Annals of the Academy of Romanian Scientists
Series on Physics and Chemistry
Online ISSN **2559 – 1061** Volume **10**, Number 1/**2025** 25

INVESTIGATION OF THIN FILMS PROPERTIES OF TITANIUM-BASED MATERIALS PRODUCED BY LASER INDUCED-THERMIONIC VACUUM ARC (LTVA) TECHNOLOGY - A REVIEW

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Rezumat. *Datorită proprietăților remarcabile conferite suprafețelor pe care le acoperă, nanocompozitele pe bază de titan au fost produse și investigate în diferite combinații și forme, cum ar fi compozitele de tip multicomponente. Combinațiile binare prezentate în acest studiu se referă la Ti:X (X=Ag, C, Cr), depuse prin metoda inovativă a arcului termoionic în vid indus de laser (LTVA). Filmele subțiri obținute au fost caracterizate prin microscopia de scanare (SEM), prin spectroscopia de raze X (EDX), microscopia de forță atomică (AFM) și microscopia de transmisie de electroni (TEM). Proprietatea de udabilitate a filmelor subțiri depuse de tip Ti:X a fost investigată prin metoda evaluării energiei libere de suprafață (SFE). Scopul acestui studiu a fost stabilirea potențialelor aplicații a filmelor pe bază de titan în nanoelectronică, energie, medicină și știința materialelor.*

Abstract. *Titanium based nanocomposites owing to their remarcable properties of the coating surfaces have been synthetized and investigated in different combination and forms, such as multi-component composites. The binary combination presented in this work will refer to Ti:X (X=Ag, C, Cr), deposited by the innovative Laser Induced-Thermionic Vacuum Arc LTVA method. The deposited thin films were characterized by means of a scanning electron microscope technique (SEM) energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), and transmission electron microscopy (TEM). The wettability of the deposited Ti:X thin films was investigated by the surface free energy evaluation (SFE) method. The purpose of our study was to prove the potential applications of Ti-based thin films in fields, such as nanoelectronics, fuel cells, medicine, and materials science.*

Keywords: TVA, titanium based nanomaterials, SEM, wettability, electrical properties.

DOI **10.56082/annalsarsciphyschem.2025.1.25**

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1. Introduction

Titanium is often called the metal of the future due to its varied properties and its important role in technological progress. Titanium exhibits outstanding corrosion resistance, excellent strength to weight ratio, high toughness superior biocompatibility and exceptional physicochemical properties due to its high specific strength. [1-3] Due to its uniqueness, titanium is used in a huge type of engineering applications, specifically with the aerospace, automotive, sporting goods, military, and biomedical fields. Each application requires unique properties. [4, 5]. For example, in aerospace applications, titanium alloys are preferred for their high strength-to-weight ratio and ability to withstand high temperatures. In the biomedical applications, the corrosion resistance and biocompatibility of titanium alloys make them suitable for implants and prosthetics. Furthermore, advancements in titanium alloy technology have led to their enhanced use in automotive applications, where their high strength and low weight. [6].

The trends illustrate a growing interest in developing new titanium-based materials and optimizing their properties. Ongoing research focuses on enhancing the corrosion resistance, mechanical properties, and manufacturability of titanium alloys. [7]. The purpose of future scientific research is to explore innovative alloying techniques and processing methods to expand the applications of titanium alloys further, in these conditions titanium mixed with other elements such as silver (TiAg), carbon (TiC) and chromium (TiCr) are of broad interest to the scientific community.

TiC exhibits high melting point, high hardness values and thermal stability, low friction coefficient, and high thermal and electrical conductivity. Because of their special properties, they are increasingly used as wear and corrosion-resistant films on cutting tools and diffusion barrier in semiconductor technology. Also, silver and its nanostructured material system has gained much attention because of its strong antibacterial and biomedical properties. Moreover, in wear situations, the incorporation of silver into Ti compounds can change their properties by acting as a solid lubricant. Chromium metallic thin films are now widely used in industries as hard coatings for wear and corrosion protection due to their high hardness, chemical stability, good wear resistance, and desirable color. [9-11]
Many methods of depositions have been studied, but still applying vacuum arc techniques to this field has been rarely reported, neither has the embracing of all these properties together.

The present paper is considered a review of the structural and morphological properties of the titanium films doped with silver, carbon and chromium using Thermionic Vacuum Arc (TVA) as the deposition method. Thermionic Vacuum Arc remains one of the best versatile method for obtaining not only metallic thin films, [12-22] but also for multicomponent processing, such as alloy/composite thin films at a nanometric scale. [23-26] An overview of the capabilities of the TVA method is presented in references [27]

An improved laser-induced TVA (LTVA) method favors the crystallization processes of the deposited titanium-based films. The new technology will provide an experimental setup procedure by optimizing the implemented LTVA technology for thin film deposition as an algorithm for enhancing the properties of deposited thin film due to photonic processes. Reported in this study are the data for the grain size nanostructures, atomic percentage, elements distribution, and free surface energy evaluation for understanding the complex nanocrystalline structure with varying features depending on the introduced element (Ag, C, Cr). The direct applications are related to the use of these elements with titanium phase for coating components with high corrosion/wear resistance, high hardness, electrical properties and good adherence especially for gear wheels and camshaft coating as mechanical components of irrigation pumps.

2. Experimental set-up

Titanium-based composites were prepared using the TVA/LTVA method in one electron gun configuration on glass and silicon substrates. In the classical TVA method, the cathode consisted of a heated tungsten filament, mounted inside a molybdenum Wehnelt cylinder. The anode is a carbon crucible, filled with a mixture of Ti and another element (X), where X means Ag granules (99.9% metal basis) [28], C powder (99.9% purity) [29] or Cr granules (99.8% min) or in a weight ratio of Ti:X =1:1. The samples were prepared following essentially the same technique as described in Ref. [30]. By increasing the values of the high-power supply up to the breakdown voltage, a bright plasma discharge ignited.

In the LTVA configuration, an adjustable power laser beam provided by a QUANTEL Q-Smart 850 Nd:YAG compact Q-switched laser coupled with a second harmonic module is applied in the middle of plasma already created, inside the vacuum chamber. [31] It is important to point out that the laser beam does not touch the bulk material from the anode directly as in the case of the Pulsed Laser Deposition (PLD) method. The main parameters for the growth of the thin films are presented in the Table I. The schematic illustration of the TVA/LTVA experimental arrangements in comparison is presented elsewhere. [32].

Table I. The main parameters of the thin films deposition

- **I_f** - the intensity of the current necessary for the filament heating
  $I_f = 57$ A
- **U_a** – the applied voltage for the ignition
  $U = 1{,}2$ kV
- **I_a** – the intensity of the arc current before the plasma ignition.
  $I = 390$ mA
- **P** – Power of the laser
  P= 50mJ/ P= 102 mJ
- **p_1** - pressure before to start the deposition ()
  $p_1 = 4{,}1 \times 10^{-6}$ Torr
- **p_2**- work pressure during deposition
  $p_2 = 1{,}5 \times 10^{-5}$ Torr
- **t**-the film thickness measured on situ
  t = 100 nm
- **τ**-the film growth time
  τ = 210 s

As an example, in Fig. 1 three photos of the TiCr were captured during the deposition with different laser powers, a) in TVA where the laser was off, in LTVA b) P= 50mJ and c) P= 102 mJ.

TVA P=0 mJ	**LTVA** P= 50 mJ	**LTVA** P= 102mJ

Fig. 1. Photos captured during TiCr thin films deposition by TVA/LTVA methods

The surface morphology of the obtained multifunctional titanium based thin films were investigated using Scanning Electron Microscopy (SEM), wettability by SEE System, and electrical properties by Ossila system.

3. Results and discussions

Scanning Electron Microscopy (SEM)

SEM images were performed using a Scanning electron microscope EVO 50 XVP (Carl Zeiss NTS) with EDX attachment (Bruker). Based on the SEM images, the equipment can generate characteristic X-ray, secondary and back-scattered electrons. The scanning electron microscopy (SEM) images of the surface morphology of Ti:Ag and Ti:C thin films grown on a silicon substrate are shown in Figs 2 and 3, respectively.

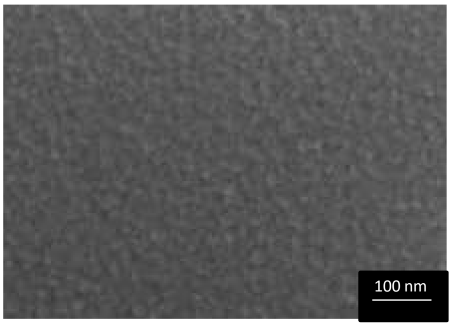

Fig. 2. SEM image for TiAg, thin films deposited on glass

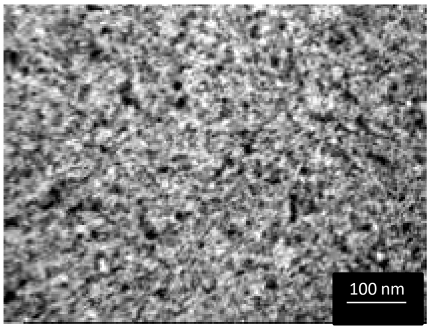

Fig. 3. BFTEM images for TiC, thin films deposited on glass

It can be seen that the TiAg film was homogeneously and uniformly coated on the on glass without delamination from the substrate. The homogeneity of the TiC coated film surface was lower than that on other substrates, but it is an inherent feature of the films containing carbon.

In Fig 4 a comparative view of TiCr films is presented, by different points of view: SEM images, roughness, and the distributions of the grain size. The Ti:Cr thin film surface prepared using LTVA looks smooth, proving it has superior deposition characteristics compared to the TVA method. Using an electron beam voltage of 5 kV, the lower electrical conductivity of the TVA sample leads to electrical charging of the surface revealing the higher conductivity of the LTVA sample. Also, the images reveal the higher roughness of the TVA sample than one of the LTVA samples, which shows a smoother surface. According to the histogram of the LTVA sample, the nonsymmetric distribution is centered at 18 nm due to the laser beam interaction with the plasma, but their number is increased to around 5000 counts with a half-width value of 3 nm. The photonic processes induced effects that produced more nanoparticles in the LTVA sample but were more compact and uniformly distributed.

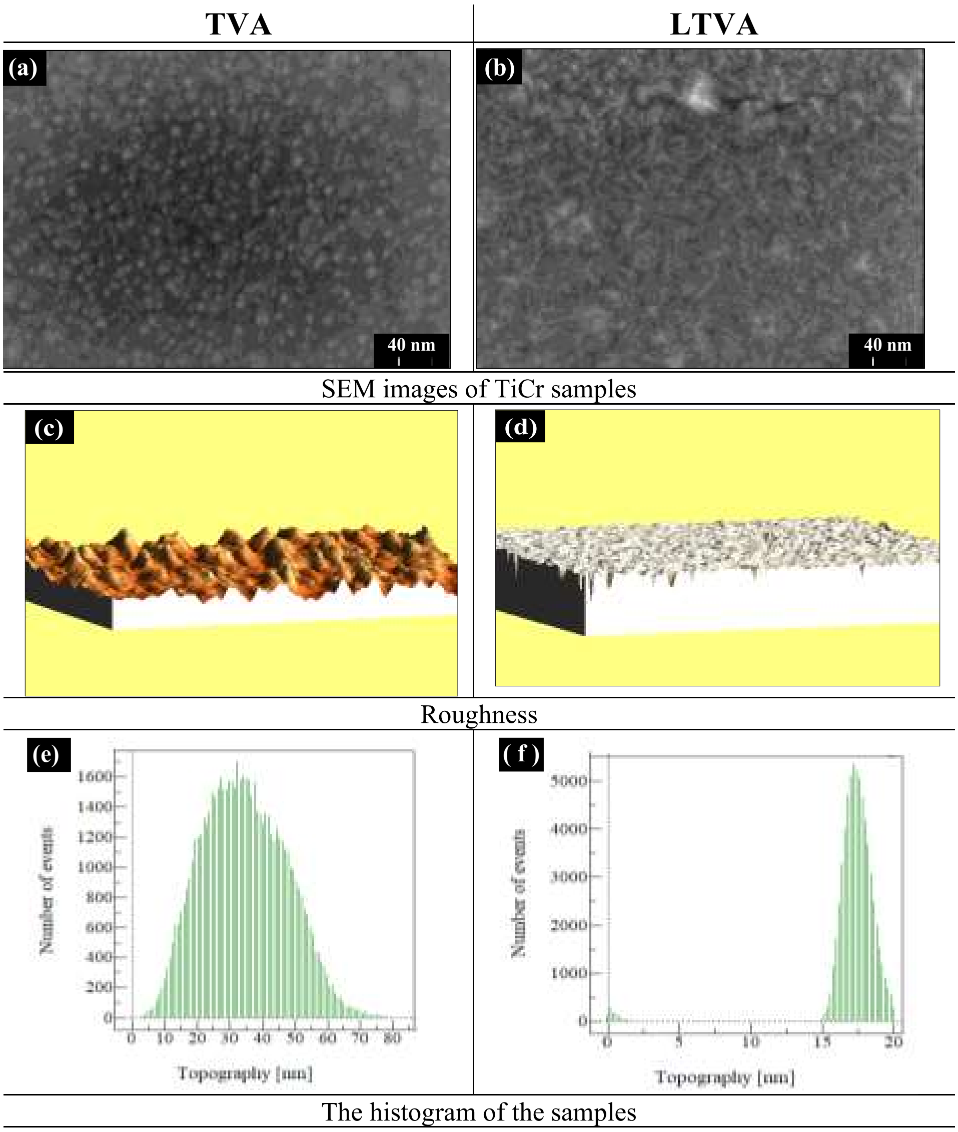

Fig.4. SEM image of TiCr sample a) TVA and b) LTVA; Roughness c) TVA and d) LTVA; Histogram e) TVA and f) LTVA Adapted from Ref [31].

Moreover, the TiCr thin films deposited by LTVA method were irradiated under very low-energy primary electron beams accelerated up to 300V (below500 eV), the irradiation setup and details of the procedure being presented in Ref [33].

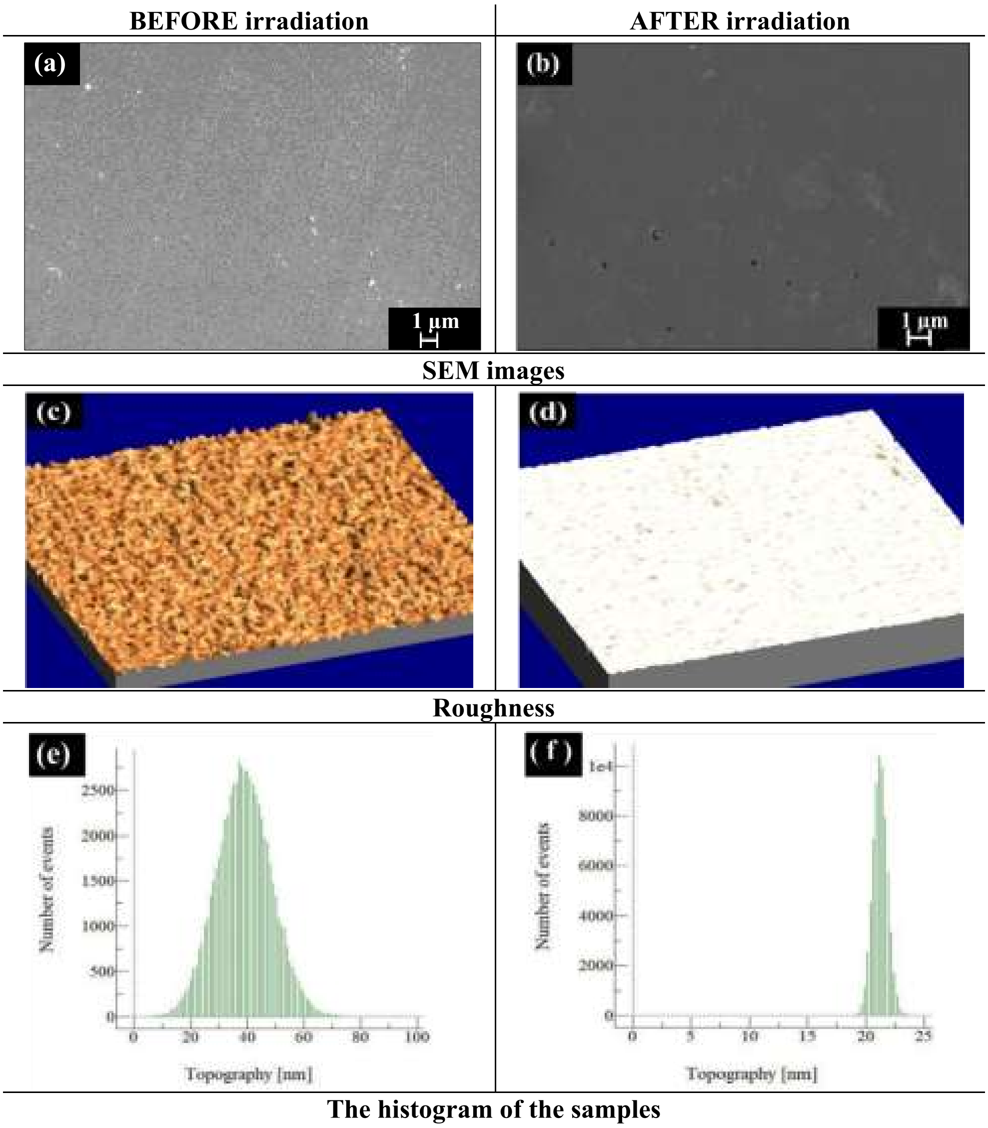

Fig.5. Results of the chracterization of the TiCr deposited by LTVA before and after irradiation. Adapted from Ref [33].

The effects were monitored before and after electron irradiation for comparison in Fig. 5. The profile analysis of these 3D cross-sections on the Z-scan, reveals a decrease in the roughness up to half after the low energy electron irradiation. A close inspection of the roughness significantly reveals modification: a smoother surface after the irradiation procedure than a disordered surface before it. Meanwhile, the histograms reveal the same reduction of roughness from 40 nm before to 17 nm after irradiation.

Electrical Measurements

The voltage–current curves for the TVA and LTVA samples (Fig. 6), which account for the voltage in the inner electrodes versus the current in the outer electrodes, reveal the lower resistivity of the LTVA samples (ρ =6.08.5x10^{-7} Ωm) compared to the TVA sample resistivity (ρ =10.4.5x10^{-7} Ωm). Both films have higher resistivity than the bulk resistivity value for the chromium element ρ =1.2.5x10^{-7} Ωm.

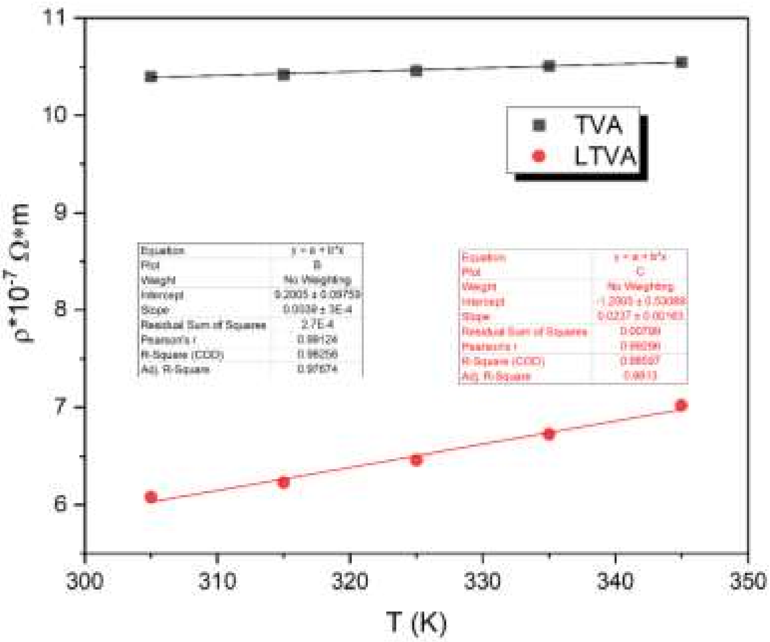

Fig. 6. Resistivity vs temperature for TiCr samples deposited by TVA and LTVA. Adapted from Ref [31].

Wettability

Materials wettability is a characteristic parameter that influences surface related processes such as adhesion [34] The contact angle measurements have been determined by means of Surface Energy Evaluation System (SEE System). By this measurement, we can evaluate the hydrophilicity or hydrophobicity of a thin film by investigating the tangent angle between the solid-vapour interface and liquid-solid interface. The testing liquids were water and ethylene glycol, and the contact angle results and captures of the drops are presented in **Fig. 7**.

According to the obtained data, for water contact angle, TiC (θ_w=53.7°) and TiAg (θ_w=56.43°) thin films showed a hydrophilic character [35] while the TiCr-TVA (θ_w=90.6°) and TiCr-LTVA (θ_w=100.48°) thin films the surface has a hydrophobic character. For the thin films obtained by LTVA method, the contact angle has a higher value and this shows the impact of the laser energy during the thin film formation.

Ti and Ag have a high influence over the character of the surface, considering that in a previous study, using the same deposition technique and the same measuring method, we found for the C thin films a contact angle of 100° and a hydrophobic character of the surface.

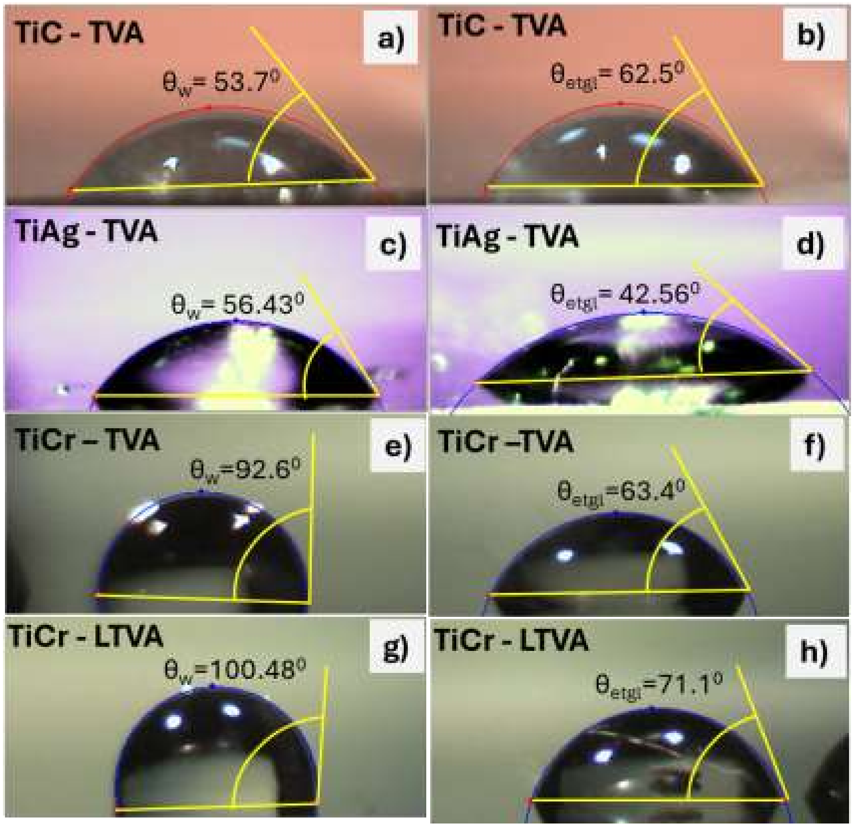

Fig. 7. Contact angle values and drop captions of the TVA and LTVA thin films measurements Adapted from Ref [25, 31, 35].

Conclusions

These results confirm that the thermionic vacuum arc technology as a deposition process is an efficient method to improve the comprehensive properties of titanium-based films, which act as candidate material for protective coatings. But in the same time, they validate the superior characteristics of the Laser-Induced Thermionic Vacuum Arc method such as: the lower roughness of the samples obtained using the LTVA method revealed by the SEM images and the higher conductivity of these samples. The laser-induced TVA method does not influence the doping process with the titanium ions, but, just for a small quantity of Ti, the obtained thin films show uniform and superior characteristics.

The SEE System reveals hydrophobic properties correlated to the topography. In this way, the study the structural and morphological properties of the titanium films doped with Ag, C and Cr by Thermionic Vacuum Arc/LTVA method would promote applications related to the use of these combinations for coating components. It helps to predict the course of reaction during the chemical processing of surfaces in a liquid environment (washing, dyeing), as well as when producing good mechanically resistant composite materials, with requested defined high corrosion/wear resistance, generated by specific grain sizes.

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