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Formation of Ceramics Coating by Laser Processes

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Abstract
        Ceramics have found increasing applications due to their
wear and corrosion resistance, high temperature strength etc...
and more recently superconducting ceramics were also discovered.
The different laser.processes able to produce the formation of
ceramics as a coating or film will be discussed according to the
different applications. These different laser processes are
divided in solid phase (powder deposition), liquid phase and
vapor phase (gas alloying, LCVD and LPVD) processes.
KEY WORDS: (Ceramics)(Laser Processes)(CVD)(PVD) (Gas Alloying)
           (Powder)

1. Introduction

    There has been widespread interest in use of the laser for the ceramics
coating to improve the wear, corrosion and thermal resistance of metals. Since the
discovery of superconducting ceramics, several groups have also succeeded in
producing high Tc(85K) thin film superconductors via laser vapor deposition. The
available laser processes able to produce a ceramic coating will be reviewed and
discussed according to the different applications. In this paper, the laser
processes are classified in solid phase (powder predeposition and powder injection
method), liquid phase, and vapor phase (laser gas alloying, laser physical vapor
deposition i.e. LPVD, laser chemical vapor deposition i.e. LCVD) processes.

2. Solid phase processes

2.1 Principle and general characteristics

    Solid phase processes may be classified as powder predeposition and powder
injection (ref. 1). The historical and technical review of C.W. Draper and J.M.
Poate (ref.1) indicates that the earliest attempt at the surface alloying of
powders with substrates dates back to 1964. In the case of powder deposition
process (Fig.1), powder is put down on the substrate in a separate step before
the laser treatment in an inert or reactive gas stream (ref.2,3,4,5). By the
powder injection process (Fig.2), powder grains carried by an inert gas stream
are injected into the melt pool formed by a high energy laser beam at the time of
laser treatment (ref.4,6). These two processes are characterized by the fusion of
the substrate and a partial or complete fusion of powder grains, and then surfaces
may be either "in situ" composites (ref.1-6) or applied coatings without substrate
dilution (ref.7), leading to strong metallurgical bondings.
    The applications of these processes are mainly the wear resistance improvment

of metal substrates such as titanium (ref.2,5) and its alloys (ref.4,5,6), aluminium (ref.3), inconel (ref.6) etc... Powders composition may be, for example, carbon (ref.2,4,5), TiC (ref.2,4,6), WC (ref.2,6), SiC (ref.2,3), Ti, Al, Cr (ref.3) and borides powders such as B, TiB_2 and WB (ref.2), etc... Laser sources were 2kW-15kW cw CO_2 lasers (ref.3-6) and pulsed YAG laser (ref.2), and laser irradiations were performed in neutral atmospheres (ref.2,4,5,6) or reactive atmospheres such as N_2 (ref.2,3) or O_2 (ref.3). Some experimental conditions are summarized in Table 1.

2.2 Fusion zone geometry

Area coverage is produced by overlapping melt trails of CW-CO_2 laser (ref.3-6) or by overlapping YAG laser pulses spots (ref.2). For both deposition and injection processes, the laser melted pool width was generally in the range 1.5-3mm and the laser melted pool depth in the range 0.02-0.80 mm, either with pulsed YAG and cwCO_2 laser irradiations. However, melt pool depth of several millimeters may be reached by overlapping of several laser passes (ref.5). From published results which are summarized in Table 2, the fusion zone geometry was rather correlated to the substrate and powder compositions (absorbtivity at the laser wavelength and thermal conductivity), to the powder thickness and to the laser power density than the type of process itself (powder predeposition or injection, pulsed or cw laser). As a matter of fact, a flat surface was obtained after irradiation with a pulsed laser (ref.2) and a rather rough surface was formed with a continuous wave laser (ref.3-6).

2.3 Fusion zones microstucture, composition and hardness

Fusion zones microstructure, composition and hardness are summarized in Table 3, according to the different experimental conditions (ref.2-6). When C powder is deposited on Ti or Ti alloys and then irradiated with a YAG or CO_2 laser, a dispersion of TiC particles is formed in the melt pool, whose hardness is about 300-400kg/mm^2 (ref.2,5). However, when the number of laser passes are increased or at higher laser power density, TiC dendrites are grown and the fusion zone hardness is increased to about 400-700kg/mm^2 (ref.4,5). (Note: Ti and Ti6Al4V hardnesses are respectively about 250 and 350 kg/mm^2)

By the TiC predeposition and injection processes, either with a pulsed YAG and cwCO_2 laser irradiation of Ti and Ti6Al4V, TiC dendrites are formed (ref.2,4,6) and some carbides inclusions are also observed in the case of large powder grains size (40-200μm) due to the incomplete fusion of initial powder(ref.4,6). The hardness of the dendritic zone is about 350-700 kg/mm^2, and the carbides inclusion hardness is about 3000kg/mm^2. Laser irradiation in N_2 instead of Ar or He leads to the formation of TiC and TiN dendrites and the surface hardness increases to 700-1400kg/mm^2 (ref.2).

By the WC predeposition and injection processes, with a pulsed YAG and cwCO_2 laser irradiation of Ti, Ti6Al4V and inconel, carbides dendrites and inclusions are observed. In case of ref.2, WC powder sizes were about 0.8μm and inclusions sizes may reach values as high as 50μm, EDX analysis showed that the inclusions were considerably enriched in tungsten by comparison to dendritic zone, however inclusions hardness (600 kg/mm^2) was close to dendrites ones (400-600kg/mm^2). In case of ref.6, inclusions sizes are about the same than initial powder (75-150μm) and corresponds to non melted powder grains; as a result, dendrites zones and inclusions hardnesses were 400-500 and 1300-2000 kg/mm^2 respectively (no analysis results).

By the SiC predeposition process of Ti, with a pulsed YAG laser, a dendritic microstructure is obtained without inclusions, although SiC powder size was 85μm, and surface hardnesses were 900-1400 and 1100-2100 kg/mm^2, when irradiation took place in Ar and N_2 atmosphere respectively (ref.2). When SiC is deposited on Al and irradiated with a CO_2 laser, the fusion zone hardness is about 400 kg/mm^2 (Note: Al hardness is 30 kg/mm^2), and no information were given on the microstruc-

ture (ref.4). When the substrate is Ti, the main phases in the laser fusion zone were SiC and TiC, and in the case of Al substrate, SiC and Al_4C_3 were mainly formed.

The predeposition of boron and borides powder led to high hardness values due to the formation of borides dendrites and inclusions in the laser fusion zone (ref.2). The laser fusion zone hardness was correlated to the dendrites density, as shown in Fig.3; the higher the dendrites density, the higher the hardness, due to the relatively large surface of the Vickers diamond compared with the dendrites size. Fig.4 shows the influence of N_2 and Ar atmosphere on the surface hardness for different powder compositions, and then the irradiation in N_2 instead of Ar increases the surface hardness of about 500 kg/mm^2. A considerably increase of Al hardness ($2300kg/mm^2$) was obtained by the predeposition of Cr and $cwCO_2$ laser irradiation in O_2 atmosphere due to the formation of Cr_2O_3 on the Al surface.

2.4 Wear resistance

Each authors having his own way to measure the wear resistance of the coating, it is then difficult to compare the different results. Several Al alloys (2024Al, 6061Al and 5052Al)were injected with TiC, and the wear resistance was 7 to 40 times higher than the base alloy, depending on the alloy composition and TiC concentration (ref.6). By the powder predeposition on Al, the wear resistance was more than 1000 times higher than the base metal (ref.3). In the case of Ti6Al4V injected with TiC or WC, the wear resistance was 2.5 to 14 times higher than the non treated alloy (ref.4,6). However, the impact wear resistance was very low, about 100 times lower than WC-Co material, due to the fact that the injected surfaces consisted of 40-50 % of the base metal (ref.6). In fact, the highest wear resistance is obtained when no dilution occurs in the substrate, no matter about the powder deposition process.

3. Liquid phase process

By the liquid phase process (Fig.5), the substrate is laser irradiated after introduction in an appropriate liquid, such as water, liquid N_2, NH_3 or O_2, organometallic solution, toluene etc... (ref.8). Few results using this method were published such as metal deposition (ref.9), oxydation and nitridation of titanium (ref.10) and oxydation of tantalum (ref.11). Applications are mainly electronics and optics.

Only chemical analysis and geometrical results were published without information on mechanical, electronical or optical properties. Lasers were Nd-glass, Q-switch Nd/YAG, pulsed ruby and excimer lasers, and the film thicknesses were in the range of 0.2-0.5 µm (ref.8-11). Some experimental conditions and results are summarized in Table 4.

4. Laser gas alloying

4.1 Principle and experimental conditions

By this process, the substrate is laser irradiated in an appropriate gas atmosphere (oxydizing, neutral or reducing atmosphere). If the surface is not melted, there is very little alloying as the rate of diffusion in the solid is low. If melting takes place, alloying over considerable depth becomes possible.

Numerous research proups have been studied the laser gas alloying of Ti and its alloys in different atmospheres (N_2, O_2, CH_4 and a mixture of these different gases) in order to improve the wear resistance of these metals (ref.5, 12-16). The lasers used were pulsed YAG laser (ref. 12,15), pulsed CO_2 laser (ref.13,14), $cwCO_2$ laser (ref.5,12-14,16). Experimental conditions are summarized in Table 5.

4.2 Results and discussion

The geometry, composition, microstucture and microhardness of the laser

treated zone of Ti and its alloys are given in Table 6, for different experimental conditions. The alloyed zone depth varied in the range 0.1-1.2 mm, depending on the laser power and the number of overlapping passes, and the melt pool width was in the range 0.75-2.5 mm. When a $cwCO_2$ laser was used instead of a pulsed YAG laser, the hardened zone thickness was increased from 0.15-0.25 mm to 0.1-1.5mm. For the same average power, a $cwCO_2$ led to thicker hardened zone than a 4kW pulsed CO_2 laser (ref.13). With increasing thickness, the influence of thermal stresses is more critical and the tendency for crack formation increases.

Laser irradiation in N_2 atmosphere leads to the formation of a very hard TiN dendritic zone in the vicinity of the surface, and the surface microhardness of all the titanium alloys studied is generally in the range 700-1300 Kg/mm^2 either with pulsed YAG, pulsed and $cwCO_2$ lasers (ref.12,15). Differences were mainly observed in the surface roughness which is strongly decreased from about 10μm to 1-3μm by using a pulsed laser instead of a continuous one(ref.12-14).

CO_2 and YAG laser irradiation in methan atmosphere of Ti and its alloys led to the precipitation of TiC particles, and the hardness of this particles zone was only about 500 kg/mm^2 (ref.14,15). By increasing the number of overlapping passes, the fusion zone hardness was increased to 800-1200 kg/mm^2 corresponding to the growth of TiC dendrites (ref.14). The surface hardness is also increased by addition of N_2 to methan (Fig.6) corresponding also to the formation of a dendritic microstructure (ref.15).

Laser irradiation in pure O_2 atmosphere seems to be not efficient on the surface hardness of Ti alloys, but causes the largest reduction in fatigue limit (ref.14).

Surface gas alloying with TiN or TiC does not only increase the wear and erosion resistance but also the corrosion resistance of Ti alloys (ref.14). However, the ductility is markedly reduced (ref.14,16). Although the stress-strain curve of Ti6Al4V is not changed after laser melting in N_2, strength was reduced by 5% and elongation to fracture by up to 50% (ref.16). Laser alloying with nitrogen leads also to a sharp reduction in fatigue life (ref.14,16).

5. Laser PVD

5.1 Principle and characteristics

By the Laser Physical Vapor Deposition (LPVD) process (Fig.7), the laser beam is focused on a ceramic target, which is preheated up to a few hundreds degrees Celsius by an electric heater to avoid thermal fractures. The evaporated ceramic molecules are deposited on a substrate, set at a distance of 20-80mm from the target surface. The substrate is generally preheated up to a few hundred degrees by an other electric heater to obtain a strong adhesion of the evaporated ceramic film on the substrate. Laser evaporation of materials in order to deposit thin films has been studied about 25 years ago with thickness of about 0.01-0.3 μm (ref.17).

5.2 Wear resistance applications

Results concerning the LPVD of thin ceramics films, such as Si_3N_4, Al_2O_3 and $LaAlO_3$ were already published in 1968 (ref.18). Since the development of high power lasers, higher ceramics film thickness (10 times) and higher deposition rate (1000 times) have been achieved (ref.19-20). The laser used is generally a CO_2 laser, and some examples of experimental conditions are given in Table 7. A few hundred watts power is sufficient to evaporate the ceramics target (Al_2O_3, mullite, Si_3N_4, SiAlON, BN etc...) by absorption of the laser beam and deposit on the metallic substrate (Mo,Al etc...) a thin film (<10μm) whose composition is close to the target composition. The roughness of this film (ref.20) is very low (0.5μm) compared to surface alloying methods (powder deposition or gas alloying processes). Depending on the experimental conditions, such as the substrate-target distance, the laser power and the targets composition, hardness values in the

$1100-4500 kg/mm^2$ range may be obtained with a deposition rate of 0.1 to 1.5 $\mu m/min$ (ref.19-20). Experimental results are summarized in Table 8.

5.3 Superconducting applications

Recently, several groups have succeeded in producing high Tc (85 K-95 K) thin-film superconductors from Y-Ba-Cu-O bulk superconductors (Tc = 90-100 K) on different substrates via a LPVD process. Using pulsed laser beams at high power density ($70-100 MW/cm^2$), such as Nd:YAG (ref.21), KrF excimer (ref.22), Q-Switch YAG (ref.23) or XeCl excimer lasers (ref.24), large amounts of materials can be transferred from target to substrate without decomposition so that the stoichiometry of the target can be preserved in the deposited film. Nd:YAG laser ablation of Y-Ba-Cu-O type materials may be advantageous because low energy infrared photons are less likely to initiate photochemistry (leading to damage) or fluorescence in the system's optical window. In this case, high-quality stoichiometric film formation was easier because direct bond breaking by higher photon energy did not occur (ref.21,23). However, redistribution of different constituents occurs during subsequent annealing treatments that are needed to recover the superconducting properties. Subsequent annealing treatments in O_2 atmosphere and cooling speed need to be carefully optimized to achieve the desired superconductivity properties of thin films (ref.24). Experimental conditions are summarized in Table 9 and results in Table 10.

Ceramics of composition close to $YBa_2Cu_3O_7$ were deposited at a speed of 0.06 to 0.6 $\mu m/min$. The ceramics film thicknesses obtained with an excimer laser and a YAG laser are respectively in the range 0.05-0.5 μm and 4-5μm. Low surface roughness (0.05 μm) may be obtained (ref.22). The onset of superconductivity was generally about 90-98 K and the offset (for the best results) about 75-90 K (Table 10).

6. Laser CVD

The term laser chemical vapor deposition (LCVD) describes a wide variety of processes in which material is deposited from the gas phase under the influence of laser irradiation. This process has been widely used for semiconductors applications (ref.25). For the last ten years, research results concerning the LCVD of ceramics such as TiC, TiO_2, $TiSi_2$, SiC, Si_3N_4, BN etc... has been published and the types of laser used were generally excimer, Ar^+, YAG, CO_2 lasers. Ceramics can be deposited from a variety of source gases using either photolytic or pyrolytic excitation of the reactant species.

In pyrolytic deposition (Fig.8), the laser is used to heat the substrate in order to thermally drive the reaction. The heating results from a number of processes such as energy transfer from hot electrons, non radiative recombination and vibrational lattice excitation. The reactant gases must be transparent to the laser wavelength, and the substrate must be absorbing.

In the photolytic deposition process (Fig.9), the laser beam is absorbed by gaseous species in a single or multiphoton process. Single ultraviolet photon (from an excimer or Ar^+ laser for example) can dissociate individual molecule due to its high energy (4 to 7 eV per photon), by exciting electronic transitions (electronic photochemistry). With many lower energy photons (from a CO_2 laser for example), dissociation occurs via a multiphoton absorption (vibrational photochemistry).

6.1 Pyrolytic LCVD

Since the first results concerning the pyrolytic LCVD of graphite from a hydrocarbon vapor reported in 1972 (ref.26) and the deposition of SiC on Al in 1973 by the Philips Research Laboratories at Aachen (ref.27), several groups have been studied the deposition of ceramics by thermal decomposition using a laser heat source.

The thermal process of LCVD is not different from conventional CVD, apart

several advantages characteristic of lasers processes, such as spatial resolution and control, limited distortion of the substrate, etc...The influence of mass transfer and kinetic effects on the shape of the deposit obtained by pyrolitic LCVD have been modeled by several authors (ref.28). The lasers used are generally few 10 W CO_2 lasers, YAG and Ar^+ lasers, and LCVD reactions have been conducted either at atmospheric pressure or low pressure (5-100torr). The pressure in the CVD reactor influences first the concentration of reactants in the gas phase and second the diffusivity of reactants toward the substrate and reaction products away (ref.29).

Deposition rates as high as several 100μm/s were reached in the CO_2 laser CVD of TiC and SiC from thermal decomposition of CH_3SiHCl_2 and $TiCl_4$ with CH_4 respectively (ref.30,31), and several 10μm/s were obtained with the YAG laser CVD (power density: 150-350 W/mm^2, energy density: 0.2-1J/mm^2) of borides from BCl_3 and CH_4 (ref.32) with hardnesses as high as 2000kg/mm^2 (ref.29-31). In refs.30 and 31, the thickness of ceramics coating was lower than 40μm and in ref.32, it was lower than 25 μm. Thicknesses and deposition rates are closely correlated to the experimental conditions, such as the laser power density, irradiation time , gas partial pressure and flow rate etc...The Arrhenius plot of the deposition rate as a function of reciprocal temperature is similar to that of conventional CVD (Fig.10). At low temperature, the deposition rate is limited by the chemical reaction rate and at high temperature, it is limited by diffusion process. In the LCVD of borides, the activation energy of the deposition rate was about 0.8 eV (ref.32).

Surface morphology is similar to that of conventional thermal CVD, i.e. a nodular aspect (ref.31-33). However, nodules size are about 10 times smaller in the LCVD process than in the conventional CVD and strongly increased with the temperature (ref.31-33). Nodules size lower than 0.5 μm may be obtained in the LCVD process.

The potential applications of the LCVD processes of ceramics are mainly the wear resistance (ref.30,32), electronics such as low resistivity materials (20 microOhm.cm) (ref.33) and optics such as the fabrication of microlens (ref.34).

6.2 Photolytic LCVD

The photolytic LCVD processes has been widely used for electronic applications, such as Cr, W and Mo deposition from generally metal carbonyles, fluorides or chlorides... and the deposition of Si and Ge from hydrides or chlorides by using either excimer, Ar^+, Cu vapor or CO_2 laser; few papers are concerning with the photodeposition of ceramics (ref.35).

In case of the LCVD of $TiSi_2$, West and all (ref.36) have compared the photolytic and pyrolytic LCVD process, by using respectively an excimer and a CO_2 laser. Different chemistries are produced by the two methods. Reaction products observed in the CO_2 laser pyrolysis of $TiCl_4$ and SiH_4 mixtures are those predicted by thermodynamic considerations whereas the excimer laser-induced chemical vapor deposition proceeds through the photolytic decomposition of $TiCl_4$. Films with smooth morphology are produced with both methods for the same substrate temperature range (400-450C). Crystalline sizes in the CO_2 laser deposited films are about 1/10 the size of those produced by excimer laser induced deposition. However, both films have the same low resistivity (20 microOhm.cm).

Boron nitride (BN) were deposited by ArF excimer laser irradiation (5-25mJ/cm^2) in a B_2H_6+NH_3 gas mixture at substrate temperature between 300-400C (ref.37). Compare to conventional thermal CVD, the deposition rate was very slow, i.e. in the 0.01-1 nm/min range. However, typical laser photodeposition rates are 1-5 μm/s (ref.35), values which are much lower than pyrolytic LCVD (a few 100 μm/s). The activation energies of the deposition rate for thermal conventional CVD and photolytic LCVD of BN were respectively 1.9 and 2.5 eV (ref.37). However, the stoichiometric ratio was considerably improved by photolytic LCVD.

Several authors (ref.38) have also developped kinetic theory of laser photo-

chemical deposition to calculate the deposition rate and the profile of deposited material.

By opposition to pyrolytic LCVD where reaction only takes place locally in the irradiated zone of the substrate, in photolytic LCVD, reaction occurs everywhere in the CVD reactor and deposition occurs also on the window through which the laser beam passes. In order to avoid the deposition on this window, an argon flow is oriented on the window surface in the case of photolytic LCVD.

7. Conclusion

Different laser processes allowing the deposition of ceramics were described. For wear applications, powder deposition methods, pyrolytic LCVD and LPVD seem to be more appropriate. By powder deposition methods, very thick (several mm), hard ($>2000kg/mm^2$), wear and erosion resistant coating may be produced on sample of complicated shape (such as turbine blades etc...) with a rather high speed. By pyrolytic LCVD, thinner coating ($<50\mu m$) are obtained at a speed of about 10-100 $\mu m/s$, with a better surface roughness, but this process is more difficult to control due to the numerous experimental parameters. However, this method is already in production for electronic applications (deposition of metals for mask repairing) and is also used for optical applications. At present, the LPVD rate is still lower than pyrolytic-LCVD and the coating thickness is also smaller. The LPVD process allow the deposition of all types of ceramics, while LCVD process is only possible for materials having gas or high pressure liquid reactant sources. LPVD is not only appropriate for wear resistance but also for electronic applications, and specially for the production of superconductors films. Photolytic LCVD is mainly used in electronic applications due to the lower deposition rate and the thinner thickness of the coating.

References

1. C.W. DRAPER and J.M.POATE, "Laser Surface Alloying", International Metal Reviews, 30(1985)85-108.
2. M. WEHR, S. KATAYAMA and A. MATSUNAWA, "Ceramic Coating of Titanium by Pulsed YAG laser", Transaction of JWRI, 16 (1987)43-49.
   M. WEHR, S. KATAYAMA and A. MATSUNAWA, "Ceramics Coating of Titanium by pulsed YAG Laser", Preprints of the National Meeting of J.W.S., 40 (1987)82-83 (in japanese).
3. N. YASUNAGA, A. OBARA, S. MINETA and M. IKEDA, "Ceramic Layer Formation on Al Surface by Gas Reaction Assisted CO2 Laser Treatment", Bull. Japan Soc. of Prec. Engg., 20 (1986)55-56.
4. M. COLLIN and G. COQUERELLE, " Laser Nitriding and Carburizing of Ti-6Al-4V Titanium Alloy", The Laser vs the Electronbeam in Welding, Cutting and Surface Treatment, Ed. R. Bakish, Englewood, N.J. 07631 U.S.A.,p215-230.
5. A. WALKER, J. FOLKES, W.M. STEEN and D.R.F. WEST, "Laser surface alloying of Titanium Substrates with Carbon and Nitrogen", Surface Engineering, 1 (1985)23-29.
6. K.P. COOPER and J.D. AYERS, "Laser Melt-particle Injection Processing", Surface Engineering, 1 (1985)263-272.
7. J. COM-NOUGUE, E. KERRAND and J. HERNANDEZ, "Chromium Steel Laser Coating With Cobalt Base Alloy", Proc. Laser Advanced Materials Processing (LAMP'87), p389-394.
8. P.R. STRUTT, "Environment Effects in the Interaction of Laser and Electron Beams with Materials", Proceedings of the Conference "The Laser vs the Electron Beam in Welding, Cutting and Surface Treatment", Ed. R.Bakish, P.O. Box 148, Englewood, N.J. 07631 U.S.A., p334-346.
9. H. YOKOYAMA, S. KISHIDA and K. WASHIO, "Laser induced Metal Deposition from Organometallic Solution", Appl. Phys. Lett., 44 (1984) 755-757.

10. S.B. OGALE, A.POLMAN, F.O.P. QUENTIN, S. ROORDA and F.W. SARIS, "Pulsed Laser Oxydation and Nitridation of Metal Surfaces immersed in Liquid Media", Appl. Phys. Lett., 50 (1987)138-140.

11. S.V. GHAISAS, A.P. MALSHE, P.P. PATIL, S.M. KANTKAR and S.B. OGALE, "Pulsed Ruby Laser-induced Aqueous Oxydation ofTantalum: X-ray Diffraction and X-ray Photoelectron Spectroscopic Study", J. Appl. Phys., 62 (1987)2799-2802.

12. S. KATAYAMA, A. MATSUNAWA, A. MORITOMO, S. ISHIMOTO and Y. ARATA, "Laser Nitriding of Titanium and its Alloys", 3nd CISFEL, LYON, FRANCE, 1983,p219-226.
    "Surface Hardening of Titanium by Laser Nitriding", ICALEO '83, L.I.A., Vol.38, (1983)127-134.

13. H.W. BERGMANN, S. LEE and T.BELL, "Properties of Laser Gas alloyed Titanium", Proceedings of the 3rd International Conference on Lasers in Manufacturing, Ed. A. Quenzer, 3-5 June 1986, Paris, France, p221-232.

14. B.L. MORDIKE, "Laser Gas Alloying", Laser Surface Treatment of Metals, Ed. C. Draper and P. Mazzoldi, NATO ASI Series, E, No115, 1986, p389-412.

15. M. WEHR and A. MATSUNAWA, "Ceramics Coating of Ti by YAG Laser enhanced CVD and Laser Gas Alloying", Preprints of the National Meeting of Japanese Welding Society, 42 (1987)144-145.

16. T. BELL, H.W. BERGMANN, J. LANAGAN, P.H. MORTON and A.M. STAINES, "Surface Engineering of Titanium with Nitrogen", Surface Engineering, 2(1986)133-143.

17. H.M. SMITH and A.F. TURNER, "Vacuum deposited Thin Films using a Rubis Laser", Appl.Opt., 4 (1965)147.

18. G. GROH, "Vacuum Deposition of thin Films by Means of a CO_2 laser", J.Appl. Phys., 39 (1968) 5804-5805.

19. M. IKEDA, S. MINETA, N. YASUNAGA and S. FUJINO, "Ceramic Coating with high Power CO_2 Laser", L.I.A.Vol38 ICALEO (1983) 135-140.

20. T. MORITA, O. HAMADA, S. HIRAMOTO, M. OHMINE and T. OKUDA, "Ceramic Vapor Deposition on Aluminium Alloy with CO_2 laser", Proceedings of LAMP'87, Osaka (May,1987)497-502.

21. L. LYNDS, B.R. WEINBERGER, G.G. PETERSON and H.A. KRASINSKI, "Superconducting Thin Films of Y-Ba-Cu-O produced by Neodymium : Yttrium Aluminium Garnet Laser Ablation", Appl. Phys. Lett., 52(4) (1988)320-322.

22. D. DIJKKAMP, T. VENKATESAN, X.D. WU and all, "Preparation of Y-Ba-Cu Oxide Superconductor thin Films using pulsed Laser Evaporation from high Tc Bulk Material", Appl. Phys. Lett.,51(8) (1987) 619-621.

23. S. KOMURO, Y. AOYAGI, T. MORIKAWA and S. NAMBA, "Preparation of high-Tc Superconducting Films by Q-Switched YAG Laser Sputtering", Japanese Journal of Applied Physics, 27(1) (1988)134-136.

24. J. NARAYAN, N. BIUNNO, R. SINGH, O.W. HOLLAND and O. AUCIELLO, "Formation of thin Superconducting Films by the Laser Processing Method", Appl. Phys. Lett., 51 (22) (1987)1845-1847.

25. R. SOLANKI, C. MOORE and G. COLLINS, "Laser induced Chemical Vapor Deposition", Solid State Technology, June (1985), p.220.

26. H. LYDTIN, Proc. of the Third International Conference on Chemical Vapor Deposition, Ed. F.A. GLASKI, (1972), p.121.

27. "Depositing Materials by Laser aided Technique", Metals and Materials, April 1973,p159160.

28. D.C. SKOUBY and K.F. JENSEN, "Modeling of Pyrolytic Laserassisted Chemical Vapor Deposition: Mass Transfer and Kinetic Effects influencing the Shape of the Deposit", J. Appl. Phys., 63(1) (1988)198206.

29. J. BLOCHER, M. BROWNING and D. BARRET, "Chemical Vapor Deposition of Ceramic Materials", Mater. Sci. Res., Emergent Process Methods HighTechnol. Ceram.,17(1984) 299.

30. J. MAZUMDER and S.D. ALLEN, "Laser Chemical Vapor Deposition of Titanium Carbide", SPIE Vol.198, Laser Applications in Materials Processing (1979)7380.
    S.D. ALLEN, "Laser Chemical Vapor Deposition Applications in Materials Proces-

sing", ibid., p4956.

31. S.D. ALLEN, S.M. COPLEY, R.H. EDWARDS and F. SHAAPUR, "Deposition, Microstructure and Properties of Laser CVD SiC films", Technical Progress Report (June84june85), DOE GRANT No ER/45093Tl, Dec85 014680.

32. M. WEHR and A. MATSUNAWA, "Laser induced Chemical Vapor Deposition of Ceramics", 4th International Colloquium on Welding and Melting by Electrons and Laser Beam, France, Cannes, 1988, September 26-30.

33. G. A. WEST, A. GUPTA and K.W. BEESON, "CO_2 Laser-induced Chemical Vapor Deposition of Titanium Silicide Films", Appl. Phys. Lett.,47(5) (1985) 476-478.

34. A. SUGIMURA, Y. FUKUDA and M. HANABUSA, "Selective Area Deposition of Silicon Nitride and Silicon Oxyde by Laser Chemical Vapor Deposition and Fabrication of Microlenses.

35. D.J. EHRLICH and J.Y. TSAO, "A Review of Laser-Michrochemical Processing", J. Vac. Sci. Technol.B, 1 (1983)969-984.

36. G.A. WEST, K.W. BEESON and A. GUPTA, " Laser-induced Chemical Vapor Deposition of Titanium Silicide Films", J. Vac. Sci. Technol. A3(6)(1985)2278-2282.

37. S. YOKOYAMA, Y. YAMAKAGE and M. HIROSE, "Laser-assisted Chemical Vapor Deposition of Stoichiometric Boron Nitride", Extended Abstr. of the 17th Conf. on Solid State Devices and Materials, Tokyo, (1985)169-172.
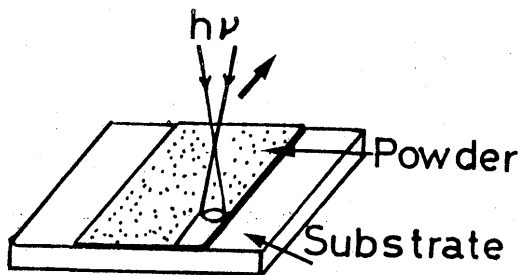
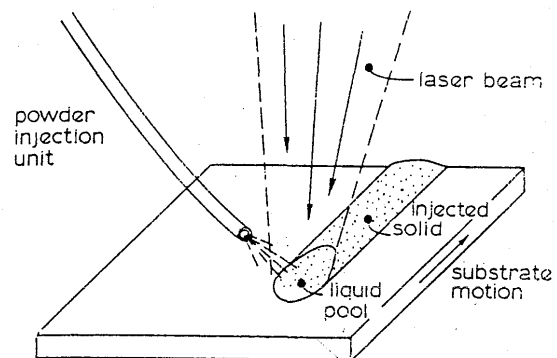Fig.1 Powder deposition process: principle.

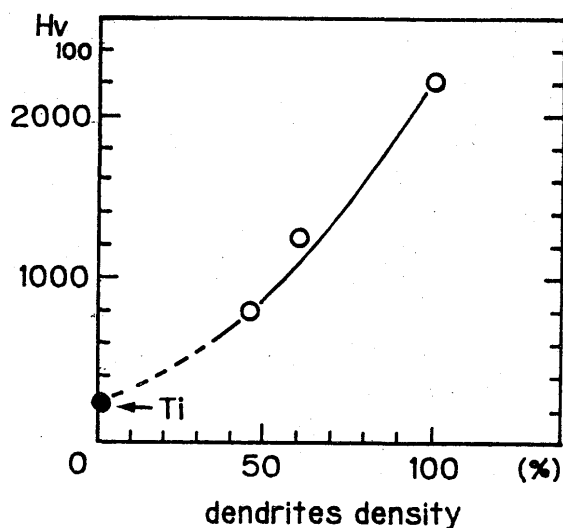
Fig.2 Powder injection process: principle (ref.6).

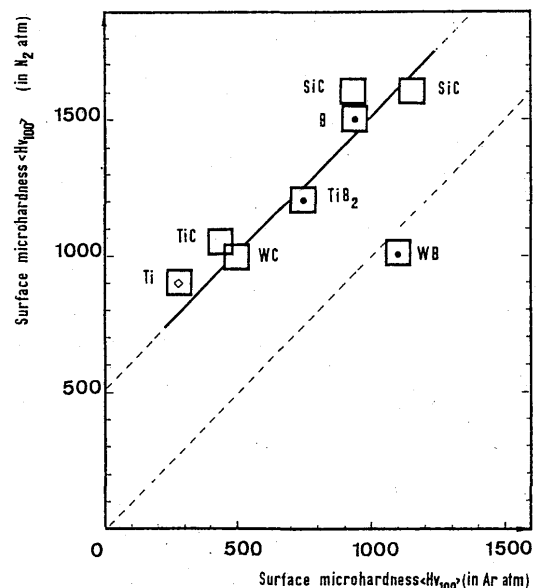Fig.3 Influence of the dendrites density on the hardness (ref.2)
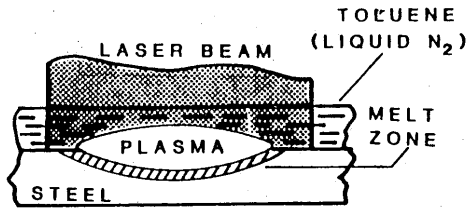

Fig.4 Influence of gas atmosphere on the surface hardness, for different powder composition (ref.2).

Power Density∼1.3X10⁸ W.cm⁻² Pulse Duration∼1us(1)
Power Density 2.5X10⁹W.cm⁻² Pulse Duration∼20ns.(2)

Ambient Pressure ·1atm.   Plasma Pressure 10⁴ to 10⁵ atm

Plasma Temperature∼1 to∼1.5ev.
Thickness of Liquid Layer∼.02 to∼1.3mm.

(1)Nd-Glass Laser (2)Excimer Laser

Fig.5 Liquid phase process: principle. (ref.8).

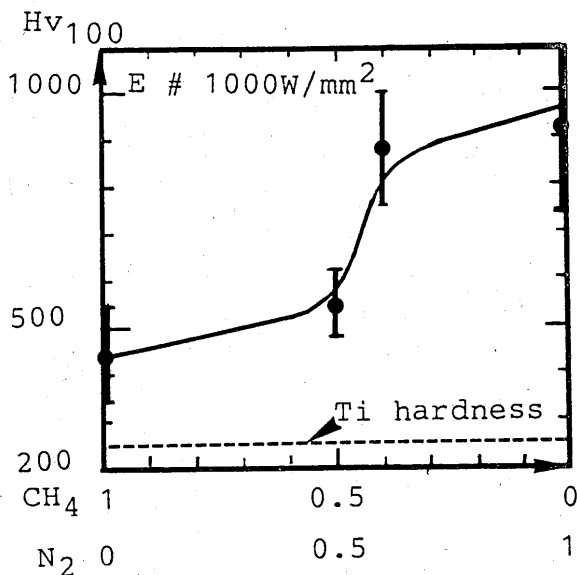

Fig.6 Influence of gas atmosphere on the surface hardness in laser gas alloying process (1 laser passe) (ref.15).
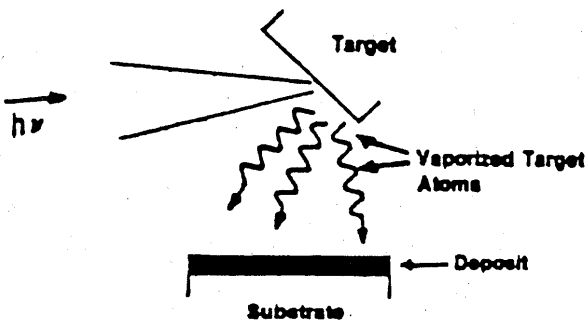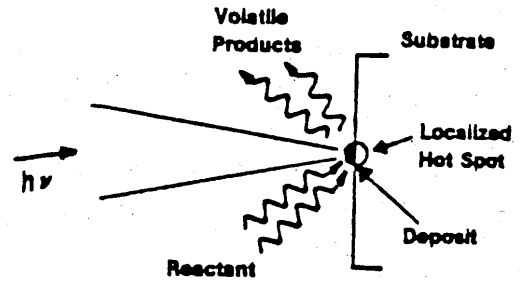

Fig.7 LPVD: principle(ref.25).
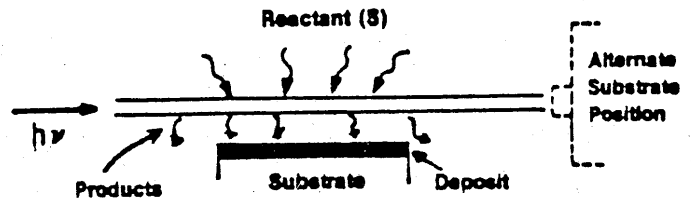

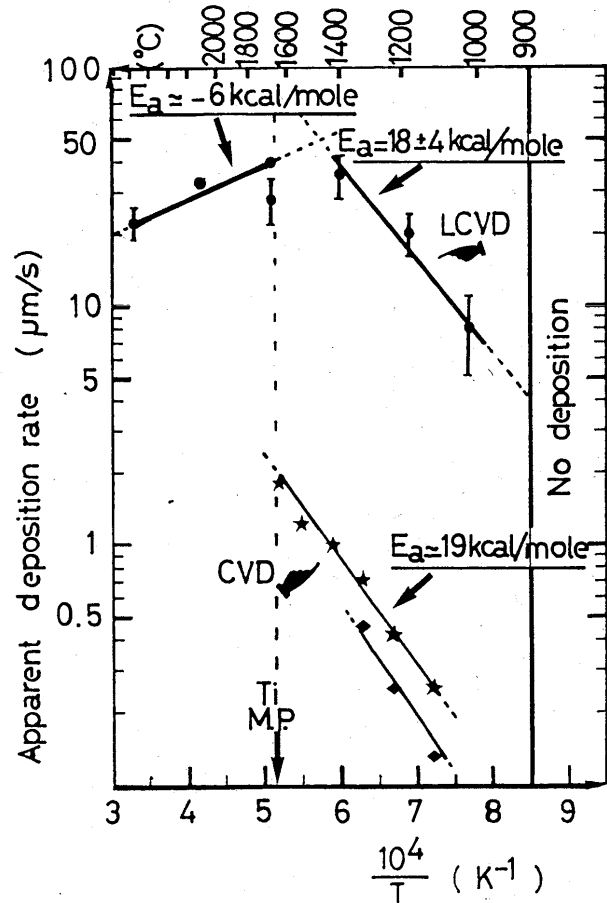Fig.8 Pyrolytic LCVD: principle. (ref.25)

Fig.9 Photolytic LCVD: principle. (ref.25)

Fig.10 Pyrolytic LCVD: Arrhenius plot of the deposition rate versus the reciprocal temperature, from $BCl_3-CH_4-H_2$ gas mixture (ref.32).

Table 1 Experimental conditions of powder deposition and injection processes

	YAG laser Dep.	CO_2 laser Dep.	Dep.	Inj.	Inj.	Inj.	Dep.	Dep.
Reference	[2]	[3]	[4]	[4]	[6]	[6]	[5]	[5]
Laser maxi power W	200	2000	5000	5000	15000	15000	2000	2000
Power exp.	4500-5500 W/pulse	?	2000-4000W	2000-4000W	6000-11000W	6000-11000W	1720 W	1200-1800W
Power density W/mm^2	1500-3500	?	?	?	850-1600	850-1600	730	700 1000
Traverse speed mm/min	140	1000 4000	1200	1200	300	300	1200	1200
Pulse duration	3.6ms	cw	cw	cw	cw	cw	cw	cw
Substrate	Ti	Al	Ti6Al4V	Ti6Al4V	Ti6Al4V	Inconel	Ti	Ti6Al4V
Powder	C,TiC,WC,SiC B,TiB$_2$,WB B+C,Si	Ti,Al,Cr SiC	C,TiC	TiC	TiC,WC	WC	C	C
Powder size um	<10, (except SiC:85)	?	45-90	45-90	37-210	37-210	?	?
Gas atmosphere	Ar,N$_2$	N$_2$,O$_2$	He,Ar	He,Ar	He	He	Ar	Ar

Table 2 Comparison of the laser melt pool geometry obtained by powder predeposition and injection processes.

Process	Substrate	Laser	Melt pool depth (um)	Melt pool Width (mm)	Ref.
Deposition	Ti	YAG	120-350	1.5-2.5	[2]
	Ti	cwCO$_2$	200-650	3	[5]
	Ti6Al4V	cwCO$_2$	700	2.0-2.4	[5]
			2200(8passes)	2.7	[5]
	Ti6Al4V	cwCO$_2$	25-130	0.2-0.5	[4]
	Al	cwCO$_2$	20-50	?	[3]
Injection	Ti6Al4V	cwCO$_2$	40-190	0.2-0.4	[4]
	Ti6Al4V	cwCO$_2$	200-500	2-3	[6]
	Inconel	cwCO$_2$	400-800	2-3	[6]

Table 3 Composition, microstructure and hardness of the coating obtained by laser powder predeposition and injection processes

Powder	Laser	Substrate	Gas	Phase	Micro hardness	Micro-structure	Ref.
Cdep.	YAG	Ti	Ar	TiC,Ti	300-330	Particles	[2]
	CO_2	Ti	Ar	TiC*	350(1pass) 600(8passes)	Particles Dendrites	[5]
	CO_2	Ti6Al4V	Ar	TiC*	380(1pass) 530(8passes)	Particles Dendrites	[5]
	CO_2	Ti6Al4V	He,Ar	TiC*	400-700	Dendrites + cells	[4]
TiCdep.	YAG	Ti	Ar	TiC,Ti	340-550	Dendrites	[2]
	YAG	Ti	N_2	TiC,TiN Ti	700-1400	"	[2]
	CO_2	Ti6Al4V	He,Ar	TiC*	450-600	Dendrites + globules (some non melted powder grain)	[4]
TiCinj.	CO_2	Ti6Al4V	He,Ar	TiC**	450-700	Cellular	[4]
	CO_2	Ti6Al4V	He	?	440-630 3000	Dendrites Carbides inclusions (partial dissolution of carbides)	[6]
WCdep.	YAG	Ti	Ar	WC,W_2C TiC,Ti	400-600	Dendrites + inclusions	[2]
			N_2	Idem + TiN	700-1300	Idem	
WCinj.	CO_2	Ti6Al4V	He	?	400-460 1600	Dendrites Inclusions	[6]
		Inconel	He	?	450-500 1300-2000	Dendrites Inclusions	[6]
SiCdep.	YAG	Ti	Ar	SiC,TiC $TiSi_2$, Ti_5Si_3,Ti	900-1400	Dendrites	[2]
			N_2	idem + TiN	1100-2100	Dendrites	[2]
	CO_2	Al	N_2	SiC,Si Al_4C_3,Al	400	?	[4]

Note: Hardness: base Ti= 250, Ti6Al4V= 350, Inconel625= 270, Al= 30 kg/mm^2
* Ti is probably also present
** No Al, no V in the dendrites

Table 4 Liquid phase process: experimental conditions and results

Laser	Wave length (um)	Pulse width (ns)	Energy density (J/cm^2)	Sub-strate	Liquid	Phase	Thick-ness (um)	Ref.
XeCl excimer	0.308	25	up to 3	Ti	N_2,NH_3 H_2O	TiN,Ti TiO,Ti	0.2 0.3-0.5	[10]
Pulsed ruby	0.694	30	6.7	Ta	H_2O	Ta_2O_5, Ta	0.5	[11]

Table 5 Experimental conditions of laser gas alloying process.

Laser	YAG	YAG	CO_2	CO_2	CO_2	CO_2	CO_2
Reference	[15]	[12]	[12]	[14]	[5]	[13]	[13]
Laser maxi power W	200	200	5500	650	2000	700 6000	700 6000
Power density W/mm^2	1000	2000-4000	? (P=1 - 3kW)	? (600W)	1000	? (200-700W) (2-5.5kW)	? (200 - 500W)
Traverse speed mm/mn	140	?	1000	400-10,000	1500-3000	500-4000	1000
Pulse duration	3.1 ms	3.6 ms	cw	cw	cw	cw	0.4 ms
Substrate	Ti	Ti Ti6Al4V Ti6Al6V2Sn	Ti Ti6Al4V Ti6Al4V	Ti6Al4V	Ti Ti-15Mo	Ti6Al4V	Ti6Al4V
Gas atmosphere	CH_4 N_2,Ar	N_2,air Ar	N_2,air Ar	CH_4 N_2,Ar	N_2	N_2	N_2

Table 6 Composition, microstructure, microhardness and geometry of the laser fusion zone obtained by laser gas alloying process.

Gas	Laser	Substrate	Phase	Microhardness (surface)	Microstructure	Alloyed zone depth(mm)	Melt pool width (mm)	Ref.
N_2	YAG	Ti,Ti6Al4V, Ti6Al6V2Sn	TiN, Ti	700-1200	dendrite+ martensite	0.15-0.25	1.2-2.5	[12]
Air	YAG	Ti	TiN, TiO_2, Ti	800-1000	idem	idem	id.	id.
N_2	CO_2	Ti and alloys	TiN, Ti	700-1300	idem	0.1 1.5	?	[12]
N_2	CO_2	Ti,Ti-15Mo	TiN, Ti	400-600	dendrites	0.2-0.3	0.75-1.2	[5]
N_2	YAG	Ti	TiN, Ti	700-1100	dendrites	0.05-0.12	2.0-2.5	[15]
CH_4	YAG	Ti	TiC, Ti	350-550	particles dispersion	0.03 0.12	2.0-2.5	[15]
N_2	CO_2	Ti6Al4V	TiN, Ti	500-1400	dendrites	0.2-1.2	?	[14], [13]
CH_4	CO_2	Ti6Al4V	TiC, Ti	500	particles	id.	id.	id.
O_2	CO_2	id.	TiO, Ti_2O	400	dense layer	id.	id.	id.

Note: Base materials hardness: Ti=200-250, Ti6Al4V=300-350, Ti6Al6V2Sn= 370-420 kg/mm^2.

Table 7 Laser PVD, experimental conditions for wear applications

Laser	Power (W)	Power density (W/mm^2)	Irradiation time,min	Substrate temperature,C	Target Temperature,C	Vacuum (torr)	Target composition	Substrate	Ref.
CO_2	100-1000	100-250	5-20	300-600	<800	10^{-4}	Al_2O_3, mullite, Si_3N_4,BN, SiAlON	Mo	[19]
CO_2	90	?	25	50-500	?	10^{-5}-10^{-4}	Al_2O_3	Al	[20]

Table 8 Laser PVD, results (wear applications)

Laser power (W)	Coating thick-ness,um	Compo-sition	Coating hardness (kg/mm^2)	Deposition rate (mm/mn)	Rough-ness (um)	Ref.
320	a few um	Al_2O_3/Mo mullite/Mo Si_3N_4/Mo SiAlON/Mo BN/Mo	2200 1100 1000 1100 2500- 4500	0.6 0.6 0.4 0.2 0.1	?	[19]
90	6-8	Al_2O_3/Al	1200	0.3	0.5	[20]

Note: Target hardness: Al_2O_3= 1600, mullite ($3Al_2O_3$-$2SiO_2$)= 460, Si_3N_4= 600, SiAlON= 1600, BN= 37-54 kg/mm^2.

Table 9 Laser PVD, experimental conditions for superconductivity applications

Laser	Power density (MW/cm^2)	Pulse width	Repeti-tion rate,Hz	Spot size (mm)	Pres-sure (torr)	Substrate	Target	Film	O_2 annea-ling	Ref.
Nd:YAG (1.06um) (0.1-1J/p)	10-100	0.12-0.15 ms	30	0.1	10^{-5}-10^{-4}	ZrO_2/MgO/ sapphire	$YBa_{2.4}$-$Cu_{4.8}O_x$	YBa_2-Cu_3O_y	800C 8-24h	[21]
KrF excimer (1J/p)	70	30ns	3-6	?	10^{-6}-10^{-7}	$SrTiO_3$ (450 C)	YBa_2Cu_3-O_7	$Y_{1.1}$-$Ba_{1.5}Cu_3$ $O_{6.4}$	900C 1h	[22]
						Al_2O_3 (450 C)	id.	id.	850C 1h	
Q-switch YAG (532nm)	94	6ns	10	3	$2.$-10^{-4}	YSZ* (300C)	Cu/Y=3 Ba/Y=2	Cu/Y=3 Ba/Y=2	900C 3h	[23]
XeCl excimer (308nm)	45-90	45ns	?	?	10^{-6}	MgO,Si, Al_2O_3, $SrTiO_3$	YBa_2Cu_3-O_{9-x} (x=2.1-2.4)	YBa_2Cu_3 $O_{6.9}$	860-900C	[24]

* YSZ= Yttria Stabilized Zirconia

Table 10 Laser PVD, results (superconductivity applications)

Laser	Deposition rate	Substrate	Thick-ness (um)	Grain size (um)	Onset Tc(K)	Offset Tc(K)	Rough-ness	Ref.
Nd:YAG	10nm/s	ZrO_2/MgO/ sapphire	5	5-10	90	20	?	[21]
KrF excimer	1nm/s	$SrTiO_3$	0.20	0.5	95	85	50nm	[22]
		Al_2O_3	0.33	0.15	95	75		
Q-switch YAG	0.06 nm/pulse	YSZ	4	?	98	90	?	[23]
XeCl excimer	?	Al_2O_3	0.05-0.45	<2	90	85	?	[24]