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Inductively coupled plasma mass spectrometric study of laser sputtering from the surface of an Al–Cu–Fe alloy and quasicrystal

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Abstract

The fractionation behavior induced by laser desorption and ablation of the $Al_{70}Cu_{20}Fe_{10}$ intermetallic alloy and of the $Al_{65}Cu_{23}Fe_{12}$ 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 power density regimes by using a Nd-YAG laser with 266 nm wavelength and single 6 ns laser pulses. In the high power density regime (>0.04–0.07 GW/cm^2) the effect of the laser power density on ablation behavior was similar for the two materials. In the low power density regime (<0.04–0.07 GW/cm^2) large differences have been found between the alloy and the quasicrystal. The results are 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.

Keywords: Ablation; Quasicrystal; Laser; Mass spectrometry; Sputtering

1. Introduction

Laser interactions with a solid surface result in the emission of atoms, molecules or ions. If a negligible ejection of particles occurs, the process is named *laser desorption*. Conversely, a process with a large amount of material removed is termed *laser ablation*, which is also associated with the formation an ejected gas plume. A more general term reported in the literature is laser *sputtering*. Laser-induced desorption and ablation depend on the power density of the excitation laser [1]. Photon energy may be deposited by exciting free electrons or exciting electronic or vibrational transitions in atoms, molecules or defects. In metals, laser excitation involves either conduction or valence band electrons. In insulators and semiconductors, the response involves both electronic and ionic contributions. In metals, following photoexcitation, energy delocalization is possible and laser desorption and ablation take place from the liquid or solid surface by thermal vaporization. In the case of solids with moderate or strong electron–lattice coupling, electronic excitation is localized and leads to lattice instability through changes in the electronic configuration [2]. If localization is such that the observed energy remains on the site long enough for the bonds to be broken, desorption and ablation occurs.

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Studies on the effects due to absorption of laser radiation by metals were reported as soon as lasers were discovered [3]. The pulsed laser metal interaction has been studied more recently in terms of one and two temperature systems of the electron and the lattice [4,5]. 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 move freely [6]. Intermetallic alloys, as binary and ternary metallic systems are similarly represented. 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, quasicrystals (QCs), was discovered in 1984 by Schechtman [7]. 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 so-called pseudo-gap [8,9]. In this case, localized and delocalized modes for the absorbed photon energy can be expected. The quasicrystal structure is described as hierarchical packing of atomic clusters of graded sizes. The basic elements are arranged in the same fashion by outer and inner shells with different number of atoms. The specific structure of a QC has an important role in the electrical and thermal conductivities. Some quasicrystal may even be considered to be insulators [10].

A study of the metallic alloy $Al_{70}Cu_{20}Fe_{10}$ and the QC $Al_{65}Cu_{23}Fe_{12}$, both with almost the same metal components but different electronic structure was conducted. Laser-induced sputtering (ablation), with chemical analysis was carried out by transporting the sampled material to an inductively coupled plasma with mass spectrometry (ICP-MS). Our goal was to establish the elemental 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 (VG Elemental) ICP-MS, as described in the previous paper [11,12]. 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 ($f = 150$ 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 was varied from 76 to 1600 μm. The sample chamber was mounted on an *xyz* micrometer translation stage.

The targets consist of the QC and the alloy. Solutions of the samples used as standard were prepared by dissolving the metallic alloy and the QC with diluted HNO_3 solution. During laser ablation, a stream of the ablated mass was transported by an Ar flow from the sample chamber to the ICP torch. The targets were ablated by a single laser pulse and the signal intensity data were acquired in the time resolved mode.

The target surface was cleaned using methanol before running the single pulse ablation experiments. The crater profile, which provides a measure of the volume removed (0.1 ML/pulse) from the sample surface was measured after a single laser pulse using a white-light interferometric microscope (New View 200, Zygo).

3. Results and discussion

3.1. Mass ablation rate behavior

We have studied the interaction of photons with two different metallic alloys that are differentiated only by structural characteristics. In both compounds, the low laser 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 laser power density range, an ablation process takes place. A large amount of material is removed and an energy threshold for 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 signal behavior.

The ICP-MS signal from the metallic alloy and the QC in terms of the spectral intensity per unit area have been measured as a function of the laser power density (Fig. 1). The data show the ablation behavior of the three constituents Al, Cu, and Fe from the two samples. The trends are similar, and three regimes are recognized in the plots. We can recognize three regimes according to the power density. In the low power density regime, the mass ablation rate increases with an exponential law $Y = A\Phi^N$ with laser power density. The data show a roll-off at approximately 0.04 and 0.08 GW/cm^2 for the QC and the alloy, respectively. A second step, at intermediate power density, results in a stable signal for the three elements. Finally, there is a rapid increase in the intensity, in the third regime, namely a roll-up, at power density of about 0.9 GW/cm^2 for both compounds. These data are summarized in Table 1.

The ablation rates show some differences between Al and Cu before the roll-off. In the high irradiance range no significant diversity was observed between the two samples. In each sample, the power densities for roll-off and for the crater threshold represent the turning point from the desorption to ablation. The turning point is at lower power density for the QC than for the alloy, which may be related to the different thermal conductivity between the two materials. A value of 1.8 W/m K was measured for the QC and a higher value of about 225 W/m K was determined for the average of the three metals [10]. This difference in thermal conductivity could explain the enhanced ablation effect on the surface of the QC rather then of the alloy. The alloy is a free-electron structure with high thermal conductivity. The QC has a more complex structure made of metal clusters in the form of small and large structures. These metallic aggregates are subunits built up as super-lattice structure which do not posses a metallic character. This hierarchy of clusters may account for the evolution of vacancy or other structured defects, by emitting the nearest-neighbor atoms which are more weakly bonded compared to those of perfect sites [13]. This mechanism of defects initiated by desorption and ablation may explain the low ablation threshold and fractionation of the QC with respect to the alloy [2]. The exponential power density law dependence, which is a measure of the ablation rate, shows distinct slopes for the two compounds (Fig. 1 and Table 1) below the first roll-off. The slope is greater for the QC than for the alloy. This may be due to two factors: the first is the energy dissipation behavior mentioned above and the second is the electronic mechanism of non-thermal bond-breaking, which can be faster than that caused by thermal evaporation. The ablation rate is almost invariant in the intermediate power density regime, which supports the hypothesis of an inverse *bremsstrahlung* mechanism above the roll-off point. The laser-induced plasma may be shielding the laser beam when there is a large removal of material.

Another critical point is observed at approximately 0.9 GW/cm^2 for both samples, when the ablation rate increases sharply. Such a sharp increase has been interpreted as a phase explosion regime with ejection of particulate in the vapor [14]. However, in previous work, the phase explosion threshold was at a factor of 2 greater than the current measurements.

Table 1
Summary of the results of Fig. 1

	Roll-off (GW/cm^2)	Roll-up (GW/cm^2)	N[a]
QC crater threshold of 0.05 GW/cm^2			
Al	0.038	0.9	1.87
Cu	0.030	0.9	2.50
Fe	0.035	0.9	1.80
Alloy crater threshold of 0.135 GW/cm^2			
Al	0.06–0.07	0.9	1.6
Cu	0.07	1.0	1.91
Fe	0.08	1.0	1.6

[a] N is the exponent of the mass-intensity per unit area (Y) vs. power density (Φ) fitting: $Y = A\Phi^N$.

3.2. Al/Cu ratio for the alloy and the QC, and numerical calculations

The Al/Cu ratio from laser desorption–ablation of the Al–Cu–Fe alloy and QC targets are reported in Fig. 2. The horizontal dotted lines indicate the actual Al/Cu ratio in the bulk alloy and the QC from the analysis of the stoichiometric solutions. An invariance of the ratio, over the entire irradiance range, was measured for the alloy. The ratio from the experimental data is approximately 3.5, corresponding to the value of the calibration solution. Over the same power density range, the QC shows a lower value than the

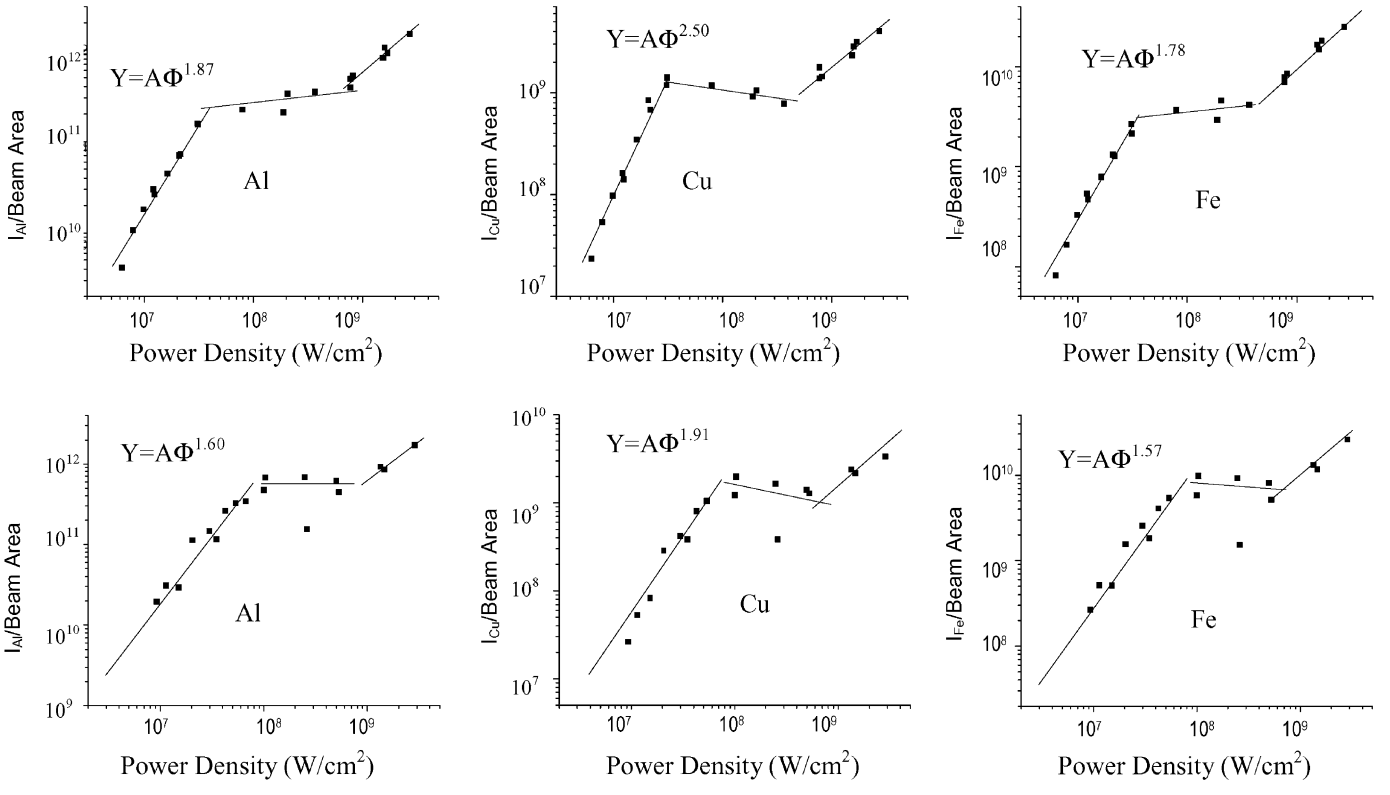

Fig. 1. ICP-MS intensity normalized to laser beam area as a function of the measured power density during a single nanosecond Nd-YAG laser pulse desorption–ablation of the Al–Cu–Fe alloy and QC, $\lambda = 266$ nm. Data show different rate behavior of the two samples in the three power density regimes.

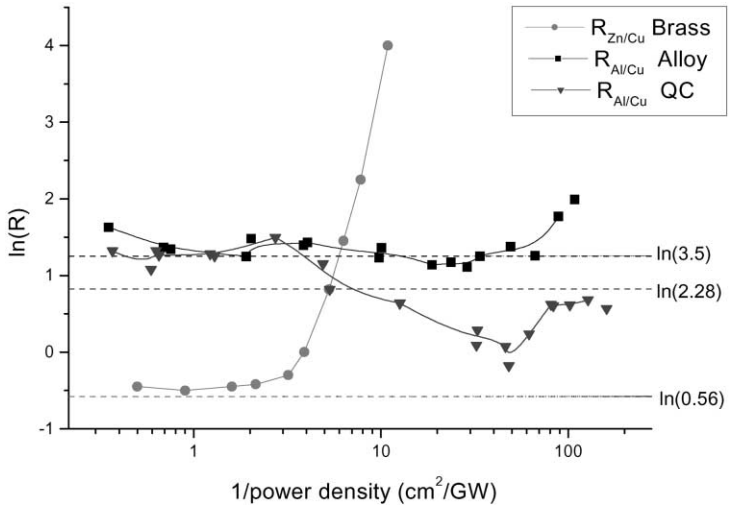

Fig. 2. The Al/Cu ratio measured by ICP-MS as a function of the laser power density for the Al–Cu–Fe alloy and QC during a single nanosecond Nd-YAG laser pulse; (●) Zn/Cu from [12].

stoichiometric Al/Cu ratio, which stabilizes above the bulk stoichiometric composition 2.28 at a laser density higher than 0.1 GW/cm^2.

The laser desorption–ablation trend for the ratio of the two components in the alloy has been treated on the basis of a *thermal* vaporization mechanism. The material optical and thermal properties, and the laser irradiance (power density) all are important parameters that affect the process. Pulsed laser ablation of metals has been treated in terms of a thermal vaporization process for the absorption, heat and dissipation of the laser energy in samples when the pulse laser duration is on the nonosecond time scale [4]. For picosecond and shorter pulse duration times, the metal must be looked at as a two-temperature system of electrons and lattice [5]. In this time scale, electron–phonon termalization 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 and 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 temperatures of the metals as shown in the following equations.

The rate of change of $R_{\mathrm{Al/Cu}}$ with temperature is mainly due to the difference of the heats of vaporization of the two species [15,16]:

$$\ln(R_{\mathrm{Al/Cu}}) = \text{const.} + \frac{\Delta H^{\mathrm{v}}_{\mathrm{Cu}} - \Delta H^{\mathrm{v}}_{\mathrm{Al}}}{RT} \tag{1}$$

where const. is a parameter not depending on temperature:

$$\text{const.} = \ln\left(\frac{\chi_{\mathrm{Al}} M^{0.5}_{\mathrm{Al}}}{\chi_{\mathrm{Cu}} M^{0.5}_{\mathrm{Cu}}}\right) + \frac{\Delta H^{\mathrm{v}}_{\mathrm{Al}}}{RT^{\mathrm{b}}_{\mathrm{Al}}} - \frac{\Delta H^{\mathrm{v}}_{\mathrm{Cu}}}{RT^{\mathrm{b}}_{\mathrm{Cu}}} \tag{2}$$

where χ is the molar fraction, M the mass of the atom, ΔH^{v} the latent enthalpy of vaporization and R the gas constant. The thermodynamic Al/Cu ratio has been calculated by using the parameters of Al and Cu as reported in Table 2.

Table 2
Thermodynamic properties of the metals employed in the calculations (The data are from C.D. Hodgman, Handbook of Chemistry and Physics, The chemical rubber publishing, Co., 1995.)

	T_{m} (K)	T^{b} (K)	ΔH^{v} (kJ/mol)
Al	659	2740	293.4
Cu	1082	2840	300.3
Fe	1535	3023	349.6
Zn	693	1180	115.3

The heat of vaporization ΔH^{v} of Al and Cu are almost the same with a difference of only 7 kJ/mol. The boiling temperatures T^{b} of the two metals are different by 100 K. 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 Raoult'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. In the previous work on a brass alloy containing Zn and Cu, which have very different heats of vaporization ΔH^{v}, a large change of $R_{Zn/Cu}$ ratio with power density was measured in the low laser power density regime. The calculated curve closely fits the experimental data [12].

At high power density, above the roll-off point (0.5–0.9 GW/cm^2), there is a possibility of two effects. First, the increased power density and thus the temperature should increase the amount of material evaporated. Second, laser shielding by the plasma causes a reduced ejection of material in comparison with that predicted by the thermal approach. The final result is the invariance of material removed and also of the Al/Cu ratio.

A thermal model does not describe the experimental Al/Cu ratio data of the QC. At low laser 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/cm^2. At high power density, the Al/Cu ratio is higher than the stoichiometric value of 2.8. This trend of the Al/Cu ratio in the QC may be related to bonding and antibonding orbitals in the quasicrystalline 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 is much lower than that of pure aluminum, supporting the view that a large number of defects is present in this material. Defects are storage sites that concentrate absorbed energy in localized modes, thus increasing preferential bond-breaking [1]. This may also explain why a non-thermal process takes place using a nonosecond laser pulse duration.

4. Conclusion

This work studied the laser–solid interaction of the intermetallic Al–Cu–Fe alloy and related QC. The ICP-MS technique was demonstrated as a suitable technique for analysis of the vapor products from the desorption and ablation over a wide range of power density, and particularly in the very low range. The experiments showed a marked diversity of these two systems that may be described by the following characteristics: ablation rate, roll-off point, crater threshold and component ratios. In the low power density desorption regime, only a small amount of material was removed. In this regime there was a marked difference in the behavior of the two materials. This is to be expected on account that the physical properties of the two materials do not change during the single low power nonosecond laser pulse. At higher laser power, a phase transition may occur in the QC and the ablation process may 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 [17]. 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 [18]. 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 QC is typically a surface phenomenon, whose features are extended from the bulk structure to the surface [19].

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