

## Complex dynamics of laser-produced plasma on high-entropy alloy

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### Abstract

High-entropy materials (HEMs) represent an innovative class of multi-principal element systems that enable the exploration of a wide range of tunable properties within a single material platform. The fabrication of high-entropy alloy (HEA) thin films using plasma-based techniques offers scalable routes to control microstructure, morphology, and functional characteristics through a deep understanding of the plasma environment. In this work, we investigate the dynamics of laser-produced high-entropy plasmas using angle-resolved optical emission spectroscopy. The results reveal complex behavior, including selective acceleration and angular separation of plasma species, driven by differences in ionic nature and kinetic energy. The emission spectra exhibit a rich composition of nanoparticles, neutral atoms, and highly ionized ions, highlighting the intricate structure of the multielement plasma.

**Keywords:** optical emission spectroscopy, high-entropy alloy, laser produced plasma

### Introduction

The first successful demonstrations of high-entropy alloys (HEAs) and HEA thin films, nearly two decades ago [1], opened a new pathway for designing advanced materials, including metallic alloys, oxides, carbides, and nitrides. HEAs are typically composed of five or more principal elements, each in concentrations between 5 and 35 at.%, resulting in a high configurational entropy. This entropy stabilizes the formation of random solid solutions (SS) by lowering the Gibbs free energy, often suppressing the formation of ordered intermetallic phases. A distinctive feature of HEAs [2] is the local lattice distortion caused by atomic size differences among randomly distributed elements. This leads to a wide distribution of interstitial open volumes. The extent of distortion can be empirically described by the atomic size misfit parameter:  $\delta = \sqrt{\sum_i x_i (1 - r_i/\bar{r})^2}$  where  $x_i$  and  $r_i$  are the atomic fraction and radius of element  $i$ , and  $\bar{r}$  is the average atomic radius. Combined with slow self-diffusion, HEAs exhibit unique open-volume and defect structures compared to conventional alloys. HEA

coatings are primarily fabricated using magnetron sputtering (MS) [2] and pulsed laser deposition (PLD) [3], due to their ability to produce high-quality films. Understanding the influence of defects on physical properties is crucial, especially given the different growth regimes of MS and PLD.

In this work, we investigate the dynamics of laser-produced HEA plasma using angle- and space-resolved optical emission spectroscopy (OES). The results reveal complex behavior, including selective acceleration and angular separation of plasma species, driven by differences in ion nature and kinetic energy. OES analysis indicates a rich plasma composition, comprising nanoparticles, neutral atoms, and highly ionized ions, reflecting the complex dynamics of multi-element plasmas.

### Experimental details

Single round-shaped HfNbTiVZr target with a 1-inch diameter prepared via spark plasma sintering (SPS) from mixed powders of pure elements were used as targets. The SPS processing of both targets was performed at 1100°C for 2 min at a pressure of 80 MPa. Irradiation with a YAG laser (266 nm, 10 Hz, 5 ns) occurred under conditions similar to those of PLD, which involved continuous rotation of the target to provide a fresh surface for each irradiation pulse and to avoid crater formation or local heating. Each investigation was preceded by a cleaning procedure (1200 pulses at a 10 Hz repetition rate using a fluence of 4.3 J/cm<sup>2</sup>). The light emitted from the plasma was imaged via a spherical lens ( $f = 15$  cm) and transmitted through 19 optical fibre bundle placed in the focusing plane of the lens. An area of 1 mm<sup>2</sup> plasma emission was imaged on the optical fibre for every position of the fibre. Optical spectra were collected with an integration time of 10  $\mu$ s and averaged from 200 spectra by an iHR550 imaging spectrometer (Horiba) connected to an LN<sub>2</sub>-cooled Symphony CCD camera (Horiba) with 2048×512 pixels using 200–1000 nm using a 3600 mm<sup>-1</sup> grating and 250–750 nm using a 2400 mm<sup>-1</sup> grating.

### Results and Discussions

To better understand the structural composition of the HEA plasma with respect to the optimum deposition conditions, systematic plasma diagnostics were performed at a range of pressures and identical irradiation conditions (4.3 J/cm<sup>2</sup>). A representative spectrum is shown for the HfNbTiVZr plasma in *Figure 1 a*. Representative lines from all the components were observed at neutral (Hf\*– 706.4 nm; and Ti\*– 720.4 nm; Zr\*– 349.9 nm; Nb\*– 350.9 nm and V\*– 419.3 nm) and ionized (Hf<sup>+</sup>– 387.5 nm; and Ti<sup>2+</sup>– 335.8 nm; Zr<sup>+</sup>– 416.1 nm, Zr<sup>2+</sup>– 355.8 nm; Nb<sup>+</sup>– 374 nm, Nb<sup>3+</sup>– 334.5 nm and V<sup>+</sup>– 349.3 nm) states. Above 2 Pa or Ar, new emission lines were observed for the Ar species (Ar\* – 738.2 nm; Ar<sup>+</sup>– 368.2 nm, Ar<sup>2+</sup> – 375.6 nm). In the 300-500 nm spectral range an increase in background is noticeable. This feature is always

present in the plasma, regardless of the expansion conditions. The feature is attributed to the presence of heated nanoparticles and clusters which emit black body radiation. The background was fitted using Plank law and an 0.8 eV temperature was extracted. Notably, the presence of highly ionized states of  $\text{Nb}^{3+}$ ,  $\text{Zr}^{2+}$  or  $\text{Ti}^{2+}$ , which require ionization energies higher than 20 eV, is consistent with the  $\text{Ar}^{2+}$  ionization state, which requires 40 eV

In order to estimate the local thermodynamic equilibrium electron density needs to be above a certain threshold, expressed through McWhirter criterion [4]. In our case the LTE limit is around  $10^{15}\text{cm}^{-3}$ , regardless of the working pressure. Once established that the LTE model can be applied, the electron density can be estimated from the Saha-Eggert equation [4] and the electron excitation temperature by Boltzmann Plot method, where the slope of this representation will give the excitation temperature, and its linearity or the deviation from it is considered as an indication of LTE validity (an example can be seen in *Figure 1b*). A unique feature of the Ar lines is represented by a slight blue shift, due to the Ar ions encountering high-energy metal ions from the HEA plasma. Therefore, the plasma contains high ionized species, with thermal and kinetic energy. The high-energy deposition can lead to the deposition of polycrystalline films without supplementary heat treatment of the substrate. By changing the position of the 19 vertical fibre bundle at various positions in the plasma volume, the emission of each species was reconstructed. An example is given in *Figure 1c* for the Hf I line. The emission is seen to be focused in 30 degrees with respect to the main expansion axis while the spatial distribution reveals on plasma structure, thus stoichiometric films can be produced for a small area deposition. Finally, the impact of Ar addition on the expansion dynamics and thermal energy of the plasma, was investigated. The results are presented in *Figure 1d*. Both the electron excitation temperature and the electron densities, calculated at 2 mm from the target, follow a similar dependence on the Ar pressure with a steep increase up to 2 Pa followed by a quasi-saturation regime. The change at 2 Pa coincides with the appearance of multiple Ar species in the plasma and thus, the background gas becomes an active part of the deposition process.

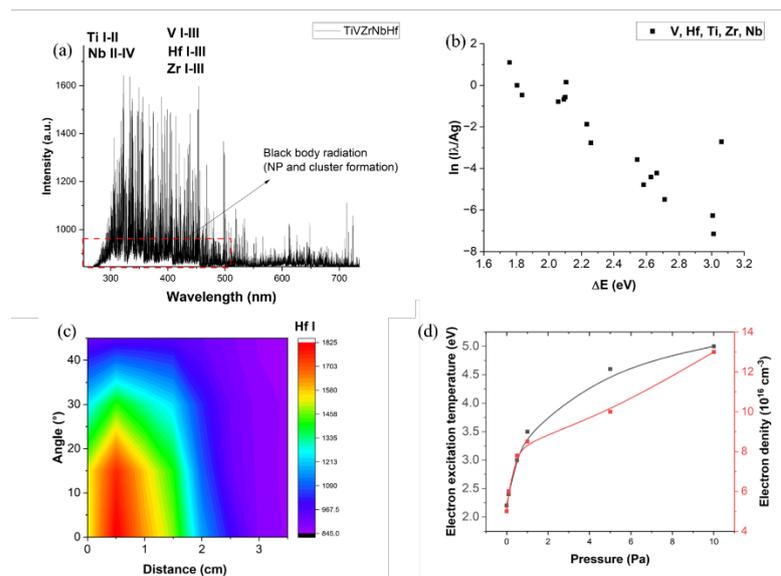


Figure 1. Optical emission spectra recorded with a 10  $\mu\text{s}$  gate with in  $10^{-5}$  Pa of a HEA laser produced plasma (a) the Boltzmann Plot associated with the spectra (b) the angle and space resolved emission mapping of Hf I – 706.4 nm (c) and the Ar pressure effect on the electron density and the electron excitation temperature (d)

## Conclusions

Laser ablation of the SPS-prepared HfNbTiVZr high-entropy target generates a plasma rich in both neutral and highly ionized metallic species alongside  $\text{Ar}^{2+}$  at higher pressures. A broad emission background attributed to blackbody radiation from heated nanoparticles ( $\sim 0.8$  eV) was consistently observed. Angular-resolved optical emission revealed that all elemental species follow a similar expansion profile ( $\sim 30^\circ$  off-axis), suggesting uniform composition across the plume. This spatial consistency supports the potential for stoichiometric thin film deposition in targeted regions. Varying the Ar background pressure revealed a transition in plasma properties: both electron temperature and density increase steeply up to 2 Pa, followed by saturation.

**Acknowledgement :** This work was supported by the NATO grant SPS MYP G6153.

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