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The Microstructure Variation of Ti6Al4VELI During Excimer Laser 308nm Irradiation

By

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Abstract:

In these work ,the effects of laser irradiation on microstructure and performance of Ti6Al4VELI alloy have been studied by qualitative and quantitative analysis techniques, volume fraction of secondary phase, shape factors, number of particles of secondary phase, mean free path and grain size number were studied at different laser irradiation conditions. The effect of the amount of absorbed energy were represented by the variation in the number of pulses from 2000 pulses to 50000 pulses. Excimer laser irradiation is performed directly in the air and without any intermediate media. The volume fraction of the secondary phase β and α phase changed in the microstructure of Ti6Al4VELI alloy gradually with increase in laser dosages. Physical metallurgy considerations is the tool to understand the microstructure of any alloy system at specified laser irradiation conditions, the phase relationships and constitution of the system being studied.

Keywords:

Surface treatment, Titanium, microstructure and UV laser

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1. Introduction:

Titanium is an allotropic element: that is, it exists in more than one crystallographic form. At room temperature, titanium has a hexagonal close-packed (hcp) crystal structure, which is referred to as “alpha” phase. This structure transforms to a body-centered cubic (bcc) crystal structure. Called “beta” phase, at 883°C (1621°F). It is common to separate the alloys into three categories [(1),(2)]. Referring to the common phases present. The alloy categories are alpha, beta and alpha + beta :

*α. Or alpha

Alloys are non-heat treatable and are generally very weldable. They have low to medium strength; good notch toughness, reasonably good ductility and possess excellent mechanical properties at cryogenic temperatures [(3)]. The more highly alloyed alpha and near-alpha alloys offer optimum high temperature creep strength and oxidation resistance as well [(4),(5)].

*β. Or beta

Beta or near-beta alloys are readily heat treatable, generally weldable, and capable of high strengths and good creep resistance to intermediate temperatures. Excellent formability can be expected of the beta alloys in the solution treated condition. Beta-type alloys have good combinations of properties in sheet, heavy sections, fasteners and spring applications [(6)].

*α - β. Or alpha plus beta

Alloys are heat treatable and most are weldable. Their strength levels are medium to high. Their hot-forming qualities are good, but the high temperature creep strength is not as good as in most alpha alloys [(7),(8)].

These categories describe the origin of the microstructure in terms of the basic crystal structure favored by an alloy composition. Crystal structure and grain structure (microstructure) are not synonymous terms. The important fact to keep in mind is that basic crystal structure changes from α to β and back again play the major role in defining titanium properties [(9),(10)] .

Alloying elements generally can be classified as α and β stabilizers [(11)]. This transformation temperature from α + β or from α to all β is known as the β transus temperature. The β transus is defined as the lowest equilibrium temperature at which the material is 100%β. The β transus is critical in deformation processing and heat treatment. Below the beta β transus temperature, Titanium is a mixture of α+ β if the material contains some β stabilizers; otherwise it is all α if it contains limited or no β stabilizers [(12):(14)] . The β transus is important. Because processing and heat treatment often is carried out with reference to some incremental temperature above or below the β transus. Alloying elements that favor the α crystal structure and stabilize it by raising the β transus temperature include Aluminium, gallium ,Germanium, Carbon, Oxygen, and Nitrogen [(15)].

2. Experimental work:

A. Materials

The alloys used throughout this work was supplied by Sandvik Co, France in the form of bars of Ti6Al4VELI. Table (1) shows the chemical composition of the alloy used in the current work.

Table (1): *The chemical composition of Ti6Al4VELI (grade 23)*

Material	C%	N%	H%	Fe%	Al%	V%	O%
Ti6Al4VELI Rod Φ(6mm)	0.08 max	0.05 max	0.015 max	0.25 max	5.75: 6.75	3.5: 4.5	0.13 max

B. Laser Surface Irradiation

The surface irradiation of the alloys was studied. Samples used in this investigation were in the standard size for every test according to ASTM. All the experiments were performed at room temperature in air at atmospheric pressure; it was shown elsewhere [(10)] that the presence of air has no measurable influence on the process of irradiation by UV laser [(11)]. The irradiation is done on one side of the sample and covers all the surface area of the sample. The main goal of this work is optimize condition for laser irradiation of the samples by Excimer laser at 308nm Table (2) shows data for used rare gas halide Excimer laser.

Table (2): *Data for Excimer Laser (rare gas halide)*

Gas type	λ (nm)	r(A)	ω (Cm^{-1})	σ (Cm^2	τ (ns)
XeCl	308	2.9	194	50	11

λ = transition wavelength

r(A) = equilibrium inter-nuclear separation

ω = fundamental vibration frequency of the excited state

σ = stimulated emission cross section

τ = radiative life time (pulse duration)

The number of pulses and the effect of energy per pulse on the hardness were recorded to indicate the energy required (fluence) to improve the mechanical properties. Source in the shape of a rectangle with width (w=4mm) and length (l=10mm) was used in the laser process the power density ranges from (0.75 W/Cm^2 to 0.1 W/Cm^2) without any focusing. Excimer laser irradiation is performed directly in the air and without any intermediate media. The laser irradiation condition is listed in Table (3).

Table (3): *The laser irradiation conditions of the samples*

Type	Wavelength nm	No of pulses	Energy per pulse mJ	Repetition rate (Hz)
Excimer	UV 308.6	0,2000,5000, 10250, 15000,50000	6	200
time=6nano second & total energy =energy per pulse *number of pulses				

C. Qualitative analysis

Metallographic Examinations

The specimens were prepared for examination first by grinding on different grades of silicon carbide "SiC" papers coarse grinding followed by fine grinding at 180,240,320,400,600, and 800 finally polishing was conducted with Alumina powder (3μm) size. The details of the microstructure were revealed after etching by standard etching solution of the alloy selected. Table (4) the etching solution composition and characteristics of Ti6Al4VELI. All specimens had to be etched and polished several times to obtain best results and to produce a uniform level of sample examination. The surfaces of the samples before and after laser irradiation were examined using an Olympus optical microscope Model BHM at selected magnification.

Table (4): *The etching solution composition and characteristics of Ti6Al4VELI.*

Alloy	Etchant	conditions	Remarks
Ti6Al4V ELI	Dist.water Hydrofluric acid (40%) Nitric acid (1.40)	100ml 1-3ml 2-6ml	Swap sample 3-10s (Toxic)

D. Quantitative analysis

Quantitative Metallography Measurements

A quantitative analysis of the microstructures was produced carried out over four (4) fields across the surface to indicate:

1) The volume fraction V_f of each phase (count analysis was applied).

2) Average grain size by linear intercept technique.

3) Average particles radius D_A using number of modules per unit area and can calculated as follows: [118]

$$D_A = (4 V_f / N_g)^{1/2} \qquad (1)$$

4) Inter nodule spacing (MFP) by measuring P_L no of particles per unit length and sustain in the equation[118]

$$MFP = (1 - V_f) / P_L \qquad (2)$$

5) The shape factor by using equation[118]:

$$S.F = 2/3(P_L)/ V_f N_g \qquad (3)$$

V_f volume fraction of secondary phase
N_g average grain size number
D_A Average particles radius
P_L no of particles per unit length
MFP Inter nodule spacing
S.F the shape factor
The terms were determined according to ASTM E112. Calculations were carried out in several areas in each specimen investigated at 100X projected on a screen measuring 500 mm^2. The measurement is an average of over five readings for each condition. The scattering value for each specimen was +1%. All calculations were measured around a circle to consider all directions 360^o

3. Results & discussions:

a. Qualitative analysis

Figure (1)-(a) shows the initial microstructure of the alloy before laser irradiation, the structure is alpha-beta (equiaxed) system contain one or more alpha stabilizers or alpha-soluble elements plus one or more beta stabilizers. The structure constituent is related to chemical composition and the effect of alloying elements on the microstructure. Alpha stabilizers such as Aluminium and oxygen, increase the temperature at which the α phase is stable. Beta stabilizers such as Vanadium result in stability of the β phase at lower temperatures.

When the surface of the alloy irradiated by Ultraviolet Excimer laser 308nm as shown in figure (1) from (b) to (e). The processes was done at room temperature in the normal atmosphere these rate allow the Martensitic transformation. The white plates are *α*. and the dark regions between them are β. This is a typical Widmanstatten structure.

Beta phase decomposes, usually by martensitic transformations in the alpha-beta alloys. Martensitic reactions are fast. diffusionless (no composition change' transformations in crystal structure and microstructure,the morphology (shape location) of the phase changes with prior treatment. The *a* phase may remain relatively globular (equiaxed). but the transformed beta (martensites or alpha may be very acicular or elongated. The amount of equiaxed alpha and the coarseness or fineness of the transformed beta products will affect titanium's alloy. Metastable beta can show more variety in decomposition than does the supersaturated alpha or martensitic alpha structure. The omega phase can form, as can alpha phase and a low-solute-contend beta phase. Other intermetallic compounds also may form. and. under certain circumstances, ordering of the beta phase can occur. (Ordering removes the randomness in atom location which normally exists and puts atoms in specific locations.

Hardenability of a titanium alloy is a phrase that refers to its ability to permit full transformation of the alloy to martensitic phases or to retain beta to room temperature. Alpha prime (α') and alpha double prime (α") martensites are brought out by cooling and decompose, on subsequent aging, to alpha and beta phases.

The β transus is important. Because processing and heat treatment often is carried out with reference to some incremental temperature above or below the β transus . Alloying elements that favor the α crystal structure and stabilize it by raising the β transus temperature.
Transformation kinetics, transformation products, and specific response of a given alloy can be quite complex. A mechanism of laser irradiation at high power rating was explained according to the following procedures: a point on the surface within the path of the beam is rapidly heated as the beam passes. This area is subsequently cooled rapidly by heat conduction to the interior after the beam has passed. By selecting the correct power density and repetition rate of the process. The material will harden to the desired depth. According to The Law of conservation of energy the laser photons absorbed according to Einstein principles

- $E = h\nu = \Delta G\ (T)$ (4)

Photon energy (laser energy) will transform to Energy for phase transition, the Gibbs Energy (which cause phase transition) is function of temperature

- $\Delta G\ (T) = A+BT \log T + CT$ (5)
- $\Delta G\ (T) = H-T\Delta S$ (6)

So ΔG Gibbs free Energy related to amount of absorbed energy which related to phase diagram by temperature (appendixI). Microstructure change is a function of phase constituent which depends mainly on ΔG Gibbs free Energy

b. Quantitative analysis

The amount and distribution of the secondary phase β phase plays the most significant role during the laser irradiation process, table (5) shows the variation in microstructure features as function of the laser energy absorbed (number of pulses).

Table (5): *The variation in microstructure features with number of pulses*

Number of Pulses	Number of particles per unit length	Volume fraction V_f	MFP(Mean Free Path)	S.F (shape factor)	ASTM grain size number
0	14	38.6%	0.04385	2.41	10
2000	17	42.5%	0.0336	2.7	9.5
5000	20	30%	0.035	4.44	7.5
10250	16	34.3%	0.04107	3.14	10
15000	10	28.6%	0.07142	2.33	10
50000	14	38.6%	0.04388	2.4	10

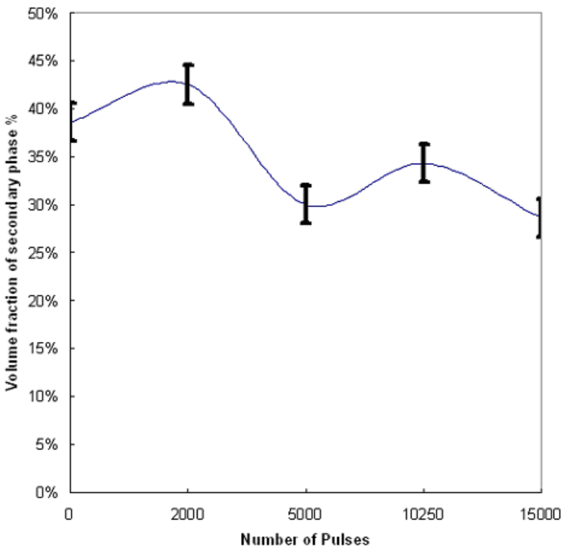
Figure (2) shows the relation between the amount of absorbed energy and the volume fraction of the secondary phase according to the phase diagram of the Ti6Al4VELI. The maximum amount of secondary phase appears at 2000 pulses, While the amount of secondary phase in the material irradiated by Excimer laser 308nm as function of the number of pulses in the range from 5000 pulses to 50000 pulses were less than the non irradiated samples. The phenomena can be explained in terms of the phase diagram (appendix I) and kinetics of the reaction when the material absorb more energy at the same composition. Ti6Al4V is α structure which is HCP structure vanadium which found in 3.5:4.5% which β-BCC phase stabilizer at room temperature so the final micro structure is a combination between α and β structure this micro-structure produce 34%improvement in the micro-hardness [16]. Not only the constituent of the alloys or the amount of alloying elements but the microstructure also have the most significant effect on the irradiation process.

Laser irradiation work as method of hardening and softening at the same time. The initial microstructure of the irradiated alloy (the room temperature microstructure) plays the significant role in that case. The chemical composition and the amount of alloying elements in the alloy plays a significant effect on the laser irradiation process.

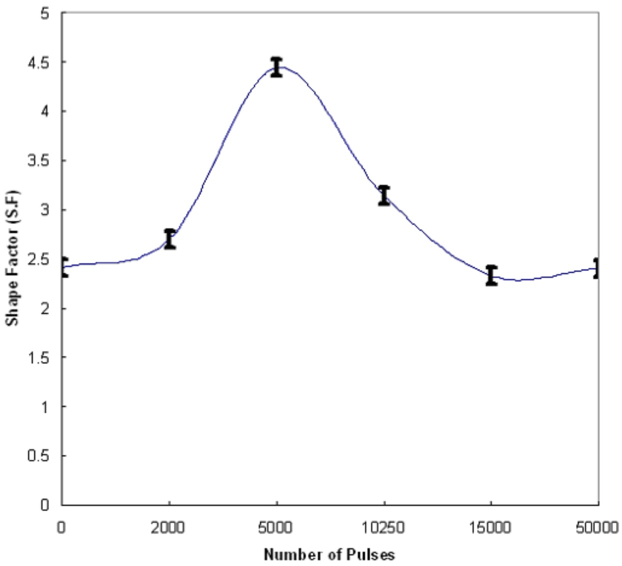
Figure (3) shows one of the most important features during microstructure changes which is the shape factor of the secondary phase during laser irradiation, the maximum value was recorded at 5000 pulses, at this amount of energy the homogeneity in the secondary phase is less while at different number of pulses the homogeneity in the structure were less than the non irradiated samples, the variation in shape factor give impression about martensetic transformation due to laser irradiation and the formation of typical Widmanstatten structure.

The phase distribution in the microstructure can be expressed by the number of secondary phase particles per unit length and the mean free path (edge to edge spacing) as shown in the Figures (4) and (5) respectively, The maximum amount of the secondary phase was recorded at 5000 pulses while the minimum amount was recorded at 15000 pulses. The alpha- beta alloys is the strongest structure in Titanium alloys. The absorption of more amount of energy above the alpha- beta transformation temperature lead to grain coarsening and affect the grain size number as shown in table (5). According to the theory of dislocations, laser irradiation effects have explained. The strain hardening effect is due to an increase in dislocation density under the action of external force resulting from the transformation of energy of the laser photons. The external force resulting from laser photons lead to the interaction of dislocations which form dislocation pile up of various degrees of stability and mobility, and form also Frank –real source. The improvement in micro-hardness due to laser irradiation because the light photons of energy is go through the surface and absorbed into the metal causing the atoms to move around their position and some atoms may be moved inside the structure. The photon energy is transformed into kinetic energy and cause some change in the arrangement of atoms inside the structure; this disturbance cause the improvement in the properties due to redistribution of atoms and some hard phases were appeared.

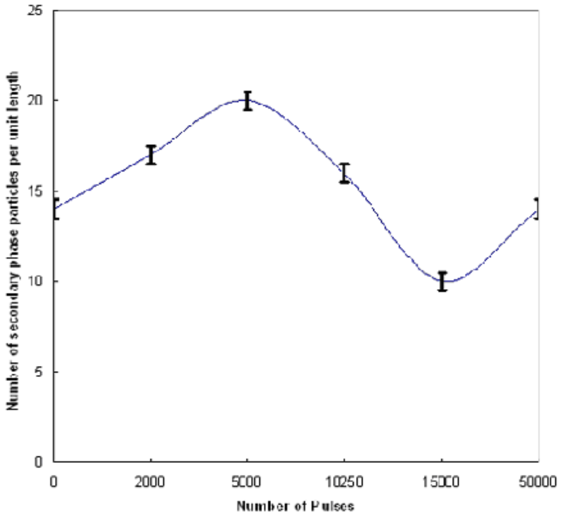
Figure(1): *Qualitative analysis for the Effect of Excimer Laser irradiation at 308nm, 6mJ, 200Hz, 750x at Different Number of Pulses on the microstructure of TI6Al4VELI (a) untreated (b)2000pulses (c)5000pulses (d)15000pulses (e)50000pulses*



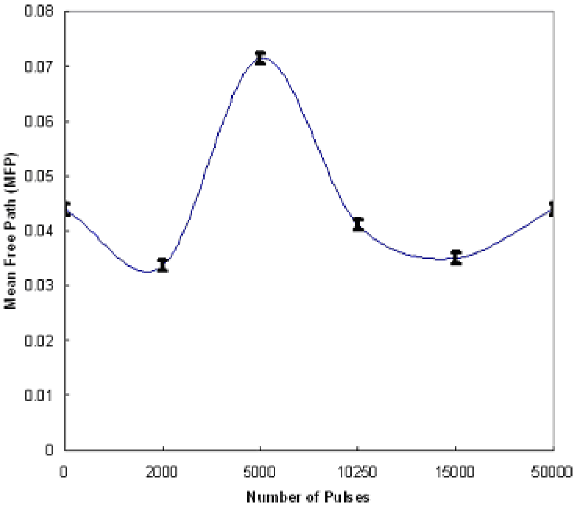
Figure(2):*The relation between number of pulses and volume fraction secondary phase for Ti6Al4VELI irradiated by 308nm,6mJ,200Hz.*



Figure(3):*The relation between number of pulses and shape factor secondary phase for Ti6Al4VELI irradiated by 308nm,6mJ,200Hz.*



***Figure(4):**The relation between number of pulses and number of particles per unit area of secondary phase for Ti6Al4VELI irradiated by 308nm,6mJ,200Hz.*



***Figure(5):** The relation between number of pulses and mean free path for Ti6Al4VELI irradiated by308nm,6mJ,200Hz*

4. Conclusions:

1. Pulse laser treatment in normal atmosphere is an attractive technique that differs from usual coating methods, a new very thin layer with different microstructure and different mechanical characteristics will be formed on the alloy surface.
2. The microstructure features and the formation of secondary phase depends on the amount of the amount of laser absorbed besides the initial microstructure and chemical composition of the treated alloy.
3. The laser with high power and short pulses interaction is the basis for an effective treatment suitable for Ti6Al4VELI. to induce the physical reaction in the atmospheric environment without external media leads to change in structure and characteristics.
4. Laser treatment process is relatively economic. It does not need a huge industrial

equipment in a great place for the installation and operation of such equipment.
5. Laser irradiation process is cold technique, so it prevent hydrogen embrittlement of titanium observed in industrial service have generally been limited to situations involving high temperatures.

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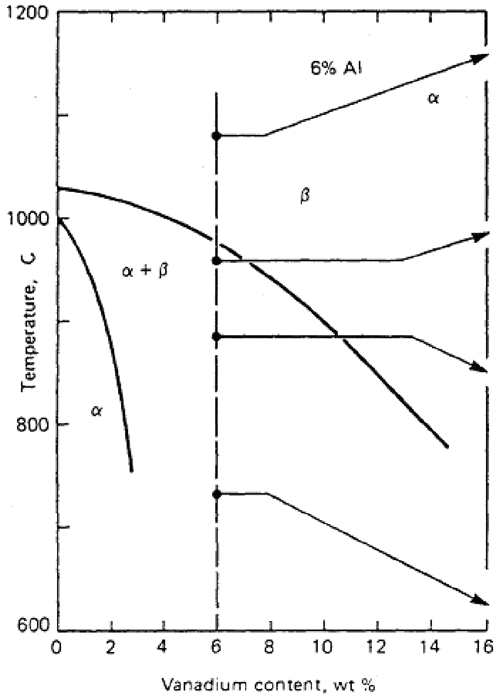
Nomenclatures:

N_g … average grain size number
D_A … Average particles radius
P_L … no of particles per unit length
MFP … Inter nodule spacing
S.F … the shape factor
V_f … volume fraction of secondary phase
T … Temperatures
ΔG … Gibbs free Energy
H … Enthalpy
ΔS … Entropy
A,B,C … Constants depends on the material
E … Photon energy

h … Plank constant
ν … Frequency
λ … transition wavelength
r(A) … equilibrium inter-nuclear separation
ω … fundamental vibration frequency of the excited state
σ … stimulated emission cross section
τ … radiative life time (pulse duration)

Appendix -1-



Phase diagram of TI6Al4VELI