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Pulsed laser ablation of Al–Cu–Fe quasicrystals

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Abstract

Quasicrystalline Al_{65}–Cu_{23}–Fe_{12} targets have been ablated by a doubled Nd:YAG laser and deposited on silicon substrates. The results show evidence of distinct ablation mechanisms, which lead to different gas phase composition, as a function of the laser fluence. Films containing the quasicrystalline phase can be deposited only at fluences higher than about 6.5 J/cm^2 while at lower fluences the aluminium content exceeds the stoichiometric value. The films obtained by laser ablation of quasicrystalline Al_{65}–Cu_{23}–Fe_{12} were compared with those obtained from the metallic alloy Al_{70}–Cu_{20}–Fe_{10}. The differences between the two systems could be explained on the basis of the low thermal conductivity of the quasicrystalline phase.

Keywords: Quasicrystals; Laser ablation; Film deposition

1. Introduction

Quasicrystals are new compounds with interesting properties from both chemical–physical and technological points of view. Their main characteristics, related to their peculiar crystallographic structure, are low thermal conductivity and high hardness [1,2]. However, given that they are brittle materials they are usually employed as film coatings.

As a consequence, we have studied the possibility of exploiting pulsed laser ablation and deposition (PLAD) technique to obtain thin films of a quasicrystalline system on a suitable substrate. Only two papers are reported in literature on this subject: the first reports the successful deposition of Al–Pd–Mn by excimer laser ablation [3], while the other, which refers also to the Al–Cu–Fe system, obtains, however, completely negative results [4]. In neither case studies of the gaseous phase were reported. In this work, we have analysed the whole ablation process with the aim on clarifying its mechanism and the deposition conditions.

2. Experimental

The ablation targets were quasicrystalline Al_{65}–Cu_{23}–Fe_{12} and the metallic alloy Al_{70}–Cu_{20}–Fe_{10}, supplied from Ames Laboratory, Iowa State University, USA.

The laser ablation deposition was performed in a vacuum chamber equipped with a rotating target support and a substrate holder, which can be resistively heated up to 800°C and cooled up to −196°C by

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a liquid nitrogen cryogenic system. An N:YAG laser ($\lambda = 532$ nm, $\tau = 10$ ns, repetition rate $= 10$ Hz) beam was focused onto the target at normal incidence. The chamber was kept under dynamic vacuum (1.5×10^{-4} Pa) during the ablation process. An ICCD camera (Princeton, 20 ns time resolution) was used to study the dynamics of the ablated material. The optical emission of the plume has been collected and analysed by an optical multichannel analyser OMA III (EG&G), equipped with a 30 cm monochromator. The ions produced during the ablation were analysed by a LAMMA 500 system (Leybold) which was also used for the quantitative analysis of the gaseous phase. Scanning electron microscopy (SEM, Stereoscan 250) was used to study the film morphology, coupled with EDX microanalysis, while X-ray diffraction (XRD), utilising Cu Kα radiation, was used for structural analysis.

3. Results and discussion

The ablation rate, measured as target weight loss, for the Al_{65}–Cu_{23}–Fe_{12} system is reported in Fig. 1. There is a clear evidence of different trends as a function of the laser fluence that presumably may be attributed to different ablation mechanisms.

We can roughly divide the fluence range into two zones, called low and high fluence, respectively, with a separation line centred at about 5.5 J/cm^2 (between 4.5 and 6.5 J/cm^2). If our hypothesis about different ablation mechanisms was correct we would expect some differences in the gas phase coming from the ablation in the two fluence regimes.

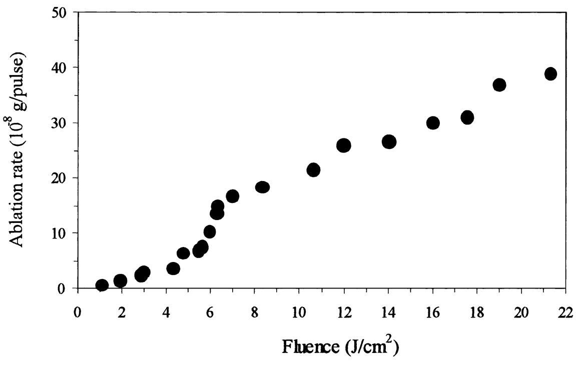

Fig. 1. Ablation rate of the quasicrystalline target.

Table 1
Gas phase composition from the ablation of a quasicrystalline target, at two laser fluences

	Target	Gas phase	
		6.0 J/cm^2	20.0 J/cm^2
Al (%)	65.0	72.0	65.5
Cu (%)	23.0	18.8	22.5
Fe (%)	12.0	11.2	12.0

The results obtained from emission spectroscopy show only the presence of neutral and ionised Al, Fe and Cu species without any difference related to the laser fluence. ICCD imaging as well shows no differences in the shape and velocity of the plume for different fluences. In contrast, after proper calibration procedure, time-of-flight mass spectrometry detects the ions present within the plume revealing each single target element, with the relative intensity strictly related to the laser fluence. Consequently, a quantitative analysis performed in this way, is reported in Table 1 for two values of fluence, one in the low fluence zone and another in the high. It is evident that the composition of the plume in the first zone is richer in aluminium in respect to the target, while in the second zone, it is practically stoichiometric. Among the elements present in the target, aluminium has the highest vapour pressure, so the presence of a high content of this element in the plume could indicate a thermal ablation mechanism.

The elemental composition of the deposited films, obtained by EDX, confirms our considerations. In fact, as shown in Table 2, the films deposited at low laser fluence have a high content of aluminium, while those deposited at high fluence are completely stoichiometric. In Table 2 the results from the ablation of a Al_{70}–Cu_{20}–Fe_{10} target, with a composition close to the quasicrystal one, but with the properties of typical metallic alloys, are also reported.

The ablation of the Al_{70}–Cu_{20}–Fe_{10} target has been carried out in order to understand if the fluence dependent behaviour is related just to the peculiar properties of quasicrystals or if it belongs to every system with a similar composition. The data so obtained have highlighted that the deposits obtained from the metallic alloy ablation do not show any composition dependence from the laser fluence and in all cases they result to be richer in aluminium than

Table 2
EDX analysis of films deposited from quasicrystalline and metallic targets

	Al_{65}–Cu_{23}–Fe_{12}			Al_{70}–Cu_{20}–Fe_{10}		
	Target	Film (6.0 J/cm^2)	Film (21.3 J/cm^2)	Target	Film (3.5 J/cm^2)	Film (15.0 J/cm^2)
Al (%)	66.0	76.2	66.5	70.0	78.0	78.5
Cu (%)	22.4	16.2	22.4	20.0	15.0	14.4
Fe (%)	11.6	7.6	11.3	10.0	7.0	7.1

the target. An explanation of the different behaviour of Al_{65}–Cu_{23}–Fe_{12} and Al_{70}–Cu_{20}–Fe_{10} targets under laser action can be related to the great difference in the thermal conductivity between the two systems. In fact, the thermal conductivity of the quasicrystal is very low compared with that of a metallic alloy [5] and this characteristics could allow the system towards a more rapid increase of the local temperature, leading to a non-thermal ablation mechanism. Differences in the ablation plume composition have been already found for other systems, such as brass [6], by varying the laser fluence, but only for very high values of the fluence itself the vaporisation was found to be congruent. The low thermal conductivity of Al_{65}–Cu_{23}–Fe_{12} could allow the system to reach the congruent non-thermal vaporisation regime at fluences significantly lower than conventional metallic alloys. If our interpretation was correct, at fluences higher than 6.5 J/cm^2 it should be possible to deposit quasicrystalline films. Consequently we have deposited in these conditions a large number of films, varying the substrate temperature from -196 up to 400°C, and we have analysed them by X-ray diffraction. In Fig. 2 the X-ray diffraction spectrum of a film deposited at room temperature is shown and we can see the presence of two peaks belonging to the Ψ quasicrystalline phase together with a peak corresponding to a β crystalline phase [7]. Lower and higher substrate temperatures seem to influence negatively the growth of the quasicrystalline phase.

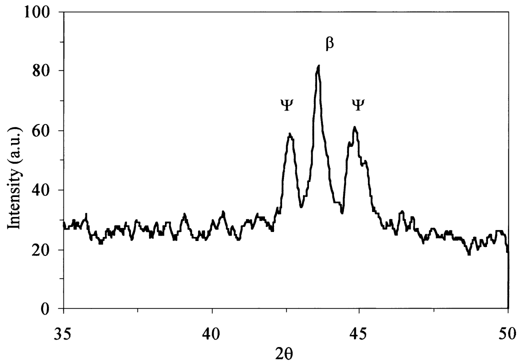

Fig. 2. X-ray diffraction spectrum of a film deposited at a laser fluence of 21.3 J/cm^2 with the substrate kept at room temperature.

4. Conclusions

In conclusion, we have shown that it is possible to deposit Al_{65}–Cu_{23}–Fe_{12} thin films with the presence of a quasicrystalline phase by PLAD, but only if the laser fluence is higher than about 6.5 J/cm^2. Below this threshold the vaporisation is not congruent and the deposits are all aluminium-rich metallic films. The congruent vaporisation of the quasicrystalline target seems to be related to its low thermal conductivity, which allows a rapid rise of the local temperature. The quasicrystalline phase is not the only phase present in our films, so further studies are needed to improve the film quality from a structural point of view.

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