Water Erosion Resistant Surface Treatments

Report for comprehensive exam

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Abstract: **Increasing the efficiency of turbines is an important issue in power generation industry. One of the effective parameters on the gas turbine efficiency is its ambient air temperature. Overspray fogging for turbine inlet cooling (TIC) is the proven and cost effective method to improve the gas turbine performance. Although, TIC methods are used to increase turbine efficiency, sometimes they do not work due to changing the geometry of turbine blades especially their edges as a result of liquid droplet erosion (LDE). Hence, increasing the erosion resistance of turbine blades is a significant issue. There are several ways to reduce the blade erosion and the surface treatments are the proven and applicable options. In the current study, the liquid impingement erosion, its mechanism and effective parameters will be investigated and then surface treatments with a concentration on the nitriding process will be mentioned. Finally, the advantages, drawbacks and the potential of nitriding processes to improve the erosion resistance of Ti6Al4Vwill be reviewed.**

Contents

1. Introduction

Liquid impingement erosion of the compressor blades of turbine systems caused by fog cooling has been known as an affective parameter on the turbine efficiency. This phenomenon has been more important since the turbine designers increased the exhaust area to have higher mass flow rate and as a result increased the rotor diameter and blade length. In this condition, more severe liquid erosion damage especially on the leading edges of blades can happen and because of their mechanical degradation, the final efficiency will be reduced. Therefore, understanding liquid impingement erosion process and its parameters is important. Several studies have been done for this purpose, but there is not complete agreement on the materials failure mechanism during water droplets impingements and the influence of process parameters. Additionally, industrial has demanded to improve water droplet erosion properties of blades to increase their turbines efficiency [1-4].

Generally, enhancement of erosion resistance could be done in two ways, changing the design and material of the blades or modifying the blades surface. Chromium stainless steels have been almost substituted by Ti alloys and specially Ti6Al4V because of its high strength to weight ratio and corrosion resistance as a result of extensive empirical and simulation researches [3]. Recently, using different subsets of surface engineering like heat treatments, thermochemical treatments, deposition of hard thin films and fabrication of thick coating on Ti6Al4V blades is the subject of many studies to improve the erosion behavior.

In this report, liquid impingement erosion, damage mechanism and effective parameters are discussed. Subsequently, some common solutions which have been proposed in the literature, especially different types of nitriding, are reviewed. Additionally, the important characteristics of the Ti6Al4V nitrided by gas, plasma and laser nitriding processes are mentioned,. To conclude, the potential of mentioned nitriding methods to improve erosion properties of blades and also some promising alternatives for this purpose are discussed.

2. Liquid impingement process in the turbines

2.1. Turbine inlet cooling

In the power gwnwration industry, the turbine efficiency is a very important issue which is affected by many parameters like the ambient air temperature. The higher ambient temperature, the less dense incoming air and the less output power and efficiency because of less mass flow rate. It is reported [2] that the turbine efficiency decreases 0.3-0.5% by raising 1°F ambient temperature. Accordingly, the different turbine efficiencies during the summer and winter are noticeable. To keep low ambient temperature, several methods were suggested, but the best method regarding to facility and cost issues, is inlet air fog cooling. During fog cooling, the micro scaled water droplets sprayed into the turbine inlet. They absorb some heat from the air and beginning to evaporate. Usually, all droplets do not evaporate and some of them enter the compressor with the air, called overspray, and result in more cooling [3].

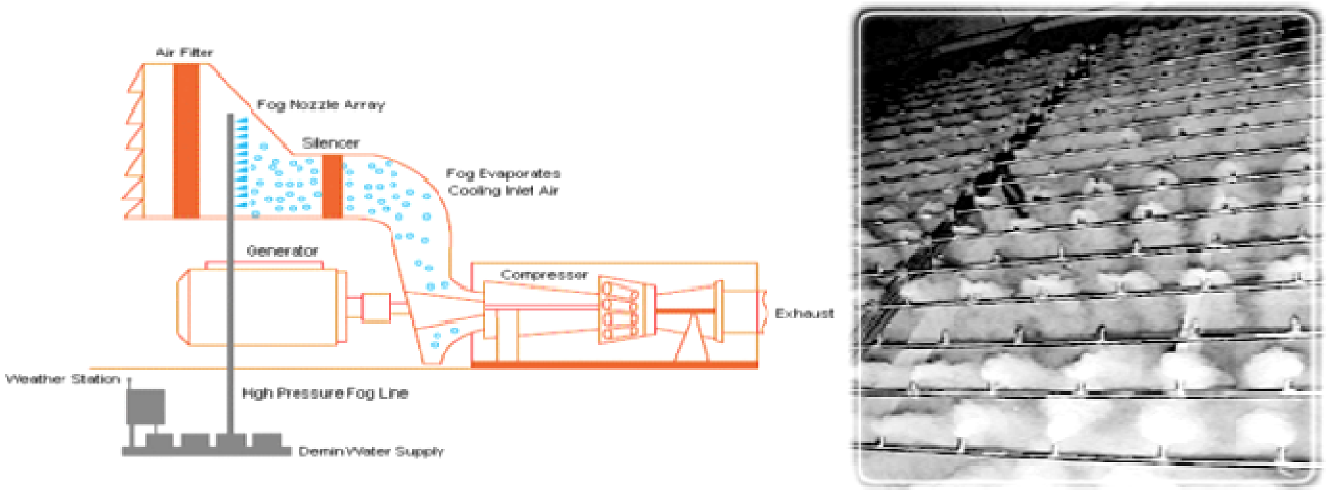


Figure 1. Fog cooling setup [3].

The entering droplets in the compressor collide to the downstream rotating blades with high speeds. Impinging the water droplets and rotating blades leads to their erosion which is called liquid droplet erosion (LDE) [3]. The droplets impact results in erosion as shown in the schematic diagram presented in Figure 2.

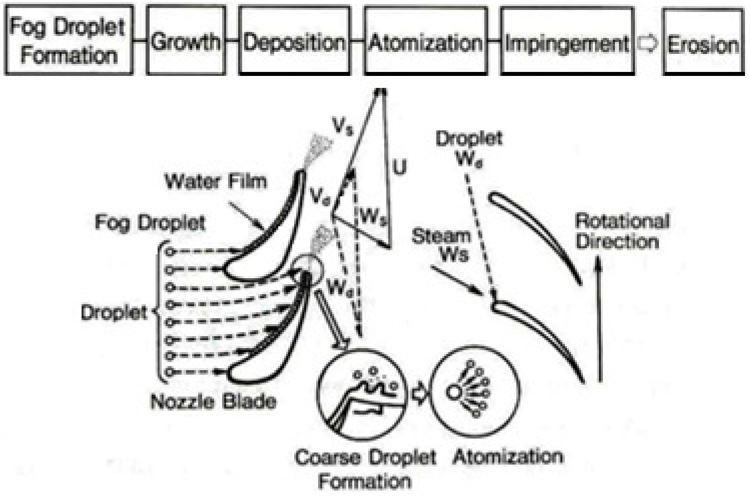


Figure 2. A schematic diagram of water film formation, droplets atomization and subsequent impingement on the rotating blades [1].

2.2. Liquid erosion damage mechanism

Liquid droplets impinging onto the surface of a solid target can exert enough force leading to plastic deformation and fracture the solid. The mechanism of material removal through one water droplet impact completely depends on the droplet and target surface properties. However, frequent water droplet impacts at the same site on the surface usually results in central pit and in some cases deep channels what usually happened in the eroded turbine blades [4].

The deformation and fracture patterns on the sample surface during the droplet impacts are classified into five groups.

- ✓ Circumferential surface fracture: central area of the specimen surface subjected to LDE should initially sustain the compression by impacting a liquid droplet, but after some microseconds large tensile stresses observed at the edges of contact area leads to initial fracture. In brittle materials, the fracture commences at the periphery of the droplet on the surface.
- ✓ Subsurface flow and fracture: subsurface shear cracks were seen in the materials, which are able to deform plastically at low stresses, as a result of high speed droplet collisions.
- ✓ Permanent depression due to plastic fracture: central depression can be seen on the metals surface during the droplet impingements because of high surface pressure. In some cases, a central pit along the depressed area has been observed.

- ✓ Shear deformation around the periphery of the impact zone: the radial wash arising on the droplet collision results in a scrubbing condition against surface discontinuity such as pre-existent scratches and pits or produced cracks and slip lines by the water impact.
- ✓ Stress wave effect: upon droplet impact, the compressive waves expend on the surface and the reflection is dilatational tensile waves in opposite side. In addition, Rayleigh waves can be seen in the sample. It was proposed that some circumferential fracture areas on the surface are created by interference of Rayleigh waves with reflected tensile expanding waves [1,5].

Upon water droplet impact, a small area of sample for a very short time experiences high pulse compression and jetting outflows as well. As a matter of fact, the materials respond to this pulse compression and jetting outflow mostly depends on their ductility and microstructure [4].

Generally, the erosion test result is reported as a curve of weight or volume loss versus exposure time. Figure. 3 shows this curve for different materials indicating the presence of three stages. The first stage is called incubation period, where some plastic deformations occurred without any mass loss. By increasing stress concentration and the number of dispersed depression parts, pitts and channels form and enlarge during the second stage so that erosion rate increases due to material removal. As it is presented in Figure 3, the erosion damage is a time dependant process. The incubation and acceleration stages of erosion could be easily explained by assuming them as fatigue like failure mechanisms. In stage 3, erosion rate decreases. This was explained by various concepts like impact cushion role of retained water at the pits and craters or work hardening of the eroded surface [1,6].

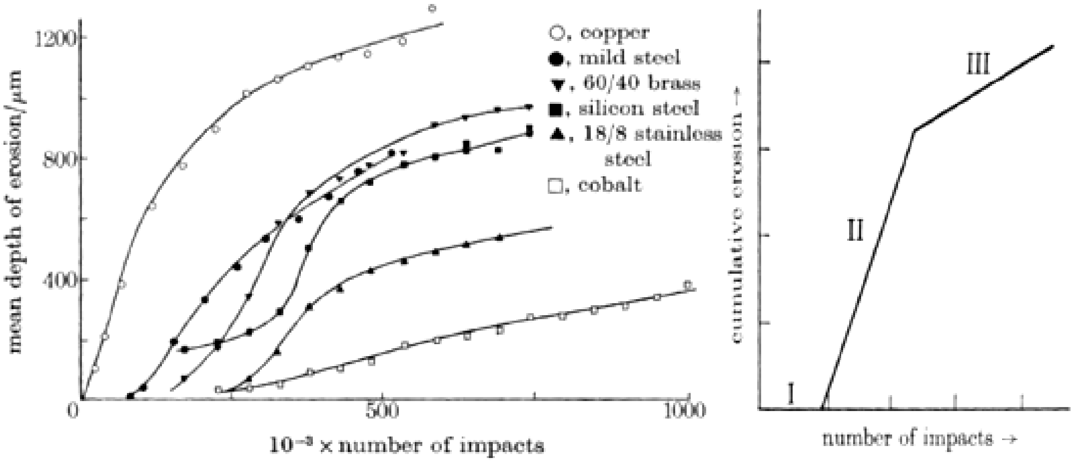


Figure 3. The erosion test results and three stages model [1].

2.3. Effective Parameters of the LDE

Liquid droplet erosion as its failure mechanism showed is an intricate mechanical phenomenon affected by many parameters including: impact velocity, impact angle, droplet size, droplet shape, frequency of impacts, and target materials properties [3,6]. They will be explained in the following sections.

- ✓ Impact velocity

The mechanism and damage extent of droplet erosion can be significantly affected by impact velocity so that a threshold velocity is reported by many authors below that no material remove would happen. As a matter of fact, the impact velocity is vector sum of incoming droplet speed and rotating blade velocity. The impact velocity dependence of erosion has been presented by a simple power law equation, $E \cong V^n$ [1,6]. n is a material dependent constant that was found to fall within the range of 4-9. For Ti6Al4V, it is 7 [7].

- ✓ Impact angle

The angle of collided droplet on the target surface is another parameter affecting indirectly the erosion. But, the determination of this angle is not always easy because of increasing surface roughness during erosion test. Some researchers assume this parameter as an unstable parameter [1]. Nevertheless, it was found that maximum water erosion occurs at 90° for Ti6Al4V. Actually, The effect of impact angle is more evident on the solid particle erosion of materials [4].

- ✓ Droplet size

Another important parameter is the size of impinging droplet. The larger the droplet size, the more the erosion damage. It is attributed to the more kinetic energy of large drops. It means for a constant volume of water, the small water droplets lead to less erosion damage in comparison with large water drops. On the other hand, Wang *et al.* [8] found that cooling efficiency declines by spraying water droplets larger than 50 µm. They also reported the best initial droplet size is in the range of 5 to 10 µm to have higher cooling efficiency and less erosion damage. But, impingement of larger droplets on the blade surface were observed due to several reasons such as coalescence of primary drops during spraying which cause more severe damages [6].

- ✓ Droplet shape

Generally, the sprayed drops were subjected to various forces during the spraying and entering to the compressor like gravity. So, they cannot be assumed as perfect spheres. Indeed, the different shapes of impinging droplets affects the erosion mechanism indirectly. For example, small flattened droplet on the surface behaves like a large sphere drop and may increases the amount of damage [6,9].

2.4. Damage resistance of target materials

The LDE phenomenon is a complicated issue to investigate, although some researchers presented erosion resistance as a property of material in its own right, most researchers studied the effect of material intrinsic properties on the erosion behavior. Generally, the erosion resistance of material could be affected by several parameters such as hardness, ultimate resilience ($S_u/2E$, where S_u is ultimate strength and E is modulus of elasticity), microstructure, true stress at fracture, strain energy to fracture, and work hardening rate. Amongst these parameters, hardness and ultimate resilience are the most important effective parameters. Thus hardness can be assumed as a good index for erosion resistance of similar alloys. Usually, the higher the hardness and toughness, the higher the erosion resistance. It has been found that surface treatments increasing the hardness and toughness is a promising way to improve erosion resistance [6,10].

2.5. Potential solutions

✓ Bulk Modification

To decrease the amount of erosion on the blades, the primary option is to decrease the area subjected to LDE in the turbines (blades surface area). But it is not an applicable approach because there are other kinds of criteria for the blades geometry in the turbine systems. In fact, the turbine designers recently reported more turbine efficiency by increasing the compressor chamber and as a result having longer blades and more area exposed to LDE [4].

Choosing a suitable material for the blades which are subjected to LDE is another option. The problem is that choosing the blade material cannot be done with only improving erosion properties approaches. In fact, by considering all criteria for the compressor blades, they has been made from Ti6Al4V [11].

✓ Surface Modification

As explained, geometry and bulk material of blades considered in the current study are fixed. The only option to improve the erosion resistance is by modifying the blades surface and especially their leading edges as the high damages locations. There are several attempts to improve the erosion behavior using surface treatments.

3. Surface Engineering to improve water droplet erosion resistance

Surface engineering is being used to improve the surface properties and protect industrial parts from various types of failures like wear and erosion without changing the bulk materials. It is classified to three groups: surface cleaning, surface treatments, and coating and thin film depositions. Surface engineering of light alloys such as titanium based materials has been studied by many researchers because of their desired properties such as low density and high strength to weight ratio [12]. The previous attempts based on surface modification to improve erosion properties of Ti alloys particularly nitriding processes will be reviewed and discussed here.

3.1. Coating and thin films

- ✓ Sprayed coatings

According to the unique properties of spraying method which is interesting for industry such as high deposition rates, several studies have been done on the influence of various sprayed coatings on the erosion properties.

Takeda *et al.* [13] investigated the erosion behavior of low pressure plasma sprayed cobalt base alloys like stellite-6 and ZrB_2-CoCrAlY composites. They reported excellent erosion behavior for the sprayed stellite-6 coating compared to satellite-6 sheet (bulk) because of its proper microstructure as a result of rapid solidification. In spite of high hardness of ZrB_2-CoCrAlY cermet coating, it showed inadequate erosion resistance during service. This was attributed to the weak bonding between the Co alloy and ZrB_2 grains as the matrix and reinforcement which accelerates crack propagations along the interface resulting in faster spallations.

Mann *et al.* [14] described the WC-10Co-4Cr fabricated by high velocity oxygen fuel (HVOF) method as a promising droplet erosion resistant coating for low droplet energy flux like what is happening at steam turbine blades. In addition to high hardness and high crystal bonding energy of tungsten and cobalt, residual compressive stresses within the coating and even in the substrate was mentioned as another reason for the improved erosion properties because of the fatigue like mechanism of erosion damages.

Lima *et al.* [15] introduced the fracture toughness of sprayed coating as an important parameter affecting cavitation erosion properties. They increased the fracture toughness of WC-Co coating by post remelting and as a result increased the cavitation resistance. As a matter of fact, post melting treatment of sprayed coating can disrupt its lamellar microstructure which is an important drawback. In this microstructure, lamellae can be removed easily during the erosion test because their cohesion is weakened by interlamellar pores and pre-existing discontinuities. Recently, Shipway *et al.* [16] studied the water droplet erosion properties of WC-Co coating fabricated by HVOF at higher droplet impact velocities. In this case, the sprayed coatings did not show proper erosion resistance because of subsurface cracking in the coating during the erosion test as a result of their low toughness.

Mann *et al.* [17] in a recent study, investigated the LDE properties of SHS 7170 (Iron base alloy) deposited by twin wire arc spraying method and the effect of subsequent laser treatment as well. The iron base sprayed coating in this study showed the weaker erosion resistance than the untreated Ti6Al4V due to its lamellar microstructure and high residual stress which accelerate detachment. But, post laser treatment sufficiently improved the erosion properties and postponed the incubation time of water droplet erosion test. The finer grain and uniform morphology of coating obtained as a result of higher cooling rates were mentioned as the main reason for desired water droplet erosion (WDE) resistance of laser remelted TWAS SHS 7170 sprayed coating.

Although, several sprayed materials like metals, ceramics and composites [14-17], have been studied as erosion resistant coatings, it is not completely understood which combination and conditions are the best for erosion properties. In order to obtain an erosion resistant sprayed coating, their inherent problems like lamellar microstructure, voids, pores, inter boundary defects, low fracture toughness, cracks formed during coating process because of thermal mismatch, high residual stresses and low controlling on the formed phases must be considered and modified.

- ✓ Vapor deposited hard films

To improve the wear and erosion properties of Ti alloys especially Ti6Al4V, hard and thin layers especially nitride coatings deposited by vapor deposition methods like PVD, EBPVD, CAPVD have been considered as promising approaches. Generally, some advantages and disadvantages have been reported for hard films deposited by vapor deposition methods which are used to enhance erosion properties. Some of them will be reviewed in the following paragraphs.

Swaminathan *et al.* [18] investigated the erosion properties of single and multi TiN and TiSiCN layers deposited by new physical vapor deposition technique, Plasma Enhanced Magnetron Sputtering (PEMS). It is reported that commercial TiN coating deposited on the Ti6Al4V by usual PVD technique improved solid particle erosion resistance up to 5 times due to their high hardness. Moreover hard coatings deposited by PEMS significantly enhance the erosion resistance because they have high adhesion strength to the substrate and very fine microstructure resulting in very high hardness. For instance, the nanocomposite TiSiCN coating deposited by this technique increased solid particle erosion of Ti6Al4V at 30 and 90 deg incident angels up to 20 times.

The comparison study of wear properties of Ti6Al4V treated by different surface modifications including plasma assisted physical vapor deposition method (PAPVD) as well as their hardness were done by Wilson *et al.* [19]. The knoop microhardness of the TiN coating at different loads was investigated. They reported the composite (substrate/coating) surface hardness of TiN layer at 200g and 15s (hardness measurement) is less than plasma nitrided and plasma nitrocarburized Ti6Al4V because the substrate cannot mechanically support the thin hard layer at this load. However at lower loads TiN layer deposited by PAPVD is much harder than diffused layers as shown inFigure 4. Although, the TiN layer showed suitable wear resistance because of high hardness, the nitrided and nitrocarburized samples presented better wear resistance as a result of better load support especially at higher loads.

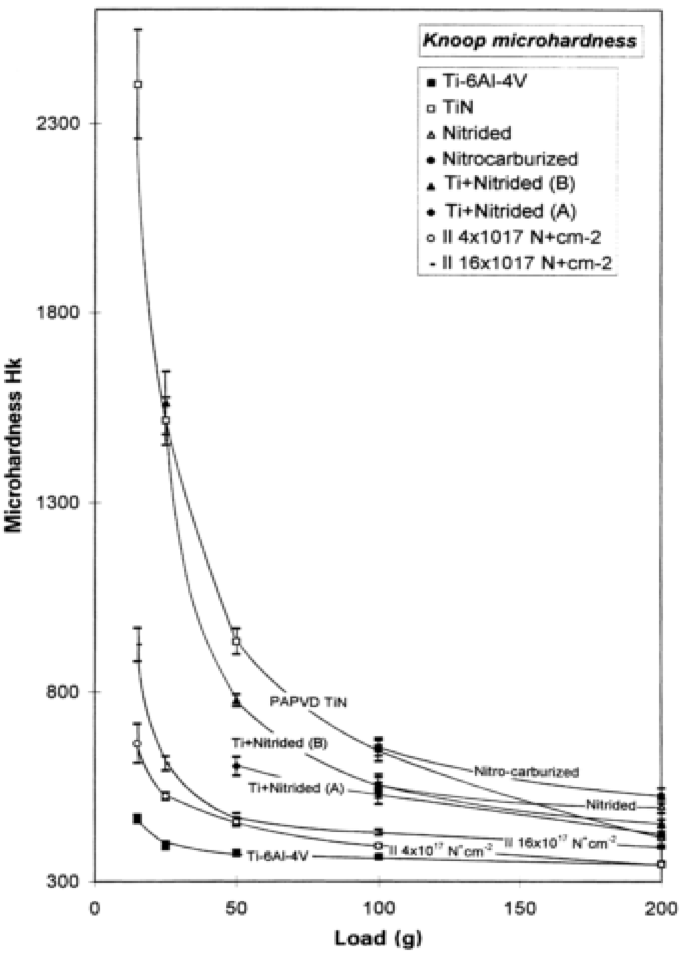


Figure 4. Microhardness of several surface treatments at different loads [19].

At first glance, deposition of a ceramic layer such as TiN on the surface because of its ceramic nature and very high hardness were thought to be useful for the wear and erosion damages, but they usually detach during the wear and erosion because of their low adhesion strength on the surface. A lot of studies have been done to increase the adhesion of the thin and hard layers on the substrate and various solutions have been suggested for this problem like applying a diffusion layer as an intermediate film between the coating and substrate [12].

3.2. Surface treatments

Several surface treatments to improve erosion properties with different approaches like increasing the surface hardness have been studied. They can be classified into two different groups according to the final chemical composition of surface: increasing the hardness without changing the chemical composition and enhancing the surface hardness by changing the chemical composition (thermochemical treatments). In the following sections some of these methods used to improve erosion properties of Ti6Al4V will critically be reviewed.

3.2.1. Surface hardening

- ✓ Laser hardening

Laser hardening has been mentioned as an excellent method to protect steel blade against liquid erosion because of the higher hardness, finer microstructure and the compressive residual stresses on the surface so that the cavitation erosion resistance of laser melted AISI 420 steel was reported 70 times better than untreated steel [20]. According to Yerramareddy *et al.* [21], laser melting improves the wear resistant of Ti6Al4V due to the formation of some α′ martensite phase in the heat affected zones resulting in high hardness, but laser nitriding effect to enhance tribological properties is much more significant. The influence of laser melting and laser nitriding process on the water droplet erosion of Ti6Al4V was studied by Robin *et al.* [21]. Laser remelting enhanced the WDE of specimen up to two times and it was attributed to the 10% hardness increase as well as martensitic structure constraining hydraulic penetration mechanism of WDE [22].Mann *et al.* [23] reported that in spite of no significant hardness increase as a result of laser remelting, the high power diode laser (HPDL) melted Ti6Al4V showed more droplet erosion resistance than untreated Ti6Al4V especially at higher energy flux of droplets. This was attributed to the excessive compressive stresses developed by concave bending on the sample after HPDL treatment as well as more α′ phase as shown in Figure 5.

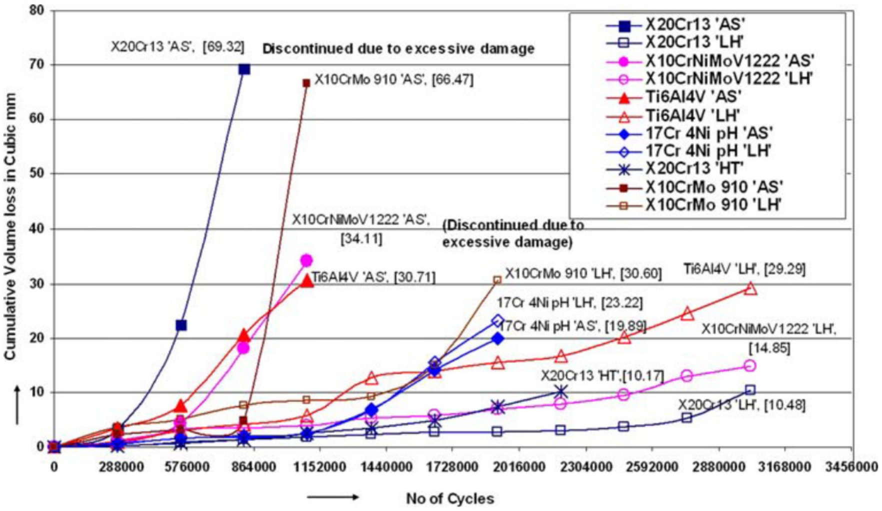


Figure 5. Volume loss of different materials after HPDL hardening at an energy flux of $57.167*10^6$ J/m^2s[23].

- ✓ Shot peening and laser peening

Shot peening is a cold working process used to produce a compressive residual layer and improve mechanical properties by impact of some shots like round metallic or ceramic particles to the surface which leads to plastic deformation. Laser peening or laser shock peening (LSP) is a process for inducing compressive residual stresses using shock waves created by laser pulses. It is a relatively new surface treatment for metallic materials that can greatly improve their resistance to crack initiation and propagation brought on by cyclic loading and fatigue [24,25].

As mentioned earlier, the surface hardness is an important parameter for LDE properties as well as the compressive residual stresses. So, considering the peening process to improve erosion properties is reasonable. The effect of these techniques on the fatigue and tribological properties of Ti alloys have been studied. Zhang *et al.* [25] described that the hardness and fatigue life of Ti6Al4V could be increased up to two times using laser shock peening. Tsuji *et al.* [26] also used shot peening process on the plasma carburized Ti6Al4V and obtained final surface with 600 HV micro hardness, high wear resistant and high fatigue life as well.

3.2.2. Thermochemical treatments

Modifying the surface properties by changing the chemical composition of the surface at high temperatures is called thermochemical treatment. Generally, titanium and its alloys are chemically active and they efficiently react with most interstitial elements like nitrogen, carbon and oxygen. Hence, modification of Ti alloys surface by penetrating proper elements to have ceramic and diffusion layers has been reported as one of the most important methods to improve surface properties. Oxidation, carburizing and nitriding are the most popular thermochemical treatments carried out on Ti alloys [12,24]. Surface nitriding will be reviewed in the following sections.

- ✓ Nitriding

Nitriding is the most common thermochemical treatment used to improve surface properties. It cannot be done correctly in the oxygen-containing environment because of high reactivity of titanium with oxygen and tendency to form TiO_2. Nitriding can strengthen the surface of Ti alloys because of high solubility of nitrogen in α-Ti and formation of thick diffused layer. Nitriding also leads to the formation of TiN and Ti_2N as compound layers with a significant thickness on the substrate surface. The very high hardness compound layer supported mechanically by thick diffusion layer resulting in an appropriate hardness gradient is the main reason of using nitriding process to improve wear, tribology and erosion properties of titanium alloys [12,27].

Nitriding of Ti alloys is a complicated process in terms of phase transformation due to several possible chemical reactions occurring simultaneously at the boundary between the gas and titanium substrate. A simplified physical model has been suggested to describe the formation and growing of nitrided layers during gas nitriding of pure titanium. First, nitrogen interstitial solution in the α-titanium phase (hcp) called diffusion layer is formed and the longer the nitriding time, the thicker the diffusion layer. Formation of an intermetalic phase, Ti_2N, is introduced as the second step when the concentration of nitrogen in the gas/substrate interface exceeds nitrogen saturation limit. By increasing the nitriding time, more nitrogen concentration in the surface is introduced and a phase transformation from Ti_2N to TiN takes place as shown in Figure 6. These phases on the surface are called compound layer [27].

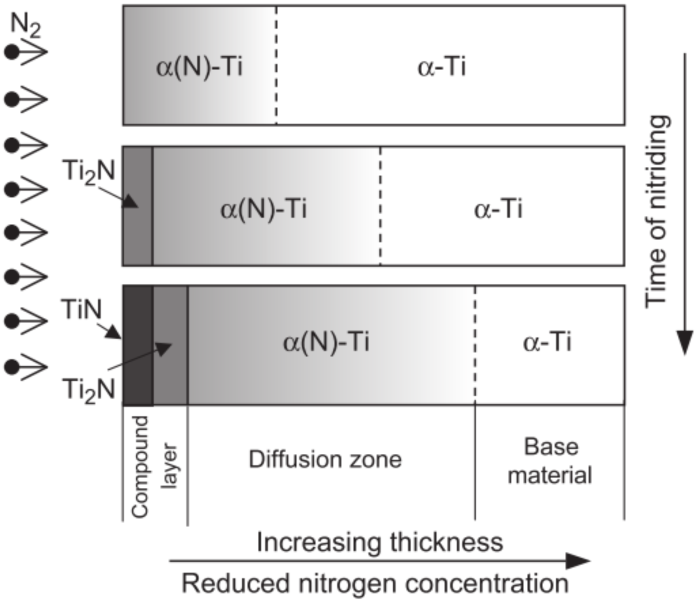


Figure 6. A schematic model of surface layers formation during nitriding of pure titanium [27].

Consequently, the phase transformation during simplified nitriding process of pure titanium can be shown in the following sequence:

$$\alpha\text{-Ti} \longrightarrow \alpha(\text{N})\text{-Ti} \longrightarrow Ti_2N \longrightarrow \text{TiN} \qquad (3.1)$$

In case of Ti alloys nitriding, the presence of Al, V, Mo, Zr alloying elements results in some deviations from this reaction mechanism. However these effects are negligible because of the low concentration of these elements. For example, the partial isothermal section of Ti-Al-N ternary phase diagram at 1000 °C is shown in Figure 7. The important area in this diagram is Ti-rich corner where aluminum amount is very low. In addition to binary compounds, there are two ternary compounds (τ_1, τ_2) which might be formed during the nitriding process. The phase transformation during nitriding of Ti-Al alloys can be deduced from Figure 8 as following:

$$\alpha\text{-Ti} \longrightarrow \tau_1 - Ti_2N \longrightarrow \tau_1 - TiN_{1\text{-}x} \longrightarrow \tau_2 - TiN_{1\text{-}x} \qquad (3.2)$$

In Ti-rich side of Figure 8, nitrogen dissolves initially in titanium. As the nitrogen content increases, Ti_2N and TiN_{1-x} progressively become stable. It has been reported that τ_1 formation is very sluggish and in the real process, it may not form at all. Therefore, the above-mentioned model (3.1) can be used for Ti6Al4V [28,29].

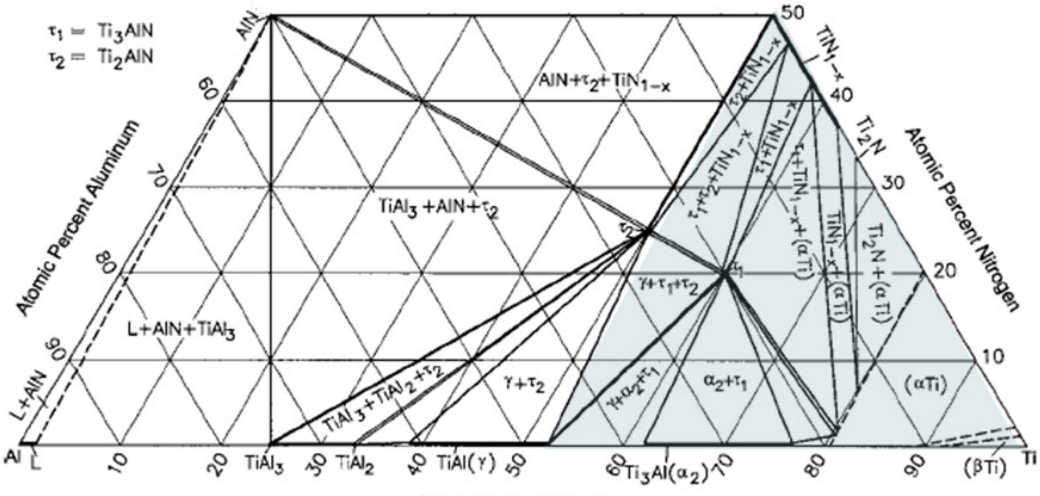


Figure 7. Isothermal section of ternary Ti-Al-N system at 1000°C [28].

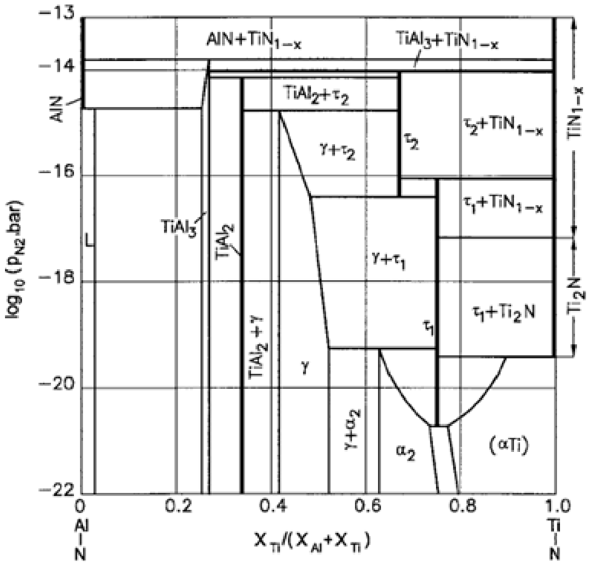


Figure 8. Stability diagram with stable equilibria at 1000°C [29].

4. Various types of Ti alloys nitriding

4.1. Gas Nitriding

Gas nitriding is considered as a high potential technique for industrial applications. Its independency of sample geometry and no need to special equipment have been described as its advantages and long time nitriding as well as declining of fatigue limit of Ti alloys as its drawbacks. The thickness of compound layer, an important parameter for nitrided sample, and the microhardness in Ti6Al4V were reported as 2-15 µm and 800 HV, respectively [12,30].

Zhou *et al.* [30] described a significant enhancement in caviatation erosion including increase of incubation period time and decrease of erosion mass loss for Ti and Ti6Al4V as a result of their gas nitriding. Although, high microhardness of nitrided layers on the surface were introduced as the main reason for better erosion properties, they may fail as a result of brittle fracture during erosion test. For Ti6Al4V specimens, to increase the surface toughness, using longer nitriding process (around 10 hours) and lower nitriding temperature (around 800°C) are recommended because in these conditions Ti_2A1N with superior toughness compared with TiN can be formed on the surface. The improved erosion resistance for nitrided Ti6Al4V due to high hardness and toughness is presented in Figure 9.

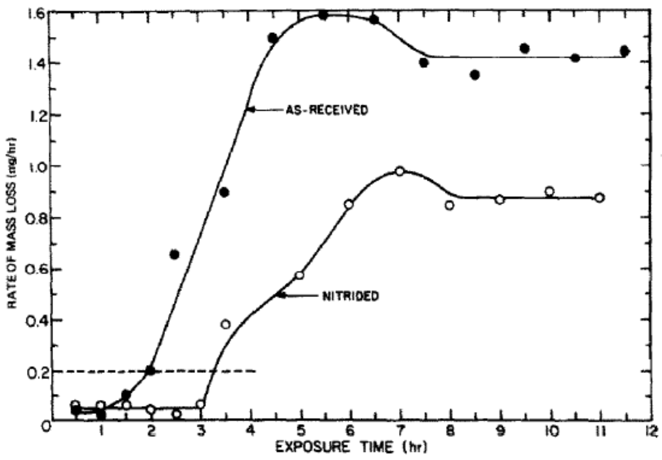


Figure 9. Rate of mass loss during cavitation erosion test versus exposure time for as-received and nitrided Ti6Al4V at 720°C for 8h Ti6Al4V [30].

4.2. Laser nitriding

Another method to improve surface properties of Ti alloys is laser nitriding which works by melting the surface with a focused laser beam in a nitrogen gas environment to form titanium nitride phases. The unique advantage of laser nitriding among other nitriding processes is an excellent metallurgical bond between the hardened surface layer and the substrate. In this method the main problem is the surface cracking. Depending on the process parameters like laser pulse energy or nitrogen concentration, a surface hardness between 900 to 1300 HV has been reported for laser nitrided Ti6Al4V. The thickness of laser nitrided layer can exceed 450 µm [27,31].

Laser nitriding has been used to improve wear properties of Ti alloys due to enhancing the surface hardness and a very good bonding between substrate and hardened layer. Jiang *et al.* [31] described the noticeable enhancement for wear resistant of laser nitrided Ti6Al4V due to the formation of a composite coating with TiN dendrites reinforcement on the surface leading to high hardness. Gerdes *et al.* [32] investigated the effect of laser nitriding on the water droplet erosion properties of Ti6Al4V and they reported significant improve in WDE resistance (specially enhancing the duration of incubation period). It was attributed to the high hardness of the surface leading to the prevention of deep craters formation during the WDE which is the main reason for high volume loss of Ti alloys. Figure 10 show the increasing of the incubation time to a higher extent in the laser nitrided Ti6Al4V.

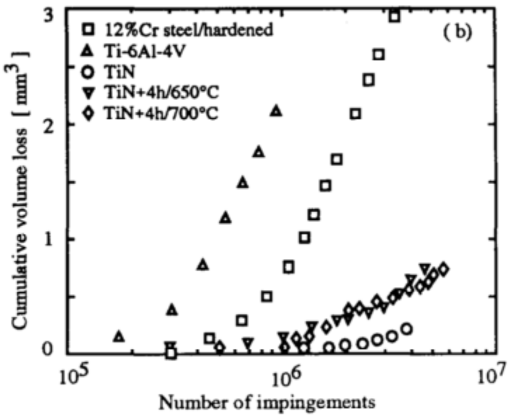


Figure 10. Cumulative volume loss during WDE versus number of impingements [32].

4.3. Plasma nitriding

Nitriding in the plasma environment is another method to improve surface properties of the metals especially titanium. Plasma nitriding has some advantages like more control on the phase formation and depth of the nitrided layer, shorter process time and elimination of undesirable oxidation. Microhardness of 600-1500 HV has been reported for plasma nitrided Ti6Al4V and up to 50 µm compound layer was obtained for this alloy. Needing to special equipment, high ionizing energy and reduction of the fatigue life can be assumed as disadvantages for plasma nitriding process [12,27]. The microstructure of plasma nitrided Ti6Al4V and its microhardness profile can be seen at Figure 11.

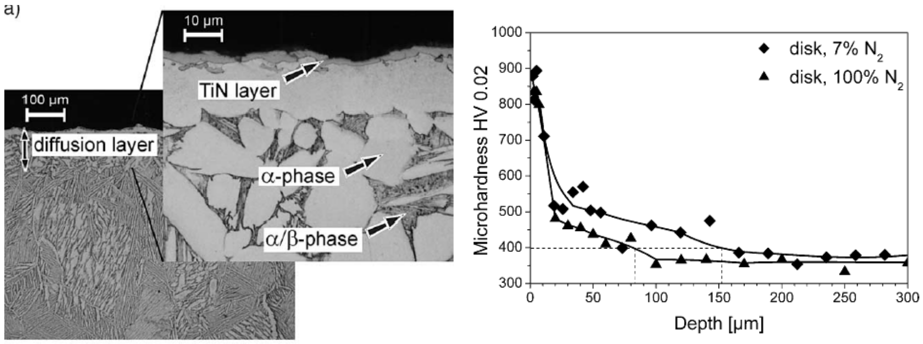


Figure 11. The microstructure and microhardness profile of plasma nitrided Ti-6Al-4V [27].

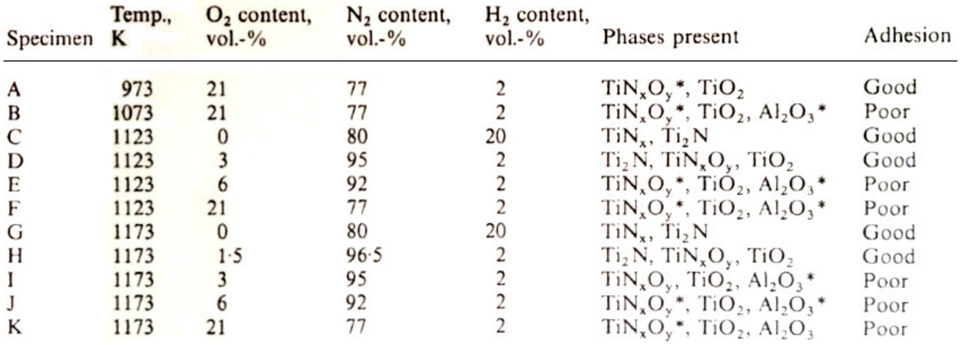
According to Kashaev *et al.* [33], the wear volume loss of Ti6Al4V decreased from 0.62 mm^3 to 0.07 mm^3 using plasma nitriding process at 500°C within 6 h in atmosphere containing argon and nitrogen. They attributed this enhancement to the formation of 150 µm diffusion layer resulting in higher microhardness.

5. Alternatives to improve final properties

Although the mentioned thermochemical techniques especially nitiriding processes are widely used to improve mechanical properties of Ti alloys, they still can be modified or combined with other surface treatments to have better final properties and be used as erosion resistant surface treatments.

The oxynitriding of Ti alloys that leads to formation of surface layers based on TiN_xO_{1-x} is a promising surface treatment to improve mechanical properties and has been studied recently [34-37]. These layers are isomorphic to the binary compounds (TiN and TiO). They have been reported as great compounds to achieve high microhardness and wear resistance which is better than both nitrides and oxides [34]. Bassi *et al.* [35] modified the surface of Ti6Al4V using plasma nitriding and oxidising treatments. The oxynitriding processes were performed in an atmosphere containing nitrogen and oxygen and their different combinations ($0<vol.\%O_2<20$) were studied. The formed phases in the compound layer fabricated in various gas mixtures and process temperatures as well as their adhesions strengths are presented in Table 1.

Table 1. Formed phases and adhesion strength of compound layer as a result of Ti6Al4V oxynitriding at different conditions [34].



Specimen	Temp., K	O_2 content, vol.-%	N_2 content, vol.-%	H_2 content, vol.-%	Phases present	Adhesion
A	973	21	77	2	TiN_xO_y*, TiO_2	Good
B	1073	21	77	2	TiN_xO_y*, TiO_2, Al_2O_3*	Poor
C	1123	0	80	20	TiN_x, Ti_2N	Good
D	1123	3	95	2	Ti_2N, TiN_xO_y, TiO_2	Good
E	1123	6	92	2	TiN_xO_y*, TiO_2, Al_2O_3*	Poor
F	1123	21	77	2	TiN_xO_y*, TiO_2, Al_2O_3*	Poor
G	1173	0	80	20	TiN_x, Ti_2N	Good
H	1173	1·5	96·5	2	Ti_2N, TiN_xO_y, TiO_2	Good
I	1173	3	95	2	TiN_xO_y, TiO_2, Al_2O_3*	Poor
J	1173	6	92	2	TiN_xO_y*, TiO_2, Al_2O_3*	Poor
K	1173	21	77	2	TiN_xO_y*, TiO_2, Al_2O_3	Poor

They reported that low process temperature and low oxygen content result in good adhesion of the compound layer to the diffusion layer. On the other hand, the more oxygen, the thicker the diffusion layer and the higher hardness. Indeed, the plasma oxynitrided Ti6Al4V at atmosphere containing 21% O_2, 77% N_2 and 2% H_2 and 973 K shows thicker diffusion layer with higher hardness and smoother hardness gradients compared to nitrided specimen.

Yaskiv *et al.* [36,37] investigated the oxynitriding of Ti alloys using gas diffusion treatments. Their study is based on the modification of titanium nitride with oxygen according to the reaction: $TiN_x + O_2 \longrightarrow TiN_xO_{1-x}$. The oxynitriding of Ti alloys in this study was performed by increasing the oxygen pressure at the final stage of nitriding (cooling step). Actually, this process is divided into two steps, thermodiffusion saturation with nitrogen (nitriding) and then improvement of nitride surface with oxygen (oxynitriding). The main reason for oxynitriding process in wear and erosion critical applications is the enhancement of hardness. It is found that higher hardening is achieved when the surface composition approaches to equiatomic TiN_xO_{1-x} (low extent of oxygen). They reported the higher the nitriding temperature, the higher the partial pressure of N_2, the lower the partial pressure of O_2 and lower oxidation temperature resulted in higher hardness. The effect of oxygen partial pressure during the oxynitriding process on the surface hardness is presented in the Figure 12. The low hardness at higher oxygen partial pressure is due to the formation of TiO_2 instead of TiN_xO_{1-x}.

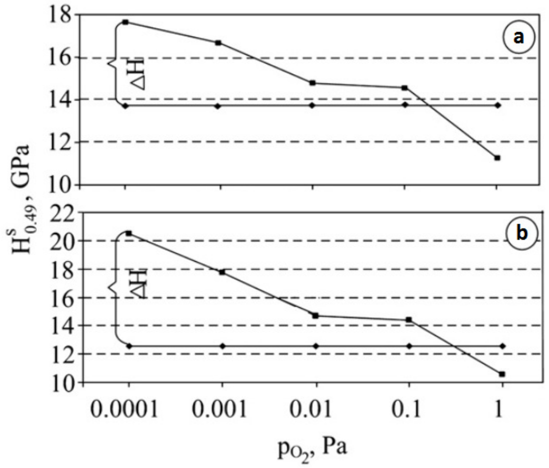


Figure 12. Effect of oxygen partial pressure at oxynitriding process on the surface microhardness (a) α+β alloy (Ti–Al–V) (b) pseudo-α-alloy (Ti–Al–V–Mo-Zr) [36]. (horizontal lines: surface microhardness of nitrided samples).

The increase of microhardness of diffusion and compound layers as a result of oxynitriding process compared to only nitriding can be assumed as a reason showing the good potential of this technique to improve liquid impingement erosion resistance.

6. Summary

In order to increase the turbine efficiency and output power, fogging cooling system is commonly used. During the cooling process, water droplets impingement to the rotating blades results in erosion especially at the leading edges. The mechanical degradation of eroded blades leads to output power reduction. Several surface treatments have been studied to improve the erosion properties of compressor blades and their main approach is the enhancement of surface hardness and toughness. Nevertheless, consideration of other materials properties on its erosion behavior still needs further investigations.

Ti6Al4V, the main material for the compressor blades, can be harden using various techniques like deposition of hard coating on the surface or conversion of titanium surface to high hardness layer. Amongst the mentioned methods, conversion techniques especially nitriding and oxynitriding process seem to be more desirable because of the following reasons. Very high surface microhardness can be achieved. Acceptable adhesion strength of hardened layer on the surface can be obtained. Surface hardening with suitable toughness is possible. To improve surface hardness and toughness, composite sprayed coatings also seem promising. Although some studies which use sprayed metallic or composite coatings to increase LDE resistance have been done, there are a lot of challenges to achieve an ideal erosion resistant coating fabricated by the most common coating process in the industry.

7. References

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