Data Article

Data on nitridation effect of AlTiTaZrHf(-N) high entropy films by X-ray photoelectron spectroscopy

Mohamed El Garah a,b,*, Djallel Eddine Touaibia a,b, Sofiane Achache a,b, Alexandre Michau d, Elizaveta Sviridova c, Pavel S. Postnikov c, Mohamed M. Chehimi e, Frederic Schuster d, Frederic Sanchette a,b

a LASMIS, Pôle Technologique de Sud – Champagne, Antenne de Nogent – 52, Nogent 52800, France
b Nogent International Center for CVD Innovation (NICCI), LRC CEA-LASMIS, Pôle Technologique de Sud – Champagne, Nogent 52800, France
c Research School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University, Tomsk 634050, Russia
d Commissariat à l’Energie Atomique et aux Énergies Alternatives (CEA) Saclay, Gif-sur Yvette 91191, France
e ITODYS, CNRS, UMR 7086, Université de Paris,15 rue JF de Baïf, Paris 75013, France

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A B S T R A C T

The data presented in this article are related to the published research of “Effect of nitrogen content on structural and mechanical properties of AlTiZrTaHf(-N) high entropy films deposited by reactive magnetron sputtering”. This database contains X-ray photoelectron spectroscopy (XPS) measurements, performed in order to determine the extents of nitrides formed in AlTiTaZrHf high entropy films. The latter were prepared by DC magnetron sputtering technique in reactive mode by adding the nitrogen to argon gas. The nitrogen flow rate is calculated by \( R_{N2} = \frac{N2}{(N2+Ar)} \). XPS measurements were done one month later. Oxides were detected on the top surface of the samples. 2p, 3d and 4f core level
peaks were fitted in order to determine accurately the chemical composition of the nitride films. Al2p, Ti2p, Zr3d, Ta4f, and Hf4f reveal the formation of nitrides of all elements constituting the films. Atomic percentage of each element was calculated revealing an increase of nitrogen loading and decrease of the metallic fractions of the elements as \( R_{\text{N2}} \) grows from 5% to 50%. Nitridation behaviour of each element, as a function of the nitrogen flow rate, is investigated and presented.

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## Specifications Table

| Subject | Type of data | How the data were acquired | Data format | Description of data collection |
|---------|--------------|----------------------------|-------------|--------------------------------|
| Materials Sciences | Table | XPS measurements describing the effect of nitrogen content from 0% to 50% on the surface chemical composition of AlTiTaZrHf high entropy film. | Additional analyzed data corresponding to fitted XPS peaks are available at the following link: https://figshare.com/s/a4d038f514016b19db6b | X-ray photoelectron spectroscopy (XPS) measurements were carried out using XPS instrument fitted with monochromated X-ray source. Measurements taken were XPS spectra with various conditions: pass energy/step size = 200/1 eV, and 40/0.1 eV, respectively. All spectra were checked visually, for the high signal-to-noise (S/N) ratio, at the end of each analysis run before removing the samples from the analysis chamber. For the peak-fitting, we used the constraints as follows: Shirley baseline, \( \pm 0.1 \text{ eV} \) for binding energy position, \( \pm 0.1 \text{ eV} \) for FWHM, and the Lorentzian to Gaussian (L/G) peak shape ratio was adjusted (in the 0–30% range). For the spin-orbit doublets Hf4f, Ta4f, Zr3d and Ti2p, we have considered the binding energy splitting as well as the theoretical peak area ratios expected for f, d, and p orbitals (4/3 for \( 4f_{7/2}/4f_{5/2} \); 3/2 for \( 3d_{5/2}/3d_{3/2} \); 2/1 for \( 2p_{3/2}/2p_{1/2} \). Taking into consideration the step size (0.1 eV) and setting the peak position to \( \pm 0.1 \text{ eV} \) in the course of the peak fitting, the accuracy could be estimated to \( \pm 0.2 \text{ eV} \). |
XPS data were processed without smoothing and without any static charge calibration, because the materials were electrically conductive. No C1s peak position was used for calibration. Note however that in the absence of any binding energy scale correction, the C1s peak from adventitious hydrocarbon contamination was found to be naturally centred at 284.8 eV [1].

Data source location

- Institution: LASMIS, Université de Technologie de Troyes, Antenne de Nogent – 52, Pôle Technologique de Sud – Champagne, 52800 Nogent, France.
- City/Region: Nogent/Grand Est
- Country: France

Data accessibility

Repository name: Figshare server.
Data identification number: 10.4121/19196615
Publisher: 4TU.ResearchData
Direct URL to data: https://figshare.com/s/a4d038f514016b19bd6b

DOI Related research article

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Value of the Data

- The data provide a deep understanding of the formation of nitrides of different elements constituting the high entropy films.
- The data give a detailed analysis on nitrogen-element bonds as nitrogen loading increases.
- It is useful to understand how nitriding occurs in the case of high entropy alloys.
- The data can be exploited to understand the nitriding effect of nitride-forming metal in high entropy materials field.
- These data can be highlighted with other microstructural investigations for high entropy alloys.

1. Data Description

This article presents the data associated to published work on effect of nitrogen content structural and mechanical properties of AlTiZrTaHf(-N) high entropy films deposited by reactive magnetron sputtering [2]. The films are deposited on silicon wafers by using DC magnetron sputtering of 99.99% pure high entropy equiatomic AlTiTaZrHf alloy target. Deph4 (DEPHIS, Étupes, France) reactor equipped with 4 circular cathodes 200 mm in diameter has been used to prepare the films in reactive mode by changing the ratio of argon-to-nitrogen gas mixture. For more details, the preparation and investigations of all samples are presented in the published work [2].

Additional amazed data which correspond to the fitting of the peaks of all elements of XPS measurement are presented figshare sever. All these data are uploaded with excel files including then the fitting peaks of N1s, Al2p, Ti2p, Zr3d, Ta4h and Hf4f as a function of the nitrogen flow rate (RN2 varies from 5 to 50%). A table of all parameters (peak position, FWHM, intensity, etc.) of each fitting for each peak is provided. The data are accessible with the following link: https://figshare.com/s/a4d038f514016b19bd6b.

2. Experimental Design, Materials and Methods

XPS is a powerful tool to provide information on the composition and the relevant chemical bonds between the different elements in the top surface of materials. Fig. 1 presents survey XPS
spectra of all films from \( R_{N2} = 5\% \) to 50\%. All elements of the present high entropy alloys are detected; namely, Hf, Ta, Al, Ti, and Zr. Nitrogen and oxygen signals are also found on the survey. The binding energy positions are compared to published articles and to XPS NIST data [3].

High resolution XPS N1s spectra are presented in Fig. 2. Fitting of high-resolution spectra of principal elements of the different films were carried out and the resulting binding energy positions compared to those reported in the literature. A large peak is found around 405 eV that is attributed to Ta4p [4]. From \( R_{N2} = 5\% \) to 50\%, the spectrum can be fitted into two peaks at 396.2 eV and 397.1 eV presenting the binding energy of nitrogen in a metal nitride state and oxide, respectively [2]. As the nitrogen flow \( R_{N2} \) increases, the first peak increases while the second one decreases (Fig. 2). More nitrides are formed according to the increase of the nitrogen flow rate in the gas mixture.

Fig. 3 shows the peaks of Al2p and Ti2p as function of \( R_{N2} \). The spectra of Al2p are fitted with three peaks. One at 71.9 eV attributed to the metal [5] and two others correspond to Al-N and Al-O between 74.2 eV and 75.2 eV, respectively [6]. As the nitrogen flow rate increases from 5 to 50\%, the peak of Al metal shows a small shift to the lower binding energy. In these conditions, the peak area of Al-N increases, as can be seen on the spectra in the Fig. 3. Ti2p XPS is composed by four spin-orbit doublets when \( R_{N2} = 5\% \). The Ti metal peaks are centred at 454.2 eV (Ti2p_{3/2}) and 460.0 eV (Ti2p_{1/2}), respectively. The nitride TiN is formed when the nitrogen is introduced. The components of Ti-N are found at 456.6 eV (Ti-N(Ti2p_{3/2})) and 462.4 eV (Ti-N(Ti2p_{3/2})). Intermediate states were also found and correspond to Ti-O-N, its components are at 457.8 eV (Ti-O-N(Ti2p_{3/2})) and 463.5 eV (Ti-O-N(Ti2p_{1/2})) [7]. As \( R_{N2} \) increases from \( R_{N2} = 20\% \) to 50\%, Ti is totally transformed to nitride and no metallic peaks is observed (Fig. 3). Besides, the peaks area of nitride (Ti-N) increases as the nitrogen ratio increases which means its content grows into the films.

Zr3d was fitted with three spin-orbit doublets at \( R_{N2} = 5\% \) and two spin-orbit doublets when \( R_{N2} \) increases from 20 to 50\%. Zr metal peaks are found at 179.1 eV and 18.6 eV for Zr3d_{5/2} and Zr3d_{3/2} respectively. Zr metal state is observed in the film at \( R_{N2} = 5\% \) and is characterized by two peaks at 179.1 eV and 181.6 eV for Zr3d_{5/2} and Zr3d_{3/2} respectively. After increasing the nitrogen, the metal components disappear, and nitrides are formed. Zr-N are presented by two
peaks at 181.9 eV for orbital 3d_{5/2} and 184.3 eV for orbital 3d_{3/2} [8]. When \( R_{N2} \) increases from 20% to 50%, the quantity of Zr-N increases in the films (Fig. 4).

Ta4f and Hf4f XPS spectra are plotted together and presented in the Fig. 4 (right side). At \( R_{N2} = 5\% \), the spectra of each element are fitted by three spin-orbit doublets. Ta metal components are found at 22.5 eV for orbital 4f_{7/2} and 24.4 eV for orbital 4f_{5/2} [9]. Ta-N is fitted with two peaks 4f_{7/2} at 24.9 eV and 4f_{5/2} at 26.8 eV [10]. As the nitrogen increases, a total transformation of Ta metal to nitride occurred. The peak areas of Ta-N increase when \( R_{N2} \) grows from 20 to 50%. In the case of Hf4f, the spectrum at \( R_{N2} = 5\% \) was fitted into Hf metal and nitrides (oxides are presents, green color). The peaks of Hf metal are fund around 14.6 eV and 16.3 eV for orbital 4f_{7/2} and 4f_{5/2} respectively. They disappear when \( R_{N2} \) increases from 20 to 50% and Hf-N nitrides are formed. The peaks of these nitrides are located at 15.9 eV for orbital 4f_{7/2} and 17.6 eV for orbital 4f_{5/2}.

Fig. 5 presents the evolution of nitridation effect of each element as a function of \( R_{N2} \). The atomic percentage was estimated from the fitting of all XPS data according to \( R_{N2} \). Two metals Ta and Hf show a quick increasing when \( R_{N2} \) increases from 5 to 20% followed by a stable evolution as \( R_{N2} \) continuous to grow from 20 to 50%. However, Ti behaviour under nitridation effect displays a very slight or even quasi-stable evolution as \( R_{N2} \) increases. A part of Ti-N is oxidised but the quantity of oxynitride decreases when \( R_{N2} \) increases. The Al element shows a percentage varying between 58.9 and 70% and is the first nitride element compared to others.
Fig. 3. Al2p and Ti2p XPS spectra of AlTiTaZrHf(-N) as a function of R_N2.
Fig. 4. Zr3d, Ta4f and Hf4f XPS spectra of AlTiTaZrHf(-N) as a function of $R_{N2}$. 
Fig. 5. Atomic percentage of individual elements of AlTiTaZrHf(-N) films as a function of $R_{N_2}$ according to XPS analysis.

After introducing a small amount of nitrogen ($R_{N_2} = 5\%$), Hf-N and Ti-N are found at low extents compared to the other nitrides Al-N, Ta-N and Zr-N. However, when $R_{N_2}$ increases, Ti-N and Al-N exhibit a quasi-stable evolution, whereas the quantities of other nitrides increase to reach the saturation point followed by steady state.

Ethics Statements

The data are the authors’ own original work, which have not been previously published elsewhere.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Raw data of XPS fitting (Original data) (4TU.ResearchData).

CRediT Author Statement

Mohamed El Garah: Conceptualization, Investigation, Formal analysis, Validation, Writing – review & editing, Writing – original draft; Djallel Eddine Touaibia: Writing – review & editing; Sofiane Achache: Writing – review & editing; Alexandre Michau: Conceptualization, Funding acquisition; Elizaveta Svirdova: Investigation, Methodology, Data curation; Pavel S. Postnikov: Investigation, Data curation; Mohamed M. Chehimi: Investigation, Formal analysis, Writing – review & editing; Frederic Schuster: Conceptualization, Funding acquisition; Frederic Sanchette: Conceptualization, Funding acquisition, Writing – review & editing.
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