AMAS Course on Mechanics of Advanced Materials
MAM'2001 – (pp.205–234) – Warsaw, October 8-12, 2001.

Laser technology in generating microstructure of advanced materials

B. MAJOR

Institute of Metallurgy and Materials Science
Polish Academy of Sciences
Reymonta 25, 30-059 Cracow, Poland

Laser application in technology is growing exponentially. In modern materials engineering, lasers are used for surface remelting as well as for explosive ablation of materials and deposition. Origin of microstructure modification by laser remelting or laser alloying is attributed to specific solidification fine structure comprising often high concentration of alloying elements. Application of laser to produce thin films is very sophisticated. The method based on laser ablation of material and plume transfer to substrate seems to be very perspective. Any materials from pure elements to multicomponent compounds can be deposited using this method. The basis for laser surface modification as well as for pulsed laser deposition are given in these lectures. Wide spectrum of possible applications of laser technology is also presented. Both laser modification and pulsed laser deposition is illustrated with own experimental results.

Key words: *laser, remelting, ablation, deposition, microstructure modification, residual stresses.*

1. Introduction

Surface treatment seems to offer the changes to save strategic materials, however, the most important is to produce materials with improved properties in comparison to the bulk properties [1, 2]. Laser surface treatment i.e. remelting/solidification, laser alloying and cludding, as well as fabrication of thin films by pulsed laser deposition(Fig.1) allows a materials engineering to be developed especially if one concentrates on the specificity of the laser processing: the laser wavelength, an extremely high power density leading to short interaction times with material [3-5].

A rapid solidification processing is a basis for microstructure selection in laser modification of surface layer of materials. Immediately after the first high-power ruby laser became available, there was interest on interaction of intense laser beams with solid surfaces. The ease with which materials could be vaporised suggested that the intense laser radiation with short pulses (nanosecond) could be used to deposit thin films [3-10]. A thorough understanding of the peculiarities of laser-surface interactions relies on a knowledge of the intrinsic properties of lasers and surfaces. Moreover, the solidification microstructure with the accompanying solute segregation profile, largely, and often definitely, controls the properties and the quantity of the final product obtained in a form of laser modified surface layers. Thus, from the

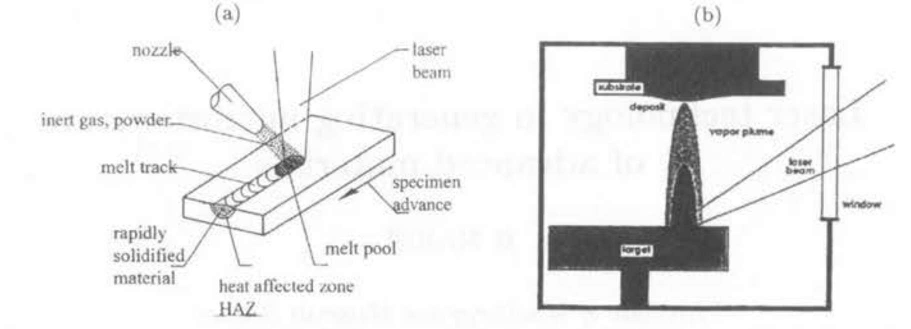

FIGURE 1. Schematic presentation of laser technologies: (a) laser surface modification and (b) pulsed laser deposition (PLD).

practical viewpoint of technological needs, it is important to know the processing conditions which will produce a microstructure that gives the desired properties to the material. The development of specific microstructural characteristics depends upon the conditions at and the shape of the solid-liquid interface, and on the transformation or even reaction processes which occur in the solid as it cools to room temperature.

Pulsed laser deposition (PLD) is often described as a three-step process consisting of vaporisation of a target material, transport of the vapour plume, and film growth on a substrate. These steps are repeated thousands of times in a typical deposition run. Laser-induced desorption and ablation result from the conversion of an initial electronic or vibration photoexcitation into kinetic energy or nuclear motion, leading to the ejection of atoms, ions, molecules, and even clusters from a surface. The properties of the deposited films depends strongly on the deposition characteristics and can be controlled by driving the process parameters.

Thin film structures, which are impossible or difficult to produce via conventional sputtering techniques (electron or ion beam sputtering), might be generated via laser sputtering or pulsed laser deposition (PLD). It is nowadays a well-established and advanced tool for the growth of dielectric, metallic, semiconductive and superconductive thin films. Prominent features of PLD include 10^5 times higher deposition rates as compared with conventional techniques, particle energies of the order of 100 eV due to the high laser power densities and interaction of the evaporated plume with the laser beam.

2. Laser surface modification

2.1. Solidification microstructures

Microstructures are at the centre of materials science and engineering. They are the strategic link between materials processing and materials behaviour. Microstructure control is therefore essential for any processing activity. One of the most important processing route for many materials, especially metals and alloys, is solidification. Recently, rapid solidification processing and microstructure formation is of great interest due to formation of refined microstructure and possible application [11]. In rapid solidification processing the growth rate of the solid-liquid interface becomes sufficiently high so that certain limits are reached which modify the global transformation behaviour of materials. These limits are of threefold nature (Fig. 2):

1. Localisation of diffusion with respect to the size of microstructure.
2. Localisation of diffusion with respect to the width of the interface.
3. Collision limit of atom attachment.

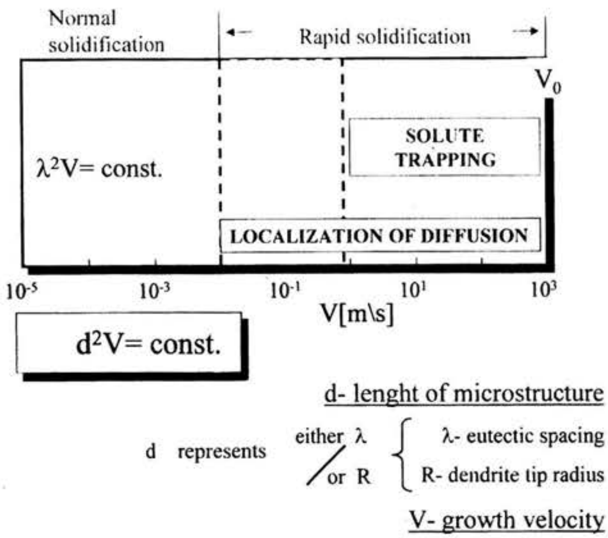

FIGURE 2. Range of solidification velocities encountered in normal and rapid solidification processing and characteristic phenomena appearing in metals under conditions of rapid solidification.

There are many rapid solidification processing which have been developed in the past, such as splat quenching, melt spinning, planar flow casting, laser or electron beam resolidification, atomisation, bulk undercooling etc. These processes can be classified into three main groups which show distinct and important differences in processing parameters (Fig. 3).

The most important variable in rapid solidification processing is the interface growth rate V; the temperature gradient in the liquid ahead of the solid/liquid interface G. Further important variables are the cooling rate $\dot{T} = dT/dt$ and the G/V ratio which controls planar interface stability at low rates (constitutional undercooling). The most important differences between the three processes types with respect to the above-mentioned solidification condition are schematically shown in Fig. 3, presenting the variation of: velocity (V), temperature gradient (G), cooling rate ($\dot{T}$) and G/V ratio in respect to the direction z which is perpendicular to the surface.

In laser surface treatment (Fig. 3a), the rapid movement of a high energy heat source is found. The laser beam moves over the specimen surface with velocity $V_{\mathbf{beam}}$.

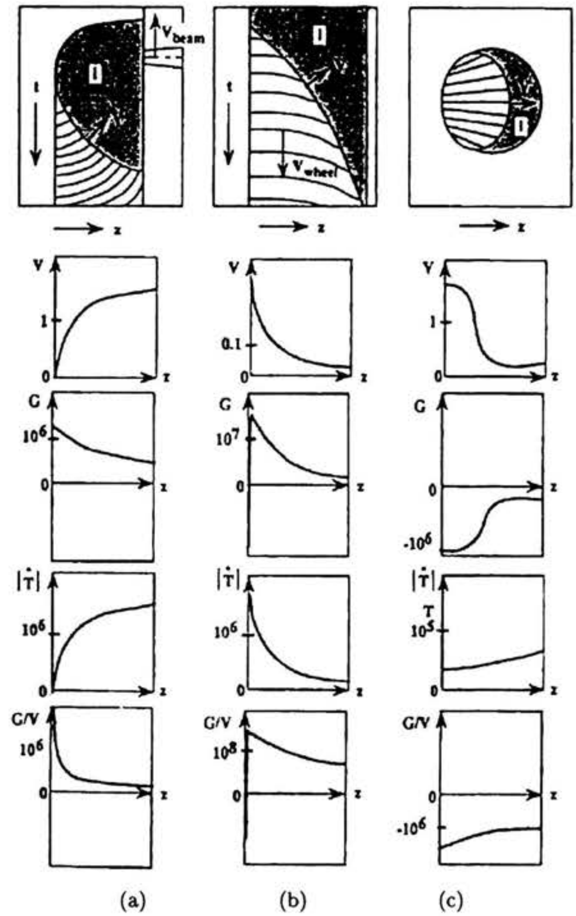

FIGURE 3. Characteristic solidification conditions of the three main rapid solidification processes: (a) laser surface treatment, welding; (b) planar flow casting, melt spinning; (c) bulk undercooling, atomisation.

Solidification rate varies from zero at the solid/liquid interface and reaches maximum on the surface. Temperature gradient is highest at the bottom of the trace and decreases approaching the surface. The absolute value of cooling rate increases strongly approaching the surface. Electron beam resolidification and electron beam or laser welding belong to this group of processes.

In planar flow casting of ribbons (Fig. 3b), a high undercooling of melt may be obtained by large cooling rates. Splat quenching and melt spinning belong to this group of processes.

In bulk undercooling (Fig. 3c), a high undercooling of the melt can be produced by the absence of nucleates. This case may appear by slowly undercooling of a bulk melt in a very pure environment such as has been obtained in levitation melting in ultrahigh vacuum or by encapsulating the melt in glass.

Atomisation is a widely used industrial process which belongs to both categories (b) and (c); some grains are free of nucleates and others are very small so high cooling rates are achieved. Powders produced by this method are subsequently consolidated to form constructional materials or even final products.

The presented diagrams show already that laser surface treatment leads (in most circumstances) to columnar (directional) growth of dendrites and in the case of atomisation free (undercooled) growth of crystal appears, while melt spinning shows a mixed behaviour which is often dominated by directional growth.

Depending on the solidification condition mentioned above, various microstructures are formed, namely, plane (P), cell (C), dendrites (D) and band (B), which are schematically presented in Figs. 4 and 5. All these morphologies may be obtained in single-phase solidification or in polyphase (eutectic) solidification.

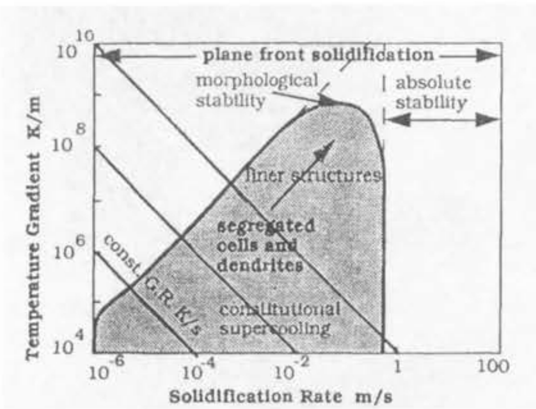

FIGURE 4. Plot of temperature gradient versus solidification rate and solidification morphology.

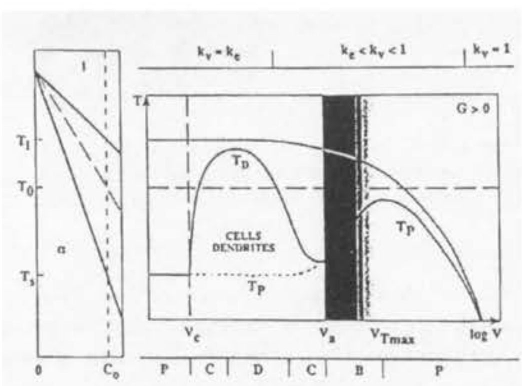

FIGURE 5. Interface response function (T-V curve) for plane front, T_P and cellular-dendritic growth, T_D, for directional growth as typically observed in laser surface treatment. The variation microstructures observed as a function of V can be determined by the maximum growth temperature criterion (P – plane front; C – cells; D – dendrites; B – bands).

2.2. Laser modification by remelting

Laser remelting can be used to create supersaturated and highly alloyed materials with novel structure. Most of the beneficial effects of a laser treatment can be attributed to specific solidification of the fine structure. The high-melt-pool temperature, resulting from a high power density of laser beam, enables the dissolution of even thermodynamically stable intermetallic phases and formation of metastable phases due to the high cooling rates. Solidification proceeds as either a stable planar front or as an unstable front leading to dendrites or cells resulting in microstructure variation in remelted layer, which was shown in own examination of Al-Zn alloy (Fig. 6) [6, 7].

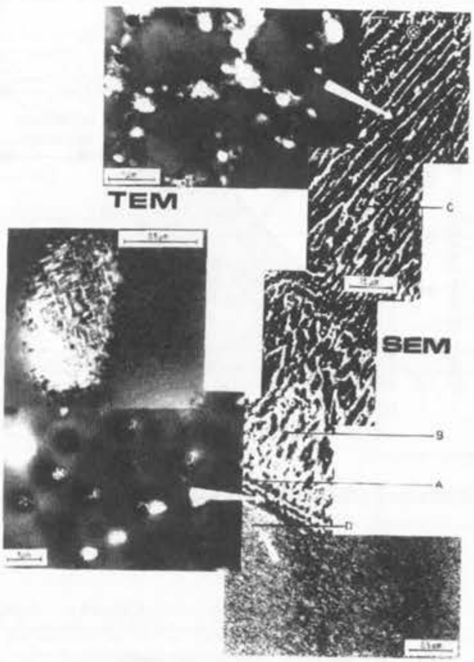

FIGURE 6. SEM photograph of a cross-section through the solidification pool and TEM details using foils cut parallel to specimen surface from layers of various depths belong the surface. (A) section with frozen droplets due to restored planar growth, (B) cells, (C) dendrites, (D) unmelted substrate.

The process which occurs depends on the occurrence of constitutional supercooling. The constitutional supercooling is caused by the thermal gradient being less steep than the melting point gradient, which is the result of partition effects taking place at the solidification front giving rise to composition variation in this region which is schematically shown in Fig. 7.

Laser modification has been applied by the author in many metallic systems shown in Table 1 and some chosen results of microstructure examinations are presented in Figs. 8-12.

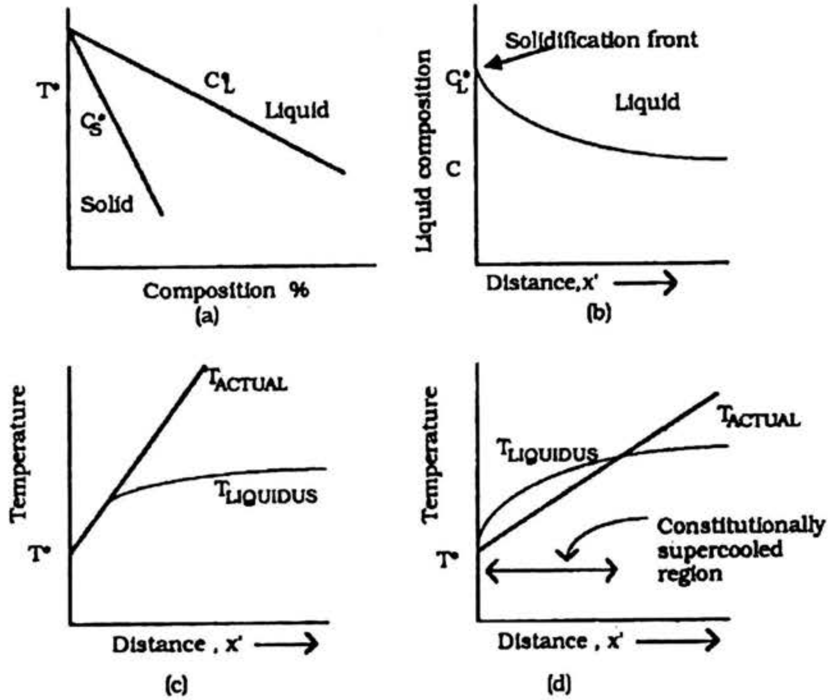

FIGURE 7. Constitutional supercooling in alloy solidification: (a) phase diagram, (b) solute enriched layer in front of liquid/solid interface, (c) stable interface, (d) unstable interface.

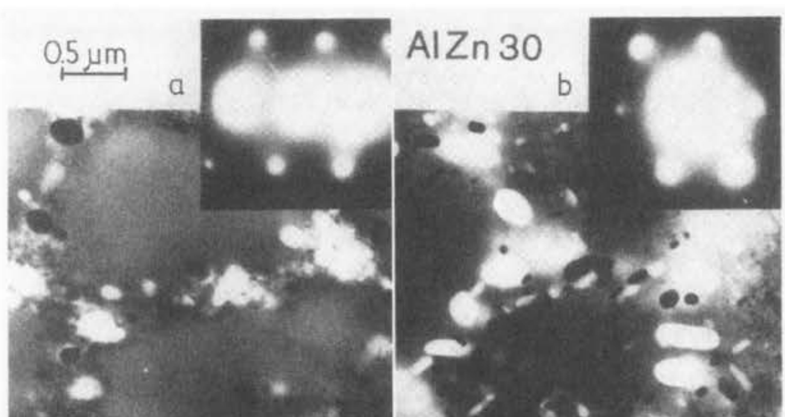

FIGURE 8. TEM microstructure of surface layer (extracted from the laser treated sample) of Al-30Zn alloy, parallel to the surface: (a) after solidification, solid solution inside the grain and allotriomorhic precipitated along the grain boundaries, (b) after ageing at 150°C/15 hr, precipitates of the β-zinc phase inside the grains.

TABLE 1. Metallic systems modified by the author.

LASER TREATMENT		
ALUMINIUM ALLOYS		
AlZn30	– remelting	
AlZn5Mg3Cu1	– remelting	
AlFe6	– remelting	
AlFe6Ni2	– remelting	
AlSi12 (Cu 1; Mg 1; Ni 1; Fe 0.4; Mg 0.12)	– remelting	
	– alloying SiC	
	– alloying Ni	
STEELS		
High speed steel (HSS) *PN SW7M, AISI M2, DIN S 6-5-2* (wt.%: C 0.9; Si 0.78; Mn 0.3; Cr 4.12; W 6.22; Mo 4.8; V 1.74)		
	– remelting	
	– alloying VB_2	V 3.8 → 9.4; B 0.9 → 3.25 wt.%
	– alloying CrB	Cr 5.4 → 13.8; B 0.3 → 2.16 wt.%
	– alloying VC	V 1.8 → 64.0; B 0.9 → 11.9 wt.%
	– alloying Mo_2C	Mo 5.0 → 55.0 wt.%
Carbon steel 45	– alloying VB_2	
	– alloying CrB	
	– alloying B_4C	
Valve steel *PN H9S2, AISI HNV3, DIN X45CrSi93* (C 0.9; Si 2-3; Cr 8-9)	– remelting	
	– alloying WC	
	– alloying Ni	
Constructional steel (Mn) *PN 50G, DIN C50*	– remelting	
	– alloying WC	
	– alloying Ni	
Constructional steel (Cr-Ni-Mo) *PN 36HNM DIN 36CrNiMo4* (C 0.32; Cr 1.16; Ni 1.05; Mo 0.19; Mn 0.64; Si 0.23)	– remelting	
	– alloying CrB	
	– alloying Ni	
Constructional steel (Mn-B) *PN 36HNM DIN 36CrNiMo4* (C 0.29; Mn 1.2; B 0.0012; Cr 0.2; Ni 0.2; Si 0.23)	– remelting	
	– alloying CrB	
	– alloying VC	
TITANUM ALLOYS		
TiAl1Mn1	– remelting in Ar	
	– remelting in N_2	
	– remelting Ni in Ar	

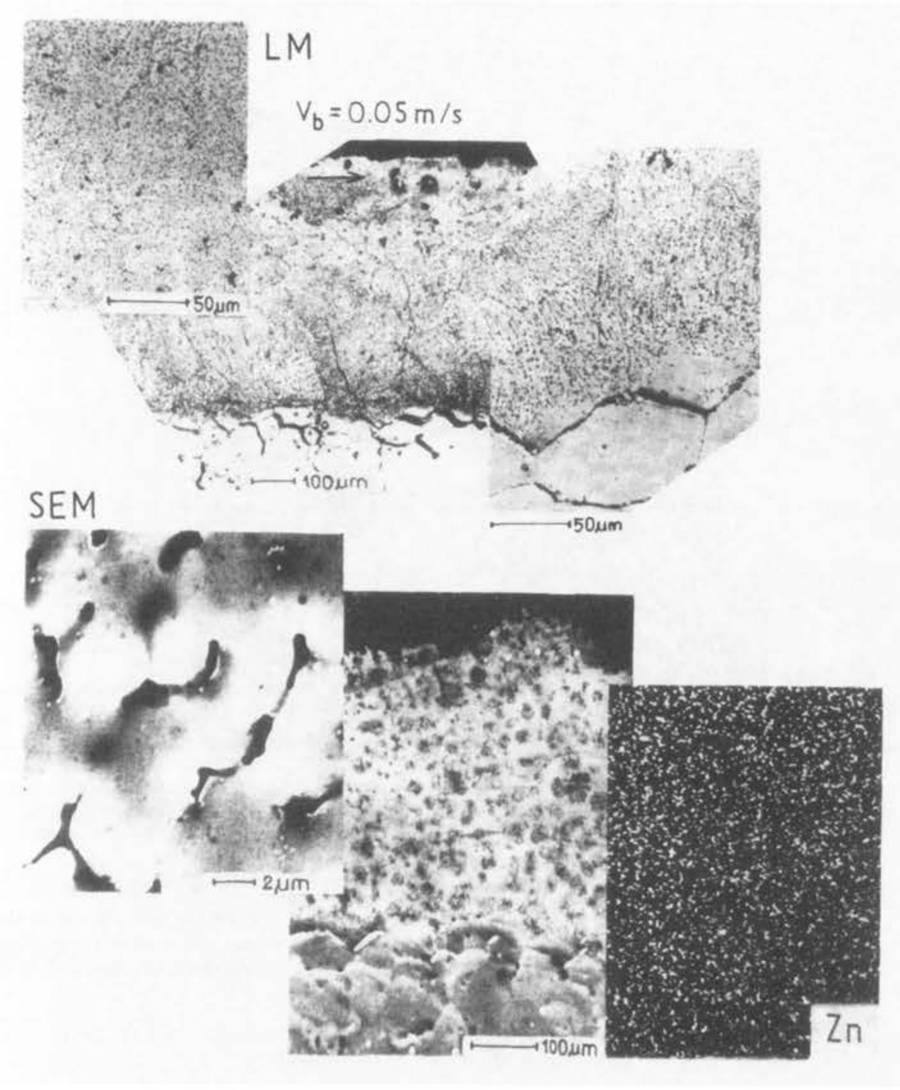

FIGURE 9. Microstructure of Al-5Zn-3Mg-1Cu alloy with the distribution of Zn, alloy subjected to ageing at 150°C for 3 hr after laser remelting; microstructure refinement within the laser remelted zone.

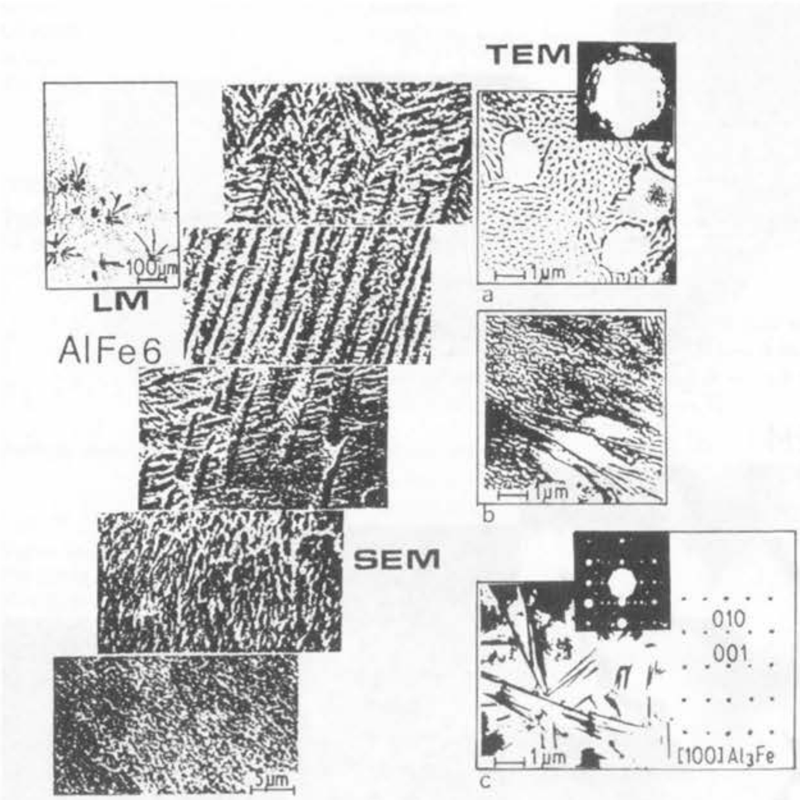

FIGURE 10. Microstructure of Al-6Fe alloy of the cross-section (LM, SEM) and parallel to the surface (TEM) through the solidified pool after laser remelting; within the laser remelted zone three types of microstructure: cellular, plate and needle (TEM); microdendrites elongated in the direction of heat flow.

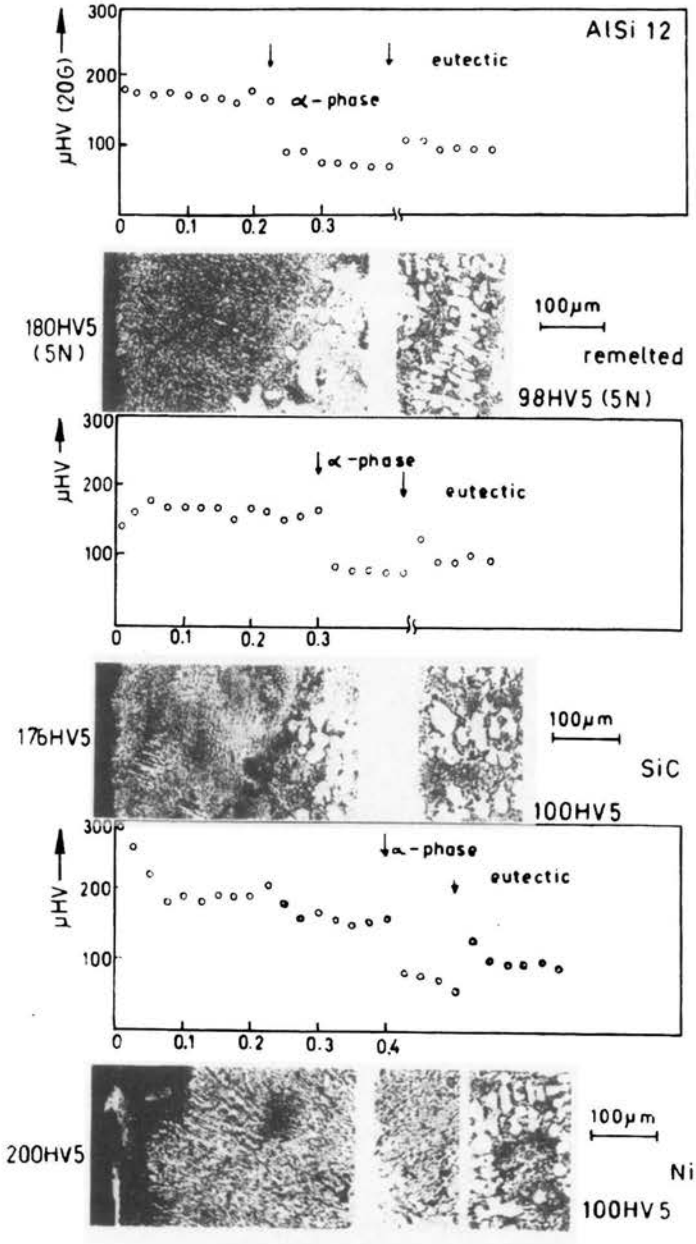

FIGURE 11. Microstructure and distribution of micro-hardness μHV of Al-12Si alloy through the cross-section of laser remelted and laser alloyed layer.

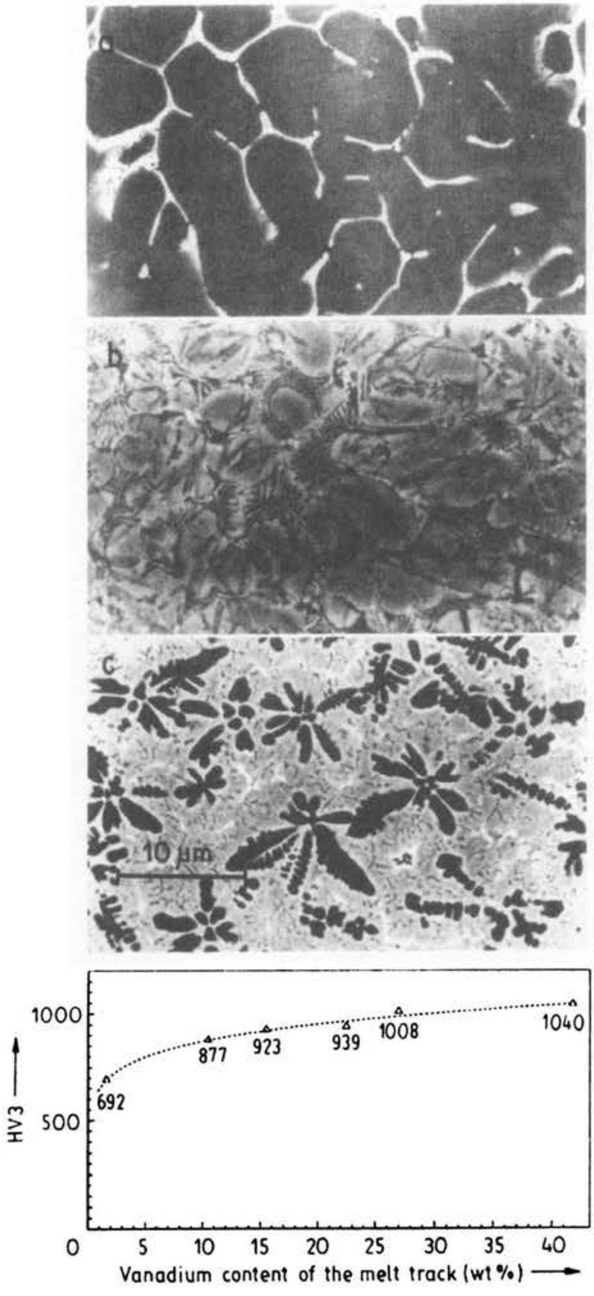

FIGURE 12. Microstructure of high speed steel 6-5-2 laser alloyed with VC; content of V in laser track: (a) 3.5 wt.%V; (b) 5.5 wt.% V; (c) 17.0 wt.%V and hardness of this steel after laser alloying.

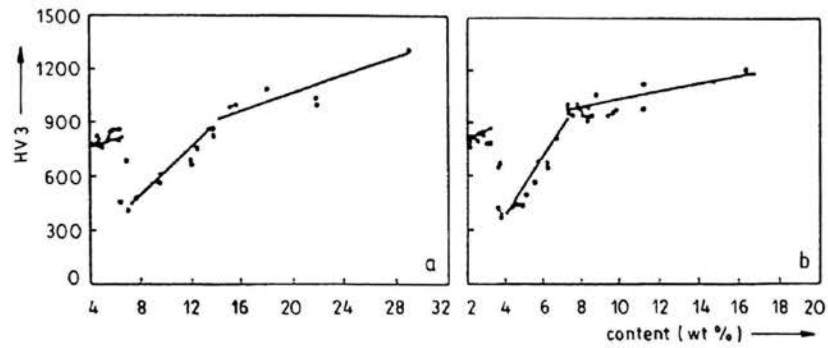

FIGURE 13. Hardness HV3 of (a) CrB and (b) VB_2 laser alloyed high speed steel of grade 6-5-2.

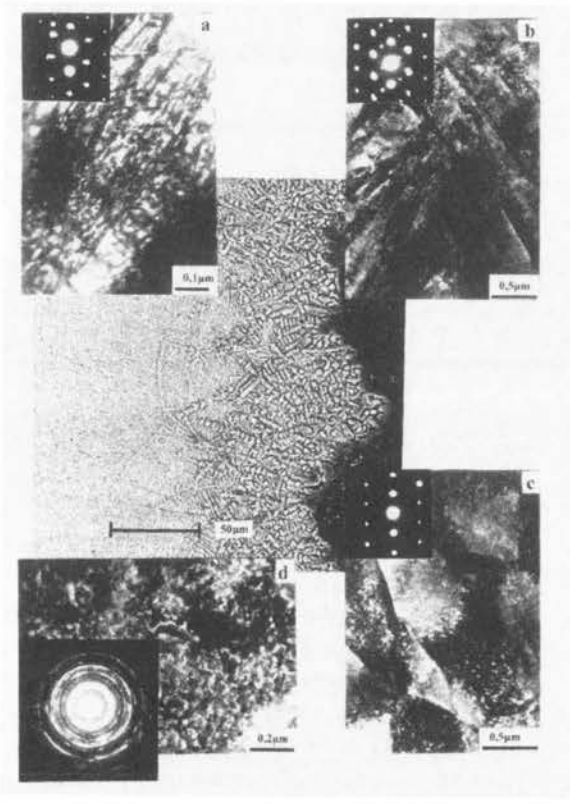

FIGURE 14. Microstructure SEM and TEM of the cross-section of TiAl6V4 alloy laser remelted in nitrogen environment, showing overview of cross-section (SEM) and microstructure: inside the dendrite arm (a), and three types of microstructure between the dendrite arms: plate (b), cellular (c) and nanostructure (d).

Laser remelted region is usually shielded by the neutral gas. One can apply such environment which leads to reaction with remelted materials. This happened, for instance, in modification of titanium alloys where the molten pool was covered by nitrogen [12]. Due to high affinity of titanium to nitrogen, the titanium nitride was formed in laser remelted surface layer and the peculiar microstructure with dendrites grown from the surface was observed. Between the dendrite arms three types of microstructure were stated i.e. plate (b), cellular (c), and nanostructure (d) (Fig. 14).

Explanation of this phenomenon could be given basing on the interaction of three forms of nitrogen i.e. molecules, atoms and ions (Fig. 15) with the molten titanium alloy.

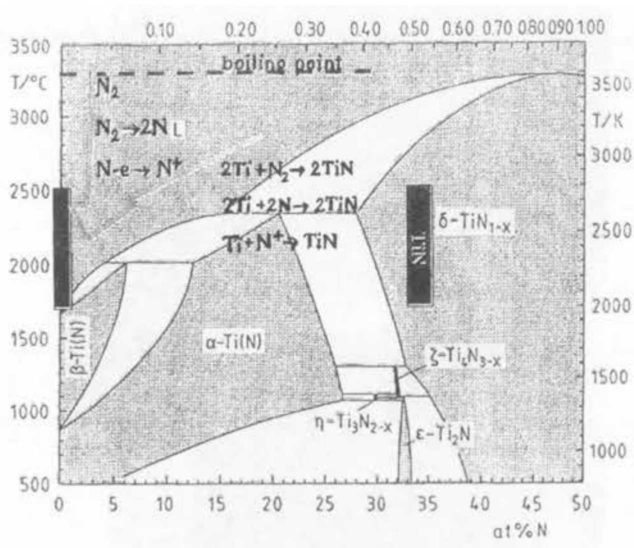

FIGURE 15. Phase diagram Ti-N with marked possible reactions of N_2, N and N^+ with molten titanium.

2.3. Laser alloying

Surface alloying with laser is similar to laser surface melting except that another material is injected into the melt pool. Laser surface alloying is also similar to surface cladding in that if the cladding process is performed with excess power then surface alloying would result. It is therefore an extreme case of surface cladding. The main characteristics of the process are as follows:

- The alloyed region shows a fine microstructure with nearly homogeneous mixing throughout the melt region.
- Most materials can be alloyed into most substances; some surface alloys can only be prepared via a rapid surface quenching, e.g. Fe-Cr-C-Mn.

The alloying material can be placed in the melt zone by:

- electroplating,
- vacuum evaporation,
- preplaced powder coating,
- thin foil application,
- ion implantation,
- diffusion, e.g. boronising,
- powder blowing,
- wire feed,
- reactive gas shroud.

Laser surface alloying is capable of producing a wide variety of functional materials. The high solidification rate allows even some metastable alloys to be formed in the surface. All this can be done by a non-contact method which is relatively easy to automate. The laser offers precision in the placement of the alloying, good adhesion and vastly improved processing speeds. Numerous systems have been explored by the author of this elaboration [6, 7], e.g.:

- aluminium alloys (AlSi12) alloyed with SiC and Ni,
- steels: high speed M2, carbon Ck45, valve HNV3, constructional of grades Cr-Ni-Mo, Mn, Mn-B; alloying with carbides or borides in wide range of concentration (Fig. 16).

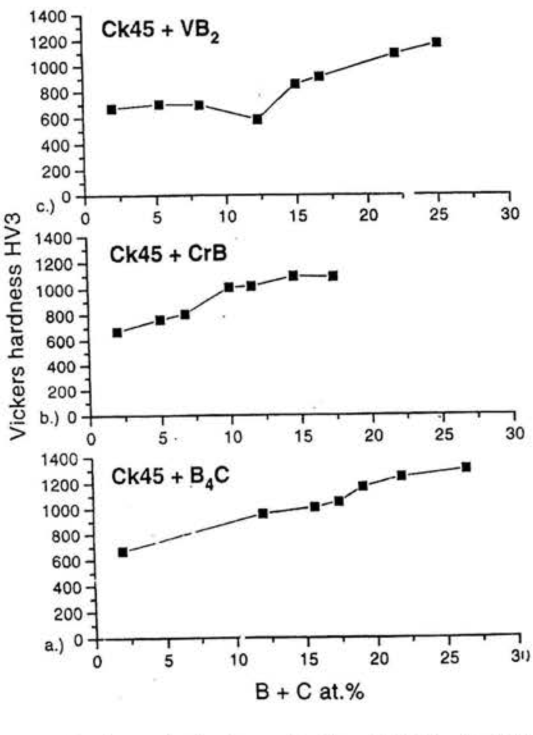

FIGURE 16. Change of hardness during laser alloying of Ck45 with VB_2, CrB and B_4C.

2.4. Residual stresses in laser treatment

Each laser process develops residual stresses in laser treated material. The measured stresses in different processes performed by the author are summarised in Table 2, and an example of residual stress distribution is shown in Fig. 17.

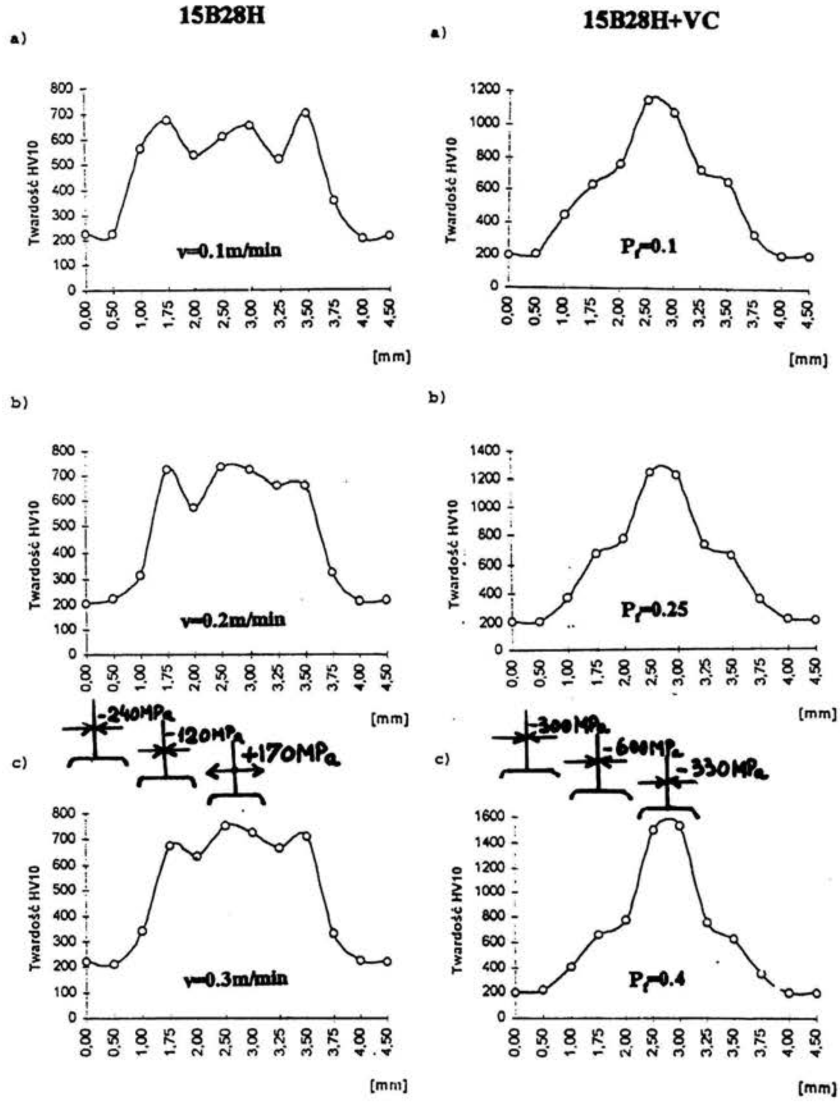

FIGURE 17. Hardness and residual stress distribution after laser remelting and laser alloying of constructional steel.

TABLE 2. Residual stresses measured in surface layers of materials subjected to laser treatment.

LASER TREATMENT – RESIDUAL STRESSES X-ray measurements	
Laser remelting (overlapping tracks)	
in Ar atmosphere; laser cw CO_2	
• valve steel (ferrite)	**−700 MPa**
• manganese steel (ferrite)	**−400 MPa**
• AlSi 12 (α-Al)	**−300 MPa**
in N_2 atmosphere; laser Nd:YAG	
• TIAl1Mn1 (TiN)	**+500 MPa** (to **+800 MPa**)
Laser alloying (individual tracks)	
in Ar atmosphere; laser cw CO_2	
• high speed steel M2 + VB_2 (V - 8.7 wt.%, B - 2 wt.%)	**−330 MPa**
• Ck 45 + CrB (Cr - 9.6 wt.%, B - 2 wt.%)	**−570 MPa**
• Ck 45 + VB_2 (V – 5.7 wt.%, B - 2.3 wt.%)	**−730 MPa**
Laser welding (overlapping tracks)	
in Ar atmosphere; laser cw CO_2	
• AlMg1Si1	**−300 MPa**

3. Pulsed laser deposition

With most deposition techniques the condensation of metallic systems from the vapor phase favours the formation of metastable phases, as long as the chosen preparation conditions lead to a kinetic suppression of the equilibrium state. It has been verified experimentally that phases far away from the equilibrium state and even amorphous ones could be formed during thin-film deposition using pulsed laser (PLD) [8-13]. In this technique, thin films are prepared by an ablation of one (or more) target(s) illuminated by a focused pulsed laser beam. The method was first used in 1965 for the preparation of semiconductors and dielectric materials. A typical set-up for the deposition of metallic alloys and multilayers is schematically shown in Figs. 1 and 18.

The deposition system consists of a target holder and a substrate holder housed in a vacuum chamber. In an UVH chamber ablated targets are struck at an angle of 45° by a pulsed and focused laser beam. The atoms and ions ablated from the target are deposited on substrates clambed on a heater with the surface parallel to the target surface with a target-to-substrate distance of typically 2-10 cm. High-power pulsed lasers with nanosecond pulses are used as an external energy source

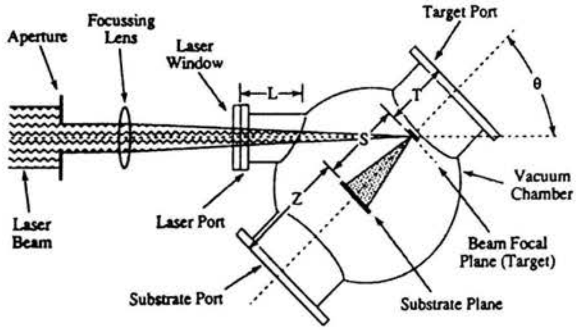

FIGURE 18. Schematic illustration of important parameters to consider when designing a PLD chamber (Keys: T = target port flange-to-beam focal plane (target) distance, Z = substrate port flange-to-substrate distance, S = target-to-substrate distance, L = laser port length, Θ = angle between target normal (plume direction) and laser beam).

to vaporize materials and to deposit thin films. In general, the useful range of laser wavelenghts for thin-film growth by PLD lies between 200 nm and 400 nm. Most materials used for deposition work exhibit strong absorption in this spectral region. Absorption coefficients tend to increase as one moves closer to the 200 nm mark. The stronger absorption at short wavelenghts also results in a decrease in ablation fluence thresholds. Most of the work accomplished to date has been focused on excimer and Nd:YAG lasers. High output energies are achieved by using two YAG rods in an oscillator/amplifier configuration. Q-switching allows this configuration to produce nanosecond pulses outputs even much higher than 2 J/pulse. At these high energies pulse repetition rates are limited to 30 Hz with pulse duration of nanoseconds. Excimer lasers emit their radiation directly in the UV. The fundamental laser emission of Nd:YAG occurs at 1064 nm, well outside the desired range indicated earlier. Using a nonlinear crystal, the 1064 nm output can be frequency doubled with about 50% power conversion efficiency yielding an output at 532 nm. In order to produce light in the UV, the 532 nm output is mixed with the residual 1064 nm light or frequency doubled again, and Q-switching allows to produce short pulses.

3.1. Laser desorption and ablation

The widely accepted term for beam-induced ejection of particles from surface is "sputtering". The term "laser-induced desorption" is defined as particle ejection without any detectable mesoscopic modification of surface composition or structure; with a particle yield that is a linear function of the density of electronic or vibrational excitation; and without any significant gas-dynamic effects in the steam of particles leaving the surface.

"Laser ablation" is a sputtering process in which material removal rates typically exceeded one-tenth monolayer per pulse; the surface is structurally or compositionally modified at mesoscopic length scales and particle yields are superlinear functions of the density of excitation.

Laser-induced desorption and laser ablation are not entirely distinct phenomena, however, laser-induced desorption initiated by low-fluence "conditioning" of surface may lead to material modifications that affect subsequent laser ablation. Moreover, laser ablation need not involve massive, catastrophic destruction of a surface; indeed, much of pulsed-laser film deposition relies on laser ablation as a reasonably well controlled and repeatable method of injection target material into the gas phase. It is, therefore, probably more correct to view desorption and ablation as two point on a continuum of phenomena seen in laser interactions with material surfaces, beginning with desorption and perhaps ending at avalanche ionisation and massive thermomechanical damage of surface as suggested by Fig. 19.

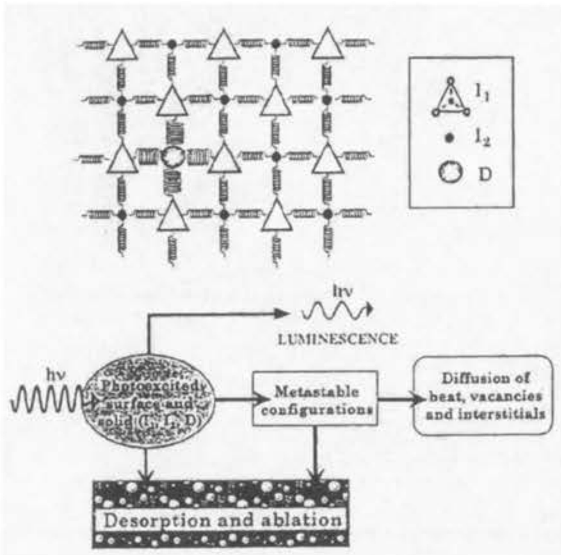

FIGURE 19. Schematic of pathways leading from photoexcitation to laser desorption and ablation. Laser light can excite intrinsic molecular (I_1), or atomic (I_2) sites or defect sites (D) by coupling to their respective electronic or vibration modes; energy is dissipated as heat to the lattice by electron-lattice (electron-phonon) coupling. The horizontal arrow represents channel loss competing with desorption or ablation.

3.2. Processes occurring during PLD

A sequence of particular processes occurs during laser ablation from the target and deposition of the ablated material on the substrate surface [10]. They are as follows:

- absorption of laser intensity,
- target heating,
- ablation of material,
- plasma formation,
- plasma expansion,

- high kinetic energy of the deposited particles,
- instantaneous deposition rate.

3.3. Characteristic properties of laser-deposited systems

They are characteristic properties, which are more or less independent of the investigated system [8-10]. Although in the case of laser deposition similar phases are formed as by conventional deposition technique, some characteristic differences occur, which are as follows:

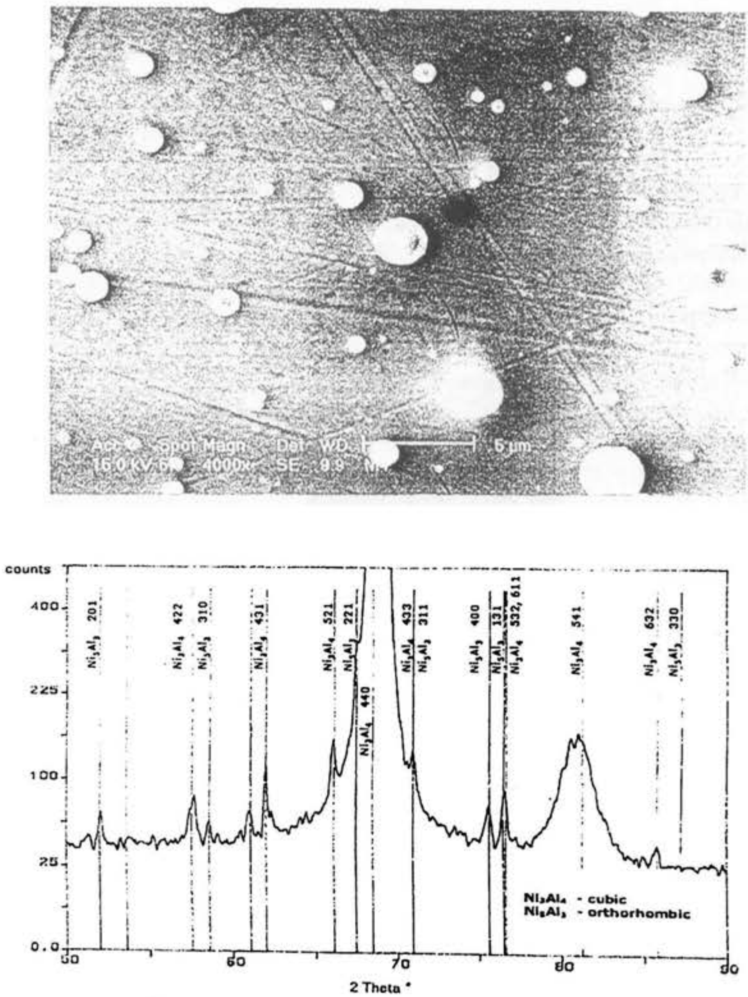

FIGURE 20. Microstructure of laser deposited layer after ablation of target Ni_3Al using KrF excimer laser (top); droplets are visible on the surface and XRD pattern (bottom) obtained from the surface revealing the Ni_3Al_4 – cubic, and Ni_5Al_3 – orthorombic phases.

- Average deposition rates; significant growth rates of order of 0.01-0.05 nm per pulse are observed above a deposition threshold of laser fluence of about 3-5J/cm^2.
- Angular distribution of the film thickness; the PLD process leads to a strong angular dependence of the film thickness; in practice, films with uniform thickness can be obtained by PLD for instance by scanning the laser beam over a large target area and by rotating the substrate during deposition.
- Stoichiometry transfer; in most cases, the stoichiometry of deposited films is close to that of the targets used. Deviation from the film stoichiometry can be explained for instance by unusually high vapor pressure of one component, different angular distribution of the elements, preferential sputtering effects, phase transformation, etc. (Fig. 20 bottom).
- Droplets on the film surface; additionally to the deposition of atoms and ions, some droplets with two characteristic sizes of < 0.5 and about 1-3 μm, respectively, are found on the film surface. The number of droplets depends on the laser fluence used, target material and surface roughness and strongly increases with the number of pulses on the same target location. In order to reduce the droplet number, the used laser fluence and the position of the substrate can be optimised, and the target surface has to be as smooth (and dense) as possible; mechanical velocity filters between the target and substrate or electrostatic deflation filter can mitigate the problem (Fig. 20 top).
- Strong adhesion exists in PLD films although the residual stress is expected in the thin layer (Fig. 21).

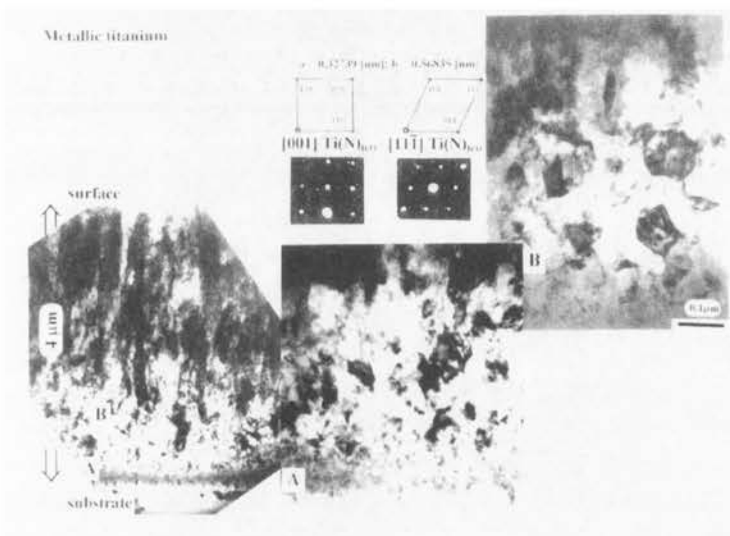

FIGURE 21. Microstructure TEM of cross-section of deposited metallic films together with electron diffraction patterns; the strongly developed interface is visible between the substrate and deposited film.

- Homogeneity of films is observed in laser deposited films of different types (Fig. 22).
- Texture is often developed in deposited layers (Fig. 23).

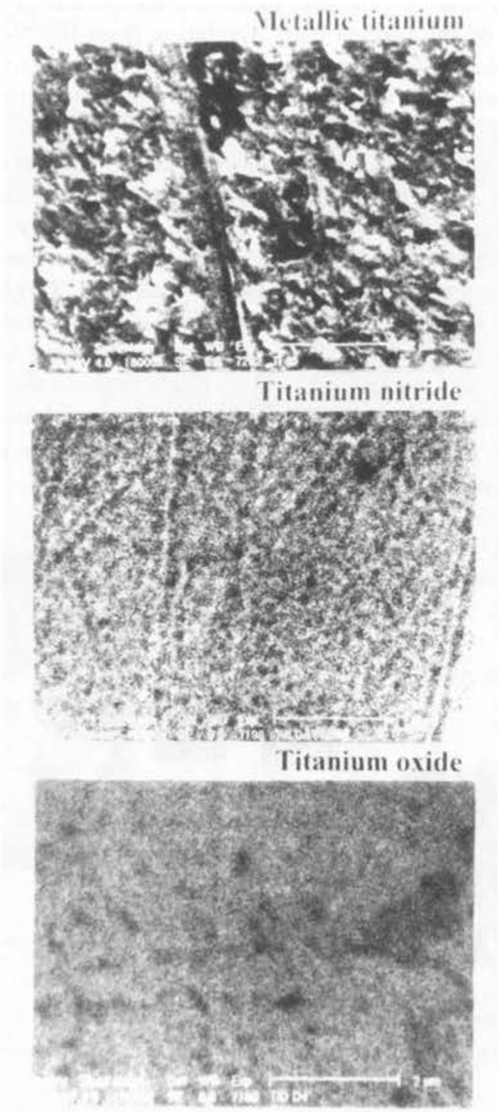

FIGURE 22. Microstructure SEM of deposited titanium based-films.

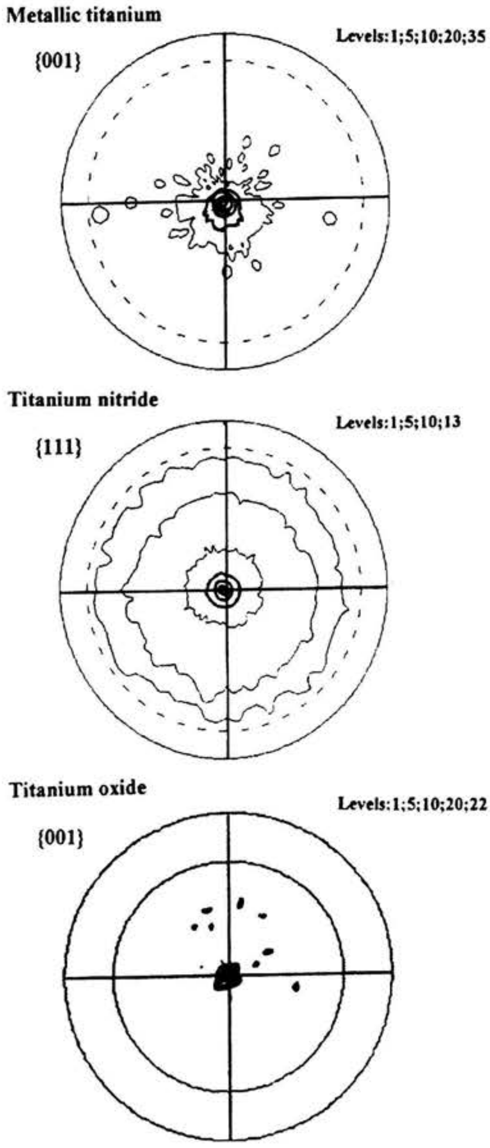

FIGURE 23. Texture measured on the surface of laser deposited titanium-based films; a strong axial texture is visible in all cases.

3.4. Applications

Interest in pulsed laser deposition (PLD), as technology producing thin layers of complex materials is growing exponentially in recent years. Condensation from the vapor phase favours formation of metastable phases, because it is often joined with a high solidification rate. Deposition of virtually any materials, from pure elements to complicated multicomponent compunds, on various substrates, make PLD very suitable technology in fabrication of thin layers. One of important advantage of the method is stoichiometry transfer from target to substrate and production of multilayered materials. It could be also possible to influence on the transferred plume producing a special environment in the reactive chamber, thus producing a layer of a requested phase. The method has been applied till now in a wide spectrum of materials, which can be grouped as follows:

- high-temperature superconducting thin films for active and passive applications (Fig. 24),
- semiconductors,
- epitaxial oxides on semiconductors,
- noncrystalline carbon films with the bonding and properties of diamond (diamond like carbon DLC),
- tribological coatings; lubricated coatings and hard coatings (Figs. 21, 25, 28),
- metallic films,
- ferroelectrics,
- magnetic materials like ferrite thin films,
- bandgap materials (Fig. 26),
- biocompatibile thin films (Figs. 23, 27),
- polymer films.

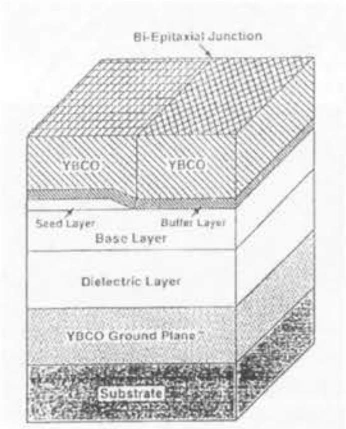

FIGURE 24. Schematic view of the biepitaxial junction structure with a seed layer and a buffer layer placed on a base layer that is grown on top of a delectric layer and a YBCO ground plane [8].

An example of microstructure variation on cross-section of pulsed laser deposited TiN thin layer from own examinations is presented in Fig. 24.

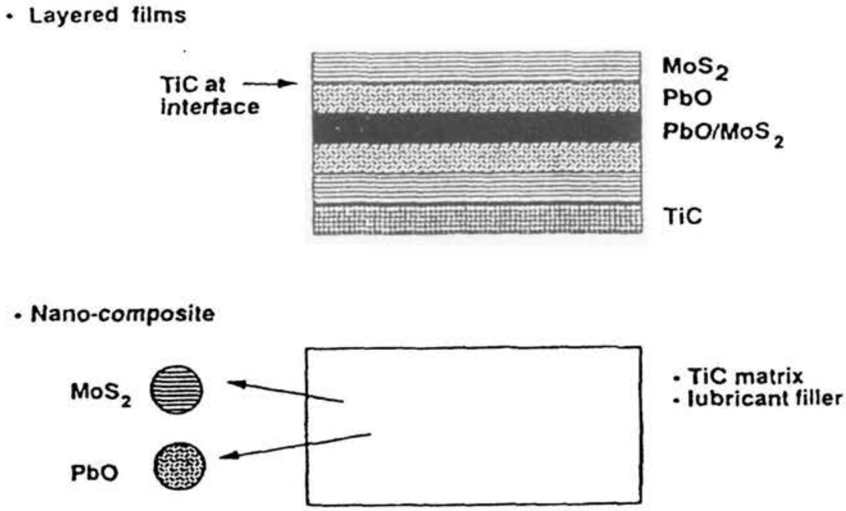

FIGURE 25. Examples of engineered coatings specifically targeted to permit extended thermal cycling of adaptive lubricant [8].

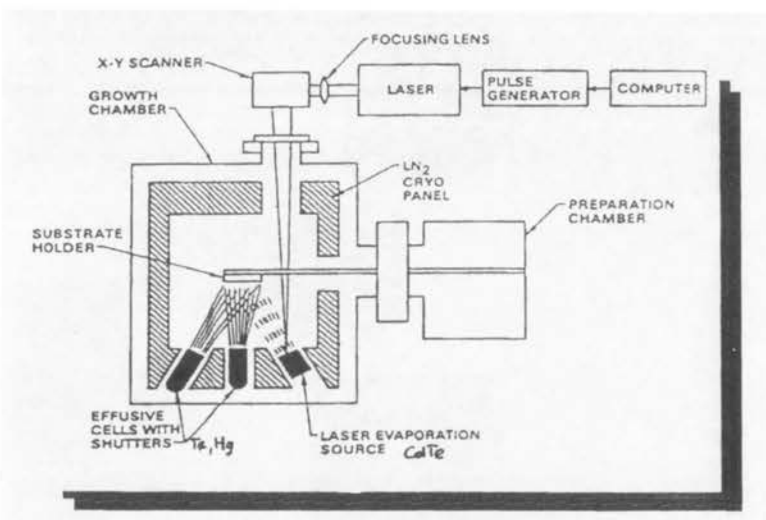

FIGURE 26. Schematic drawing of the apparatus for HgCdTe bandgap engineering.

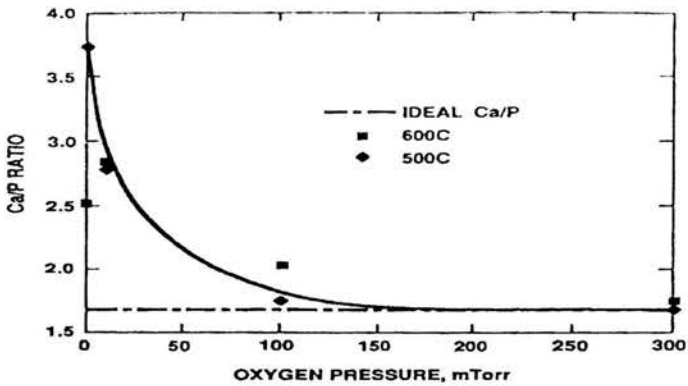

FIGURE 27. Rutherford backscattering spectroscopic data for the Ca/P ratios in films deposited by PLD from a target of hydroxylapatite using an excimer laser. The Ti-6Al-4V substrates were maintained at 500°C or 600°C, and the gas environments consisted of oxygen gas at various pressures [8].

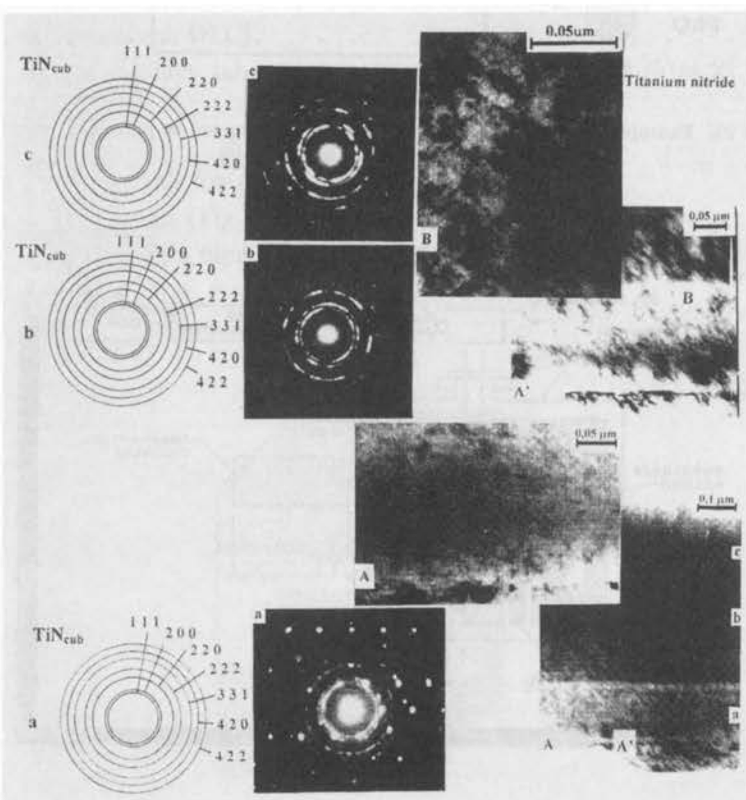

FIGURE 28. Microstructure TEM of the cross-section of titanium nitride coating produced by pulsed laser deposition using Nd:YAG laser [13].

3.5. Future directions of PLD method

In the last years a considerably effort has been devoted to developing PLD for thin films. A wide variety of materials and applications have been explored, although the main emphasis has been directed at development of a multilayered novel materials with combination of special properties. As a by-product, many difficulties have been identified and solutions found to many of them. The best results obtained up to date, however, are connected with the realisation of the power in using PLD for these materials. This technique has the ability to improve the fundamental understanding of thin film production by virtue of its ability to easily produce epitaxial films. In addition, PLD provides an opportunity to fabricate many exciting and novel devises and systems where high-quality epitaxial films are required. From this point of view the future for PLD of thin films looks auspicious.

The actual research activity in laser ablation is focused on the following topics:

- laser surface interactions,
- mechanism and diagnostics of laser desorption,
- modelling and computer simulation of laser-induced desorption and ablation,
- laser plasma and gas dynamic effects,
- matrix-assited laser desorption ionisation (MALDI),
- analytical spectrometry based on laser ablation,
- film synthesis in laser plasma by pulsed laser deposition; new and artificially-structured materials,
- cluster/nanoparticle/nanowire(tube) formation and deposition,
- nanoscience and nanotechnology using laser-solid interactions,
- electronic excitation effects and kinetic energy effects,
- laser-induced surface modification,
- laser eaching and cleaning,
- lithography and micromachining,
- biomedical ablation; mechanisms and applications (corneal, tissue, dental, ...),
- fs-laser applications,
- industrial applications.

4. Concluding remarks

A brief survey of laser technologies clearly shows and proves that it is very perspective giving researchers a new experimental tool with special properties (Tables 3 and 4).

Understanding the peculiarities of laser-surface interaction relies on a knowledge of the intrinsic properties of lasers and surfaces. The use of laser techniques to study fundamental rapid solidification, adsorption, desorption and diffusion processes on surface seems to be very practical. Since in the last two decades spectroscopy with laser light has been introduced into many laboratories, important linear and nonlinear spectroscopic methods are of research interest.

TABLE 3. Output power and power density of commercial lasers.

Source	Pulse length	Power	Power density
CO_2 laser	cont.	6 kW	10^7 W/cm^2
CO_2 laser (giant pulse)	10^{-7} s	1000 MW*)	10^{12} W/cm^2
Solid state (normal pulse)	10^{-4} s	0.1 MW*)	10^{10} W/cm^2
Solid state (giant pulse)	10^{-8} s	100 MW*)	10^{13} W/cm^2
GaAs – laser	10^{-8} s	300 W*)	10^5 W/cm^2
GaAs – laser	cont.	11 W	$2 \cdot 10^3$ W/cm^2
Soldering flame	cont.	1.6 kW	$5 \cdot 10^4$ W/cm^2
e-beam	cont.	3 kW	10^9 W/cm^2
Sun light focused by a lens ($D = 5$ cm)	cont.	2 kW	300 W/cm^2

*) peak power

TABLE 4. Types of lasers applied in materials engineering.

Laser	Emitted wavelength [nm]	Efficiency [%]
Excimer:		
F_2	157	
ArF	193	
KrF	248	0.3
XeCl	308	
XeF	351	
Nd:YAG		
(ω_0)	1064	2
($2\omega_0$)	532	0.2
($3\omega_0$)	355	0.1
N_2	337	0.1
Ar	488 and 514	0.006
CO_2	10 600	10-15
Diode	800-900	30-40

Development of ultrashort laser pulses has allowed one to observe directly the dynamic and vibronic surface excitation and relaxation processes. Materials treatment, beginning with fundamental changes of the plain surface induced by laser radiation, namely heating, melting and plasma generation are studied due to possible technical application. Moreover, structuring of the surface in terms of controlled crystallisation processes, ablation of surface materials, generation of periodic structure and generation of thin films is of great perspective technical interest.

Many of the basic mechanisms studied in solid state are used in laser medical applications. Here, the laser light sources are applied to heat treatment of organic tissues (photocoagulation), a major and very perspective is the use of laser in such branches of medicine like: cardiology, dentistry, dermatology, gastroenterology, gynecology, neurosurgery, ophthalmology, orthopedics and urology.

Obviously, a rapid expanding, innovative and important field such as the interaction of photons with surface of inorganic solid state and organic tissues is extensively studied in many laser laboratories due to the fact that laser-surface interaction mechanism and processes are a fascinating research field with perspective in the near future. Details of some achievements can be already found in the literature, cf. [3, 4, 8, 9].

References

1. T. Burakowski and T. Wierzchoń, *Surface Engineering of Metals - Principles, Equipment, Technology*, CRC Press, Boca Raton - London - New York - Washington D.C. 1999.
2. D.S. Rickerby and A. Matthews [eds.], *Advanced Surface Coatings: a Handbook of Surface Engineering*, Chapman and all, New York 1991.
3. W.M. Steen *Laser Material Processing*, Springer-Verlag, 1992.
4. H.-G. Rubahn, *Laser Applications in Surface Science and Technology*, John Wiley, Chichester 1999.
5. J. Kusiński, *Lasery i ich zastosowanie w inżynierii materiałowej* [in Polish], Wydawnictwo Naukowe "Akapit", Kraków 2000.
6. B. Major and R. Ebner, Konstytuowanie warstwy wierzchniej tworzyw metalowych na drodze obróbki laserowej [in Polish], *Inżynieria Powierzchni*, Vol.53, No.1, 1996.
7. B. Major and R. Ebner, Laser applications in surface modification and pulsed laser deposition, *Journal of Technical Physics*, Special Supplement Vol.XL, No.3, Warszawa 1999.
8. D.B. Chrisey and G.K Hubler [eds.], *Pulsed Laser Deposition of Thin Films*, Published in the USA by John Wiley and Sons, 1994.
9. J.C. Miller and R.F. Haglund Jr. [eds.], *Laser Ablation and Desorption*, Vol.30, Academic Press, San Diego 1998.
10. H.-U. Krebs, *International Journal of Non-Equilibrium Processing*, Vol.10, No.3, 1997.
11. W. Kurz and R. Trivedi, Rapid solidification processing and microstructure formation, *Mat.Sci.Eng.*, A179/A180, Vol.46, 1994.
12. B. Major, T. Wierchoń, R. Ebner, A. Klimpel, A. Maranda-Niedbała, E. Branstätter, G. Krużel and R. Gruca, Structure and properties of titanium based layers produced using advaned methods, *XVIth International Physical Metallurgy and Materials Science Conference on Advanced Materials and Technology ATM 2001*, Gdańsk 2001, [in:] *Inżynieria Materiałowa* [in press].

13. B. MAJOR, R. EBNER, R.P. ZIĘBA and W. WOŁCZYŃSKI, Titanium-based films deposited using a Nd:YAG pulsed laser, *Appl.Phys.*, Vol.A69, No.1-3, 1999.