6 March 2009

Chapter 18 Laser surface modification of Ti alloys

T N Baker, Department of Mechanical Engineering, The University of Strathclyde, Glasgow, UK.
E-mail:neville.baker@strath.ac.uk.

Abstract: The laser surface engineering of titanium alloys has been developed over the past 30 years to produce a modified layer up to 1mm depth, thicker than alternative techniques. CW CO_2 lasers have been the main lasers used for both surface cladding and alloying. Much of the early work was based on laser nitriding forming titanium nitrides throughout the molten pool . Subsequent alloying developments have included the incorporation of carbides, nitrides, oxides and silicides, and also intermetallics and rare earths, added as powders. Laser processing can now tailor surfaces with superior tribological and erosion resistant properties compared to the untreated titanium alloys.

Key words : Laser melting, cladding, alloying, microstructure, tribological properties.

Professor T N Baker

18.9 References

18.1 Introduction

18.11Why use titanium alloys

Titanium alloys have been developed widely as commercial alloys for over 60 years, fulfilling the requirement for materials with high strength to weight ratios at elevated temperatures, initially used in the aerospace and defence industries. Over 80% of titanium alloys are used in these industries, mostly in the wrought form, but many other applications are restricted due to their poor tribological and oxidation properties and high relative cost, which is about five times that of steels and aluminium alloys.

Titanium and its alloys have excellent corrosion resistance in rainwater and sea water environments, through the formation of protective oxide films These films have been recognized and utilized by the chemical industry and also have led to applications in dentistry and by the medical profession in prostheses for implanting in the human body. Titanium has a high melting point, 1678ºC, which indicates that the alloys will show good creep resistance over a significant range of temperature.

18.12 The need for surface engineering

While titanium alloys also possess good fatigue resistance, they have a high coefficient of friction (μ) in the region of 0.6, both against each other, against other alloys and against non-metallic materials, such as polymers, which means that they suffer from low resistance to wear. The poor tribological properties are normally associated with the transfer of the surface oxide film to mating surfaces, resulting in severe adhesive wear. In some cases, the situation can be alleviated through the application of lubricants, for example when titanium alloys are in contact with polymers. The improvement in wear resistance due lubricants, in general, decreases with temperature. For this reason, surface modifications of titanium alloys have been used to increase the near surface strength, reducing the coefficient of friction and lowering the tendency for material transfer and adhesive wear (Heyman 1992) .

In addition to aerospace applications, the attractive high temperature properties of titanium alloys has been extended to land based turbines. This has been particularly the case in Japan (Yamada 1996). The density advantage of titanium alloys over such steels as Cr-Mo-V and 12%Cr has led to their use in the low pressure end of steam turbines. Under the operating conditions, liquid impingement erosion is a well recognized damage mechanism associated with moving blades (Robinson and Reed 1995). A loss of material which occurs from the leading edges of the blades is a result of cumulative damage from the impact of water droplets formed by the condensation of steam in the later stages of the steam turbine. The impact of each droplet generates, very briefly, high local forces. Pressure forces are generally normal to the direction of impact, whereas forces due to splashing or jetting, as the droplet disperses, are tangential to the impacted surface. These two sets of forces produce characteristic pitting or tunnelling damage to the surface (Hu et al 1997). Therefore, protection of the blade surfaces is essential if they are to function effectively and within acceptable commercial economic limits. The use of laser surface engineering to develop this protection, by creating surface coatings on titanium alloys has some advantages over other alternative coating techniques (Zhecheva et al 2005).These include a precise control over the width and depth of surface modification and the ability, through computer controlled work tables, of processing complex shapes and targeting specific areas of a component. Laser surface processing methods have been reviewed by Tian et al (2005) who include a brief, but useful description of biomedical applications, not covered in the present Chapter which concentrates on more extensive consideration of what are, in effect, functionally gradient layers for structural engineering applications.

18.13 Primary sources of material

Materials Property Handbook: Titanium Alloys, 1994, 1169-1176, ASM International, Materials Park, OH.

Laser Processing of Engineering Materials, J. C. Ion, 2005, 296, Elsevier, Amsterdam.

The Development as Turbine Materials ed G.W.Meetham, R.M.Duncan, P.A.Blenkinsop and R.E.Goosey, Applied Science Publishers,London,1981, 63-87.

18.2 Lasers used in surface engineering

With the need to improve the surface properties of titanium alloys, such as the tribological, high temperature and corrosion aspects, the normal approach has been to modify the surface to one with a higher hardness and /or a lower coefficient of friction than the substrate, while retaining the attractive properties of the bulk material of the alloy. Lasers are one of many tools that have been used to modify the surface of an alloy. They involve light amplification by stimulated emission of radiation, which gives rise to the acronym *laser*. The different types of laser are grouped according to the active medium (gas, liquid or solid),wavelength ,power, energy and mode of operation(continuous or pulsed).These are shown in Fig 18.1, by Ion (2005), characterized by plotting the average power versus the wavelength, and vary from excimer, Nd:YAG, diode through to CO_2 lasers, the latter being the main tool used in most of the work reported in the literature on surface alloying. Ion (2005) attributes the popularity of CO_2 lasers to their 'efficient use of gases, which reduces running costs, that the pulsed or continuous wave emission is produced in a high quality beam at superkilowatt power levels, and far- infrared light is transmitted readily in air, being absorbed by a wide range of engineering materials'. However, he also expects there to be a growth in the use of multikilowatt diode –pumped solid state(DPSS) lasers which offer compactness, high power efficiency and high beam quality. Information on the physics associated with lasers and their construction are found in Duley (1983) and Ion (2005).

18.3 Laser surface modification methods

The simplest application of laser processing, laser heating, involves the rapid heating of the surface layers to a temperature well below the melting point, followed by rapid cooling. While this technique is widely applied to steels and results in transformation hardening due to the development of martensite, in laser processed titanium alloys, the martensitic phase transformation has no significant effect on the hardness. However, the technique has been reported to increase the fatigue life of Ti-6Al-4V alloy due to both a reduced fraction of α-Ti and to a reduction in the grain size (Konstantino and Altus 1999).

Laser processing using around three times the beam energy as in laser heating, can develop a deeper melt pool than other surface modification techniques,Fig18.2,(Gates 1986,Deng and Braun 1994, Zhecheva et al 2005),a rapidly solidified melt pool, with a >1000H_v surface zone, followed by a zone of a hardness gradually decreasing to that of the titanium substrate,325-350 H_v. This modified microstructure has been described as a functionally gradient layer, Fig18. 3. Many applications result in the removal of the surface during service. Therefore the thicker the modified layer, the longer the in- service use of the component. However, defects may be introduced during the surface modification process. These include cracks, Fig18. 4 and porosity in the surface layer, and in the case of the incorporation of particles, undissolved particles and heterogeneous particle distribution which may result in an early deterioration of the surface properties.

Several laser surface modification methods have been developed and include:

(1) surface alloying using an element which is well distributed throughout the Ti matrix, such as Al in low concentrations, to provide solid solution hardening, resulting in improved surface properties. Secondly, alloying with a solute element which will form a compound

with a higher hardness than the titanium alloy. This latter situation occurs following alloying with higher concentrations of Al, forming TiAl, and with Si, which forms Ti_5Si_3, either as needles, or together with ά- Ti as a eutectic, Fig18.5 and Fig18.6, (Hu et al 1998)

(2) the use of compounds which will completely dissolve providing solute atoms which react with titanium to form hard particles, such as borides, carbides, nitrides, oxides or silicides. An example is SiC particles, 3-7µm in size, which dissociates to give elemental Si and C. These atoms then react with Ti forming TiC and Ti_5Si_3 precipitates respectively, both significantly harder than Ti and its alloys ,Table 1. Another example is 10µm BN powder dissolved in Ti-6Al-4V alloy to give compounds of Ti_2N, TiB and Ti_3B_4, producing a surface hardness between1500-1700VHN, due to presence of the hard TiB and TiN phases (Selvan et al 1999).

(3) the incorporation of hard compounds, such as SiC, which will dissolve partially, leaving sufficient of the original particles well distributed throughout the Ti-matrix together with solute elements which will react with α-Ti to form a fine dispersed phase. SiC particles, in the range 30-100µm have been found to partially dissolve giving the same phases described in (2), Fig18.7(Mridha et al 1996).

(4) Intermetallic coatings of Ti-Al (Garcia 2002) have been developed on Ti alloys by laser processing as a means of improving high temperature properties while Ti_2Ni_3Si toughened by a ductile NiTi (Dong and Wang 2008) have potential for improved corrosion and wear resistance.

(5) Inoue (2000) discovered a series of amorphous alloys, based on R-E oxides, with a high glass forming ability (GFA).A Zr based amorphous alloy with the widest supercooled liquid region has an extremely high glass forming ability and was applied by Wang et al (2004) to coat CPTi using Zr based alloy powders.

(6) Laser nitriding to form a hard TiN surface layer ~5μm, followed by dendrites, needles and quasi-spherical particles at lower depths in the melt pool, Fig 18.3. This technique has received widespread attention for many years, initially through the use of CWCO_2 lasers (Katayama et al 1983, 1984), but also using Nd-YAG pulsed lasers (Ettaqi et al 1998,Santos et al 2006).Bianco et al (1995) investigated laser processing with CO_2 gas to form TiC precipitates, while the effect of TiC_xN_y by laser processing with a combination of carbon and nitrogen was addressed by Covelli (1996), and using gas mixtures of CO and N by Greiner (1997). However, the reader should be aware that a review of 'laser nitriding of metals' by Schaaf (2002) does not consider titanium alloys. Examples of these different approaches are discussed below.

18.4 Laser processing conditions

The main laser parameters which can be controlled during processing include the laser power, q, the beam radius, r_b the specimen or work-piece velocity, v, `and the beam mode, which may be stationary, spinning; top hat , or Gaussian (Ion 2005).In addition, in the case of alloying, the composition and concentration of the alloy, and if the processing involves a gas such as nitrogen, the concentration and the flow rate (Mridha and Baker1998). Other important factors are the dimensions, particularly the thickness of the work-piece (Hu et al 1997) and its absorptivity of the laser energy. Many of the studies on laser surface modification describe work which involved either a small hemispherical melted volume (Abboud and West 1994) or a single laser track with a width of a few millimetres (Mridha and Baker 1996). In practice, there is frequently a requirement to produce surface modification over a much greater area. This necessitates overlapping of many laser melted tracks. The best results for laser processing Ti-6Al-4V alloy plate using a stationary beam were obtained with medium scanning velocities of 15-50 mms^{-1} and with a minimum overlap of 50%, otherwise it was found that a part of each track will only be molten once, Fig18.8

(Morton et al 1992).Work by Baker and Selamat (2008), used a spinning beam to produce a broad laser track, lower scanning velocities, usually in the range 3-10mms^{-1} ,and in agreement with Morton et al (1992) and Robinson and Reed (1995), they also found that an overlap of 50% provided the best surface finish. However in earlier work (Xin et al 1996), also using a spinning beam, where the economics were not a prime concern, found that a 35% overlap gave a satisfactory surface. A consequence of overlapping of laser tracks is a build- up of heat in the work piece, resulting in preheating, which increases the temperature of subsequent tracks. This effect has received little attention in the literature but has been the subject of two papers, (Hu and Baker1997, 1999). The melting of 13 tracks on a 10mm thick plate of Ti-6Al-4V under atmosphere of Ar, showed that a constant preheat temperature of 235ºC was reached by track 7. With a 20% nitrogen atmosphere, under the same processing conditions, a temperature plateau of 290ºC was reached by track 11, Fig18. 9. Higher temperatures were reached with 5mm thick plate. Therefore it is not surprising that variations in the melt depth, in the microstructure and therefore in the properties such as hardness occur, from the first to the last melted tracks, although these changes are rarely reported in the literature.

The laser energy density E is related to the laser power q, the scanning velocity, v, which is normally the traverse speed of the work-piece, and the radius r_b of the laser probe by

$$E = (q / r_b v) \qquad [18.1]$$

expressed in MJm^{-2} , and for CO_2 lasers is normally in the range 50-600 MJm^{-2} .

The variation in the input energy density, that is the energy density absorbed by the alloy surface, controls the depth of the melt pool and therefore the volume of the molten alloy. The laser processing is characterized by high heating and cooling rates in the range 10^4 to 10^{10} Ks^{-1}, thermal gradients between 10^5 and 10^8 K/m and solidification velocities up to 30ms^{-1} (Draper and Poate 1985).These laser surface alloying parameters have the effect of extending the solid solubility limit and may result in metastable non-equilibrium phases leading to novel microstructures due to the rapid solidification conditions. The most important characteristic of the modified layer is the depth of penetration which is related to the maximum temperature reached during processing. As described by Steen et al (1994), several attempts have been made to predict the melt depth. These include those 'based on experimental studies which analysed statistically a large number of measurements to develop a master correlation. At the other extreme, those based on the laws of physics which provide 'exact' predictions, but the dominant physics is often lost in the wealth of information generated and the nature of the simulations limit their engineering application'. However, Shercliff and Ashby (1991) 'provide a balance between these two extremes and their work results in plots of dimensionless parameters which capture the significant trends of a large number of experimental data, including their own measurements'. Ion et al (1992) and Ion (2005 p525) have summarized some of the available approaches and collated the main relationships required to develop model process diagrams, while Hu and Baker (1996) considered the case of a spinning beam. A modified laser processing diagram showing the conditions for laser melting and laser cladding is given in Fig18.10.

While the melt depth, surface temperature, heating and cooling rates are of primary importance to the mechanical properties developed on solidification, the surface roughness can have important consequences for erosion resistance. Anthony and Cline (1977) explored the development of surface ripples during laser processing. They considered that 'during laser surface melting and alloying, a temperature gradient extends radially away from the centre of the laser beam. Under the beam, the temperature of the liquid is at its highest level and the surface tension of the liquid is at its lowest value. As the temperature of the liquid decreases away from the centre of the laser beam, the surface tension of the liquid increases. This increase of the surface tension of the liquid away from the centre of the beam, pulls the liquid away from the centre of the beam, thereby depressing the surface of the liquid under the beam and heightening the liquid surface elsewhere. This effect is known as Marangoni flow and is the dominant convective mechanism in the melt pool. It can have a controlling effect on the microstructure, Fig18.11. Chan et al (1984) in modelling heat flow, predicted that the melt pool rotates approximately five times before solidification. This effect manifests itself on occasions in the heterogeneous distribution of dendrites, Fig18.12. As the beam passes to other areas of the surface, this distortion of the liquid surface is frozen in, creating a roughened rippled surface', Fig18.13 The roughness of the surface has been shown to be a major factor in erosion of titanium alloys, considered in Section 18.74.

18.5 Laser Surface Melting and Cladding

18.51 Laser surface melting

The process whereby the alloy surface is laser melted and then resolidified without any attempt to modify the surface layer chemical composition is normally referred to as laser glazing or melting. The sequence of surface changes following the instant the laser beam contacts the alloy surface is summarized below. Firstly, the near surface region rapidly reaches the melting point and a liquid/solid interface starts to move through the alloy. Diffusion of elements commences in the liquid phase. The laser pulse is nearly terminated while the surface has remained below the vaporization temperature. At this stage the maximum melt depth has been attained, inter-diffusion continues, the re-solidified interface velocity is momentarily zero and then rapidly increases. The interface moves back to the surface from the region of maximum melt depth. Interdiffusion continues in the liquid, but the re-solidified metal behind the liquid/solid interface cools so rapidly that solid state diffusion may be negligible. Finally, re-solidification is complete and a surface alloy has been created. Due to the relatively small melted zone of 50 to 1000 microns, very high quench rates are achieved, in the range of 10^3 to 10^6 Ks^{-1}, resulting in non-equilibrium martensitic microstructures (Draper and Ewing 1984,Draper and Poste 1985).The re-solidified alloy has a titanium oxide film on the surface, which confers good wear resistance. Langlade et al (1998) used a YAG-Nd laser to study oxides on T40Ti and Ti-6Al-4Valloys. Stratified layers giving different coloured films were related to oxide thicknesses and oxide compositions. TiO $+Ti_2O_3$ followed TiO, and finally Ti_2O_3 +anatase TiO_2 +rutile TiO_2 .It was noted that titanium oxides may exhibit a solid lubricant effect, while the oxygen dissolved in the titanium matrix had a hardening effect.

One of the characteristics of the laser surface melting technique is the rapid solidification. which can produce hardening through the introduction of crystalline defects such as vacancies and dislocations. Often residual stresses are developed which result in a distortion of the work-piece, but can be overcome by the application of a low powered surface heating procedure following the laser melting process.

18.52 Cladding

Ion (2005) defined cladding as 'a surface melting process in which the laser beam is used to fuse an alloy addition onto a substrate'. The alloy may be introduced into the beam- material interaction zone either during or prior to processing, usually as powder, wire or foils'. The object is to melt a thin layer of substrate together with as much alloy addition as possible, which must be able to homogenize before it solidifies. Therefore very little of the substrate is melted and ideally, vaporization is avoided, as the molten clad solidifies rapidly, a clad with a nominal composition of the alloy is produced which has a strong metallurgical bond with the substrate and increased hardness. The process may be used for large area coverage by overlapping tracks, but it is the ability to protect smaller localized areas, that according to Vilar (1999) makes the technique unique. Most of the substrates which can be subjected to laser melting techniques are suitable for producing clad surfaces and in the case of powder additions, cladding and alloying processes often overlap. As seen in the schematic diagram

Fig18.10, laser cladding, uses a lower power density, around 10^{2} Wmm^{-2} compared with $!0^{3}$-10^{4} Wmm^{-2} for laser surface melting. This lower power density not only reduces the relative extent of distortion, but also ensures a closer control of the dilution of the clad, leading to a more exact coating composition.

Cladding was considered by Ion (2005) and Bao et al (2006) and reviewed by Vilar (1999) and Wu and Li (2006). The pioneering work was undertaken by Ayers (1981), who injected into Ti, powders of TiC (Ayers et al 1981,1984) or WC (Ayers et al 1981,1984), and later Abboud and West (1989) with SiC. Abboud and West (1989, 1990, 1991, 1991a) also laser surface clad CPTi with Al powder to produce titanium aluminide coatings. This was followed by the study of the wear and oxidation properties of titanium aluminides on CPTi (Hirose et al 1993). Recently, interest in cladding with Al on titanium alloys has been revived by Guo et al (2007, 2008, 2008a) and Pu (2008). Guo et al (2008) who studied the effect of preplaced aluminium powders between 14.7 and 29.7 at% on the phase composition and tribological properties of CPTi. Cracking was found in all the laser modified specimens. Cai et al (2007) used a mixture of titanium and B_4C precursor powders to form a mixture of carbide and boride precipitates which raised the hardness of the Ti-6Al-4V substrate from~350 to ~600H_v through the formation of TiC, TiB and TiB_2.Unusually,the precursor powders were placed in grooves machined to depths of 0.2 to 1.0mm. Research by H.M. Wang and Liu (2002), is an example of a study to develop a wear resistant $T_{i5}Si_3$/$NiTi_2$ intermetallic composite coating which was fabricated on a near alpha titanium alloy, BT9. The laser clad intermetallic composite of Ti_5Si_3 primary particles were uniformly distributed in the $NiTi_2$ matrix and metallurgically bonded to the titanium substrate, were free from porosity and microcracks, with a hardness of ~1000Hv at the surface retained to a depth of 800µm. Recently, cladding of Ti-6Al-4V by cobalt has been studied by Majumdar et al

(2008) developing several titanium cobalt compounds which were associated with improved corrosion resistance.

Laser cladding is also one of the surface amorphization technologies associated with the high rapid heating and cooling rates that inhibit long-range diffusion and avoids crystallization (Morris 1988). However, the amorphous alloys found before 1990's required cooling rates above 10^5 Ks^{-1} for amorphization, and the resulting amorphous layer thickness was limited to less than 50 nm (Wang et al 2004). Since 1988, Inoue and co-workers have discovered a series of amorphous alloys with high glass forming ability (GFA) and much lower critical cooling rates in the Mg-,Zr-, Fe-, Pd-, Ti- and Ni-based alloy systems (Inoue 2000). The alloy $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ which has a widest supercooled liquid region, also has a high GFA at an extremely low critical cooling rate of 1.5 K/s (Inoue et al 1993). The discovery of these GFAs opened up significantly greater prospects for laser cladding of amorphous coatings with a thicknesses >1mm and able to cover a large area. Various alloys have been laser cladded on a variety of substrates. Wang et al (2004) has studied Zr-based alloy powders laser-clad on a pure Ti substrate in an attempt to form an amorphous coating. No cracks or voids were observed within the coating. There are clear tendencies of composition separations in different phases. The extensive growth of titanium in the form of columnar crystallites into the coating, provide a good metallurgical bond between the coatings and substrate. This clad coating showed a higher but varying microhardness 650-1000H_v. As mentioned in Section 18.3, titanium based intermetallics, such as γ-TiAl, are of interest for structural applications at elevated temperatures (Ye 1999). Whereas γ-TiAl possesses low density (3.7-4.6 g cm^{-3}), high specific strength and excellent high temperature resistance, the sliding wear resistance at elevated temperatures needs improvement. Coatings of TiN on γ-TiAl, by multiarc implantation or a 3μm film of Ti_2AlC using plasma carburization, were found to have inadequate oxidation resistance with increasing temperature. Also the ductility at room temperature is a major obstacle to the use of Ti_3Al, TiAl and $TiAl_3$ (Hirose et al !993). However, Chen and Wang (2003) found that laser surface alloying Ti-48Al-2Cr-2Nb (γ-TiAl) with carbon, resulted in a thick composite coating of TiC, which exhibited >700 Hv and a 5x improvement in sliding wear resistance at 600°C over untreated γ-TiAl. Liu and Wang (2006, 2007) investigated the effect of laser cladding the same alloy with a mixture powders of Ni-20wt-%Cr alloy and Cr_3C_2 in the ratio of 20:80, 50:50 and 80:20, as a means of further improving the high temperature wear resistance. The main clad phases were γ Ni solid solution matrix, Cr_7C_3 and TiC. The clad processed with the 50:50 alloy showed a two times improvement in room temperature sliding wear resistance. An extension to this work (Liu and Yu 2007a) involved the incorporation of between 1 and 10wt-% of a rare-earth metal oxide, La_2O_3 , to the 50:50 ratio Ni-20wt-%Cr alloy :Cr_3C_2 alloy. An addition of 4 wt-% La_2O_3 refined the carbide microstructure and produced the highest values of microhardness combined with the lowest wear rate during room temperature sliding wear experiments. Possible improvements in the high temperature wear resistance of γ TiAl alloy were investigated by developing laser clad $\gamma/W_2C/TiC$ composite coatings through the use of different concentrations of Ni-Cr-W-C precursor mixed powders and testing the response of the coatings to dry sliding wear at 600ºC and isothermal oxidation at 1000ºC .Improved wear resistance was obtained, but oxidation resistance was reduced (Liu and Yu 2007b).

18.6 Laser surface alloying

Laser surface alloying of has been reviewed by Draper et al up to 1985 and by Ion (2005).Here the gaseous, solid and gaseous plus solid methods are considered.

18.61Laser nitriding

Laser surface engineering requires the protection of the molten surface by an inert gas, such as argon or helium, to prevent oxidation during processing. In the case of titanium alloys, the replacement of the inert gas by nitrogen is a technique which has been developed over the past 30 years for modifying the near-surface region of alloys without altering the bulk characteristics of titanium alloys (for example: Katayama et al 1985,Walker et al 1985,Bell et al 1986,Mridha and Baker 1991,1994, Kloosterman and De Hosson, 1995,Xin et al 1996,Nwobo et al 1999,Kasper et al 2007, Abboud et al 2008). Laser nitriding with a 100% nitrogen atmospheres was used in most of the early work ,and produced a thin 5-10µm surface layer of titanium nitride. The hardness recorded closest to the surface was ~ 1000-2000H_v , and in addition, the TiN layer provided improved corrosion resistance, a lower coefficient of friction and wear resistance. However, cracking was often observed, Fig18.4 (Katayama et al 1985, Morton et al 1992, Hu et al 1997b, Nwobo et al 1999). Morton et al (1992) found that when laser nitriding CPTi and Ti-6Al-4V alloy produced a surface with a hardness >600H_v , cracking was likely to occur ,but could be avoided by preheating prior to nitriding, which reduced the cooling rate and controlled the level of the residual stresses developed on solidification. An alternative method of alleviating this problem is the use of dilute nitrogen atmospheres, usually in the form of an argon-nitrogen mixture, together with lower nitrogen flow rates (Mordike 1985, Bell et al 1986,Morton et al 1992, Mridha and Baker 1994, Xin and Baker 1996,Grenier et al 1997, Xin et al 1998,Selamat et al 2001).Dilute nitrogen atmospheres were found to reduce significantly or eliminate cracking, but at the expense of a decrease in surface hardness, Fig18.14, and a smaller melt depth. In the work of Selamat et al (2001),no cracking was observed following processing with a dilute nitrogen atmosphere of 20%N- 80% Ar,while laser nitriding using a 50%N50%Ar atmosphere coincided with a reduction in hardness to ~800H_v (Xue et al 1997). As described by Mridha and Baker (1994) and Kloosterman and De Hosson (1995), initially, a thin surface TiN layer <10µm, will solidify, out of which titanium nitride dendrites will grow due to constitutional undercooling. The dendrites grow by rejecting titanium into the melt. At the same time there will be a solidification front at the bottom of the melt pool and somewhere in between, these fronts will meet. If the cooling rate is sufficiently fast, and the nitrogen concentration in the titanium is below 6.2 $^{a}/_{o}$, a martensitic transformation (ά-Ti) is possible. In general, the nitrided surface develops better properties than those produced by glazing in an inert gas atmosphere (Baker et al 1994). Below the surface, the hardness normally decreases rapidly, due to the TiN layer being replaced by TiN dendrites in an ά Ti-N solid solution matrix (Katayama 1983, Walker et al 1985, Bell et al 1986, Mridha and Baker 1991, Kloosterman and De Hosson 1995), Fig18.3. Closer to the melt zone- HAZ boundary, only the ά Ti-N solid solution is present, and this is reflected in the level of the hardness.

Microstructural characterisation has been related to the processing, hardness and roughness data.. Previous studies by the present author and co-workers used TEM/SAED, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to characterise titanium nitride phases in a Ti-6Al-4V alloy produced by laser nitriding (Xin et al 1998, Xin et al 2000, Selamat et al 2001). Single phase δ TiN has an NaCl type fcc structure and is more accurately expressed as TiN_x, as it and can have a wide range of homogeneity from~ 30 to 55 atomic percent nitrogen. In the transition elements, the cubic nitrides can exist in a wide range of non-stoichiometry, and TiN_X can be obtained with $0.5 \leq x \leq 1.1$ (Selamat et al 2003). The values of x have been shown to depend on the percentage N in the nitriding atmosphere. With 100%N, x has been estimated to be close to 1, with 80%N, x =0.8 while when 20%N is employed, x decreased to 0.75 (Selamat 2001). The XPS spectra obtained from different depths in the melt zone indicated that the quantity of TiN_x precipitates decreased with increasing depth from the surface. Only a small quantity was present at 100µm, while none was detected below 300µm from the surface.

TiN coatings are used mostly for their low coefficient of friction in order to reduce adhesive wear, while TiC coatings increase both the surface hardness and the resistance to ploughing wear (Moskowitz et al 1986). Eskin et al (1995) and Bianco et al (1995) have shown the potential use of CO_2 as an alloying gas. They noted that the abrasive wear resistance of CO_2 laser alloyed titanium is improved relative to TiN layers produced by laser nitriding. It is also known that the wear resistance of titanium was enhanced by TiC coatings produced by laser alloying using preplaced graphite powders, originally added to improve the absorptivity (Flower et al 1985, Walker et al 1985, Covalli et al 1986). Unlike nitriding, which resulted in a layer of TiN, the alloying with graphite did not produce a surface layer of TiC.The use of a gas instead of preplaced graphite allows a more precise control of the relative concentration of the carbon content of the molten layer. Also, laser gas alloying can be undertaken more easily on complex shapes without the feeding difficulties associated with powders or wires. Deng and Braun (1994) have observed that the wear behaviour of TiC_xN_y is superior with carbon rich coatings to TiN or TiC which led Grenier et al (1997) to study the effect of mixtures of carbon monoxide and nitrogen gases on the microstructure and wear resistance of laser processed CPTi using a Nd:YAG pulsed laser.

18.62 Laser powder alloying

The early work using powders as a source of alloying (Ayers et al 1981, 1984, Abboud and West 1989) was based on injection of powders of around 150μm in size, which may be described more accurately as cladding rather than surface alloying. Later, this average particle size was reduced to within the range 60-100μm (Cooper and Slebodnick 1989, Kloosterman et al 1998, Kool et al 1999, Pei et al 2002). An alternative method is the preplacement of particles on the surface of the substrate alloy in the form of a slurry, where in general, the particles have a smaller average size, ~ 45-60μm (Hu et al 1997, Pang et al 2005). Both these techniques result in the partial dissolution of the powders, Fig18.7, which can provide a strong bond with the matrix, and confer significant wear resistance to the substrate (Ayers and Bolster 1984, Hu et al 1997, Ettaqi et al 1998, Pang et al 2005).

However, for some applications which require improved surface strength through dispersion hardening and /or improved corrosion properties, a complete dissolution of the particles during laser processing is beneficial. This is possible using laser powers of ~3kW, when the particle size is less than 10μm.With SiC particles, both of these techniques provided an opportunity for the precipitation, in a fine state, of new phases such as Ti_5Si_3 and TiC, Fig18.15 (Mridha et al 1993, Baker et al 1994, Hu et al 1997, Mridha and Baker 1997, Selamat et al 2003, Mridha and Baker 2007,Poletti 2008).It is generally found that the hardness of the powder alloyed surface is lower than that of the nitrided specimens. Other elements and compounds that have been incorporated into titanium alloys include, Al (Abboud et al 1994,1994a,Majumdar et al 2000,2000a), B_4C (Mehlmann et al 1990), BN (Selvan et al 1999) ,Co (Majumdar et al 2008),Si (Selvan et al 1999, Majumdar et al 2000,2000a,Alhammad et al 2008),TiC(Abboud and West 1992, Majumdar 1999, Man et al 2001,Sun et al 2001, Zang et al 2001, Pei et al 2002) , TiN (Hu et al 1997,Ettaqi et al 1998, Yilbas and Shuja 2000, Yilbas et al 2001), ZrC (Hu et al 1997) and ZrN((Hu et al 1997). Mixed alloy powders such as Al+ Si (Majumdar et al 1999, 2000,2000a) , Mo-WC (Pei et al 2002) ,Ti-Cr_3C_2 (Pei et al 2002) , and Ti-TiB (Banerjee et al 2004) have also been studied, as have complex powders which include BN-NiCrCoAlY (Molian and Hualun 1989) , NiCrBSiC (Sun et al 2000,2002a), NiCrBSi-TiC (Sun et al 2001),NiCrBSiC-TiC (Majumdar et al 1999,Sun et al 2002,2002a), NiCoCrAlY (Meng et al 2005), Ti_5Si_3+$NiTi_2$ (Wang and Liu 2002) and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ (Wang et al 2000) .Laser alloying with graphite (Courant et al 2005), graphite and silicon mixed powders (Tian et al 2006) , graphite, boron and RE oxides (Tian et al 2006a) has been undertaken. However, in all cases, the laser alloying resulted in a harder melt zone than the substrate and many papers reported significant improvements in properties.

In the case of injected powders, the protective gas used to avoid oxidation has been employed as a carrier, and some studies have found that position the powder stream out of the laser beam minimizes the reaction layer between the particles and the titanium matrix (Kloosterman et al 1998).

18.63 Laser surface nitriding plus powder alloying

The combination of powders with gaseous atmospheres has also been studied; in particular mixtures of nitrogen with SiC (Hu et al 1997, 1998,Mridha and Baker 1996, 1997,Selamat et al 2003), TiN (Ettaqi et al 1998), ZrC (Ettaqi et al 1998) and ZrN (Hu et al 1997) . Dilute nitrogen atmospheres combined with powder alloying have been found to produce crack- free surfaces which have additional hardness relative to the titanium parent alloy and the powder alloying alone (Baker et al 1994,Mridha and Baker 1996, 1997,2007, Hu et al 1998,Selamat et al 2006,2008,Garcia et al 2002,Guo et al 2008a).

18.7 Effect of laser surface modification on properties

18.71Hardness and residual stress

The hardness of laser modified titanium surfaces has a significant influence on the wear properties. The aim is to precipitate hard ceramic particles, sometimes as dendrites, as quasi-spherical particles, needles or in a eutectic with α-Ti together with a solid solution strengthened Ti matrix. In the case of laser nitriding, the formation of a hard surface TiN layer is followed by a dendrite microstructure, (Bell et al 1986, Morton et al 1992, Hu et al 1996). The hardness, H_v is controlled by the volume fraction dendritic phase V%, Fig18.16, by

$$H_v = 23\ V\% \qquad [8.2]$$

which is related to the details of the secondary arm spacing. This in turn is controlled by the rate of cooling. Peng et al (1983) used the Cline and Anthony (1977) model to calculate the maximum cooling rate, ε in Ks^{-1} following laser melting through a correlation with dendrite arm spacings, d in μm, measured from photomicrographs. The best functional correlation was

$$d=80\ \varepsilon^{-0.34} \qquad [18.3]$$

Fig18.7 shows that this holds for values of ε between 8×10^4 and 1.5×10^6 Ks^{-1}, as described by the model.

Whereas most research reports the hardness as a single series of microhardness measurements taken close to the surface down to the substrate, Baker and Selamat (2008) produced hardness maps, Fig18.18 which, by allowing a comparison of hardness over several laser tracks, provides a much more accurate picture hardness variations throughout processing.

Laser nitriding Ti with 100% N produced surface hardness values in the range 1600-2000H_v (Katayama et al 1983, Bell et al 1996, Mridha and Baker 1994a,Ettaqi et al 1998), which decreased with increasing work-piece velocity, %N in the atmosphere, Fig18.14 (Hu et al 1996,Xin et al 1996,Hu and Baker 1999, Nwobe et al 1999, Kasper et al 2007, Raaif et al 2008) and flow rate (Mridha and Baker 1998).The variation of hardness of TiN_x as a function of N/Ti ratio was shown by Sproul et al (1989) for sputtered coatings, to have a narrow range between 3140 and 3400 $Kgmm^{-2}$, the latter figure also given by Perry et al (1999). To date it has not been possible to find hardness data related to the stoichiometry of bulk TiN_x, over a wide x range.

Laser alloying Ti with powders also increased the surface hardness. For example, Tian et al (2005) obtained hardness of 1500-1600H_v after laser processing TiN/B/Si/Ni powders, while slightly higher hardness 1600-1700 $Hv_{0.1}$ were found the in work on C/ TiB/Ti powders(2006b).By comparison, the hardness of individual Zr-based amorphous was much lower and varied from ~650 to 1000HK,still higher than the single amorphous alloy at 450-500HK (Wang et al 2004).

Another effect that has received little attention is the residual stress which develops as a result of laser surface modification processing. Ubhi et al (1988) showed by X-ray diffraction, that the residual stress across a single track in laser glazed Ti-6Al-4V plate was +170MPa (+ve is a tensile stress) compared to +100MPa in the parent as rolled plate, and these values were reduced on annealing. Mridha et al (1993) determined the residual stress laser processed CPTi alloyed with 6μm SiC particles. They showed that the tensile stresses determined parallel to the track direction, decreased with depth from +259MPa at the surface to +124MPa at a depth of about 200μm.The compressive stresses determined perpendicular to the track direction also decreased fromn-244MPa at the top to-170MPa at 100μm subsurface. A detailed study of the surface residual stresses developed in both single track and multi track laser nitrided Ti-6Al-4V specimens was undertaken by Robinson et al (1996). The tracks, unlike the work of Mridha et al (1993), were allowed to cool to below 50ºC between each successive pass to avoid preheating effects. In the single track specimen, the residual stress state prior to laser treatment was compressive (-562MPa), due to the severity of the grit blasting and considered to be the maximum value of elastic stress.. A progressive increase in the level of the tensile residual stress occurred as successive adjacent melt tracks were formed, reaching a maximum tensile stress of ~ +560MPa, corresponding approximately to the compressive stress in the grit blasted surface prior to laser melting. Cracking was not observed when the alloy was melted in an Ar. However, the introduction of nitrogen, led on occasion, to longitudinal cracks parallel to the laser track in the multi-track case, but perpendicular to the melt track in the single track experiments. The work emphasises the importance of conducting multi-track studies, but avoiding inter-pass cooling, and using conditions which are more appropriate to engineering applications than single track work.

18.72 Surface roughness

The roughness of the laser modified surface layer has received less attention in the literature. This may be because many applications require the machining of a surface before service, which may remove up to 40µm of the modified surface and entails additional costs. However, very smooth surfaces following laser processing have been reported.

The origin of laser induced surface roughness is due to the development of morphologies such as ridges, Fig18.13 , large scale periodic structures, cones or columns. The surface micro-structuring of titanium in the presence of nitrogen following processing using a Nd-YAG laser was investigated in detail by György et al (2003, 2004).They showed that initially, a rippled structure developed, which under further irradiation gave way to micro-columns, uniformly distributed on the whole irradiated surface. Nitrogen pressure had a significant influence on the surface morphology. However, 'in argon, smooth flat islands appear, surrounded by a wave-like micro-relief, which evolves with increase in the number of laser pulses towards a smooth surface with polyhedral structures' (György et al 2004)..

The characterization of the surface finish of laser molten layers following CW CO_2 laser processing was considered in terms of roughness and waviness (Morton et al 1992). Roughness, according to Morton et al (1992,) is due to the amount of surface rippling, which in turn is dependent on the viscosity of the melt (Anthony and Cline 1977). In agreement, Xue et al (1997) noted that the surface roughness in laser nitrided surfaces is related to the laser process parameters, the nitrogen concentration and the track overlap ratio. To this list, in the case of powder alloying, it is necessary to include the concentration and size of the powder and details of the carrier gas flow. Whilst rippling as a result of laser nitriding is widely reported, it has also been observed after laser boronising Ti 6Al-4V with a preplaced layer of BN (Selvan et al 1999). Waviness is a function of the convectional flow of the melt surface and again is influenced by the percent overlap (Morton et al 1992). The use of a spinning rather than a stationary beam had an influence on the surface morphology, which developed cellular –like structures with oval-shaped shiny bands across the tracks, Fig18.19 (Mridha and Baker 1994a). After laser nitriding of titanium, Bell et al (1986) found the surface roughness, R_a <10µm, that is,smoother than the as-ground condition or following shot peening (Xue et al 1997), which can show an R_a value of up to 15µm (Drechsler et al 1999).These data compare with an as- machined roughness of Ti-6Al-4V which can vary widely from 1.4µm (Ribeiro et al 2003,Nalla et al 2003) to 5µm, depending on the tools and machining parameters (Che-Haron 2001) .

Laser nitriding using 100% N, produces the smoothest surface for both CPTi and Ti-6Al-4V alloys with R_a values of 2.7µm,4.6µm respectively, but these was greater than laser processing in 100% argon or under a vacuum (Hu and Baker 1999). Baker and Selamat (2008) compared in Table18. 2 the surface roughness of laser processed Ti-6Al-4V following nitriding in 20% N:80%Ar (specimen A), SiC powder melting (specimen B)and combined nitriding 40%N plus SiC powder addition (specimen C).It is interesting to note that the R_a value varied with track number. For specimen A, R_a decreases with increasing track number, while with specimens B and C, the roughness increased as the track number increased. The data in Table 18. 2 show that laser processing Ti-6Al-4V following preplacing of SiC powder produces a very smooth surface, as R_a increases from of 0.94µm to 1.8µm from track 1 to track 6, but is still significantly smaller than any other R_a values collated in this work. However, combining nitriding with powder placement resulted in a marked deterioration in the surface smoothness, with the R_a values again increasing with track number from 4.4µm for track 1 to >7µm for tracks 6 and 12.These were the highest values recorded in the work, but still fall within the limits given by Bell et al (1985).

18.73 Wear

Titanium alloys have poor fretting fatigue resistance and poor tribological properties. Theoretical calculations have shown that metals with low theoretical tensile and shear strengths exhibit higher coefficients of friction(μ) than higher strength materials. Within the class of alloys with hcp structures, titanium has relatively low values of these properties. Consequently, it is expected that it will have high frictional values, which is the case for titanium sliding against titanium in air, where μ=6 (Miyoshi and Buckley 1982). Lower strength materials also show greater material transfer to non-material counter-faces, than higher strength materials. The great affinity of titanium for oxygen leads to the formation of oxide which is transferred and adheres to non-metallic materials, such as polymers, resulting in severe adhesive wear. Surface modifications are therefore required to increase near surface strength, thereby reducing μ and lowering the tendency for transfer of material and adhesive wear (Kustas and. Misrta 1994).

Following either laser nitriding or laser powder alloying, there are reductions in μ and improvements in wear resistance. At higher loads, there are several reports of three body wear, due to the hard ceramic particles which were originally part of the modified layer, augmenting the wear debris.

Yerramarry and Bahadur (1991) were among the first to study both sliding wear and abrasive wear of titanium alloys following laser surface modification. They assessed the wear following (a) surface melting in an argon atmosphere, (b) nitriding and (c) nickel alloying, where an electroplated nickel layer 25-50μm was surface melted in an argon atmosphere. Sliding wear tests were undertaken using a block –on-ring configuration in dry conditions with the titanium alloy sliding against a tool steel. The steady state wear rate decreased from 40x 10^{-4} mm^3m^{-1} to 0.8 x 10^{-4} mm^3m^{-1} after Ni alloying ,to 0.5 x 10^{-4} mm^3m^{-1} after surface melting, while the lowest wear rate was 0.3 x 10^{-4} mm^3m^{-1}, following laser nitriding. The as –received value of μ was reduced from0.62 to ~0.43 for all the laser – treated specimens. Ploughing with some adhesive wear was observed after testing the as-received alloy. The abrasive wear test involved a dry sand –rubber wheel and the wear rate of the as-received titanium alloy was about 0.16 mm^3m^{-1} which was reduced by a factor of 1.5 for the laser nickel alloying and 3.0 for laser nitriding. A higher abrasive wear resistance for Ti-6Al-4V coincided with greater surface hardness and N%,(Xin and Baker 1996,Hu et al 1997a) The thicker the TiN layer, the greater the abrasive wear resistance even when fine cracks were found in the layer. Three slopes associated with different microstructures, were seen in the weight loss versus sliding distance graphs, Fig18.20.The wear rate for 100%N CPTi was 0.001mg m^{-1} while that of the untreated CPTi was 0.18mg m^{-1}. Recently Raaif (2008) determined the sliding wear of laser nitrided Cp Ti for 40, 60 and 80%N atmospheres. They showed that μ decreased both with increasing load and %N. Baker et al (1994) and Mridha and Baker (1997, 2007) looked in detail at the abrasive wear resistance of laser incorporation of small SiC powders. Fig18.21 shows that both processing conditions and powder volume fraction affect the weight loss. The best results are comparable to those of 100%N, Fig18.20.

The wear resistance developed by laser processing using intermetallic powders has been the subject of several investigations. Research by Majumdar et al (2000), found that laser alloying of Ti-6Al-4V with Al, Si or Al+Si powders showed improved wear resistance in the order, Ti(Si), Ti(Al+Si) ,Ti(Al) and CPTi. The rate of wear was a minimum in Ti(Si) and the improvements were considered to be due to Ti_5Si_3 +άTi eutectic following incorporation of the Si addition. In CPTi, an increase in μ was associated with severe adhesive wear and localized deformation, which was responsible for the formation and propagation of microcracks, while a gradual decrease or constant value of μ, indicated that the wear was mainly abrasive in nature. Tian and co-workers laser synthesised a series of MMC coatings on titanium alloys, TiN/B/Si/Ni (2005b), $TiB/TiB_2/Ti/TiNi$ (2005a), $TiC/Ti_5Si_3/Ti$ (2006), and C/TiB/Ti (2006b). The TiN/B/Si/Ni (2005b) work showed the coating had a μ of ~0.4, lower than the untreated alloy. Slightly higher hardness 1600-1700 $Hv_{0.1}$ values were found the in work on C/ TiB/Ti powders(2006b), which developed coarse needle TiB and dendritic TiC particles conferring excellent dry sliding wear resistance. Dry sliding wear at RT of Ti-Al cladded coatings on CPTi was studied by Guo et al (2007). The best results were obtained from the cladded 18at% Al specimen, which was composed of α –Ti and α_2-Ti $_3$Al.The hardness in all the cladded specimens showed variations, but peaked at ~700H_v, which then gradually deceased to the substrate. This approach was extended to a study of TiN/Ti_3Al on CPTi by nitriding a coating of Al and Ti powders (Guo et al 2008a), and 40 ^{v}/o TiN, TiC or SiC powders, all mixed with Al powders on CPTi, to give Ti_3Al (Pu et al 2008). The latterfound that TiN/ Ti_3Al and TiC/ Ti_3Al coatings displayed the best wear resistance at a load of 5N, due to the presence of a granular TiN/ Ti_3Al / TiAl / Ti_2AlN_2 / Ti_3AlN_2 phases, giving a surface hardness of 1124H_v..

In an attempt to form a hard amorphous coating, Zr-based alloy powders laser-clad on a pure Ti substrate were investigated by Wang et al (2004). The un-lubricated coating showed a lower μ ,0.17-0.25,than that of the amorphous alloy ~0.52, while the predominant wear mechanisms were abrasion and peeling. A series of papers (Wang et al 2003, Wang and Wang 2004, Dong and Wang 2008) have highlighted the combination of excellent tribological and corrosion properties of a multiphase structure consisting of a brittle Laves phase Ti_2Ni_3Si toughened by a ductile NiTi phase. The properties were attributed to the chemical stability of the phases and their strong inter-atomic bonds.

18.74 Erosion of titanium alloys

Erosion is an accelerated form of attack usually associated with high water or solid particle velocities and with local turbulence which removes the oxide film from the surface of metals, thus exposing bare metal to the corrodent. As a result of its ability to repair its protective oxide film quickly, titanium has an extremely high resistance to this form of attack. The erosion resistance of titanium alloys has been studied mainly from two aspects, firstly the resistance to solid particle erosion and secondly the resistance to water droplet impingement. The erosion of ductile metals is often the result of several simultaneous material removal mechanisms. Massoud and Coquerelle (1988) undertook erosion studies on Ti -6Al-4V alloy by impinging SiC particles at the alloy surface at different angles. They found that the maximum rate of erosion coincided with an angle between 20 and 30º, which is well established for ductile metals, compared with 90º for brittle materials. Within this impingement angle range, impact craters were elongated in the direction of the particle motion and the predominant modes of erosion seem to be ploughing and cutting. At higher impingement angles, the main modes of erosion were deformation and extrusion of metal to form, a raised region around the crater. Many SiC particle fragments were embedded in the surface. Adherence of the target material to the eroding particle surface has been identified as an important material removal mechanism. Here large Ti chips were adhered to SiC particles. No melting was observed in this work. The same features were recorded by Yerramarry and Bahadur (1991) again studying Ti-6Al-4V alloy impacted by SiC particles. Material removal was attributed to cutting, ploughing or pile-up leading to flake formation and separation and lip fragmentation.

18.741 Erosion resistance of hard coatings

Singhal (1978) showed that TiB-TiN coatings were erosion resistant . Massoud and Coquerelle (1988) observed that the thickness of these nitrided coatings appeared to be crucial to the erosion resistance of laser nitrided titanium alloys. They found that laser nitrided surface had better erosion resistance than titanium nitride surfaces prepared by PVD, where spalling damage removed the TiN coating from the substrate after only a few impacts. However, hard dense coatings of TiB-TiN, 20 to 30μm in thickness, with surface hardness of ~1400H_v, were rapidly damaged because of cracking due to the brittle nature of the layer, but thicker layers (80μm) showed a slower erosion rate. Yerramarry and Bahadur (1991) again studying the effectiveness of laser surface modification on Ti-6Al-4V alloy, found that in their tests involving high velocity impacts by coarse SiC particles of 120 grit (100μm),erosion of the surface produced deep craters which extended beyond the laser treated region for all the treatments. They concluded that laser treatments were ineffective in preventing severe erosion by coarse particles.

The ultrasonically induced cavitation erosion in a 3.5% NaCl solution of laser nitrided CPTi and Ti-6Al-4V in a pure nitrogen atmosphere was considered by Man et al (2003). They produced crack-free surfaces with a hardness of ~2000Hv, followed by a microstructure with a hardness of 800Hv retained to a depth of ~400μm. The cavitation resistance was improved by 12 times following laser nitriding and attributed to the increased surface hardness, which Neville and McDougall (2001) reported to be related to the erosion-corrosion resistance for Ti alloys.

18.742 Water droplet erosion

Laser nitriding using a CW CO_2 laser has been the most researched method of improving erosion resistance of Ti-6Al-4V alloy. Contrary to abrasion and sliding wear, hardness alone is not considered to be a major factor in effecting erosion resistance, as residual stress plays a major role in erosion resistance of TiN layers (Sue and Troue 1988). Gerdes et al (1995) showed that laser nitriding improved water droplet erosion resistance. More recently, Kasper et al (2007 investigated the influence of percentage nitrogen on the erosion resistance of Ti-6Al-4V following water droplet testing. Again, they found an improvement, once the nitrogen level was >5%, but little difference in the cumulative volume loss for nitrogen levels between 9 and 25%.When the nitrogen content was ≤ 5%, the matrix was mainly martensitic ά-Ti, and erosion proceeded along the boundaries of the martensitic needles, whereas with nitrogen >5%,the microstructure consisted of small α-Ti grains with β-Ti between them, which eroded more rapidly. They attributed the best erosion resistance to the presence of a more homogeneous, crack- free microstructure. Two sets of researchers, Robinson and Reed (1995) with Robinson et al (1995), and Hu et al (1997a)) used the same test rig to evaluate the water droplet erosion resistance of laser nitrided Ti-6Al-4V alloy The conditions during testing were designed to approximate the actual operating conditions in the LP stage of a steam turbine, with a spray droplet size of ~100μm.The impact velocity of ~500ms^{-1} is well into the regime of impact velocities under which the wear mechanism is dominated by erosion alone (Coulon 1986). Robinson and Reed (1995) compared three environments, Ar, 10%N +90%Ar and 20%N +80% Ar. They observed cracks after laser nitriding, but a significant reduction in the weight loss of the specimens laser nitrided in the 20% N.Hu et al (1997a), using a spinning beam, extended the work to include nitriding under 60%Ar + 40%N. They also compared the effect of grinding 100-180μm from the laser nitrided surfaces to give a smoother surface before testing. This would remove any TiN layer and expose the TiN +ά-Ti microstructure to the erosion jets.Fig18.22 shows that grinding had a beneficial effect on the erosion resistance thought to be due to reducing the level of the residual stress.

The solid particle and cavitation erosion of titanium aluminide intermetallic alloys was investigated by Howard and Ball (1995).They concluded that the γ-TiAl alloys they examined were more resistant to cavitation erosion than the super α_2 – TiAl alloy, while the particle erosion due to the impact of angular 120grit (~100μm dia.) SiC, of both types of TiAl alloys, was similar to 304 stainless steel.

18.75 Oxidation resistance

Hirose et al (1993) were among the first to explore the oxidation resistance of laser alloyed titanium aluminides on CPTi. Testing at 1000ºC they found that the layer comprising $TiAl_3$ +TiAl had the best oxidation resistance. In other work, a laser synthesised TiN/B/Si/Ni coating on titanium alloys was shown by Tian et al (2005) to be ~4 times more resistant than the untreated alloy to oxidation after 70hrs at 750ºC. Liu and Wang (2006, 2007) found that the high temperature oxidation resistance, measured after 50hrs at 1000ºC, of 50:50 mixed powders of Ni-20wt-%Cr alloy and Cr_3C_2 was 2.5x superior to the untreated TiAl alloy. This was shown to be associated with the compact oxide scale consisting of $TiO_2/\alpha\text{-}Al_2O_3/Cr_2O_3$, which protected the γ/ Cr_7C_3/ TiC composite coating from excessive oxidation attack. Al rich $TiAl_3$ layers have superior oxidation resistance at ~800ºC to that of Ti alloys(Garcia 2002) as does TiC formed on γ-TiAl alloyed with carbon (Chen and Wang 2003).

11 Summary

Laser surface modifications to produce cladded and surface alloyed coatings on titanium alloys have been studied extensively. Laser nitriding has been widely investigated, but when high concentrations of nitrogen are used, cracking is invariably found, often penetrating from the surface to the substrate. Preheating or the use of dilute nitrogen atmospheres avoid cracking but at the expense of lower surface hardness and poorer wear properties However, significant improvements in water droplet erosion have been recorded compared to the untreated titanium. Powders, incorporated via the gas flow injection technique or as a preplaced slurry have been used to precipitate borides, carbides, nitrides and silicides, singly or in combination, sometimes with nitriding, as a means of producing a thick, hard crack-free coating having good wear and high temperature oxidation resistance. It is concluded that different applications require different properties in the laser modified surfaces. Whereas high hardness is important for dry sliding wear resistance, strong bonding between the new phases developed during laser processing, are important for abrasive wear resistance. On the otherhand, improved hardness but with a smooth surface with $R_a < 5\mu m$ together with a low residual stress provide the best combination for erosion resistant surfaces.

Acknowledgments

The author acknowledges the co-operation of Professor S Mridha, Drs C Hu, M S Selamat, H S Ubhi, L M Watson, H Xin and the late Professor A W Bowen, in his research involving laser processing of titanium alloys. Aileen Petrie is thanked for her kind help with the figures.

12 References

Abboud J H and West D R F (1989) 'Ceramic-metal composites produced by laser treatment', *Mat Sci Technol*, 5, 725-728

Abboud J H and West D R F (1990) 'Laser surface alloying of titanium with aluminium', *J Mater Sci Lett*, 9**,** 308-310.

Abboud J H and West D R F (1991), 'Processing aspects of laser surface alloying of titanium with aluminium' , *Mater Sci Technol*, **7**,353-356.

Abboud J H and West D R F (1991a) 'Martensite formation in Ti-Al layers produced by laser surface alloying', *Mat Sci Technol*, 7, 827-834.

Abboud J H and West D R F (1992) 'Insitu production of Ti-TiC composites by laser melting', *J Mater Sci Lett ,* 11, 1675-1677.

Abboud J H and West D R F (1994) '.Titanium aluminide composites produced by laser melting', *Mater Sci Technol.*, 10, 60-68.

Abboud J H, Rawlings R and West D R F (1994) 'Functionally gradient layers of Ti-Al based alloys produced by laser alloying and cladding', *Mater Sci Technol*, 10,414-419.

Abboud J H, West D R F and Rawlings R (1994a), 'Microstructure and properties of laser produced Ti-Al functionally gradient clad ', *Mater Sci Technol*,10, ,848-953

Abboud J H, Fidel A F and Benyounis K Y (2008), 'Surface nitriding of Ti-6Al-4V alloy with a high power CO_2 laser ', *Optics and Laser Technol*,40, 405-414.
doi: 10.1016/j.optlastec.2007.07.005

Alhammad M, Esmaeili S and Toyserkani E (2008), 'Surface modification of Ti-6Al-4V using laser-assisted deposition of a Ti-Si compound', Surf Coat Technol , 203,1-8.
doi: 10.1016/j.surfcoat.2008.06.160

Anthony TR and Cline HE (1997),'Surface rippling induced by surface- tension gradients during laser surface melting and alloying', *J Appl Phys* , 48,3888-3894.

Ayers J D (1981), 'Particulate composite surfaces by laser processing', in Mukherjee K and Majumdar J ed. *Lasers in Metallurgy*, Met .Soc. AIME, Warrendale, Penn.,115-120.

Ayers JD, Schaffer R T and Robey W P (1981), ' A laser processing technique for improving the wear resistance of metals '*J Metal*, 33**,** 19-23.

Ayers J.D and Bolster R.N (1984), ' Abrasive wear with fine diamond particles of carbide containing aluminium and titanium surfaces ',*Wear*, 93**,** 193-205.

Baker TN, Xin H, Hu C, and Mridha S (1994), 'Design of surface *in-situ* metal- ceramic composite formation via laser treatment ', *Mat Sci Technol*, 10, 536-544.

Baker T N and Selamat M S (2008), 'Surface engineering of Ti-6Al-4V by nitriding and powder alloying using CW CO_2 laser', *Mater Sci Technol*,24,189-200.
doi: 10.1179/174328407X226563

Banerjee R, Genç A, Collins P C and Fraser H (2004), ' Comparison of microstructural evolution in laser-deposited and arc-melted in-situ Ti-TiB composites ', *Met Mat Trans* , 35A, 2143-2152.

Bao R L, Yu HJ ,Chen C Z, Qi B and Zang LJ (2006), 'Development of laser cladding wear-resistant coating on titanium alloys ', *Surf Rev Lett*, 13,645-654.

Bell T, Bergmann H W, Lanagan J, Morton P H and Staines A M (1986), 'Surface engineering of titanium with nitrogen', *Sur Eng,* 2,133-143.

Bianco M, Tosto S, Pierdominici F and Casaccia C R E (1995), '*CO_2 gaseous alloying of Ti6Al4V by means of a pulsed laser*', in Sudarshan T S and Jeandin M ed. Surface Modification Technologies V111, Inst. Metals, 320-326.

Cai LF, Zhang Y and Shi L (2007), 'Microstructure and formation mechanism of titanium matrix composites coating on Ti-6Al-4V by laser cladding', *Rare Metals*, 26, 342-346. doi: 10.1016/S1001-0521(07)60226-5

Chan C, Mazumder J and Chen M M (1984), 'A two –dimensional transient model for convection in laser melted pool', *Metall Trans*, 15A, 2175-2184.

Che-Haron C H (2001), 'Tool life and surface integrity in turning titanium', *J Mater Process Technol,* 118, 231-237. doi:10.1016/S0924-0136(01)00926-8

Chen Y and Wang H M (2003) , 'Microstructure and high-temperature wear resistance of a laser surface alloyed γ-TiAl with carbon', *Appl Surf Sci*, 220, 186-192. doi:10.1016/S0169-4332(03)00816-X

Chen Y, Liu D, Li F and Li L (2008), 'WC_p/Ti-6Al-4V graded metal matrix composites layer produced by laser melt injection', *Surf Coat Technol*, 202, 4780-4787. doi:10.1016/j.surfcoat.2008.04.057

Cline H E and Anthony T R (1977) , 'Heat treating and melting material with a scanning laser or electron beam', *J Appl Phys*, 48, 3895-3900.

Cooper KP and Slebodnick P (1989), 'Recent developments in laser melt/particle injection processing', *J Laser Applic*, 1, 21-29.

Coulon P A (1986), 'Erosion –corrosion in steam turbines 11; a problem largely resolved', *Lubr Eng*, 42,357-362.

Courant B, Hantzperque J J, Avril L and.Benayoun S (2005), 'Structure and hardness of titanium surfaces by pulsed laser melting with graphite addition', *J Mat Proc Tech* 160, 374-381.doi: 10.1016/j.jmatprotec.2004.06.025

Covelli L, Pierdominici F, Smurov I and Tosto S (1996), 'Surface microstructure of titanium irradiated by Nd:YAG pulsed laser in presence of carbon and nitrogen', *Surf Coat Tech* , 78**,** 196-204. doi:10.1016/0257-8972(94)02409-X

Deng J and Braun M(1994), 'Tribological behaviour of TiN, TiC_xN_y and TiC coatings prepared by unbalanced magnetron sputtering techniques', *Surf Coat Tech* , 70**,** 49-56**.**

Dong L X and Wang HM (2008), 'Microstructure and corrosion properties of laser-melted deposited Ti2Ni3Si/NiTi intermetallic alloy', *J Alloys Comps*, 465, 83-89. doi: 10.1016/j.jallcom.2007.10.065

Draper C W and Ewing CA (1984), 'Laser surface alloying –a bibliography', *J Mater Sci* , 19, 3815-3825.

Draper C W and Poate J M (1985), 'Laser surface alloying', *Int Met Rev* , 30, 85-107.

Duley W W (1983), '*Laser processing and analysis of materials',* Plenum Press, New York.

Drechsler A, Kiese J and Wagner L (1999) '..'Proc 7th Int Conf on Shot peening 145-152, Warsaw, Institute of Precision Mechanics.

Eskin S, Zahavi J and Berner A (1995), 'CO_2-Laser nitriding as a result of Ti coating modification in a nitrogen atmosphere (1) features of nitriding process', *Lasers Eng*, 4, 85-96.

Ettaqi S, Hays V, Hantzpergue J J, Saindrenan G and Remy J C (1998), 'Mechanical, structural and tribological properties of titanium nitrided by a pulsed ;laser', Surf Coat Technol , 100-101, 428-432. doi:10.1016/S0257-8972(97)00664-6

Flower H M, Walker A and West DRF (1985), 'The structure of Ti-6Al-4V laser surface alloyed with carbon', *Scripta Metal* ,9, 923-926.

Garcia I, Fluente J de la and Damborenea J J de (2002), '(Ti, Al)/ (Ti, Al)N coatings produced by laser surface alloying', *Mater Lett*,53,44-51. doi:10.1016/S0167-577X(01)00451-7

Gates A S (1986), 'Composition, structure and wear resistance of TiAlOC coatings deposited by chemical vapour deposition', *J Vac Technol*, A4, 2707-2712.

Gerdes C, Karimi A and Bieler H W (1995), 'Water droplet erosion and microstructure of laser-nitrided Ti-6Al-4V', *Wear,* 186-187, 368-374. doi:10.1016/0043-1648(95)07153-9

Grenier M, Dubé D, Adnot A and Fiset M (1997), 'Microstructure and wear resistance of CP titanium laser alloyed with a mixture of reactive gases', *Wear*, 210,127-135. doi:10.1016/S0043-1648(97)00043-4

Guo B, Zhou J, Zhang S, Zhou H, Pu Y and Chen J (2007), 'Phase composition and tribological properties of Ti-Al coatings produced on pure Ti by cladding', *Appl Surf Sci*, 253, 9301-9310. doi:10.1016/j.apsusc.2007.05.056

Guo B, Zhou J, Zhang S, Zhou H, Pu Y and Chen J (2008), 'Tribological properties of titanium aluminides coatings produced on pure Ti by laser alloying', *Surf Coat Technol*, 202,4121-4129. doi:10.1016/j.surfcoat.2008.02.026

Guo B, Zhou J, Zhang S, Zhou H, Pu Y and Chen J (2008a),'Microstructure and tribological properties of in situ synthesized Ti/$TiAl_3$ intermetallic matrix composite coatings on titanium by laser cladding and laser nitriding', *Mater Sci Eng*, A 480,404-410. doi:10.1016/j.msea.2007.07.010

Gyorgy E, del Pino AP, Serra P, Morenza JL (2003), 'Depth profiling characterisation of the surface layer obtained by pulsed Nd : YAG laser irradiation of titanium in nitrogen', *Surf Coat Technol*,173, 265-270. 10.1016/S0257-8972(03)00520-6

György E, Pérez del Pino A , Serra P and Morenza J L (2004), 'Influence of the ambient gas in laser structuring of the titanium surface', *Surf Coat Technol*,187,245-249.

doi: 10.1016/j.surfcoat.2004.03.015

Heyman F J (1992),'*Liquid Impingement Erosion*', in Wear, ASM Handbook, !8 , 221-232.

Hirose A, Ueda T and Kobayashi K F (1993),'Wear and oxidation properties of titanium aluminides formed on titanium surface by laser alloying', Mater Sci Eng, A160,143-153.

Howard R L and Ball A (1995), 'The solid particle and cavitation erosion of titanium aluminide intermetallic alloys', *Wear* 186-187, 123-128. doi:10.1016/0043-1648(95)07126-1

Hu C, Mridha S, Uhbi H S, Holdway P, Bowen A W and Baker T N (1996), '*Hardness, dendrite population and microstructure under different nitrogen environments in laser nitrided Ti-6Al-4V alloy*' , P A Blenkinsop, W J Evans and H M Flower, eds, Titanium'95 Science and Technology, Institute of Materials, London,1959-1966.

Hu C and Baker TN (1996), 'Investigation of the temperature field developed by a spinning beam in laser processing', *Metall Mater Trans*, 27A, 4039-4047.

Hu C and Baker TN (1997), 'Overlapping tracks to produce a continuous nitrided layer in Ti-6Al-4V alloy', *J Mater Sci*, 32, 2821-2826.doi: 10.1023/A:1018664231410

Hu C, Xin H and Baker T N (1997), '*Surface MMC's on Ti-6Al-4V alloy produced by combining laser nitriding and powder alloying*', Scott M.L, ed, Proceedings of the Eleventh International. Conference on Composite Materials, Metal Matrix Composite and Physical Properties, Woodhead Publishing, Abington, UK, ,Vol.3, 80-89.

Hu C, Xin H and Baker T N (1997a) ,'*Effect of processing parameters on the microstructure and properties of laser nitrided Ti-6Al-4V', Proceedings of EUROMAT '97 Conference*, Vol 3, 99-102.

Hu C, Stalker W L , Conroy RD and Baker TN(1997a), '*Formation of a high erosion resistant Ti-6Al-4V alloy surface by laser nitriding* ', A. Strang, W.M.Banks, R.D.Conroy and M.J.Goulette, eds ,Proc. Fourth International Charles Parsons Turbine Conference on Advances in turbine materials, design and manufacturing, , Inst Mater, London, 454-464.

Hu C, Xin H ,Watson LM and Baker TN (1997b), 'Analysis of the phases developed by laser nitriding Ti-6Al-4V alloys' *Acta mater,* 45,4311- 4322. doi:10.1016/S1359-6454(97)00076-1

Hu C, Selamat M S B, Uhbi HS and Baker TN (1998), 'Characterisation of surface MMC layers developed in Ti-6Al-4V alloy using a combination of SiC_p and dilute nitrogen environment', *Mater Sci Tech*, 14, 1045-1052.

Hu C and Baker TN (1999), 'The importance of preheat before laser nitriding a Ti-6Al-4V alloy', *Mater Sci Eng A*, 265, 268-275. doi:10.1016/S0921-5093(98)01135-6

Inoue A, Zang T, Nishiyaman N, Ohbak K and Masumoto T (1993), 'Preparation of 16mm diameter rod of amorphous Zr65Al7.7 Ni10 Cu17.5 alloy',*Mater Trans JIM*, 34,1234-1237

Inoue A (2000), 'Stabilization of metallic supercooled liquid and bulk amorphous alloys', *Acta Mater*, 48,279-306. doi:10.1016/S1359-6454(99)00300-6

Ion J C, Shercliff H R and Ashby M F (1992), 'Diagrams for laser materials processing', *Acta Metall Mater*,40,1539-1551.

Ion J C (2005), '*Laser Processing of Engineering Materials',* Elsevier, Amsterdam.

Jiang P, He X L, Li X , Yu L G and Wang H M(2000), 'Wear resistance of a laser surface alloyed Ti-6Al-4V alloy', *Surf Coat Technol,* 130,24-28. doi:10.1016/S0257-8972(00)00680-0

Kasper J, Bretschneider J, Jacob S, Bonß S , Winderlich B and Brenner B (2007), 'Microstructure, hardness and cavitation erosion behaviour of Ti-6Al-4V laser nitrided under different atmospheres', *Surf Eng*, 23, 99-106. doi: 10.1179/174329407X169430

Jianglong L, Qiquan L and Zhirong Z (1993), 'Laser gas alloying of titanium alloy with nitrogen', *Surf Coat Technol*, 57, 191-195.

Katayama S, Matsunawa A, Morimoto A, Ishimoto S and Arata Y (1983), '*Surface hardening of titanium by laser nitriding*', ICALEO(1983),Proceedings of the Fifth

International Conference on Applied Laser Electro-Optics, Laser Institute of America, 127-134.

Katayama S, Matsunawa A, Morimoto A,, Ishimoto S and Arata Y (1984), '*Surface hardening of titanium by laser nitriding',* Conf. Proc Laser processing Materials, Los Angeles,159-166.

Kloosterman A B and De Hosson J Th M (1995), 'Microstructural characterization of laser nitrided titanium', Scripta Metall Mater, 33,567-573. doi:10.1016/0956-716X(95)00238-Q

Kloosterman AB, Kool BJ and De Hosson J Th M (1998), 'Electron microscopy of reaction layers between SiC and Ti-6Al-4V after laser embedding ', *Acta mater*, 46, 6205-6217. doi:10.1016/S1359-6454(98)00265-1

Konstantino E and Altus E (1999), 'Fatigue life enhancement by laser surface treatment', *Surf Eng*, 15, 126-128. 10.1179/026708499101516461

Kool BJ, Kabel M, Kloosterman A and De Hosson J Th M (1999), 'Reaction layers around SiC particles in Ti: an electron microscopy study', *Acta mater* 47, 3105-3116. doi:10.1016/S1359-6454(99)00151-2

Kustas F.M. and. Misrta M.S (1994), '*Friction and Wear of Titanium alloys',* Material property handbook: Titanium alloys, ASM International, Materials Park, OH, 1169-1176.

Langlade C, Vannes A B, Krafft J M and Martin J R (1998), 'Surface modification and tribological behaviour of titanium and titanium alloys after YAG-laser treatments', *Surf Coat Technol*,100-101,383-387. doi:10.1016/S0257-8972(97)00653-1

Liu X B and Wang H M (2006), 'Modification of tribology and high temperature behaviour of Ti-48Al-2Cr-2Nb intermetallic alloy by laser cladding', *Appl Surf Sci* ,252,5735-5744. doi: 10.1016/j.apsusc.2005.07.064 2006

Liu X B and Wang H M (2007), 'Microstructural and tribological properties of laser clad γCr_7C_3/TiC composite coatings on γ-TiAl intermetallic alloy', *Wear*, 262,514-521.

doi: 10.1016/j.wear.2006.06.012

Liu X B and R L Yu (2007a), ‘Effects of La_2O_3 on microstructure and wear properties of laser clad γCr_7C_3/TiC composite coatings on TiAl intermetallic alloy’, *Mater Chem Phys*,10,448-454.doi: 10.1016/j.matchemphys.2006.08.013

Liu X B and R L Yu (2007b), ‘Microstructure and high-temperature wear and oxidation resistance of laser clad γW_2C /TiC composite coatings on TiAl intermetallic alloy’, *J Alloys and Cpds,* 439,279-286.doi: 10.1016/j.jallcom.2006.08.065

Majumdar J D, Weisheit BL, Mordike B L and Manna I (1999), ‘Laser surface alloying of Ti with Si, Al and Si plus Al for an improved oxidation resistance’, *Mater Sci Eng A,* 266**,** 123-134. doi:10.1016/S0921-5093(99)00045-3

Majumdar J.D, Mordike BL and Manna I (2000), ‘Friction and wear behavior of Ti following laser surface alloying with Si, Al and Si plus Al’, *Wear*, 242, 18-27. doi:10.1016/S0043-1648(00)00363-X

Majumdar JD, Manna I, Kumar A, Bhargava P and Nath A K (2008), ‘Direct laser cladding of Co on Ti-6Al-4V with a compositional graded interface’, *J Mater Proc Technol* in the press.doi:10.1016/j.jmatprotec.2008.05.017.

Man HC, Zhang S, Cheng FT and Yue TM (2001), ‘Microstructure and formation mechanism of in situ synthesized TiC/Ti surface MMC on Ti-6Al-4V by laser cladding ’,*Scripta Mater* 44, 2801-2807. doi:10.1016/S1359-6462(01)00977-0

Man H C, Cui Z D, Yue TM and Cheng F T (2003), ‘Cavitation erosion behavior of laser gas nitrided Ti and Ti-6Al- 4V alloy’, *Mater Sci Eng*, A355,167-173.doi: 10.1016/S0921-5093(03)00062-5

Massoud J P and Coquerelle G (1988), ‘*High power laser surface treatments on Ti-6Al-4V in order to improve its erosion resistance*’, P. Lacombe et al, ed 6th World Conf. on Titanium, 1847-1852, Les Editions de Physique, Les Ulis Cedex, France.

Mehlmann A, Dirfeld S Fand Minkoff I (1990), 'Laser-melt injection of B4C on titanium' *Surf Coat Technol,* 42, 275-281. doi:10.1016/0257-8972(90)90158-9

Meng Q, Geng L and Ni D (2005), 'Laser cladding NiCoCrAlY coating on Ti-6Al-4V',*Mater Lett*, 59,2774-2777. doi:10.1016/j.matlet.2005.03.056

Miyoshi K and Buckley DH (1982), ':Adhesion and friction of transition-metals in contact with non-metallic hard materials', *Wear* ,77 ,253-264.

Molian PA and Hualun L (1989), 'Laser cladding of Ti-6Al-4V with BN for improved wear performance' *Wear*, 130, 337-352.

Mordike B L (1985), '*Laser gas alloying*', Draper CW and Mazzoldi P, ed. Laser Surface treatment of Metals, 389-412, Martinus Nijnhoff, Dordrecht.

Morris DG (1988), 'Glass forming conditions during laser surface melting', Mater Sci Eng 97,177-180.

Morton PH, Bell T, Weisheit A, Kroll J Mordike BL and K.Sagoo (1992), 'Laser gas nitriding of titanium and titanium alloys', Sudarshan T S and Braza J F ed, *Surface Modification Technologies V,* Inst Mater, 593-609.

Moskowitz D, Terner L L and Hamenik M Jr (1986), '*Some physical and metal cutting properties of titanium carbonitride base materials*', Almond E A ,Brookes C A and Warren R, eds, Science of Hard Materials, Inst Phys Conf Ser No 75,Adam Hilger,Bristol,p605.

Mridha S and Baker T.N (1991),'Characteristic features of laser –nitrided surfaces of two titanium alloys', *Mater Sci Eng,* A142, 115-124. doi:10.1016/0921-5093(91)90760-K

Mridha S, Ubhi HS, Holdway P, Baker TN and AW Bowen (1993), 'Metal-ceramic composite layer formation on titanium surface through laser treatment', Froes FH and Caplan IL eds,, '*Proceedings of the Seventh International Conference on Titanium, Titanium '92 Science and Technology Conference*, Vol III, pp 2641-2648, , TMS Warrendale.

Mridha S and Baker T.N (1994), 'Crack-free hard surfaces produced by laser nitriding of commercial purity titanium', *Mater Sci Eng* A188, 229-239. doi:10.1016/0921-5093(94)90376-X

Mridha S and Baker T.N (1994a), 'Surface cracking in laser-nitrided titanium of commercial purity and possible ways of reducing these defects', *Proc Adv Mater,*4,85-94.

Mridha S and Baker T.N (1996), 'Metal matrix composite layers formed by laser processing of commercial purity Ti-SiC_p in nitrogen environment', *Mat Sci Technol*, 12, 595-602.

Mridha S, Hu C, Ubhi H S, Bowen A W and Baker T N (1996), '*Characteristic features of the MMC layer formed on Ti-6Al-4V(IMI318) alloy surfaces through laser treatment by using SiC powder injection and preplacement techniques*', P A Blenkinsop, W J Evans and H M Flower,eds,Titanium'95 Science and Technology ed. Institute of Materials , London.2835-2842.

Mridha S and Baker T N (1997), 'Metal matrix composite layer formation with 3μm SiC_p powder on IMI318 titanium alloy surfaces through laser treatment', *J Mat Proc Tech*, 63, 432-437. doi:10.1016/S0924-0136(96)02660-X

Mridha S and Baker T N (1998), 'Effects of nitrogen gas flow rate on the microstructure and properties of laser nitrided IMI318 titanium alloy(Ti-6Al-4V)', *J Mat. Proc Tech*,77, 115-121. doi:10.1016/S0924-0136(97)00408-1

Mridha S and Baker T N (2007), 'Incorporation of 3μm SiC_p into titanium surfaces using a 2.8kW laser beam of 186 and 373MJm^{-2} energy densities in a nitrogen environment', *J Mat Proc Tech* , 185, 38-45. ISSN: 0924-0136. doi: 10.1016/j.jmatprotec.2006.03.110

Munteanu D and Vaz F (2006), 'The influence of oxygen flow on the tribological behaviour and residual stress of TiCO thin-films', *J Optoelect Adv Mater*, 8, 720-725.

Nalla R K, Altwnberger L, Noster U, Liu G Y, Scholtes B and Richie R O (2003), 'On the influence of mechanical surface treatments - deep rolling and laser shock peening - on the fatigue behavior of Ti-6Al-4V at ambient and elevated temperatures', Mater Sci Eng, 355A, 216-230. doi:10.1016/S0921-5093(03)00069-8

Neville A and McDougall BAB (2001), 'Erosion and cavitation-corrosion of titanium and its alloys', *Wear*, 250,726-735. doi:10.1016/S0043-1648(01)00709-8

Nwobo A I P, Rawlings R D and West DRF (1999), 'Nitride formation in titanium based substrates during laser surface melting in nitrogen-argon atmospheres', *Acta mater*, 47,631-643. doi:10.1016/S1359-6454(98)00369-3

Pang W, Man HC and Yue TM (2005), 'Laser surface coating of Mo-WC metal matrix composite on Ti6Al4V alloy', *Mat Sci En* . A390, 144-153.doi:10.1016/j.msea.2004.07.065

Pei Y T, Ocelik V and De Hosson J Th M (2002), 'SiCp/Ti6Al4V functionally graded materials produced by laser melt injection', *Acta mater,*50, 2035-2051. doi:10.1016/S1359-6454(02)00049-6

Peng T C , Sastry S M L, O'Neal J E and Tesson J F (1983), E A Metzbower, ed,'*A correlation between dendrite- arm spacing and cooling rate for laser-melted Ti-15V-3Al-3Sn-3Cr'* ,Lasers in Materials Processing, 241-246,Amer Soc Metals ,Metals Park, OH.

Perry A J, Sharkeev Y P, Geist D E and Fortuna S V (1999), 'Dislocation network developed in titanium nitride by ion implantation' ,*J Vac Sci Technol A* ,17A, 1848-1853.

Poletti C, Balog M, Schubert T, Liedtke V and Edtmaier C (2008), 'Production of titanium matrix composites reinforced with SiC particles', *Compos Sci Technol.*, 68,2171-2177. doi:10.1016/j.compscitech.2008.03.018

Pu YP, Guo BG, Zhou JS, Zang S, Zhou H and Chen J (2008), 'Microstructure and tribological properties of in situ synthesized TiC, TiN, and SiC reinforced Ti_3Al intermetallic matrix composite coatings on pure Ti by laser cladding ', *Appl Surf Sc.,* 255 2697-2703. doi:10.1016/j.apsusc.2008.07.180

Raaif M, El-Hossary F M, Negm N Z, Khalil S M ,Kolitsch A, Höche D, Kasper J, Mändl S and Schaaf P (2008), 'CO_2 laser nitriding of titanium',*J Phys D:Appl Phys.*,41, 085208 (8pp)

Ribeiro M V, Moréta MRV and Ferreira J R (2003), 'Optimization of titanium alloy (6Al-4V) machining', .*J Mater Proc Technol*, 143-144, 458-463. doi:10.1016/S0924-0136(03)00457-6

Robinson J M, Anderson S, Knutsen R D and Reed R C (1995), 'Cavitation erosion of laser melted and laser nitrided Ti-6Al-4V', Mater Sci Technol ,11 611-618.

Robinson J M and Reed R C (1995), 'Water droplet erosion of laser surface treated Ti-6Al-4V', *Wear*, 186-187,360-367. doi:10.1016/0043-1648(95)07131-8

Robinson J M, Van Brussel B A , De Hosson J Th M and Reed R C (1996), 'X-ray measurement of residual stresses in laser melted Ti-6Al-4V alloy', *Mater Sci Eng* A208,143-147. doi:10.1016/0921-5093(95)10158-6

Santos E C, Morita M, Shiomi M, Osakada K and Takahashi M (2006), 'Laser gas nitriding of pure titanium using CW and pulsed Nd:YAG lasers', *Surf Coat Technol,* 201,1635-1642. doi:10.1016/j.surfcoat.2006.02.048

Schaaf P (2002), 'Laser nitriding of metals', *Prog Mater Sci* , 47, 1-161. doi:10.1016/S0079-6425(00)00003-7

Schüssler A, Steen PH and Ehrhard (1992), 'Laser surface treatment dominated by buoyancy flows', *J Appl Phys,*71,1972-1975.

Selemat M S, Baker TN and Watson LM (2001), 'Study of the surface layer formed by laser processing of Ti-6Al-4V alloy in a dilute nitrogen atmosphere', *J. Mater Proc Technol*,113,509-515. doi:10.1016/S0924-0136(01)00595-7

Selemat M S, Watson LM and Baker TN (2003), ' XRD and XPS studies of surface MMC layer of SiC reinforced Ti-6Al-4V alloy ', *J. Mater Proc Technol*,142, 725-737. doi:10.1016/S0924-0136(03)00814-8

Selemat M S, Watson LM and Baker TN (2006), 'XRD and XPS studies of surface MMC layers developed by laser alloying Ti-6Al-4V using a combination of a dilute nitrogen environment and SiC powder', *Surf. Coat Technol*, 20, 724-736. doi:10.1016/j.surfcoat.2005.12.038.

Selvan J S, Subramanian K, Nath A K, Kumar H , Ramachandra C and Ravindranathan SP (1999), 'Laser boronising of Ti-6Al-4V as a result of alloying with preplaced BN*', Mater Sci Eng* , A260**,** 178-187. doi:10.1016/S0921-5093(98)00964-2

Shercliff H R and Ashby M F (1991), 'The prediction of case depth in laser transformation hardening', *Metall Trans* , 22A, 2459-2466.

Singhal SC (1978), 'An erosion- resistant coating for titanium and its alloys', *Thin Solid Films* , 53, 75-381.

Sproul W D, Rudick P J and Graham M E (1989), 'The effect of N2 partial pressure, deposition rate and substrate bias potential on the hardness and texture of reactively sputtered TiN coatings', *Surf Coat Technol*,39-40,355-363. doi:10.1016/0257-8972(89)90068-6

Steen PH, Ehrhard P and Schüssler A (1994), 'Depth of melt pool and heat-affected zone in laser surface treatments', Metall Mater Trans , 25A, 427-435.

Sue J A and Troue H H (1988), 'Influence of residual compressive stress on erosion behaviour of arc evaporation titanium nitride coating', *Surf Coat Techno.* 36, 695-705. doi:10.1016/0257-8972(88)90010-2

Sun R L , Yang DZ , Guo LX and Dong SL (2000), 'Microstructure and wear resistance of NiCrBSi laser clad layer on titanium alloy substrate', *Surf Coat Tech*, 132,251-255. doi:10.1016/S0257-8972(00)00904-X

Sun R L, Yang DZ , Guo LX and Dong SL (2001), 'Laser cladding of Ti-6Al-4V alloy with TiC and TiC+ NiCr + BSi powders', *Surf Coat Tech*, 135**,**307-312. doi:10.1016/S0257-8972(00)01082-3

Sun, R L, Mao J F and Yang DZ (2002), ‘Microscopic morphology and distribution of TiC phase in laser clad NiCrBSiC -TiC layer on titanium alloy substrate’, *Surf Coat Technol*, 155**,** 203- 207. doi:10.1016/S0257-8972(02)00006-3

Sun R L , Yang DZ , Guo LX and Dong SL (2002 a), ‘Microstructural characterization of NiCr1BSiC laser clad layer on titanium alloy substrate’, *Surf Coat Tech* , 150,199- 204. doi:10.1016/S0257-8972(01)01512-2

Tian Y S , Chen CZ , Li S T and Huo Q H (2005), ‘Research progress on laser modification of titanium alloys’, *Appl Surf Sci* , 242,177-184.doi: 10.1016/j.apsusc.2004.08.011

Tian Y S , Chen CZ, Wang D Y and Lei T Q (2005a), ‘Surface modification of pure Ti by laser alloying with B and Ni mixed powders’, *Adv Eng Mater*, 7,629-632. doi: 10.1002/adem.200400221

Tian Y S, Chen CZ, Wang D Y, Huo Q H and Lei T Q (2005b), ‘Laser surface alloying of pure titanium with TiN- B-Si- Ni mixed powders’, *Appl Surf Sci*, 250,223-227. doi:10.1016/j.apsusc.2005.01.001

Tian Y S, Chen CZ, Chen L X and Huo Q H (2006), ‘Microstructures and wear properties of composite coatings produced by laser alloying Ti-6Al-4V with graphite and silicon mixed powders’, *Mat Lett.*, 60, 109-113 doi: 10.1016/j.matlet.2005.07.082

Tian Y S, Chen C Z, Chen L X and Huo Q H (2006a), ‘Effect of RE oxides on the microstructure of the coatings fabricated on titanium alloys by laser alloying technique’, *Scripta Mater*,54, 847-852. doi:10.1016/j.scriptamat.2005.11.011

Tian Y S, Chen CZ, Chen L B and Chen L X (2006b), ‘Study on the microstructure and wear resistance of composite coatings fabricated on Ti-6Al-4V under different processing conditions’, *Appl Surf Sci,* 253, 1494-1499. doi:10.1016/j.apsusc.2006.02.026

Ubhi HS, Holdway P, Bowen AW and Baker TN (1988),'The development of surface-modified microstructures in laser-treated titanium and titanium alloys', *Proc. 6th World Conference on Titanium*, pp 1687-1692, France.

Vilar R (1999), 'Laser cladding' *J Laser Applic*, 11,64-79.

Walker A, Foulkes J, Steen W M and West DRF (1985), 'Laser surface alloying of titanium substrate with carbon and nitrogen', *Surf Eng,*1, 23-29.

Wang H M and Liu YF (2002), 'Microstructure and wear resistance of laser clad Ti_5Si_3 / $NiTi_2$ intermetallic composite coating on titanium alloy', *Mater Sci Eng* , A338, 126-132. doi:10.1016/S0921-5093(02)00076-X

Wang Y, Li G, Wang C, Xia Y, Sandip B and Dong C (2000), 'Microstructure and wear resistance of NiCrBSi laser clad layer on titanium alloy substrate', *Surf Coat Tech*, 132, 251-255. doi:10.1016/S0257-8972(00)00904-X

Wang Y F, Li G, Wang C, Xia Y, Sandip B and Dong C (2004), 'Microstructure and properties of laser clad Zr-based alloys coatings on Ti substrates', *Surf Coat Tech*, 176, 284-289.doi: 10.1016/S0257-8972(03)00771-0

Wang Y and Wang H M (2004), 'Wear resistance of laser clad Ti_2Ni_3Si reinforced intermetallic composite coatings on titanium alloys', Appl Surf Sci, 229, 81-86. doi: 10.1016/j.apsusc.2004.01.045

Wu W L and Li XW (2006), 'Research progresses on laser cladding of titanium alloys ',*Rare Metal Materials and Engineering*, 35, 850-854.

Wu X (2007), 'A review of laser fabrication of metallic engineering components and of materials', *Mater Sci Technol*, 23,631-640 doi: 10.1179/174328407X179593

Xin H and Baker T N (1996), 'The development of wear resistant surface on CPTi and Ti-6Al-4V alloys by laser nitriding' P A Blenkinsop, W J Evans and H M Flower, eds, Titanium'95 Science and Technology ,Institute of Materials , London.2031-2038..

Xin H, Mridha S and Baker T N (1996), 'The effect of laser surface nitriding with a spinning beam in the wear resistance of commercial purity titanium', *J Mater Sci,* 31, 23-30. doi:10.1007/BF00355121

Xin H, Watson LM and Baker TN 1998), 'Surface analytical studies of a laser nitrided Ti-6Al-4V alloy: a comparison of spinning and stationary laser beam modes',*Acta Metall*, 46 1949- 1961.

Xin H, Hu C and Baker TN (2000) , 'Microstructural assessment of laser nitrided Ti-6Al-4V alloy', *J Mater Sc*i, 35, 3373-3382.doi: 10.1023/A:1004833018817

Xue L, Islam A, Koul A K , Wallace W and Bibby M (1997), ' Laser gas nitriding of Ti-6Al-4V alloy', *Mater Manufac Proc* ,12, 799-817.

Yamada M (1996) , ' An overview on the development of titanium alloys for non-aerospace application in Japan', *Mater Sci Eng*, A213, 8-15. doi:10.1016/0921-5093(96)10241-0

Ye H Q (1999) , 'Recent developments inTi_3Al and TiAl intermetallics research in China', *Mater Sci Eng* A263, 289-295. doi:10.1016/S0921-5093(98)01159-9

Yerramarry S and Bahadur S (1991),'The effect of laser surface treatments on the tribological behavior of Ti-6Al-4V', *Wear*,142, 253-263. doi:10.1016/0043-1648(91)90168-T

Yilbas B S, Hashmi M S J and Shuja S Z (2001),' Laser treatment and PVD TiN coating of Ti-6Al-4V alloy' ,*Surf Coat Technol* , 140, 244-250. doi:10.1016/S0257-8972(01)01038-6

Yilbas B S and Shuja S Z (2000), 'Laser treatment and PVD TiN coating of Ti-6Al-4V ', *Surf Coat Technol* , 130,152-157. doi:10.1016/S0257-8972(00)00715-5

Yue TM, Yu JK, Mei Z, Man HC (2001), ' Excimer laser surface treatment of Ti-6Al-4V alloy for corrosion resistance enhancement', Mater Lett , 52,206-212 . doi:10.1016/S0167-577X(01)00395-0

Zang S, Wu WT, Wang MC and Man H C (2001), 'In-situ synthesis and wear performance of TiC particle reinforced composite coating on alloy Ti6Al4V', Surf Coat Technol ,138,95-100. doi:10.1016/S0257-8972(00)01133-6

Zhecheva A, Sha W, Malinov S and Long A (2005), 'Enhancing the microstructure and properties of titanium alloys through nitriding and other engineering methods', *Surf Coat Techno.*, 200,2197-2207. doi:10.1016/j.surfcoat.2004.07.115

Figure Captions

18.1 A selection of commercial lasers characterized by wavelength and average power shown on a background of applications (Ion 2005)

18.2 Macrograph showing the top (T), melt zone (MZ)and heat affected zone (HAZ) following laser melting (Mridha and Baker 1991)

18.3 Micrograph showing the functionally gradient layer following laser nitriding of titanium (Hu et al 1997)

18.4 Laser induced cracks through the entire depth of the melt pool arrested at the HAZ (Mridha and Baker 1991)

18.5 SEM micrograph showing Ti_5Si_3 particles A and B, spherical TiC in C and E, and a eutectic of Ti_5Si_3 and ά-Ti, at D. (Hu et al 1998) Page 7

18.6 TEM micrographs of eutectic of Ti_5Si_3 and ά-Ti (a) bright field (b) dark field, with Ti_5Si_3 in light contrast. (Hu et al 1998)

18.7 SEM micrograph of partially dissolved SiC particle acting as a nucleant for TiC (Mridha et al 1996)

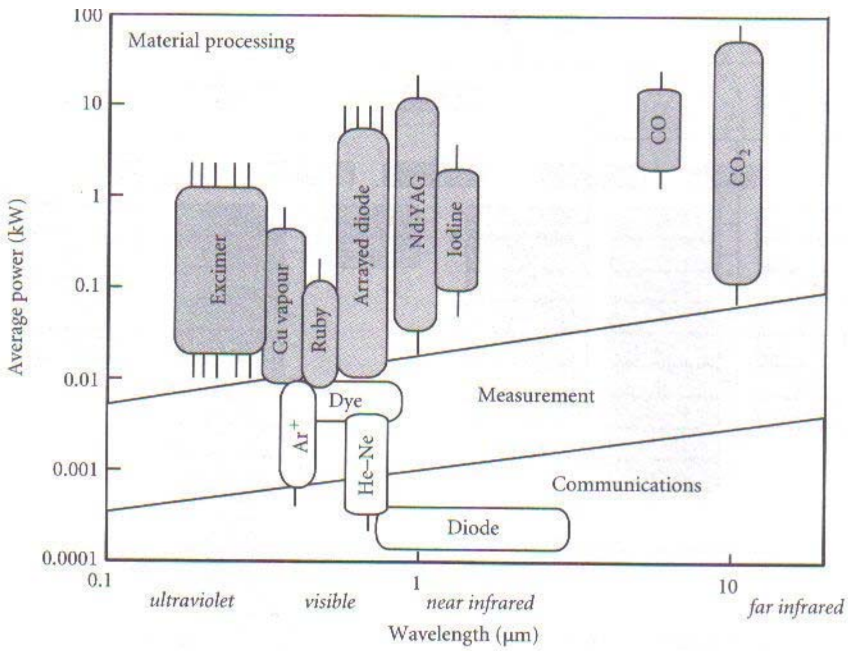
18.8 Figure showing the effect of percentage overlapping on the remelting of solidified alloy page 8

18.9 Effect of multi- track alloying on the preheat temperature (a) in Ar environment (b) in 40% nitrogen 60% argon environment (Hu and Baker 1999)

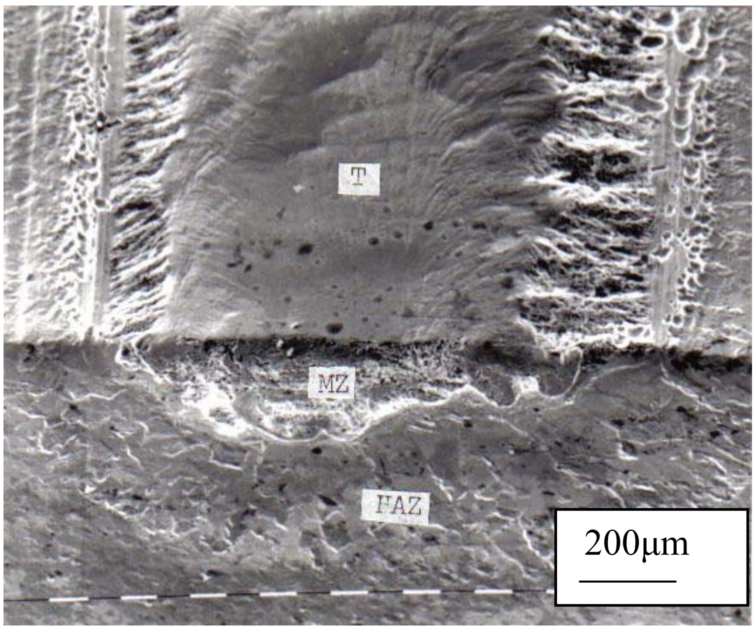
18.10 Laser processing diagram showing the conditions for laser melting and laser cladding (after Ion 2005)) page 10

18.11 SEM micrograph showing the capillary convective flow patterns in the melt pool(Marangoni flow) high- lighted by precipitation of needle particles along the flow lines (Mridha and Baker 1994) page 11

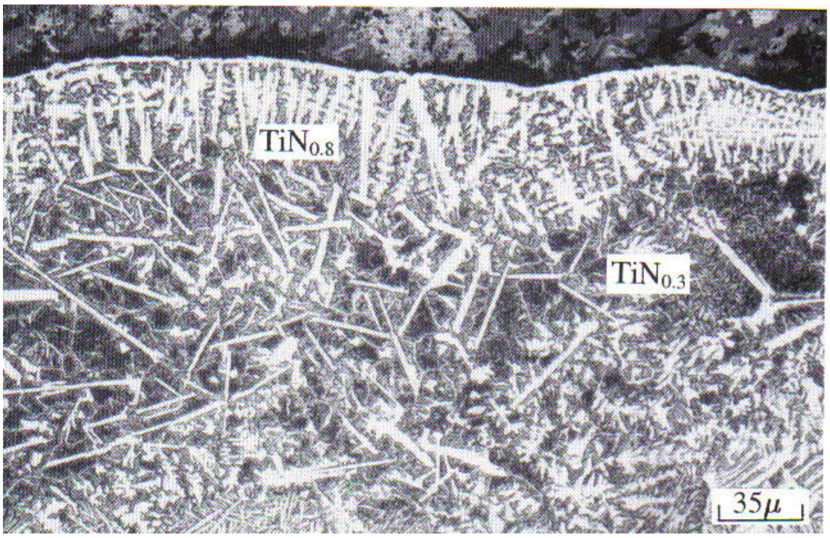
Table Captions



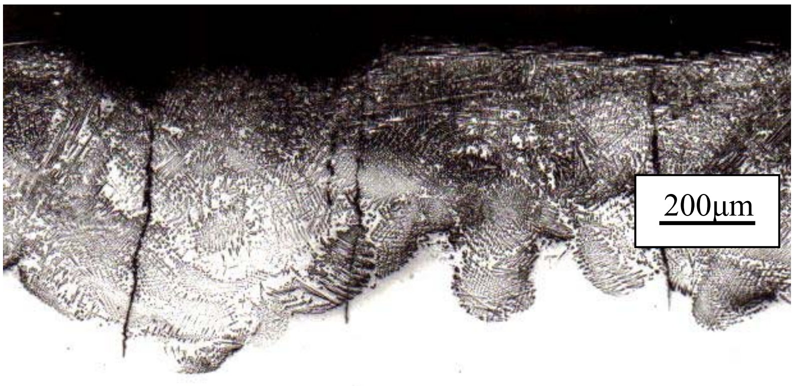
18.1 A selection of commercial lasers characterized by wavelength and average power shown on a background of applications (Ion 2005) Page 4



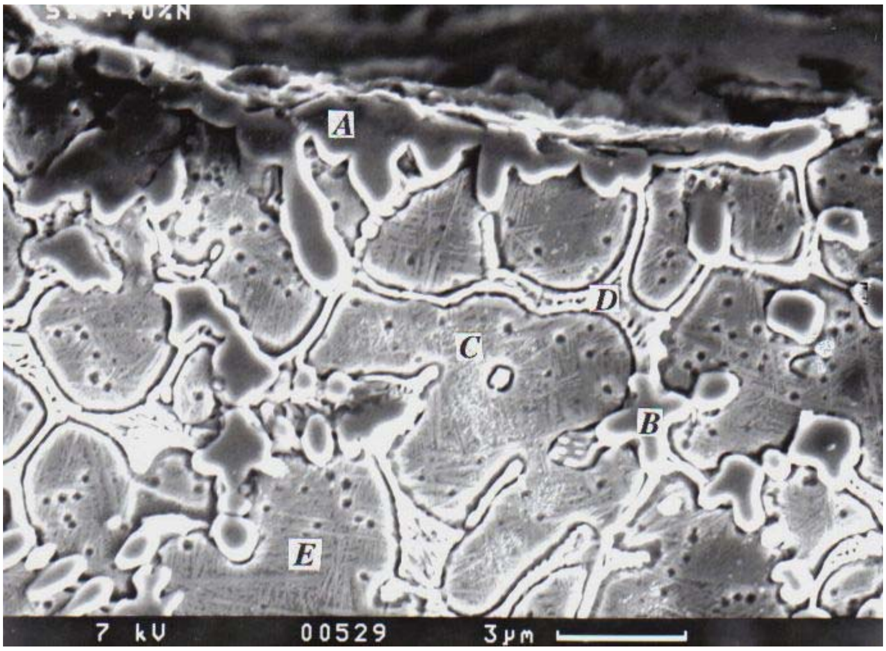
18.2 Macrograph showing the top (T), melt zone (MZ)and heat affected zone (HAZ) following laser melting (Mridha and Baker 1991)



18.3 Micrograph showing the functionally gradient layer following laser nitriding of titanium.(Hu et al 1997)

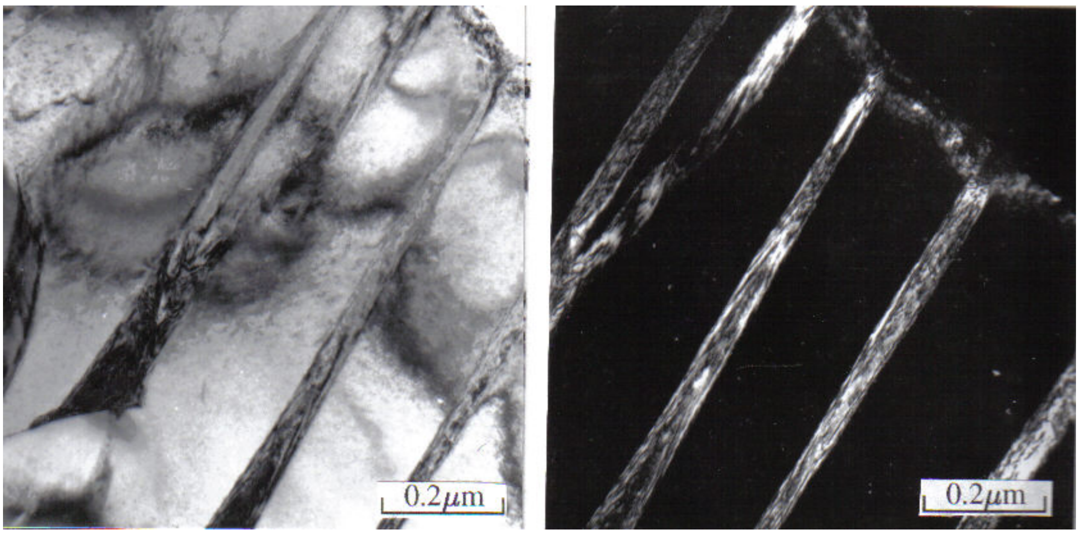


18.4 Laser induced cracks through the entire depth of the melt pool arrested at the HAZ. (Mridha and Baker 1991)

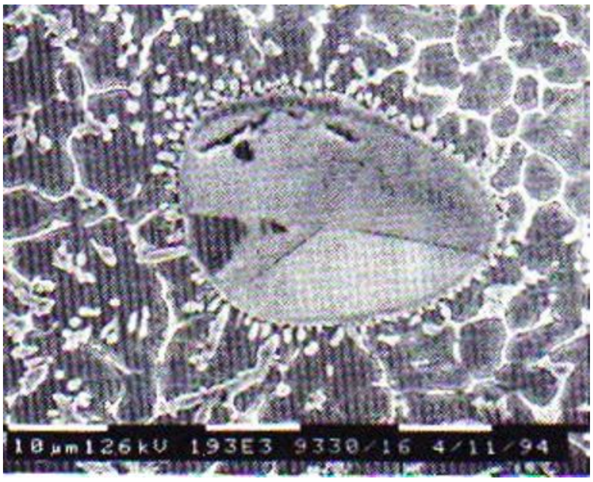


18.5 SEM micrograph showing Ti_5Si_3 particles, A and B, spherical TiC in C and E, and a eutectic of Ti_5Si_3 and ά-Ti, at D.

(Hu et al 1998) Page 7

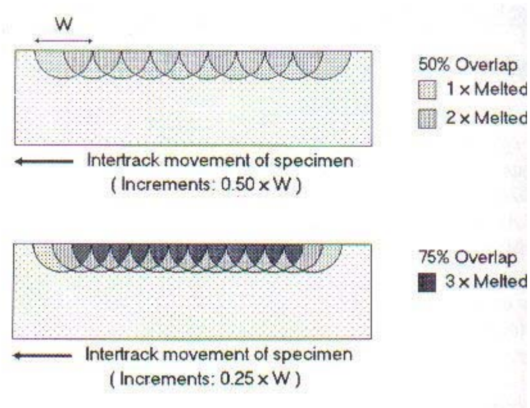


18.6 TEM micrographs of eutectic of Ti_5Si_3 and ά-Ti (a) bright field (b) dark field, with Ti_5Si_3 in light contrast (Hu et al 1998).

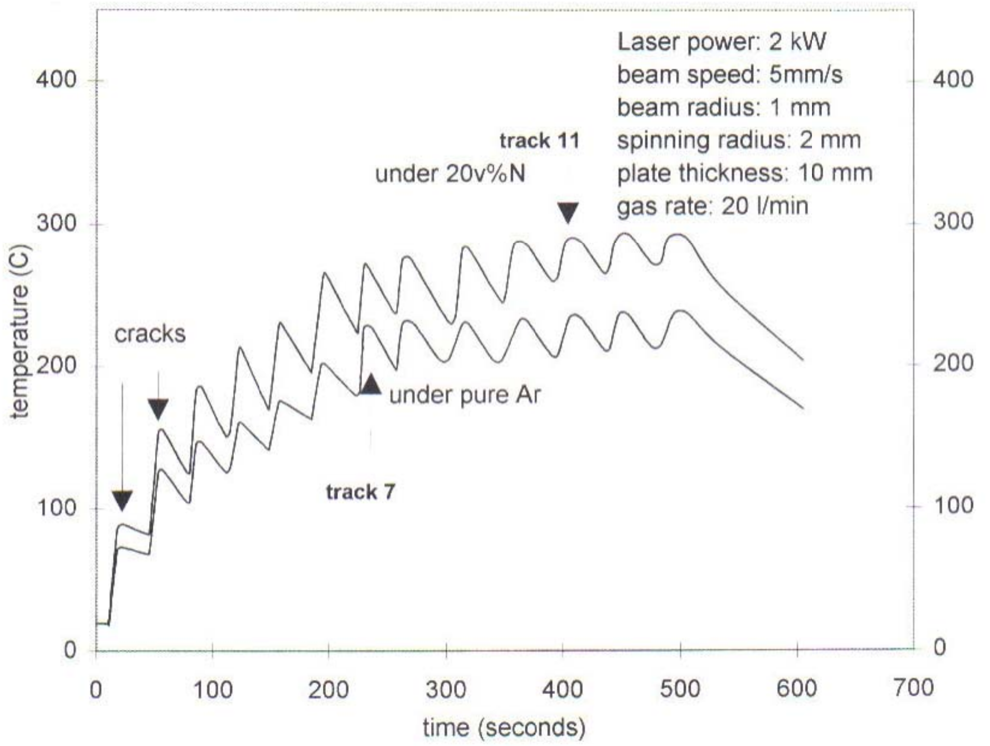


18.7 SEM micrograph of partially dissolved SiC particle acting as a nucleant for TiC

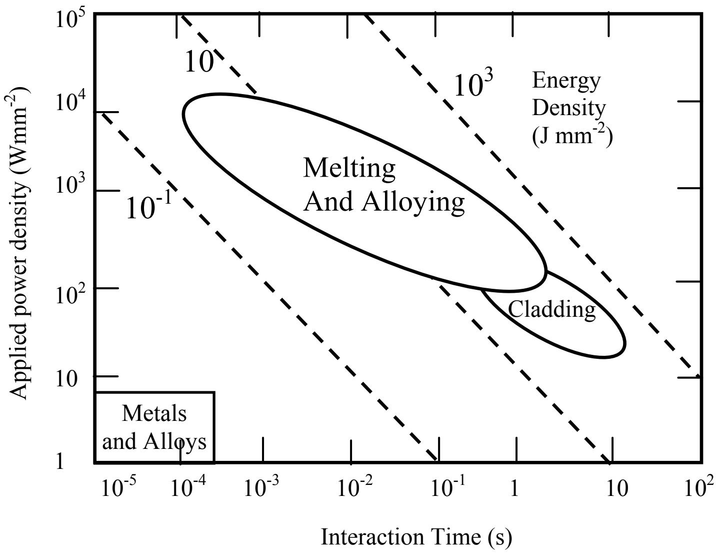
(Mridha et al 1996)



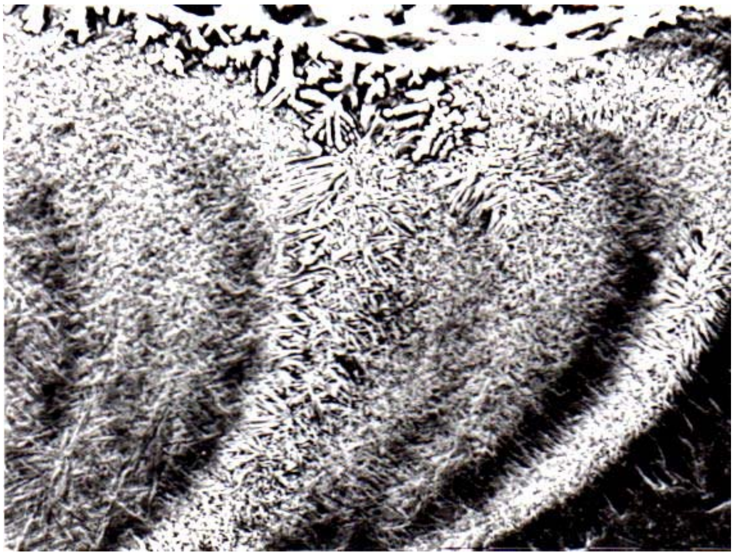
18.8 Laser tracks showing the effect of overlapping of 50% and 75% as a percentage of the width W of a single track (after Robinson et al 1995)



18.9 Effect of multi- track alloying on the preheat temperature (a) in Ar environment (b) in 40% nitrogen 60% argon environment (Hu and Baker 1999)

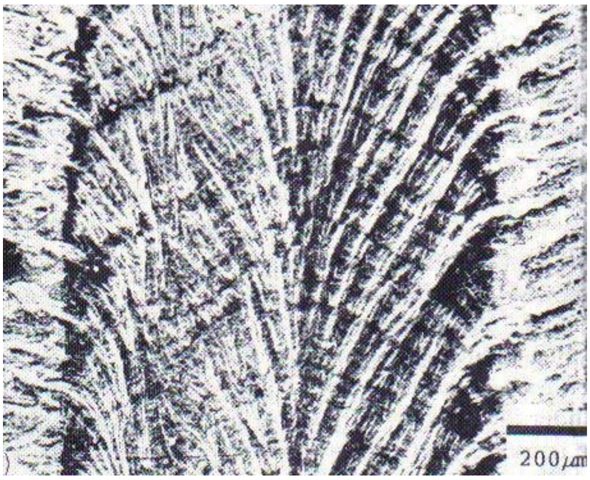


18.10 Laser processing diagram showing the conditions for laser melting and laser cladding (after Ion 2005)

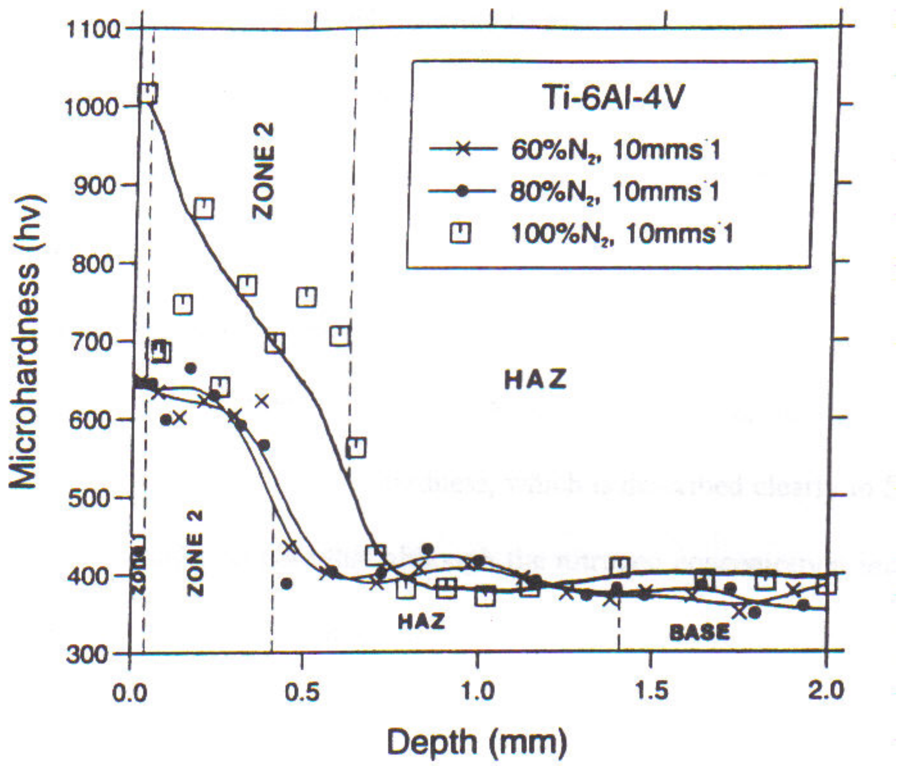


18.11 SEM micrograph showing the capillary convective flow patterns in the melt pool(Marangoni flow) high- lighted by precipitation of needle particles along the flow lines (Mridha and Baker 1994) page 11

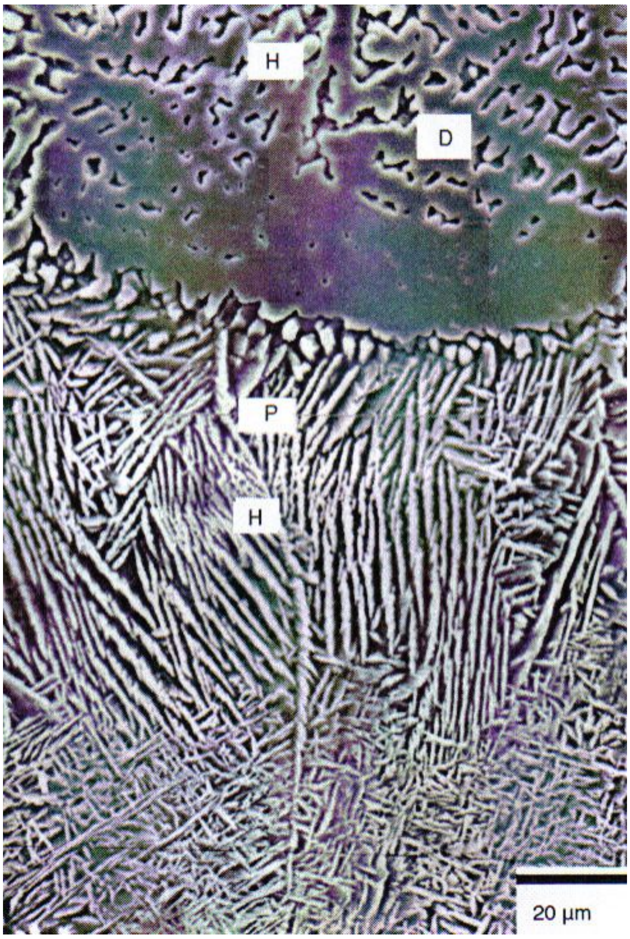
18.12 Heterogeneous distribution of dendrites following laser nitriding (Mridha and Baker 1996) Page 11



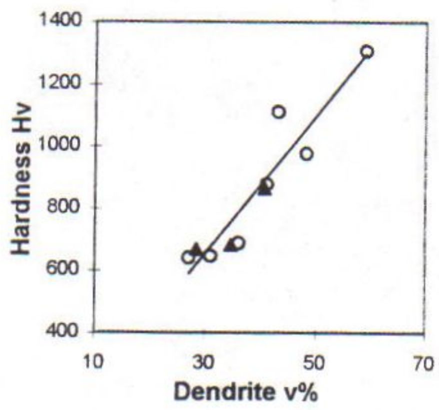
18.13 Surface topography showing rippling following laser melting of CPTi



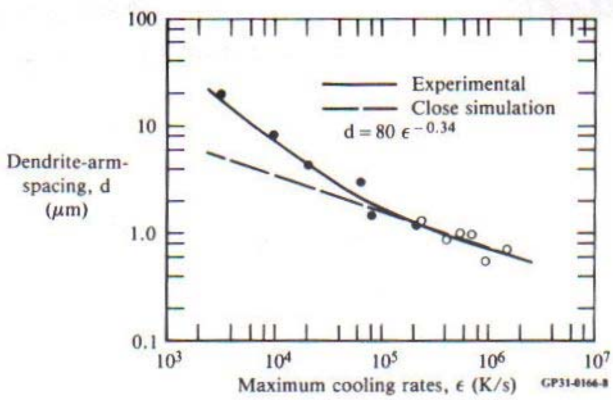
18.14 Microhardness –depth profile of specimens laser processed with varying nitrogen percentages. (Xin and Baker 1996) page 16



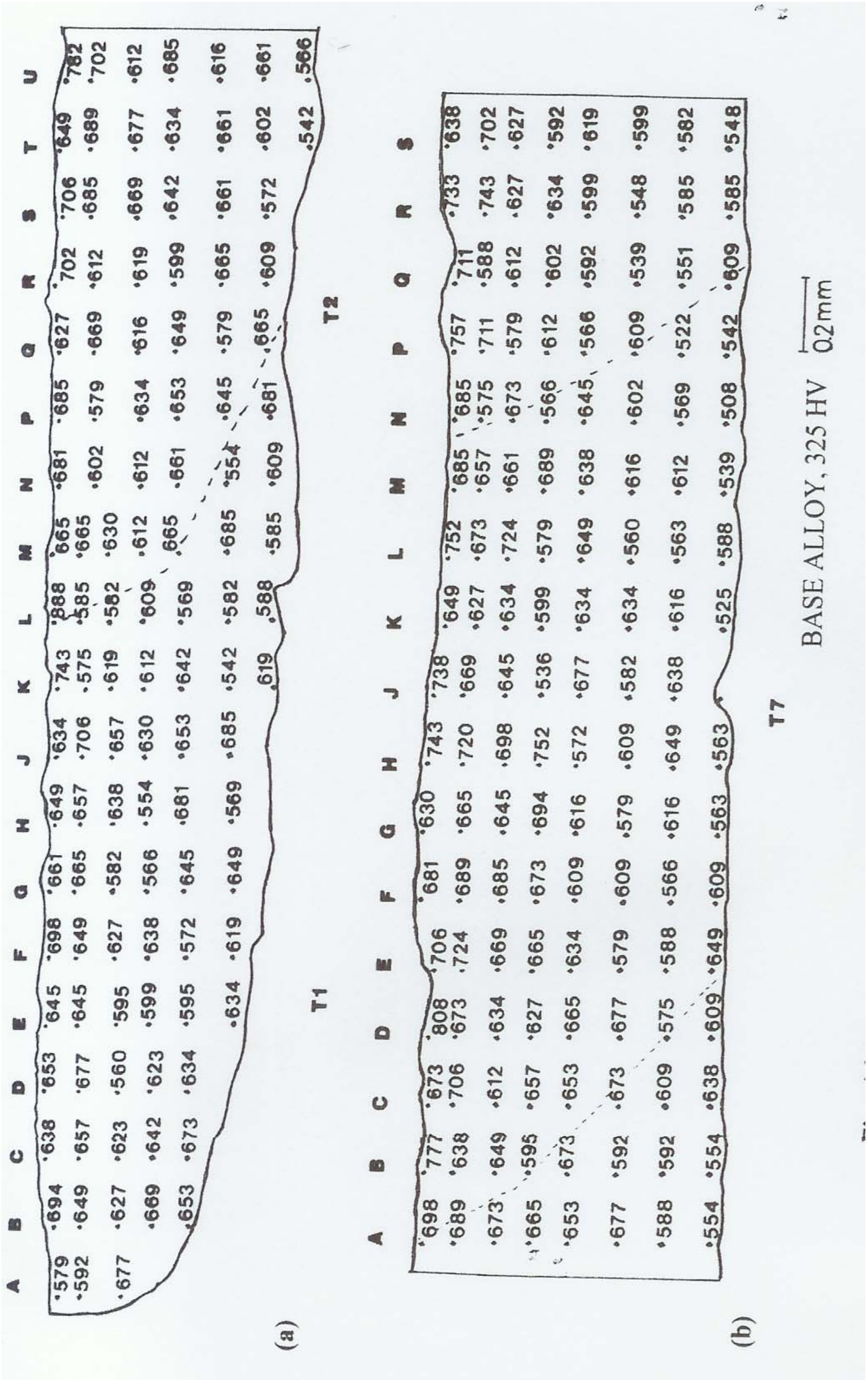
18. 15 SEM micrograph of laser processed SiC preplaced powder on CPTi, showing small needles(10-15µm)below larger needles (30-35µm) following a concentrated dendritic structure(D).Platelet particles(P) in the needle structures and variation of the hardness indentations(H) are also visible (Mridha and Baker 2007).



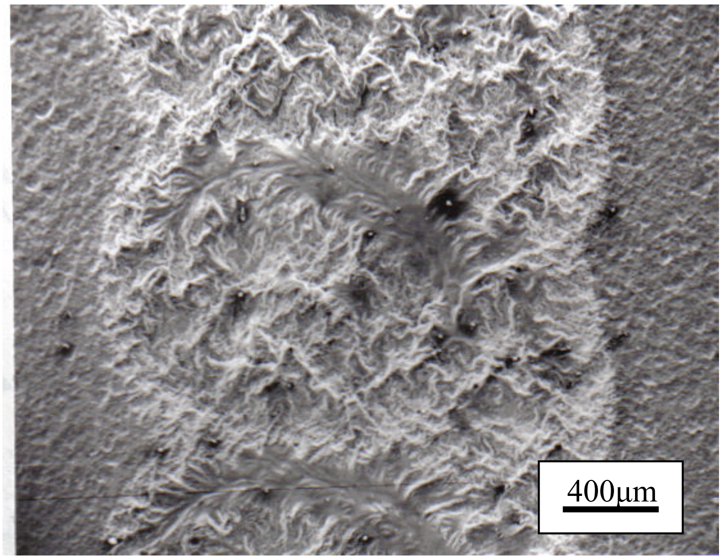
18.16 Hardness versus dendrite volume fraction in laser nitrided Ti-6Al-4V showing a near linear correlation (Hu et al 1996) page 20



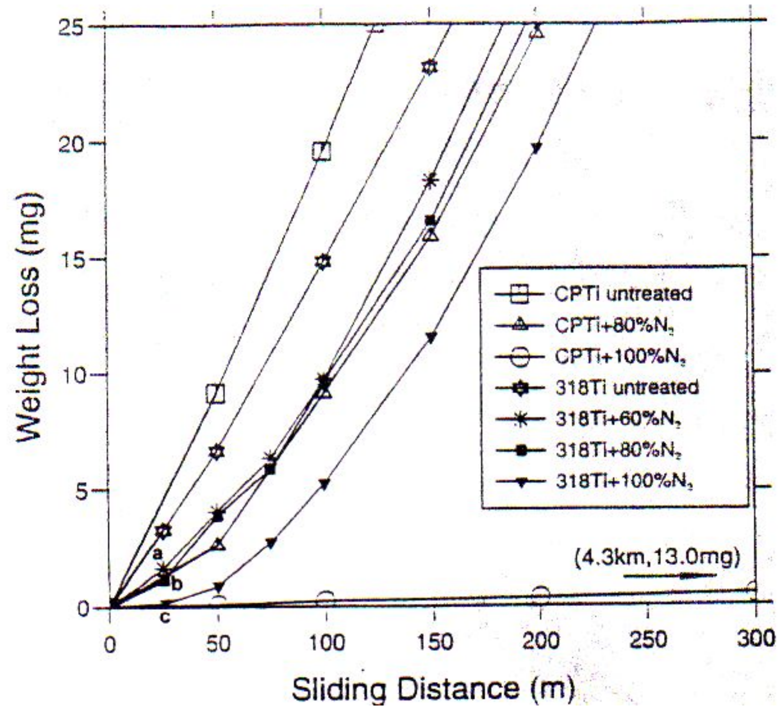
18.17 A correlation between the observed dendrite- arm- spacing and the calculated maximum cooling rate (Peng et al 1983)



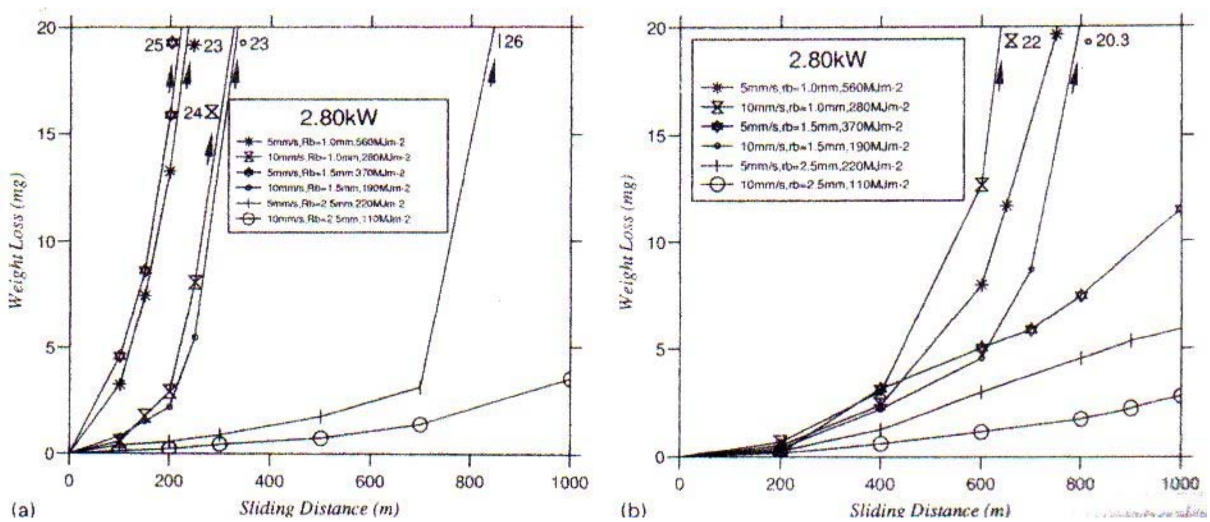
18.18 Microhardness map of Ti-6Al-4V alloy after laser nitriding with 20%N-80%Ar (a) tracks Ti and T2 (b) tracks T6 and T7 (Baker and Selamat 2008) page 20



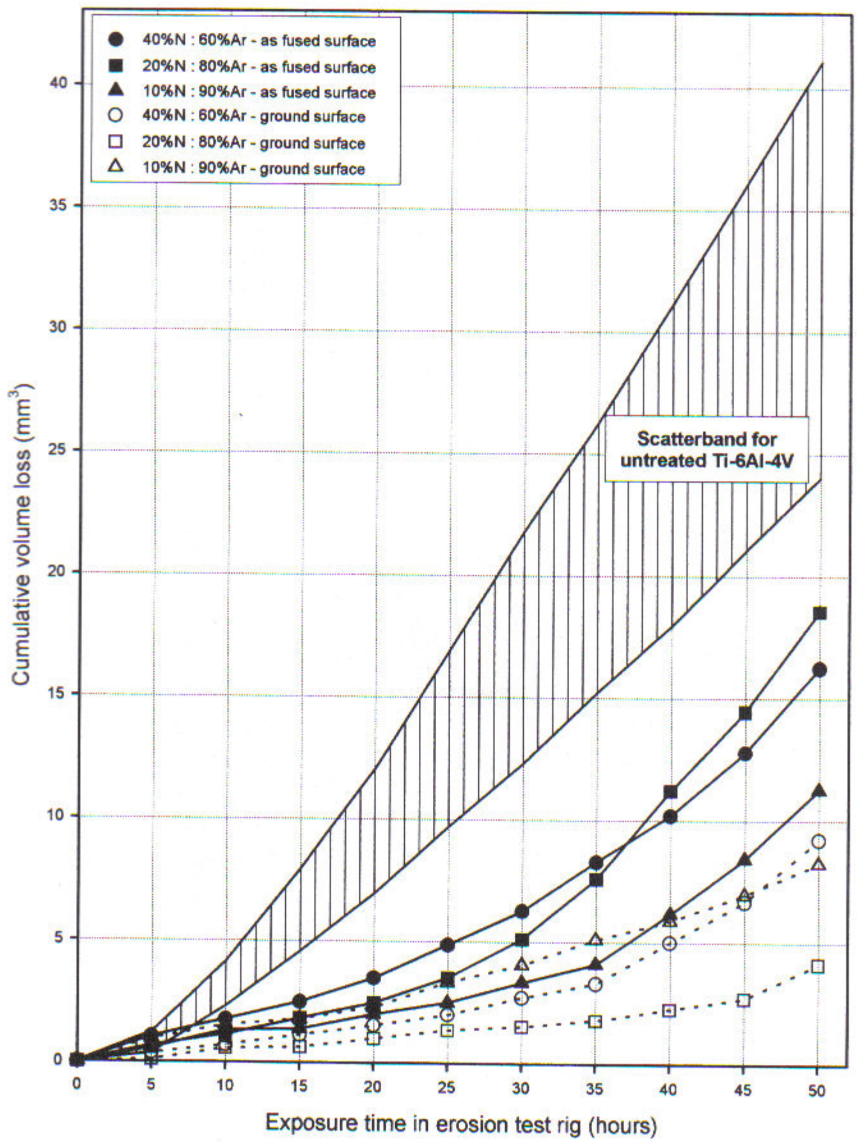
18.19 Surface morphology after laser processing using a spinning beam showing the origin of roughness bands across the track. (Mridha and Baker 1994a)



18.20 Weight loss versus sliding distance for specimens ground on 600 grit SiC paper for CPTi and Ti-6Al-4V alloys following laser nitriding (Xin and Baker 1996).



18.21 Weight loss versus sliding distance for specimens ground on 600 grit SiC paper of CPTi + (a) 5vol%SiC (b) 10vol% SiC (Baker et al 1994).



18.22 A comparison of water droplet erosion results from nitrided Ti-6Al-4V surfaces with and without grinding (Hu et al 1997a)

Table18. 1 Data of compounds incorporated into titanium alloys

Material	Melting Temperature ºC	Vickers Hardness VHN)	Density g/cm^3
Ti	1650-1670	60	4.54
TiC	3067	2800 -3200	4.92
SiC	2760	2600	3.22
TiN	2930	~ 2500	5.43
WC	2870	2400	15.77
VC	2830	2800	5.81
ZrC	3500	2600	6.73
ZrN	2980	1510K	7.35
ZrB	2990	2200	6.09
$TiSi_2$	1540	870	4.39

K is Knoop hardness

Specimen	Track number	R_a µm
A –Nitrided (20%N)	1	5.10
	6	3.10
	12	2.70
B-SiC preplaced	1	0.94
	3	0.70
	6	1.80
C- Combination of nitrided (40%N)and SiC preplacement	1	4.40
	6	7.50
	12	7.20

Table 18.2 Surface roughness measurements according to the sequence of laser track number for specimens A,B and C (Baker and Selamat 2008)