) measurements of different samples are summarized in Figure 4.44. Three measurements are taken on each sample and the average was calculated. Figure 4.44 shows some variations in the hardness measurements attributed to the presence of non-uniform composition and defects at the surface of samples as observed in previous sections. Also it is important to note that that the microhardness values obtained in this study partially resulted from the substrate (untreated coating) as the average depth of penetration of the indenter was 2.2 microns, while the thickness of the laser treated layer is in the range of 1 microns.

Figure 4.44 shows the hardness measured of laser treated and untreated AZ-40 coatings. Coatings irradiated at 800mJ/cm$^2$, 1000P and 50Hz display the highest hardness of 1115$H_v$, corresponding to around 15% increase compared to untreated coatings (935$H_v$). The results presented in previous sections suggest that the change in hardness resulted mainly from phase transformation during the laser irradiation. At higher laser energy (800 mJ/cm$^2$) tetragonal zirconia transfer to the harder phase monoclinic zirconia, and some tetragonal alumina transfer to the harder phase alpha-alumina.

The surface hardness of coating irradiated with 200mJ/cm$^2$, 1500P and 10Hz decreased by around 20% compared to untreated coatings. This reduction is attributed to propagation of cracks due to thermal stresses induced by this low laser energy. By comparing samples irradiated at 200mJ/cm$^2$ and 800mJ/cm$^2$ it is clear that laser energy have an effect on surface hardness. Coating irradiated with 800mJ/cm$^2$, 1000P
and 10Hz shows around 33% increase in surface hardness compared to the one treated with 200mJ/cm², 1500P and 10Hz.

Figure 4.44 also reveals that at 200mJ/cm² coatings irradiated with 3000P show around 20% decrease in surface hardness compared to the one treated at 1500P. As mentioned previously increasing the number of pulses led to increase the surface defects (Figure 4.42), which is attributed to the reported decrease in hardness values. At 800mJ/cm² there was an increase of around 7% between surface hardness of samples irradiated with 50Hz and 10Hz.

Figure 4.44. Micro hardness values (Hv) for laser treated and untreated alumina-40% zirconia coatings

The fracture toughness (KIC) measurements of different samples are presented in Figure 4.45. Measurements of a (half the average length of the diagonal of Vickers
marks) and c values (average length of cracks obtained in the tips of Vickers marks) were taken on the three different Vickers indentations and the average values were reported. $K_{IC}$ is then calculated based on Evans & Charles equation as explained in section 3.2.2.

**Figure 4.45. Fracture toughness of laser treated alumina-40% zirconia coatings**

Figure 4.45 indicates that untreated coatings have relatively low fracture toughness of 2.24 MPa.m$^{1/2}$. Irradiating the surface of coating with 200 mJ/cm$^2$ causes a reduction of around 10% in fracture toughness (compared to $K_{IC}$ of surface treated with 200 mJ/cm$^2$, 1500 P, and 10 Hz). This is because irradiating the surface with low energy results into thermal stresses and crack propagation. At low laser fluence further increase in number of pulses induces more cracks, which is associated with further decrease in $K_{IC}$.

At 680 mJ/cm$^2$ the surface starts to melt and porosity decreases (as previously explained in section 4.1.4), which is attributed to the slight increase in surface toughness observed. However, after treating the surface with 680 mJ/cm$^2$ deep pores
are still present at the surface of the coatings, which inhibits significant increase in fracture toughness.

Irradiating the surface with 800mJ/cm² allows an increase in fracture toughness by around 30% compared to untreated coatings. It is suggested that this increase is attributed to formation of eutectic colonies, which are acting as crack arrestors as suggested in Section 4.2.3. At 800mJ/cm², increasing the frequency from 10 to 50 Hz results into slight increase in fracture toughness of around 10%. This is due to formation of dome-like structure and eutectic colonies all over the surface.

4.2.7. Effect of laser on the Surface roughness

Figures 4.46 to 4.52 show the surface roughness measurements carried out before and after laser treatment of plasma sprayed AZ-40 coatings. The average surface roughness Ra of as sprayed coatings is around 1.261. It is also interesting to note that the surface of untreated coating is continuously alternating up and down; it has a 'zigzag' nature as shown in Figure 4.46. This zigzag surface profile was previously reported in other studies [25, 31]

![Figure 4.46. Surface profile of as sprayed alumina-40% zirconia coating](image)
Figures 4.47 to 4.50 illustrate the effect of number of pulses on surface roughness of AZ-40 coatings. Figure 4.47 shows that at 200mJ/cm$^2$ and 10Hz, the number of pulses does not have a significant effect on surface roughness. Even though the number of pulses is doubled from 1500P to 3000P, the surface roughness does not change. Also, the low energy of 200mJ/cm$^2$ is not enough to change the 'zigzag' nature of the as sprayed coating. SEM observations and simulation results indicates that 200mJ/cm$^2$ is not enough to melt the material and allow changes on surface of coatings. High number of pulses produces thermal stresses resulting in an increase in crack density, which is attributed to the slight increase in surface roughness observed.

Figure 4.47. Effect of number of pulses on surface roughness of plasma sprayed alumina-40% zirconia coatings irradiated with 200mJ/cm$^2$ and 10Hz

Figure 4.48 reveals that the average surface roughness Ra of the coatings treated with laser operating conditions of 400mJ/cm$^2$, 10Hz and 1000P is about 1.506μm, whereas for operating conditions of 400mJ/cm$^2$, 10Hz and 2000P is 1.416μm. As mentioned previously, at 400mJ/cm$^2$ and 10Hz protrusions appear at the surface of the coating and by increasing the number of pulses these protrusions flatten out (c.f. Figure 4.41). The peaks of these protrusions are attributed to the 7% increase
in Ra of the coating treated 1000P compared to the one treated at 2000P as shown in Figure 4.48. Yet, the surface profile maintains its 'zigzag' shape. At 400mJ/cm² and 10Hz, increasing the number of pulses does not change the smoothness of the profile curve.

**Figure 4.48. Effect of number of pulses on surface roughness of plasma sprayed alumina-40% zirconia coatings irradiated with 400mJ/cm² and 10Hz**

Figure 4.49 illustrates that Ra of coating treated at 400mJ/cm², 50Hz decreased by 37% (from 1.884μm to 1.183μm) by increasing the number of pulses from 500P to 1000P. By comparing the surface profile of the coatings treated with these two operating conditions, it is clear that at 400mJ/cm² and 50Hz, increasing the number of pulses tends to flatten out the surface profile as it was observed in Figure 4.42.
Figure 4.49. Effect of number of pulses on surface roughness of plasma sprayed alumina-40% zirconia coatings irradiated with 200mJ/cm² and 50Hz

Also, Figure 4.50 indicates that Ra of coatings irradiated at 800mJ/cm², 50Hz and 1000P decreased to 1.114μm compared to one treated at 100P (1.764μm). As demonstrated in earlier section, at 800mJ/cm² eutectic colonies start to grow and increasing the number of pulses inhibits the vertical growth of these colonies (c.f Figure 4.43). This results into the 6% increase in Ra observed in Figure 4.50. More importantly, the zigzag nature of the profile disappears. Figure 4.40 shows that at 800mJ/cm² and 50Hz eutectic colonies appear all over the surface and by increasing the number of pulses the density of these colonies areas increases. This means that increasing the number of pulses gives time to the surface to melt causing elimination of some defects initially present and significant change in the surface morphology. The recrystallization of the surface observed and the change in surface morphology is attributed to modification of the nature of surface profile. The smoothening of the profile curve is also accompanied by an increase in surface hardness and fracture toughness.
Figure 4.50. Effect of number of pulses on surface roughness of plasma sprayed alumina-40% zirconia coatings irradiated with 800mJ/cm² and 50Hz

Figure 4.51a reveals that irradiating the surface of coating with 800mJ/cm², 1000P and 10Hz leads to around 23% increase in Ra compared to untreated coatings. However, Figure 4.51b indicates that treating coatings with 800mJ/cm², 1000P and 50Hz results in around 13% decrease in Ra. Coatings irradiated with 800mJ/cm², 1000P and 10Hz shows around 28% increase in Ra compared to surface treated with 50Hz. A frequency of 10Hz leads to the formation of self-organized cluster cracks and coarse eutectic colonies (c.f. Figure 4.39), which are attributed to the increase in average surface roughness of the coatings treated with 10Hz.

Results also show that the pulse repetition rate has an effect on surface roughness. At 400mJ/cm² Figure 4.38 shows that surface irradiated with 50Hz is smoother and contains less cracks than one treated with 10Hz; therefore, coating irradiated at 400mJ/cm² 1000P and 10Hz shows a 23% increase in surface roughness compared to one treated at 50Hz as illustrated in Figure 4.52. More importantly, at 800mJ/cm² and 1000P the surface profile of the coating demonstrates that at 50Hz the 'zigzag' nature of as sprayed coating is less pronounced than at 10Hz. This is because as shown in Figure 4.39, at 10Hz the eutectic colonies are surrounded by a smooth
and glassy surface that maintains solid solution nature of the initial coating. At 50Hz the surface morphology drastically changed to a granular texture; dome-like structures are observed all over the surface. This change in morphology is accompanied by the modification of surface profile observed.

These results suggest that laser energy followed by the pulse repetition rate and the number of pulses plays a major role in modifying surface roughness of the coating. The lowest surface roughness value was obtained after laser treatment with 680mJ/cm². High laser fluence of 800mJ/cm² also allows for change in the surface profile of the coatings.

**Figure 4.51.** Effect of laser frequency on surface roughness of plasma sprayed alumina-40% zirconia coatings irradiated with (a) 800mJ/cm², 1000P and 10Hz, and (b) 800mJ/cm², 1000P, 50Hz
4.2.8. Effect of laser on the surface porosity

Figures 4.53-4.55 show the estimated surface porosity for laser treated and untreated plasma sprayed coatings using ImageJ software (a public domain, Java-based image processing program developed at the National Institute of Health (NIH), Maryland, USA). Figure 4.53 demonstrates that laser energy has a significant effect on surface porosity. Treating the surfaces of AZ-40 coatings even at low laser energy causes a large decrease in porosity. The average area percentage porosity for untreated coating is 16.4% whereas the percentage porosity of coatings treated with laser operating condition of 200mJ/cm², 1500P and 10Hz is 6.75% corresponding to around 60% reduction (Figure 4.53). Previous results indicate that pores absorb energy at a higher rate than flat surfaces. These results suggest that at 200mJ/cm² most of the energy is absorbed by pores. This energy is used to melt material inside the pores and these molten regions help filling the pores with material transferred from other pores running parallel to the surface (around 0.5 to 1µm underneath the surface). Figure 4.53 clearly reveals that the effect of laser energy on porosity
diminishes as energy increases. Coatings treated at laser operating conditions of 400mJ/cm², 1000P and 10Hz show a decrease in porosity of 34% compared to the ones treated at 200mJ/cm², while there is only a 16% decrease in porosity between 800mJ/cm² and 400mJ/cm². These results suggest that there exist deep pores at the surface that are not sealed even at high laser energy.

At 200mJ/cm² eutectic structure was observed (Figures 4.24 and 4.26) indicating that the eutectic temperature was reached. At 800mJ/cm² the surface morphology drastically changed, a smooth layer is formed and eutectic colonies growing in a pool of zirconia matrix formed (Figure 4.26 shows that white crystalline areas appear all over the surface).

<table>
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<td>400mJ/cm², 1000P, 10Hz</td>
</tr>
<tr>
<td>800mJ/cm², 1000P, 10Hz</td>
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**Figure 4.53. Effect of laser energy on area percentage porosity**

Figure 4.54 illustrates the effect of the number of pulses on the surface porosity. Irradiating the surface with 200mJ/cm², 10Hz and 3000P shows 18% increase in porosity compared to the one treated at 1500P. Also at 400mJ/cm² and 10 Hz increasing the number of pulses from 1000P to 2000P results in a 36% increase in porosity. As demonstrated previously, increasing the number of pulses results in crack
initiation and crack propagation, which is attributed to the increase in porosity. Yet at 800mJ/cm², doubling the number of pulses from 1000P to 2000P causes a minor decrease in porosity. This is because at 800mJ/cm² the surface completely melted and energy supplied by further heating is used for formation of more eutectic colonies (density of white crystal areas increases as shown in Figure 4.34) rather than sealing of pores.

![Figure 4.54. Effect of number of pulses on porosity at 10Hz and at different laser energies](image)

Figure 4.55 shows that at 400mJ/cm² and 1000P increasing the frequency from 10Hz to 50Hz causes a 21% decrease in porosity. This is consistent with what was observed in Figure 4.38. At 50Hz the crack density is lower and surface is smoother than at 10Hz. Figure 4.55 reveals that at 800mJ/cm² increasing the frequency from 10 to 50 Hz causes an increase in porosity. This increase in attributed to granular texture formed all over the surface.
4.2.9. Nano-Indentation

Nano-Indentation results are presented in Figures 4.56 to 4.58. Fifteen measurements are carried out on each sample on different positions to reduce the measurement error. Figure 4.56 shows the load–displacement curves for two alumina-40% zirconia coatings one treated at 200mJ/cm², 200P, 10Hz (AZ-1) and the other one treated at 200mJ/cm², 200P, 50Hz (AZ-2). The load displacement curve is very smooth; there is no indication of dislocation during loading or shear during unloading. This result indicates that the laser treated layer is highly uniform and there is no variation in the structure of the ceramic coating throughout the depth traveled by the nano-indenter. Coating treated with 50Hz shows a slightly stiffer plastic response than the one treated with 10Hz.

Figure 4.55. Effect of pulse repetition rate on porosity at 1000P
Figure 4.57 shows the variations of the indentation hardness with depth. There are no noticeable variations in hardness (except at the starting of the test), which indicates that the microstructure of the depth travelled by the nano-indenter is homogenous. This result confirms that the laser treated layer is highly uniform. Coating treated with 50Hz shows slightly higher hardness than one treated with 10Hz, which is consistent with previous results.

Figure 4.56. *Load displacement curves*
Figure 4.58 shows variations of the elastic modulus with the depth. There are very slight variations in the elastic modulus throughout the depth penetrated by the nano-indenter, which indicates that the laser treated layer is isotropic. Coating treated with 50Hz shows a slightly higher elastic modulus compared to one treated with 10Hz, which is consistent with the results given in Figures 4.56 and 4.57.
The results from the load displacement curves, hardness, and elastic modulus indicate that nano-indenter travels only in a homogenous and isotropic coating. Hence, the thickness of the laser treated layer must be larger than 800nm, which is the total travel of the indenter during the indentation tests. Therefore, this observation validates the simulations results (section 4.1.3.1) indicating that the thickness of the laser treated layer is in the range of 1μm. This is also consistent with previous studies [25, 70, 71, 76, 77].

**Figure 4.58.** *Depth-dependent modulus results at maximum load with error bar*
In this work the effect of KrF excimer laser annealing having a wavelength of 248nm and pulse duration of 24ns on surface of plasma sprayed alumina-40% zirconia coatings was investigated, the main finding are as follow:

- The microstructure of as sprayed coatings was characterized by high density of defects (i.e. pores, cracks and inclusions), partially melted regions and non-homogenous composition.
- 3D transient heat conduction model was created in COMSOL Multiphysics 4.2 in order to investigate the heat distribution in plasma sprayed AZ-40 irradiated by KrF beam. The simulation results and experimental investigations indicated that defects present at the surface of as sprayed coatings absorb more energy from laser than continuous surface exposed to the pulse.
- 680mJ/cm² was found to be the threshold energy to melt the surface of AZ-40 both though numerical and experimental investigation.
- Lowest percent porosity and surface roughness was reached after irradiating the surface with 680mJ/cm², 200P and 50Hz.
- A parametric study was conducted to study the effect of laser parameters on surface of alumina-zirconia coating.
- Irradiating the surface with laser energy of 200mJ/cm² helped revealing the structures initially present but hidden at the surface of sprayed coatings. Eutectic structures (60%Al₂O₃-40% ZrO₂) were clearly observed at the surface of coatings irradiated with 200mJ/cm².
- Increasing the laser energy to 800mJ/cm² caused drastic change in surface...
morphology. The surface completely melted and Al$_2$O$_3$-ZrO$_2$ eutectic colonies having different sizes and shapes nucleated and grew independently

- Increasing the number of pulses resulted into an increase in the density of these colonies. The formation and growth of the eutectic colonies is one of the most important findings of this parametric study. The structure of these colonies may have important technological applications. The surface irradiated at 800mJ/cm$^2$, 1000P and 50Hz exhibited ‘dome-like’ structures all over the surface accompanied by a change in the ‘zigzag’ nature of the surface profile of as sprayed coating and an increase in surface hardness

- Coatings irradiated with 800mJ/cm$^2$ showed highest surface hardness values

- Highest fracture toughness values were also reached after irradiating the surface with 800mJ/cm$^2$

- The results from the Nanoindentation study indicated that the laser treated layer is a fine homogenous and isotropic coating

**Recommendations**

- Study the fine eutectic structure of AZ-40 using high resolution SEM and TEM. Scanning Electron Microscope (SEM) with high resolution is a powerful instrument for imaging of fine structures of materials and coatings

- AFM examination of the laser treatment on the surface morphology of the coatings. Evolution of the surface morphology can be shown from multiple images for the laser treated coatings at different time and with different laser parameters

- Investigate the mechanism of formation of dome-like structure in the AZ-40

- Nano-Indentation assessment of mechanical properties of different eutectic
colonies: rod, lamella and Chinese script

- Comparative analysis of structure and phase composition for laser treated coatings alumina-40% zirconia, alumina-25% zirconia and alumina-10% zirconia
REFERENCES


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