

Laser induced desorption and ablation: mechanism of metal removal from an Al–Cu–Fe alloy and a quasicrystal of the same composition

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ABSTRACT. Quasicrystals are a special class of metallic alloys that share some of the properties of crystals. Their structures reduce to a single repeating unit like that of the unit cell of a crystal. The quasi-unit-cell is representative of a cluster like structure where electrons cannot move with freedom as in metals. Quasicrystals are formed of metallic elements but they do not have metallic properties.

The diversity of the fractionation behavior induced by laser desorption and ablation of the Al₇₀Cu₂₀Fe₁₀ of the intermetallic alloy and of the Al₆₅Cu₂₃Fe₁₂ quasicrystal has been examined in terms of the structural properties of the two compounds. Elemental fractionation during laser desorption and ablation sampling was investigated by using inductively coupled plasma mass spectrometry. The experiments were carried out in two different irradiance regimes by a Nd-YAG laser with 266 nm wavelength and single 6 nanosecond laser pulses. In the high irradiance regime ($> 0.04, 0.07 \text{ GW/cm}^2$) the effect of the laser irradiance is not discriminating. In the low irradiance regime ($< 0.04, 0.07 \text{ GW/cm}^2$) large differences have been found between the alloy and the quasicrystal. The results have been interpreted on the basis of a thermodynamic vaporization process for the intermetallic alloy. An electronic model of localized excitation is suggested for the physical process of surface material removal from a quasicrystal.

1. INTRODUCTION

Studies on the effects due to absorption of laser radiation by metals were reported as soon as laser were known as laser source [1]. Laser metal interaction has been studied more recently by pulsed laser ablation in terms of one and two temperature systems of the electron and the lattice [2, 3]. Metals are represented by the Drude-Fermi model which assumes that the atoms of a metallic element lie in a given position in the bulk structure where the detached Fermi electrons freely moves [4]. Intermetallic alloys, as binary and ternary metallic systems are similarly represented [4]. The electronic quantum states of metals or alloys are thus highly delocalised and described as extended or band-like. This means that there is no opportunity for localization.

A new class of metallic alloys, the quasicrystals (QC), was discovered in 1984 by Dan Shechtman [5]. These compounds are described as an aperiodic structure, with a long-range atomic order and electronic quantum states, intermediate between localized and delocalized. The Fermi electrons in a QC are scarce and this leads to a low thermal and electrical conductivity and to a so called pseudo-gap [6, 7]. In this case it can be expected localized and delocalized modes for the absorbed photon energy.

On these premises it appeared worthwhile a study of these two compounds the metallic alloy Al₇₀Cu₂₀Fe₁₀

and the QC Al₆₅Cu₂₁Fe₁₂, both with almost the same metal components and different electronic structure.

Laser induced sputtering, solid sampling, and chemical analysis have been carried out by transporting the removed material to a secondary source such as the inductively coupled plasma with mass spectrometry (ICP-MS). Our concern was to establish the constituents of the laser-ablated mass, after previous calibration of the ICP system, as a function of the laser power density.

2. EXPERIMENTAL

The experimental work was performed by using a PQ3 (VGE 1 elemental) ICP-MS.

A schematic of the experimental apparatus is shown in Figure 1. The laser for ablation was a Nd-YAG with pulse duration of 6 ns and operated at 266 nm. The laser beam was focused on the target with the use of a plano-convex U-V quartz lens ($f = 150 \text{ mm}$). The laser beam spot size was varied by changing the lens-to-target distance. The laser beam was monitored by a joule meter and the spot size was calculated by the geometry of the beam. The laser energy was fixed at 0.85 mJ the beam diameter from 76 μm to 1600 μm . The sample chamber was mounted on a xyz micrometer translation stage. The targets consist of two fragments of the compounds. Standard solution of the samples were prepared by dissolving the metallic alloy and

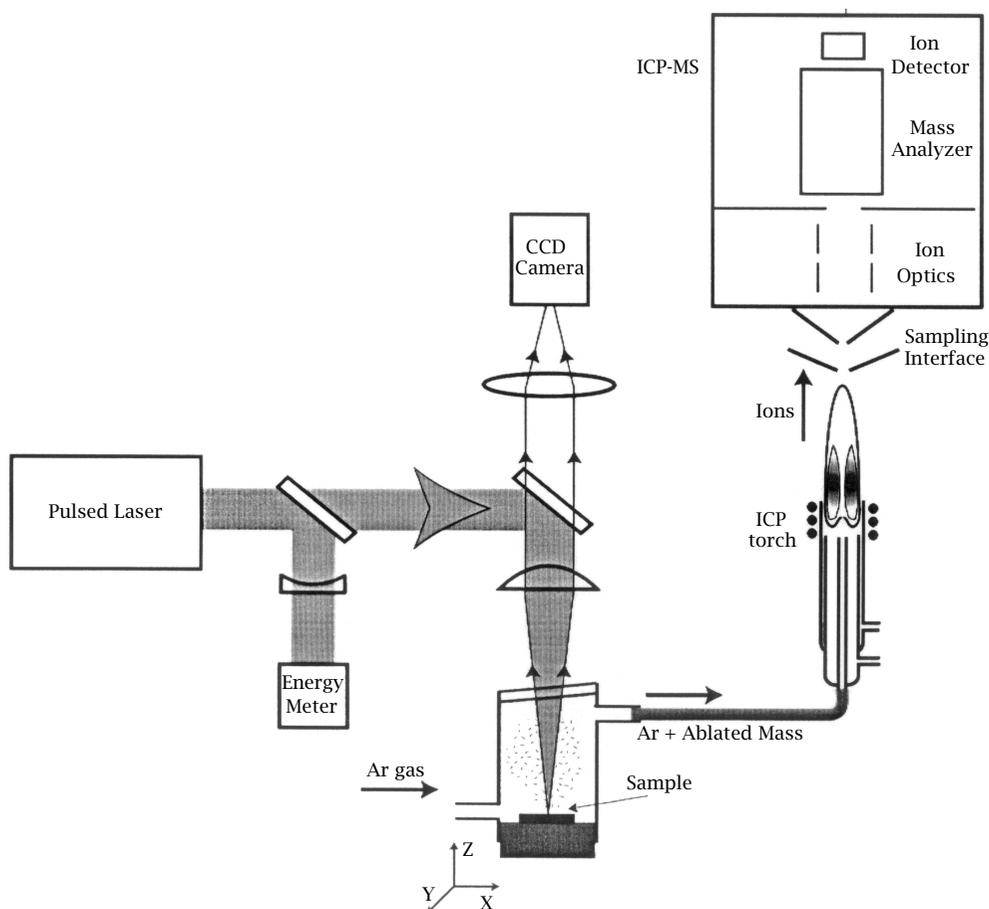


Figure 1. Schematic of the apparatus.

the QC with diluted HNO_3 solution respectively. During laser ablation, a stream of the ablated mass is transported by an Ar flow from the sample chamber to the ICP torch and to the quadrupole mass spectrometer.

The ICP-MS detection was performed by irradiating the targets by a single laser pulse and the signal intensity data acquired in the time resolved mode.

The target surface was cleaned repeatedly by methanol before running the single pulse set of the ablation experiments.

The crater at the sample surface was measured after a single laser pulse with a white-light interferometric microscope (New View 200, Zigo Corporation).

3. RESULTS AND DISCUSSION

3.1. Materials. The single crystalline phase $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ can be formed from ternary mixture of Al, Cu and Fe metals melted in argon atmosphere by using a high temperature furnace.

The samples is annealed at 1118k ($0.98 T_m$) in vacuum and conventionally (rapidly) solidified from the melt show in both cases X-ray diffraction (XRD) patterns indicating a quasi-crystalline structure with a five-fold

symmetry. The spectra can be identified as an icosahedral structure and no diffraction peaks of other phases are observed. Further if the QC is even heated after solidification at high temperature no diffraction peaks of second phase is seen. These results indicate that the icosahedral phase is a thermodynamically stable phase from high to room temperatures but only at a composition very close to $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ [8].

The quasi-crystal structure is described of as hierarchical packing of atomic clusters of graded sizes. These basic elements are arranged in the same fashion by outer and inner shells with different number of atoms. The specific structure of QC has a very important role for their weak electrical and thermal conductivity. Some quasi-crystal may even be considered to be insulators.

The phase structure of the QC samples used in the present experiments, and reported in Figure 2, was obtained by the X-ray diffraction (XRD) pattern of the powder with a Philips automated PW1729 diffractometer using a $\text{Cu-K}\alpha$ radiation (Ni filtered). The spectra show diffraction peaks only from the icosahedral phase without exception. The indices peak positions, peak

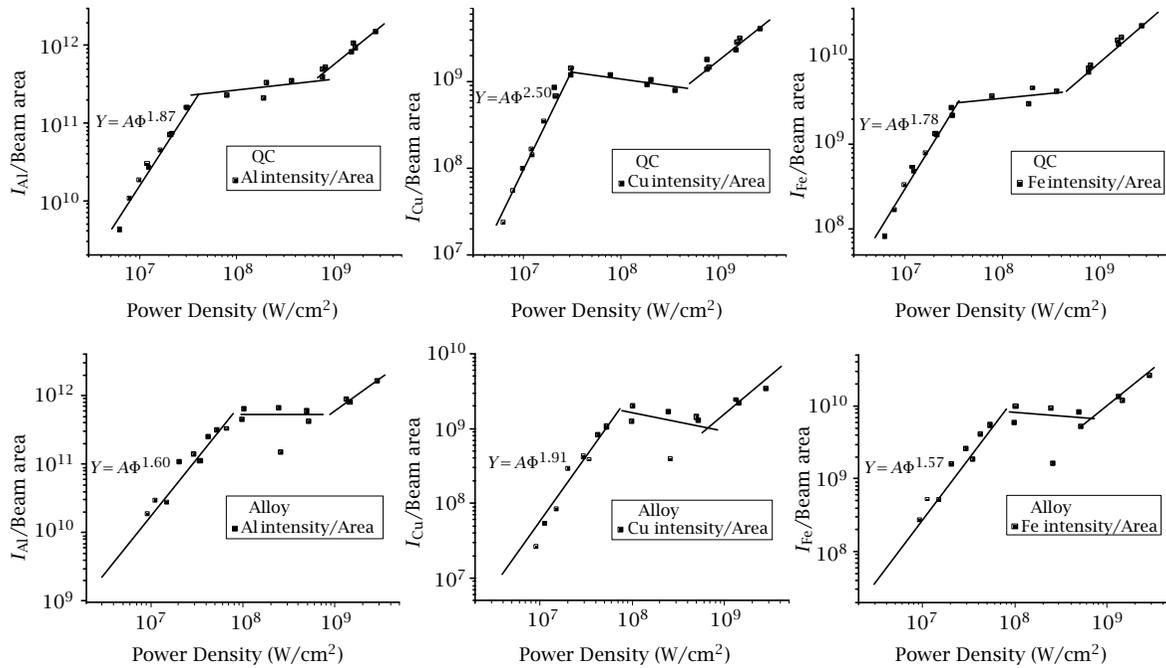


Figure 3. ICP-MS intensity normalized to laser beam area as a function of the measured power density, during a single nanosecond Nd-YAG laser pulse desorption-ablation of the Al – Cu – Fe alloy and QC: $\lambda = 256$ nm. Data show different rate behavior of the two samples in the three power density regimes.

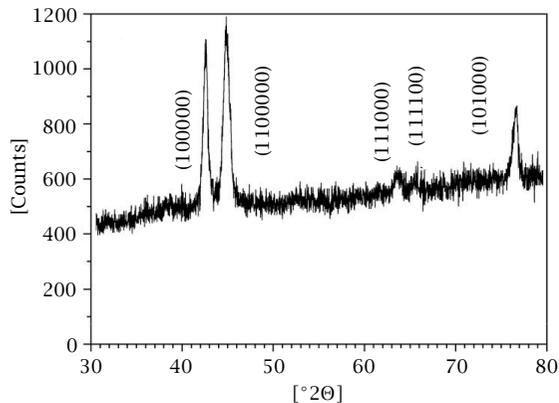


Figure 2. X-ray diffraction pattern of QC sample $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ used in the ICP-MS experiments.

intensities, peak width and lattice parameters of the diffraction peaks correspond to the QC structure [8].

Under the same condition no XRD peaks were observed in the case of the ternary intermetallic alloy $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_{10}$, confirming the amorphous character of the sample. Electronic properties and heat capacities for amorphous systems can be described by the simple Drude model. These properties are not so different from those of a crystalline alloy. A striking difference between amorphous and crystalline alloys is the substantial decrease in resistance with decreasing temper-

ature, which is much larger for the former. The only our concern for the present work is that the electronic quantum state for both systems is highly delocalized.

3.2. Mass ablation rate behavior. The data of ICP-MS from the metallic alloy and the QC per unit area are reported as a function of the power density in Figure 3. The plots refer to the three constituents Al, Cu, and Fe of the two compounds separately. The trends are very similar, and three regimes may be recognized in the plots. At low regimes the mass ablation rate increases with an exponential law $Y = A\Phi^n$ with the laser power density. The trend shows a roll-off at approximately 0.04 GW/cm^2 and 0.08 GW/cm^2 for the QC and the alloy respectively.

The second step, at intermediate power density, results in a stable stage for the three elements. An unchanged value of the intensity after the roll-off point is observed. Finally at the third step there is a rapid increase of the intensity, namely a roll-up, at higher power density at about 0.9 GW/cm^2 for both the two compounds. These data are summarized in Table 1. It can be seen from the table that the ablation rates show some differences between Al and Cu.

In the high range of irradiance no significant diversity is observed between the two systems. The data reported in Figure 3 and in Table 1 show that the crater threshold, the roll-off points, and the exponent of the straight line before the roll-off point are different.

Table 1. Summary of the results of Figure 3.

QC Crater threshold 0.05 GW/cm ²			
	Roll-off (GW/cm ²)	Roll-up (GW/cm ²)	$N^{(1)}$
Al	0.038	0.9	1.87
Cu	0.030	0.9	2.50
Fe	0.035	0.9	1.80
Alloy Crater threshold 0.135 GW/cm ²			
	Roll-off (GW/cm ²)	Roll-up (GW/cm ²)	$N^{(1)}$
Al	0.06-0.07	0.9	1.6
Cu	0.07	1.0	1.91
Fe	0.08	1.0	1.6

⁽¹⁾ Where N is the exponent of the mass-intensity per unit area (Y) vs. Power density (Φ) fitting: $Y = A\Phi^N$.

The crater threshold is obtained by visual observation of the surface damage and the roll-off point occurs at a lower irradiance for the QC than for the alloy. This may simply be explained with the different thermal conductivity found between the two compounds. A value of 1.8 W/mK is found for the QC and a higher value of about 225 W/mK for the average of the three metals [9]. This difference could indicate that ablation effect due to the laser pulse on the surface is in favor of the QC rather of the alloy, the latter having a higher thermal conductivity thus the energy dissipation is higher. Analogously for the roll-off point of the two compounds. The exponential power density law dependence, which is a measure of the ablation rate, shows two distinct slopes for the two compounds according to the plots of Figure 3. The slope results higher for the QC than for the alloy. This is because of two combined factors: the first is the energy dissipation behaviour as mentioned above and the second is due to an electronic mechanism of non-thermal bond-breaking, faster than that caused by a thermal evaporation process. The ablation rate increases exponentially in the low irradiance regime and it is almost invariant at intermediate power density. The invariance of the rate supports the hypothesis of an inverse *bremstrahlung* mechanism above the roll-off points. The laser-induced plasma is shielding the laser beam, at intermediate power density and up, when there is a massive removal of material. This is confirmed by the fact that at the power density above the roll-off point, a crater is observed on the target surface by the interferometric microscope. This crater is a measure of the volume removed and increases with the power density. A laser *ablation* process in which material removal rate exceeds one-tenth monolayer per pulse [10] takes place at these values of irradiance.

Another critical point is observed at approximately 0.9 GW/cm² when the ablation rate increases sharply. This occurs at rather high power density and it has been interpreted as a phase explosion mechanism with ejection of particulate in the vapor [11].

3.3. The Al/Cu ratio for the alloy and the QC and numerical calculations.

The present work wants to analyze the interaction of photons with two different metallic alloys that are differentiated only by structural characteristics. In both compounds, the low power density regime gives rise to a low-yield sputtering process that is closely related to the phenomenon of laser-induced *desorption*. If this is the case the process results in the ejection of atoms from isolated surface sites. In the intermediate and high power density range, an *ablation* process takes place, a large amount of material is removed and an energy threshold of the flux of material is observed. The metallic alloy and the QC behave differently in the low power density regime due to the fact the structural properties are different. At high laser power density the effect of the structural diversity of the two compounds disappears and the laser *ablation* produces the same result. The primary event in laser *desorption* and *ablation* is in both cases an electronic excitation. In the metallic alloy this excitation is delocalized while in the QC could be localized. In the first case the ejection of material takes place by heating the surface, causing vaporization, in the latter by producing localized lattice instability and bond breaking.

In Figure 4 the data of the Al/Cu ratio from laser *desorption-ablation* of the Al – Cu – Fe alloy and QC targets are reported. The horizontal solid lines indicate the actual Al/Cu ratio in the bulk alloy and the QC as results from the analysis of the solutions of the stoichiometric composition. An invariance of the ratio, in the whole irradiance range, is shown for the alloy. The experimental data are in the range of a 3.5 ratio, corresponding to the value of the calibration solution. In the same power density range, the QC shows a lower-than-

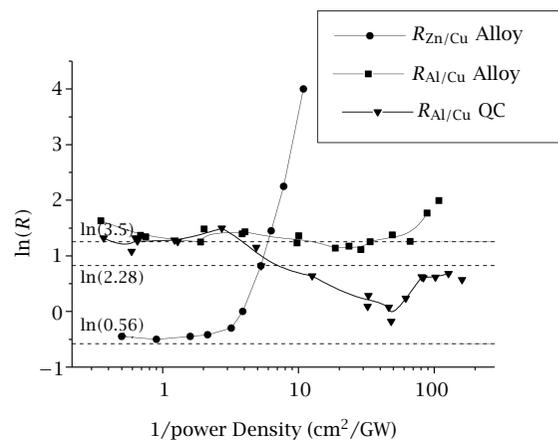


Figure 4. The Al/Cu ratio measured by ICP-MS as a function of the laser power density for the Al – Cu – Fe alloy and QC, during a single nanosecond Nd-YAG laser pulse: interpolated curve spline ■, ▼ Zn/Cu curve from reference [13] ●.

stoichiometric Al/Cu ratio, which stabilizes above the bulk stoichiometric composition 2.28 at 0.1 GW/cm².

The laser *desorption-ablation* trend of the ratio of the two components in the alloy has been treated on the basis of a *thermal* mechanism of vaporization. The material optical and thermal properties and the laser irradiance (power density) all are important parameters which affect the process. Pulsed laser ablation of metals have been treated in terms of a thermal process of vaporization accounting for the absorption, heat and dissipation of the laser energy in the samples when the pulse laser duration is in a nanosecond time scale [2]. In a picosecond pulse duration time, the metal must be looked as a two-temperature system of electrons and lattice [3]. In this time scale electron-phonon thermalization takes place with electrons gradually returning to the equilibrium with the ionic lattice.

The invariance of the ratio of the components is in agreement with a numerical treatment obtained by combining the Clausius-Clapeyron's, Hertz-Knudsen's laws: namely the rate of vaporization and the flux of the material removed. This treatment is characterized by a marked dependence of the ratio of the components on the heat of vaporization and on the boiling temperature.

In order to obtain the $R_{Al/Cu}$ ratio it is necessary to know the number of atoms of the i^{th} specie, that escapes the any condensed phase per unit time per unit area, i.e.:

$$N_i = \frac{P_i}{(2\pi M_i k_b T)^{0.5}}$$

(M_i is the molar mass of the i^{th} element, k_b is the Boltzman constant and T is the temperature of the heated phase, assumed proportional to the laser power density) P_i is the pressure of an effusing gas at temperature T , which reduces to a simple formula if the Clausius-Clapeyron's equation is properly integrated (neglecting the role played by the specific heats, because the heats of vaporization are assumed not varying with temperature in the range of energies of low-irradiance regime [12, 13]):

$$P_i = P_i^o \left[\exp \left(\frac{-\Delta H_i^v}{R} \left(\frac{1}{T} - \frac{1}{T_i^b} \right) \right) \right],$$

where P_i^o is the vapor pressure of the i^{th} element at temperature T_i^b , its boiling temperature; ΔH_i^v is its heat of vaporization, largely independent of temperature, and R is the gas constant.

The $R_{Al/Cu}$ ratio is then expressed as:

$$R_{Al/Cu} = \frac{\chi_{Al} N_{Al}}{\chi_{Cu} N_{Cu}}$$

in which χ_{Al} and χ_{Cu} are respectively the molar fraction of Al and Cu in the studied solid. It can be seen that the

Table 2. Thermodynamic properties of the metals of the metals employed in the calculations.

	T_m (K)	T_b (K)	ΔH_{ev} (kJ/mol)
Al	659	2740	293.4
Cu	1082	2840	300.3
Fe	1535	3023	349.6
Zn	693	1180	115.3

The data are from the handbook of chemistry and physics, C.D. Hodgman, The chemical rubber publishing Co. 1995.

rate of change of $R_{Al/Cu}$ with temperature is mainly due to the difference of the heats of vaporization of the two species:

$$\ln(R_{Al/Cu}) = \text{Const} + \frac{\Delta H_{Cu}^v - \Delta H_{Al}^v}{RT},$$

where Const is a parameter not depending on temperature:

$$\text{Const} = \ln \left(\frac{\chi_{Al} M_{Al}^{0.5}}{\chi_{Cu} M_{Cu}^{0.5}} \right) + \frac{\Delta H_{Al}^v}{RT_{Al}^b} - \frac{\Delta H_{Cu}^v}{RT_{Cu}^b}.$$

The thermodynamic Al/Cu ratio has been calculated, by using the parameters of Al and Cu as reported in Table 2. It can be noted that the heat of vaporization ΔH^v of Al and Cu are almost the same with a difference of only 7 kJ/mole. The boiling temperatures T^b of the two metals are different of 100K. These values show that Al and Cu need the same power density to vaporize. A stoichiometric ratio = 3.5 is assumed in the calculation of the vaporization process based on the Rault's law for an ideal solution. The results of the calculations confirm the invariance of the ratio at this value in the low power density range (A previous work on a brass alloy with Zn and Cu, which have very different heats of vaporization ΔH_v , reports a trend of large change of $R_{Zn/Cu}$ ratio with power density in low laser energy regime [14]).

At high power density, above the roll-off point (0.5–0.9 GW/cm²), there is a combination of two effects. First, above this point, the increased power density and thus the temperature should increase the amount of material evaporated. Second, the laser shielding, due to the plasma, causes a reduced ejection of material in comparison with what the thermal approach would predict. The final result is the invariance of material removed and also of the Al/Cu ratio. At variance a *thermal* model does not fit the experimental data of the Al/Cu ratio in a QC. At laser low power density the Al/Cu ratio is lower than that of the target. A Cu rich component is found in the ejected mass up to about 0.02 GW/cm². At high power density the Al/Cu ratio is higher than the stoichiometric value 2.8.

The diversity of behavior of the alloy and of the QC may find an explanation in the structure of the

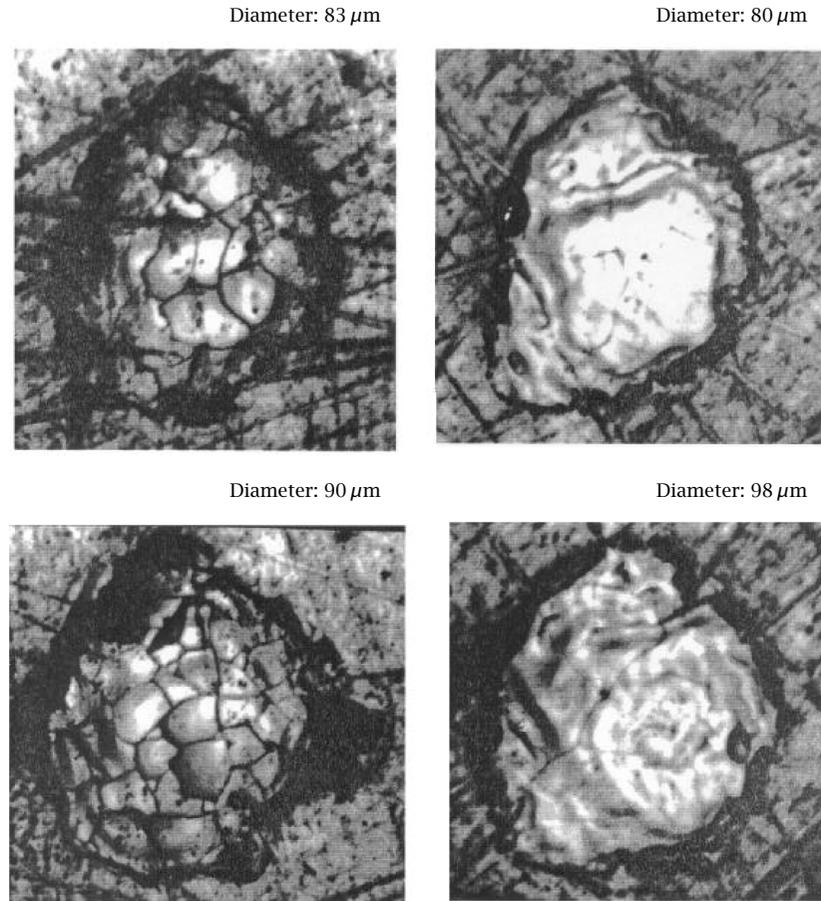


Figure 5. Surface topography of Al – Cu – Fe alloy and QC formed after a single Nd-YAG laser pulse. left QC, right alloy. Top 0.02 GW/cm^2 , bottom 0.06 GW/cm^2 . A white light interferometric microscope was used to examine the surface parameters.

two compounds. The trend of the Al/Cu ratio in QC is likely due to bonding and antibonding orbitals in the quasi-crystalline structure. In this structure the presence of a large number of defects may have a role in the laser induced *desorption* and *ablation*. The electrical conductivity of a QC that is much below of that of pure aluminum supports the view that a large number of defects is present in this material. The defects are storage sites to keep the absorbed energy for long time in localized modes thus increasing preferential bond breaking. They may act by weakening local bonds by forming nucleation centers for rapid raising of *desorption-ablation* sites [10]. This could also justify why a *non-thermal* process may take place by using a nanosecond laser pulse duration. In the structure of the QC, the binding energy of Cu with other elements, after initial photoexcitation is converted to kinetic energy, leading to preferential ejection of Cu with respect to Al [10].

Two photographs of the alloy and QC after a single pulse and at the low power density, before the roll-off point, are reported in Figure 5. Melting of the sample is

observed for the alloy, while for the QC a mosaic-like structure is the main feature.

Evaporation from the melting appears to be the *desorption* process in the alloy as described above. The ejection of materials occurring by laser surface interaction in the QC does not seem to take place by simple melting and evaporation. The mosaic-like structure seems to reflect the Fibonacci pentagrid that describes the bulk “superlattice”. The observed topography of the surface depends apparently on the laser power density, i.e. the temperature applied during irradiation [15].

4. CONCLUSION

The present study of the laser-solid interaction of two substances such as Al – Cu – Fe the intermetallic alloy and QC has demonstrated that the ICP-MS technique is a very suitable tool for an analysis of the products in a *desorption* and *ablation* process in a wide range of power density, and particularly in the very low range. This is the case of two compounds with almost identical

composition and different structure: the first a metal and the latter a non-metal.

The experiments have shown a marked diversity of these two systems that may be listed in the following characteristics: ablation rate, roll-off point, crater threshold and component ratios. In the low power density regime we are dealing with a *desorption* process in which no large amount of material is removed. In this regime there is a marked difference of behavior of the two compounds. This is likely to be expected on the account that the physical properties of the two do not change in the time lag of a single nanosecond laser pulse. At high energy, in the QC, a phase transition occurs and the *ablation* process may come to have the same characteristics as for the alloy.

An extensive discussion of a model of laser interaction with the QC surface and *desorption and ablation* is rather complex. The system is characterized by closely related phases called "approximant" phases, which are in competition with the icosahedral phase. The study of an isothermal section, at a given temperature, of the Al – Cu – Fe phase diagram shows three domains near the perfect icosahedral phase corresponding to other approximants [16].

Most of the atom sites can be viewed as a result of structures built essentially with roughly the same atomic units, but stacked in a different way. The laser *desorption* phenomenon studied with the laser on QC is typically a surface phenomenon, whose features are extended from the bulk structure to the surface [15]. It seems thus that it would be difficult, under this condition, to figure out the problem without knowing what structure of phase approximants is involved in the *desorption* process.

Unfortunately the microscopic structure of the QC is unknown, and even a simple electronic ablation model, such as that based on DIMET quantum-statistical process applied to metal ablation [3], can not be verified because of the lack of fundamental chemical-physics parameters, i.e. harmonic vibrational frequencies of the surface modes, binding energies to desorb metallic elements at surface and the electron-phonon coupling constant G .

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