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Estudo da liga Ti-15Nb com reforço *in situ* de TiC e TiB para combinar baixo módulo de elasticidade com alta resistência ao desgaste visando aplicações biomédicas

Bauru
2025

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Trabalho de conclusão do curso de graduação em Bacharelado em Física de Materiais da Faculdade de Ciências da UNESP – Campus Bauru, como requisito para a obtenção do Título de Bacharel em Física de Materiais.
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ATA DE DEFESA PÚBLICA DO TRABALHO DE CONCLUSÃO DE CURSO

Aos 08 dias do mês de dezembro de 2025, às 14h00, em sessão pública em formato presencial\virtual via Google Meet, na presença da Banca Examinadora presidida pelo **Prof. Dr. Diego Rafael Nespeque Correa** e composta pelos examinadores **Dr. Rafael Formenton Macedo dos Santos** e **Dra. Mariana Luna Lourenço**, o aluno **Carlos Eduardo da Silva** apresentou o trabalho de conclusão de curso intitulado: **"Estudo da liga Ti-15Nb com reforço in situ de TiC e TiB para combinar baixo módulo de elasticidade com alta resistência ao desgaste visando aplicações biomédicas",** como requisito curricular indispensável para a integralização do curso de Física – Bacharelado em Física de Materiais. Após reunião em sessão reservada, a Banca Examinadora deliberou e decidiu pela **aprovação** do referido trabalho, divulgando o resultado formalmente ao aluno e demais presentes e eu, na qualidade de Presidente da Banca, lavrei a presente ata que será assinada por mim, pelos demais examinadores e pelo aluno.

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Aluno

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“Não importa que tipo de sabedoria dite a opção que você escolher, ninguém será capaz de dizer se é certa ou errada até que você chegue a algum resultado.”
Levi Ackerman (Attack on Titan)

Estudo da liga Ti-15Nb com reforço *in situ* de TiC e TiB para combinar baixo módulo de elasticidade com alta resistência ao desgaste visando aplicações biomédicas

RESUMO

Este trabalho tem como objetivo desenvolver novos compósitos de matriz à base de Ti (TMCs) que combinem baixo módulo de elasticidade e alta resistência ao desgaste para aplicações biomédicas. Especificamente, a liga Ti-15Nb (% em peso) foi selecionada, e foram utilizados diferentes teores de B_4C, nas concentrações de 1, 3 e 5% em volume durante o processo de fusão em arco. A análise microestrutural confirmou a formação *in situ* de partículas de TiC e *whiskers* de TiB na matriz, com ambos os precipitados aumentando em tamanho e quantidade à medida que o teor de B_4C aumentava. Além disso, a adição de B_4C aumentou a dureza Vickers para 388 HV e o módulo de elasticidade de 66,57 GPa para 107,32 GPa. Os testes de desgaste indicaram maior resistência ao desgaste com a redução do tamanho da trilha, embora tenha sido observado um mecanismo abrasivo de terceiro corpo em concentrações mais altas. Outro ponto importante é sobre os ensaios in vitro que confirmaram que todas as amostras compósitas não foram citotóxicas, apresentando excelente viabilidade celular após 72 horas. Este estudo valida que o compósito Ti-15Nb + B_4C é um material promissor para implantes ortopédicos resistentes ao desgaste, equilibrando bem as propriedades mecânicas, tribológicas e biológicas.

Palavras-Chave: Biomateriais, Materiais Metálicos, Compósitos de Matriz Metálica, Ligas de Titânio-Nióbio, Microestrutura, Propriedades Mecânicas.

Study of Ti-15Nb alloy with in situ TiC and TiB reinforcement to combine low elastic modulus with high wear resistance aiming at biomedical applications

ABSTRACT

This work aims to develop novel Ti matrix composites (TMCs) to combine a low elastic modulus with high wear resistance for biomedical applications. Specifically, the Ti-15Nb alloy (wt%) was selected, and B_4C *at 1, 3, and 5 vol% was used during arc melting. The microstructural analysis confirmed the in-situ formation of TiC particles and TiB whiskers within the matrices, with both precipitates increasing in size and quantity as the* B_4C *content increased. Furthermore, the addition of* B_4C *increased the Vickers hardness up to 388 HV and the elastic modulus from 66.57 GPa to 107.32 GPa. Wear tests indicated improved wear resistance, as evidenced by reduced wear-track size, although a third-body abrasive mechanism was observed at higher concentrations. Another important point concerns the in vitro tests, which confirmed that all composite samples were non-cytotoxic and showed excellent cell viability after 72 hours. This study validates that the Ti-15Nb +* B_4C *composite is a promising material for wear-resistant orthopedic implants, successfully balancing mechanical, tribological, and biological properties.*

Keywords: *Biomaterials, Metallic Materials, Metal Matrix Composites, Titanium-Niobium Alloys, Microstructure, Mechanical Properties*

Sumário

1. Introdução

1.1. Biomateriais

Pesquisas recentes indicam que a expectativa de vida está aumentando, e consequentemente a população está envelhecendo (Karaflou; Goulis, 2025), fazendo com que doenças ósseas podem aparecer, como por exemplo, a osteoartrite, que é uma das doenças mais comuns em pessoas acima de 60 anos (GBD 2021 Osteoarthritis Collaborators, 2021). Deste modo, surge uma necessidade de utilizar de implantes metálicos para substituir o osso doente, assim aumentando a qualidade de vida (Abdel-Hady Gepreel; Niinomi, 2013). Porém, o uso de implantes pode acarretar alguns problemas, dentre eles o atrito entre o implante e o osso, assim desgastando o material e podendo liberar partículas tóxicas no corpo, além de afetar à funcionalidade do implante (Abd-Elaziem et al., 2024).

De um modo geral, a maioria dos implantes ortopédicos é feita de metais biocompatíveis, sendo chamados de biomateriais, que, segundo a ANVISA, através da Portaria 686/98, são materiais ou artigos de uso médico destinados a serem introduzidos no corpo de forma total ou parcial. Deste modo, os principais tipos de materiais metálicos para implantes são feitos de ligas metálicas de diversos tipos, como o aço inoxidável, (316L *stainless steel), ligas à base de cobalto-cromo (Co-Cr), e ligas à* base de titânio (Ti) (Kaur; Singh, 2019).

Pesquisas como a de M.M Soliman e colaboradores (Soliman et al., 2024), indicam que ao utilizar implantes mais rígidos, aqueles que possuem alto módulo de elasticidade, pode surgir o problema da blindagem óssea (*stress shielding*). Isso ocorre porque o implante absorve uma porção maior da carga mecânica, o que faz com que o osso não receba estímulos mecânicos e atrofie. Outro estudo feito por Kumar e Gautam (Kumar; Gautam, 2024), mostram que as principais ligas utilizadas na confecção de implantes possuem um alto módulo de elasticidade em comparação ao do osso. Por exemplo, o titânio comercialmente puro (Ti-cp), possui um módulo de elasticidade de aproximadamente 100 GPa, enquanto outras ligas como a Ti-6Al-4V (T64) possui módulo de elasticidade em torno de 110 GPa, tal que esses valores estão muito distantes dos valores dos ossos, com módulos elástico com valores entre 10 e 30 GPa.

Outras pesquisas indicam também que as principais ligas comerciais, como a T64, podem liberar íons citotóxicos ou provocar sintomas alérgicos no corpo (Lu et al., 2025). Com isso, surge a necessidade de pesquisas em novas ligas, com foco em reduzir esses efeitos prejudiciais ao corpo humano.

1.2. Ligas de Ti-Nb

Pesquisas recentes têm sido destinadas para encontrar ligas que possuem um baixo módulo de elasticidade, com o objetivo de minimizar o *stress shielding*, além de uma boa biocompatibilidade, como têm sido destacadas as ligas de Ti-Nb (Campos-Quirós; Cubero-Sesín; Edalati, 2020). Diversos estudos focaram na fase β do sistema Ti-Nb, que apresenta um baixo módulo de elasticidade. O estudo de S. Hanada e colaboradores (Hanada et al., 2003) mostrou que o módulo de Young está relacionado à fase do material. Ainda nesse estudo, foram mostradas duas regiões de interesse na liga de Ti-Nb, nas quais estão as fases α'' (ortorrômbica), em torno de 15% a 17% em peso de Nb, e a fase β, em torno de 40% a 42% de Nb; ambas as fases demonstraram um baixo módulo de elasticidade.

As ligas de Ti-Nb nessas concentrações de nióbio têm sido amplamente pesquisadas, como o estudo de C. Schulze e colaboradores (Schulze et al., 2018) que estudaram a liga Ti-42Nb e obtiveram um valor de módulo de Young por volta de 60,5 GPa. Em outro estudo, a pesquisa feita por A. Thoemmes e colaboradores (Thoemmes et al., 2021), na qual o objetivo era analisar as ligas de Ti-Nb, variando a concentração de nióbio de 10% até 40%, as ligas que apresentaram os menores valores de módulo de elasticidade são justamente as que estão na fase martensítica α'', que é em torno de 15% a 17,5% de Nb, com um módulo de elasticidade entre 47 a 65 GPa.

1.3. Compósitos a base de matriz metálica

Em alguns casos, as ligas convencionais, como por exemplo ligas de Ti e de Co-Cr não possuem uma alta resistência ao desgaste, logo utilizar de reforços cerâmicos traz essa vantagem ao comportamento das ligas (Kumar; Hiremath, 2014). De modo geral, os compósitos à base de matriz metálica (MMCs no inglês) podem ser definidos como uma combinação de fases, misturando a fase macia dos metais com as fases duras das cerâmicas (Cheng et al., 2025).

Os reforços duros em compósitos de matriz à base de titânio (TMCs, em inglês) são materiais que aprimoram as propriedades das ligas de Ti (Attar et al., 2018). Desse modo, os principais tipos de reforços cerâmicos são o carbeto de titânio (TiC), e o boreto de titânio (TiB), e uma das formas em que eles ocorrem é por reações *in situ*, entre a matriz de titânio e o pó cerâmico de carbeto de boro (B_4C) (Hayat et al., 2019).

Durante a fusão a arco, as ligas de Ti reagem com o B_4C, formando TiC e TiB, preferencialmente TiB devido à maior proporção de boro no carbeto de boro. Segundo Nartu e colaboradores (Nartu et al., 2020), o primeiro produto da reação é a precipitação de TiB, que serve como local de nucleação para os precipitados de TiC. Por fim, a matriz metálica remanescente, em estado líquido, solidifica, formando a estrutura metálica.

Diversos efeitos decorrentes da formação in situ do reforço podem influenciar o comportamento do compósito em testes mecânicos. De acordo com Hua e colaboradores (Hua et al., 2024), os precipitados aumentam a resistência ao desgaste através do endurecimento por refino de grão, endurecimento por dispersão e pelo mecanismo de transferência de carga da matriz metálica para o TiC e TiB. Em geral, isso eleva não apenas a resistência ao desgaste, mas também as propriedades mecânicas, resultando em menor deformação plástica. Esse comportamento é a combinação da parte elástica da liga metálica com a parte mais dura e resistente da cerâmica.

2. Objetivos

Este presente trabalho tem como objetivo produzir e caracterizar novos compósitos *in situ* com a adição em diferentes teores de B_4C durante a fusão à arco voltaico da liga Ti-15Nb, além de estudar seu uso como um biomaterial.

3. Capítulo único

O presente trabalho de conclusão de curso será apresentado no formato de artigo completo, sendo transcrito de forma idêntica ao que foi submetido ao periódico científico.

Synthesis of a novel titanium matrix composite targeted for biomedical implants by *in situ* reactions of B_4C and Ti-15Nb (wt%) alloy during argon arc-melting

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Abstract

This study aimed to develop novel Ti-based matrix composites (TMCs) to combine proper mechanical, tribological, and biological properties for biomedical applications. The Ti-15Nb (wt.%) alloy was selected, considering the precipitation of metastable α” phase, while the B_4C was varied (1, 3, and 5 vol.%). The structural and microstructural results indicated the presence of *in situ* reactions between the B_4C particles and Ti atoms in the matrix, resulting in the formation of TiB (whisker-shaped) and TiC (particle-shaped) phases, accompanied by a phase transformation in the matrix from a dual α’ + β to α” + β phase. The elastic modulus and microhardness increased gradually with the addition of precipitates, indicating the influence of the ceramic reinforcements and phase transitions in the bulk on dislocation movement and phase precipitation hardening. The presence of TiB and TiC also influenced the wear resistance of the samples, affecting the volume loss and wear rate by altering the wear mechanisms. *In vitro* biological tests indicated a positive interaction with osteoblastic-like cells. This study demonstrates that the Ti-15Nb alloy reinforced with TiB and TiC precipitates is a promising material for next-generation orthopedic implants, with tunable mechanical, tribological, and biological properties.

Keywords: biomaterial; Ti-Nb alloy; titanium-matrix composite; B_4C; *in situ* reaction; mechanical biocompatibility.

3.1. Introduction

Chronic bone diseases, such as osteoarthritis, commonly appear in people over 40, leading to difficulties and impacting their quality of life [1]. Therefore, it's necessary to replace the diseased bone with metal prostheses that are compatible with the human body [2]. In this scenario, titanium (Ti) alloys emerge to circumvent this problem, given that they have good biocompatibility [3]. However, one of the widely commercialized Ti alloys, with the composition Ti-6Al-4V (wt%), presents some deleterious issues in the long term, by releasing toxic ions into the body and contributing to the development of new bone diseases [2]. Lu *et al.* [4] emphasized that the Ti-6Al-4V alloy releases aluminum (Al) and vanadium (V) ions due to wear mechanisms, which can be harmful to the human body, as both may contribute to undesirable biological responses. Furthermore, according to Kumar and Gautam [5] some Ti alloys have mechanical restrictions. For instance, taking commercially pure titanium (CP-Ti) as a reference, its elastic modulus is approximately 110 GPa, which is higher than that of human bone, which ranges from 10 to 30 GPa.

To mitigate the issue with biological compatibility, niobium (Nb) is often chosen to form solid solutions with Ti, considering the lack of allergenic and toxic reactions with the human body [3]. Furthermore, the Nb alloying can bring benefits to the mechanical properties, enhancing the mechanical strength and diminishing the elastic modulus [6]. As an example, Campos-Quirós *et al.* [7] studied Ti-xNb (x = 10, 20, 25, and 35 at%) alloys processed by mechanical alloying for biomedical purposes, finding a good balance between hardness and elastic modulus by combining the synthesis parameters and the Nb content, resulting in mitigation of the stress shielding effect. However, the insufficient wear resistance remains a drawback for biomedical Ti alloys when considered for long-term implantation, as the release of ions and debris can result in adverse biological effects and implant failure [8].

In this scenario, a titanium matrix composite (TMC) reinforced with ceramic particles has been established as a novel strategy to tune the wear resistance of Ti alloys [9]. Ogunmefun *et al.* [10] detailed how the presence of ceramic particles as a secondary phase can enhance the mechanical and tribological properties of the Ti metallic matrix by altering the plastic deformation mechanisms. Currently, the use of boron carbide (B_4C) is emerging as an option, as it can be prone to decomposing and forming *in situ* reactions with Ti atoms, generating titanium carbide (TiC) and borate (TiB), which positively affect the mechanical properties of the matrix [11]. Considering biomedical applications, the addition of B_4C to Ti alloys has been demonstrated to yield advantageous results for implantation [12].

Nowadays, several studies aimed to optimize the relationship between TiC and TiB reinforcements in TMCs, since it is paramount to understand the influence of the reinforcements on the mechanical behavior [13]. Furthermore, the behavior of the solid solution in the matrix in the presence of reinforcements is another major issue for TMC composites, as investigated by Gonçalves *et al.* [14]. The authors found that the chemical reaction of Ti in the β phase solid solution resulted in a slight decrease in hardness, accompanied by reduced wear resistance at very high concentrations.

Given this, the present study aimed to develop a novel TMC via *in situ* reactions between B_4C and a Ti-15Nb (wt%) matrix. Then, the effect of the formation of TiC and TiB phases on the microstructure was evaluated, and the corresponding effects on the selected mechanical, tribological, and biological properties were also considered. Finally, the B_4C decomposition reactions and the mechanisms of forming TiC and TiB in the Ti-Nb solid solution were addressed at the nanoscale.

3.2. Materials and Methods

3.2.1. Sample processing

Ingots were produced by argon arc-melting in two steps. Firstly, Ti-15Nb (wt%) samples were prepared in a half-round copper crucible, using pure Nb (99.8%) and commercially pure Ti grade 2 (99.7%, ASTM F67). Then, B_4C powders (98% purity; particle size of 10 µm) were added to a handmade copper crucible to produce the metal-matrix composite ingots. Further processing details regarding composite fabrication were introduced in a previous study [15]. Four distinct amounts of B_4C powders were used, as described in **Table 1**. The proportion of B_4C was defined in terms of volume percentage (vol.%), with the highest B_4C addition of 5% based on previous studies [4] .

Table 1: Samples' nomenclature and elemental proportions.

Sample	B_4C (vol.%)	Ti (at.%)	Nb (at.%)	B (at.%)	C (at.%)
Control	0	91.67*	8.33*	0	0
1%	1	89.47	8.14	1.91	0.48
3%	3	85.27	7.75	5.58	1.39
5%	5	81.29	7.39	9.05	2.26

*Equivalent to Ti-15Nb (wt.%).

3.2.2. Sample characterization

The samples were sectioned using a Buehler Isomet 1000 cutting machine. After cutting, the samples were ground with water-sandpaper up to a mesh of #2000 and polished with an Al_2O_3 (1 µm) colloidal suspension. X-ray diffraction (XRD) was performed using a Rigaku Miniflex 600 diffractometer with Cu-Kα radiation ($\lambda = 0.15406$ nm), operating at 40 kV and 15 mA. The diffraction angles (2θ) ranging from 20° to 80° were collected with a step size of 0.04° and analyzed using the HighScore Plus software version 5.1 (Malvern Panalytical Inc., USA). Microstructural features were analyzed using an optical microscope (Olympus BX51M) and a scanning electron microscope (SEM; Philips XL-30 FEG) at 15 kV, operating with both secondary electron (SE) and backscattered electron (BSE) beam modes, equipped with an energy dispersive X-ray spectroscopy detector (EDS; Bruker Corp., USA) for chemical mapping and semi-quantitative analysis. Further microstructural details were obtained using transmission electron microscopy (TEM; Thermo Fisher Scientific Inc., FEI Titan Cubed Themis, USA), operating at 300 kV in both transmission (CTEM) and scanning transmission (STEM) modes. High-resolution imaging (HRTEM), EDS, and nanobeam electron diffraction (NBED) techniques were also employed during the analysis. For this purpose, the thin lamella was prepared using a focused ion beam (FIB) in a dual-beam field-emission scanning electron microscope (FESEM; Thermo Fisher Scientific, Helios NanoLab 660, USA). Then, the acquired results were evaluated using the CrysTBox version 1.10 and Fiji ImageJ version 1.54f software. Finally, the crystallographic features were also investigated using automated crystal orientation mapping (ASTAR package, NanoMEGAS) on a TEM microscope (FEI TECNAI, 52 S-TWIN model, USA).

3.2.3. Sample testing

A preliminary mechanical evaluation was conducted using microhardness and elastic modulus measurements. Vickers microhardness was measured on a polished surface using a Shimadzu HMV-G equipment (USA), under loads of 0.025 kgf (0.245 N) and 2 kgf (19.613 N), with a dwell time of 15 seconds. The elastic modulus was acquired in rectangular-shaped specimens (~ 25 × 5 × 2 mm) by using the impulse excitation mode in a Sonelastic equipment (ATCP Physical Engineering, Brazil). Average values and standard deviations were calculated from 10 measurements per sample.

Dry sliding tests were performed on a ball-on-plate tribometer (UMT, Bruker, USA) using linear reciprocating motion at room temperature. The tests were conducted in ambient air under unlubricated conditions. The samples were tested by rubbing a 6 mm alumina ball under 2 N and 5 N loads at 1 Hz, with a total stroke length of 5 mm, for 1.8 ks (30 min). The tests were carried out in triplicate ($n = 3$) to assess the reliability of the coefficient of friction (COF) values. The wear tracks produced during the dry sliding wear tests were measured for width and depth using an optical profilometer (Olympus Group, DSX500 opto-digital microscope, USA). For each sample, three 2D profiles were taken from the middle, upper, and bottom parts of the wear track, and the volume loss (V) and wear rate (W) were estimated following previous studies from the group [16]. Later, the wear track was analyzed using a field-emission SEM microscope (FESEM; FEI, Teneo, USA), equipped with an EDS detector (EDAX, Gatan Corp.).

To assess the biological response of the alloys, MC3T3-E1 pre-osteoblast cells (subcloning 4, ATCC CRL-2593) were employed. The cells were maintained in Alpha Minimum Essential Medium (α-MEM) enriched with 10% Fetal Bovine Serum (FBS), and kept in a 5% CO_2 incubator at 37°C. For the cell viability assay, an extract was prepared by conditioning the α-MEM with the materials (at 0.2g/mL) for 24 hours. This conditioned medium was subsequently collected. Cells were seeded into 96-well plates at a density of 5×10^4 cells/mL. Once they reached a subconfluent stage (after 24 hours), they were exposed to the conditioned medium for either 24 hours or 72 hours (n = 6 per group). A control group was simultaneously maintained in conventional culture medium. Following the incubation periods, cell viability was quantified using the MTT assay ((4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide). The viability was determined by measuring absorbance at 570 nm using a SYNERGY-HTX multi-mode microplate reader (BioTek, USA). The cell adhesion assay was performed using the crystal violet staining technique. After routine cultivation and trypsinization, the cells were seeded into 96-well plates containing media previously conditioned with the materials at a density of 5×10^4 cells/mL. This assessment was performed to measure the impact of media conditioned by materials on cell adhesion properties. The cell groups included a control set maintained in standard culture medium and sets exposed to the materials. After a 24-hour incubation period, the cells were stained with crystal violet [17,18]. The degree of cell adhesion was quantified by measuring the absorbance of stained cells at 540 nm using the SYNERGY-HTX multimode microplate reader.

3.3. Results and discussion

3.3.1. The role of B_4C addition on the phase proportion and microstructure

Fig. 1 displays the XRD profiles of the control and TMC samples, where a significant effect of the B_4C additions on the phase composition is evident. The control exhibited a dual α' + β phase, which is typical of as-cast Ti-15Nb alloys [19]. However, the incorporation of B_4C

led to the appearance of noticeable TiB and smooth TiC peaks, indicating *in situ* reactions between B_4C and Ti atoms. Furthermore, the TiB peaks remained more intense than the TiC, respecting the stoichiometric composition of the B_4C powders (4:1). It is also worth pointing out that the metallic phases (α' and β) were modified with the B_4C addition, having intense β phase peaks together with a martensitic α" peaks, indicating possible phase transformation reactions (α' → α" and α' → β) induced by the Ti depletion in solid solutions. This result corroborates the findings of Bonisch *et al.* [20], who evaluated the phase stability of Ti-Nb alloys and stated that the metastable α'/α" phases can be retained in the Ti-(14 – 19)Nb (wt%), while α"/β phases in the Ti-29Nb alloy.

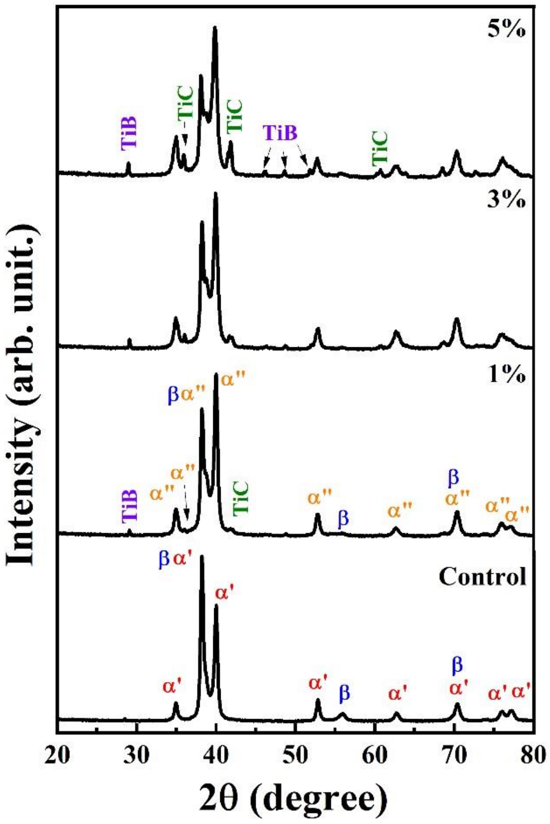


Fig. 1: XRD profiles of the TMC samples varying the B_4C content. ICSD CIF files: TiC #01-071-0298, TiB #01-089-3922, β-Ti #01-085-8555, α'-Ti #01-086-2608, α"-Ti #01-071-9956.

Fig. 2 illustrates the microstructural features of the TMC samples, along with some chemical details regarding the forming precipitates in **Fig. 3**. The micrographs show the presence of large (α’) and thin (α”) needles along with the β grain boundaries of the control sample, having the TMC samples diminished the quantity of the α’ needles, agreeing with the supposed phase transitions α’ → α” and α’ → β. In the TMC samples, the number and size of precipitates increased proportionately with the amount of B_4C, forming TiB and TiC precipitates. Overall, the microstructure consisted of particle- and whisker-shaped precipitates, measuring approximately dozens of micrometers in size. The semi-quantitative EDS analysis (**Fig. 3**) was performed on the matrix (Zone I), whisker (Zone II), and particle (Zone III) precipitates. Overall, besides the fact that Zone I was composed mainly of Ti and Nb, Zone II was enriched with B, while Zone III confirmed that the whisker and particle precipitates are formed by TiB and TiC, respectively. Furthermore, the concentration of Ti in the precipitates remained close to that of B and C in Zones II and III, and followed the TiB and TiC stoichiometries, consistent with the XRD results. Similar results were found in our earlier study [21] with the Ti-40Nb alloy, which was melted with B_4C powders, and showed a microstructure composed of the same TiB and TiC morphologies.

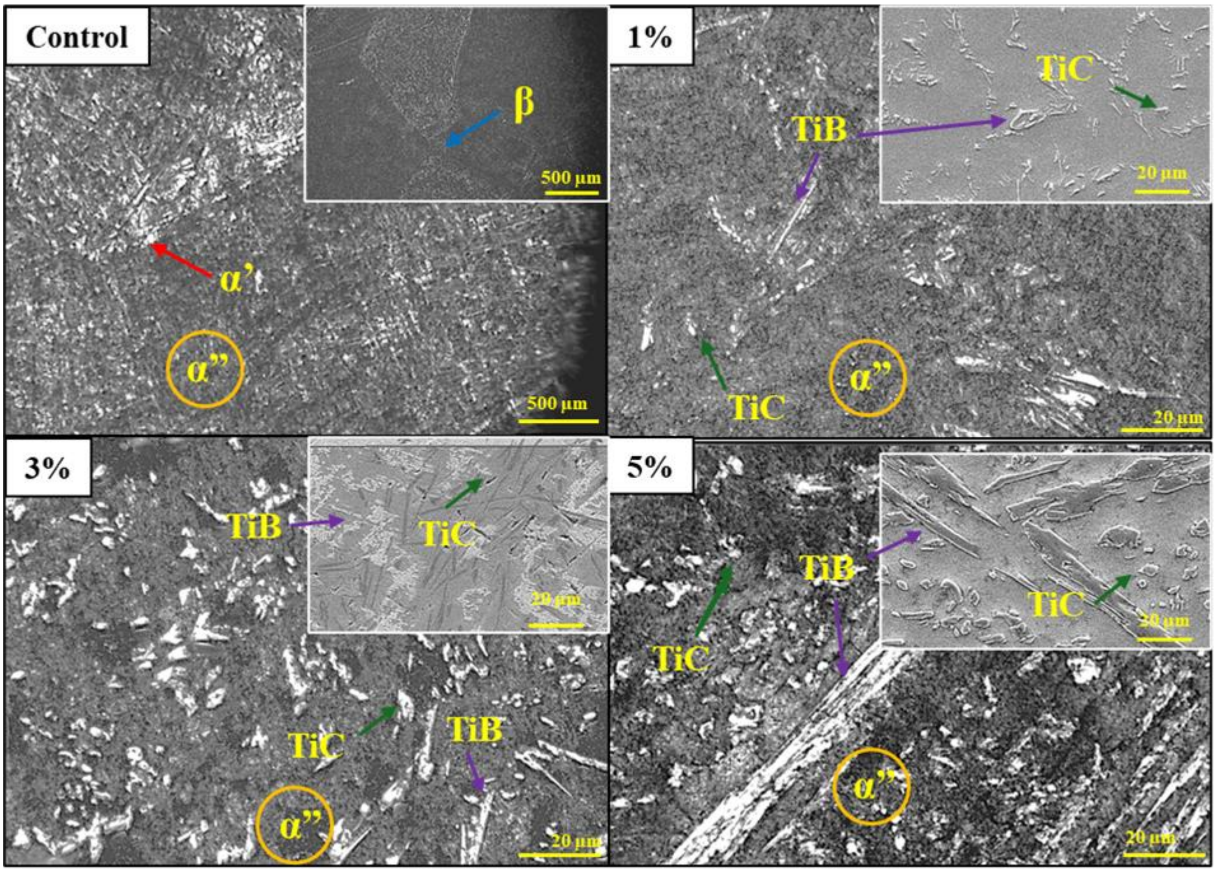


Fig. 2: Microstructural analysis of the TMC samples under optical imaging. The inset for the control sample is optical imaging at low magnification (50×), while the insets for the TMC samples are SEM images (1 k×) in SE mode.

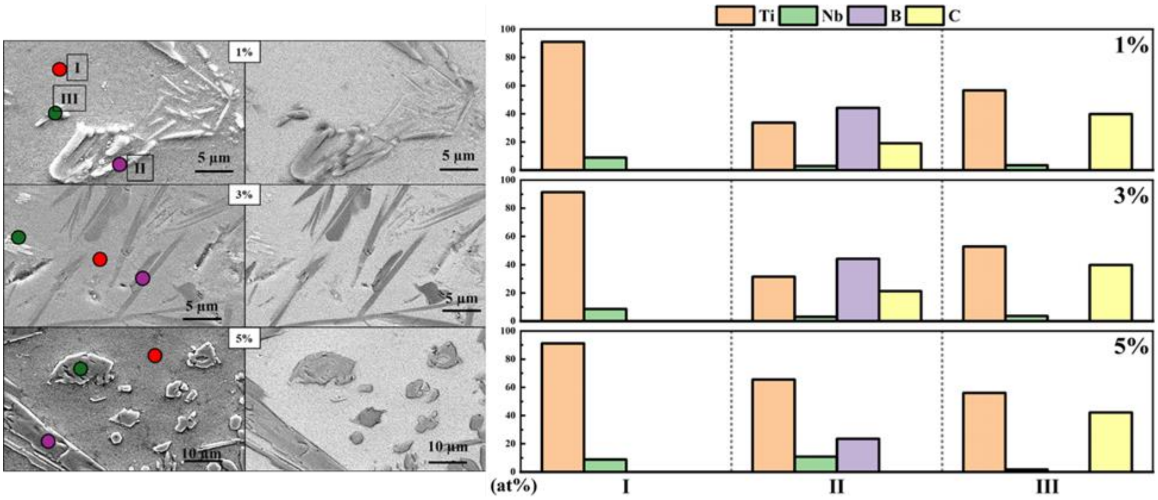


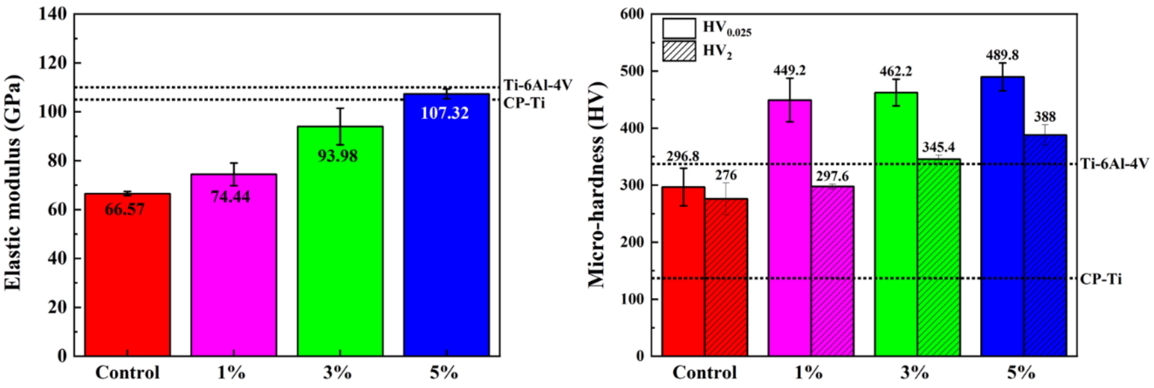
Fig. 3: Semi-quantitative EDS values of the TMC samples: SEM imaging in SE and BSE modes (left) and chemical proportion of the elements in selected zones (right).

3.3.2. Influence of the TiB and TiC precipitates on the properties of interest

The preliminary assessment of the mechanical properties is presented in **Fig. 4**, which compares the elastic modulus and Vickers microhardness of the TMC samples with those of the commercial CP-Ti grade 2 and Ti-6Al-4V alloy. The elastic modulus (**Fig. 4a**) of the control sample was the lowest, mainly due to its phase composition. The addition of B_4C increased the abundance of TiC and TiB precipitates, leading to a gradual increase in the elastic modulus. Bernard *et al.* [22] studied the mechanical properties of laser-sintered Ti-TiC composites processed under distinct laser energy densities. The authors found that the addition of TiC precipitates in the metallic matrix increased the elastic modulus and positively influenced tensile properties (e.g., yield strength, ultimate tensile strength, and elongation).

Interestingly, while the B_4C addition increased the elastic modulus, the TMC sample containing 5% B_4C remained within the range of the CP-Ti and Ti-6Al-4V alloys, which are conventional biomedical materials used in implants [4]. Regarding the Vickers hardness (**Fig.**

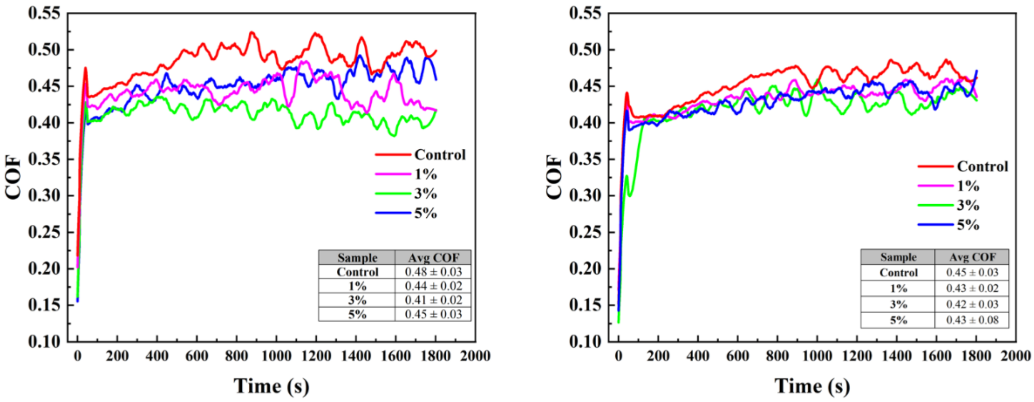
4b), the average values are presented for two distinct loads to highlight the local effect of the precipitates on plastic deformation. The control sample showed similar values in both loads, remaining above the CP-Ti mainly due to the solid-solution hardening effect of the Nb addition. However, the presence of TiB and TiC precipitates gradually increased the hardness values on both load conditions. Under 0.025 kgf, the phase precipitation hardening effect of TiB and TiC prevail, resulting in values above those of the Ti-6Al-4V alloy. In contrast, at 2 kgf, the matrix hardness is highlighted. As a comparison, Gonçalves *et al.* [23] investigated the mechanical properties of the Ti-40Nb (wt%) alloy reinforced with TiB and TiC, where the effect of the ceramic reinforcements and the matrix under distinct loads was detectable. As stated by Dutta *et al.* [24], whose evaluated the mechanical aspects of the Ti-45Al-5Nb-0.5Si (wt%) alloy reinforced with TiC and TiB_2, the presence of ceramic reinforcements can augment the hardness and elastic modulus due to second-phase particle strengthening, thereby affecting the elastic and plastic deformation mechanisms.



(a) (b)

Fig. 4: Selected mechanical properties of the TMC samples: elastic modulus (a) and Vickers microhardness (b) at two distinct applied loads.

Fig. 5 illustrates the evolution of the coefficient of friction (COF) at loads of 2 N and 5 N. In both conditions, the COF curves for the TMC samples remained below those of the control, exhibiting a non-linear dependence on the amount of B_4C added in solid solution. The average COF values of the TMC samples remained less than 0.45 for 5 N and 0.48 for 2 N, indicating a slight lubricating effect of the TiB and TiC precipitates, as well as the phase transition of the matrix. Further wear tests under distinct load conditions can help reveal the effect of the ceramic precipitates on the wear resistance of the solid solution. Souza *et al.* [25] detected differences in the COF values and wear volume loss of composites based on Ti-TiB-TiC_x under tribocorrosion tests, attributing them to the formation of protective tribolayers that protected wear and corrosion mechanisms.



(a) (b)

Fig. 5: Representative COF values recorded during the wear tests under normal loads of 2 N (a) and 5 N (b), with the corresponding average COF values shown in the inset.

The corresponding topography of the wear tracks, as acquired by SEM imaging, is shown in **Fig. 6**. Overall, all the wear tracks exhibited grooves associated with abrasive wear and adhered particles associated with adhesive wear. The increase in TiB and TiC resulted in a slightly narrower wear track width (**Fig. 7**), suggesting enhanced wear resistance. This result suggests strong interfacial bonding between the precipitates and the matrix, arising from *in situ* reactions during arc melting. At 5 N, the wear tracks exhibited a larger width and similar wear mechanisms, but with deeper grooves and larger adhered particles. Ureña *et al.* [26] studied the wear behavior of Ti-Nb and Ti-Mo alloys produced by powder metallurgy and thermochemical treatment. The authors demonstrated that applying different loads in dry-sliding wear tests influences the wear behavior of TMCs, revealing distinct wear mechanisms along the wear tracks.

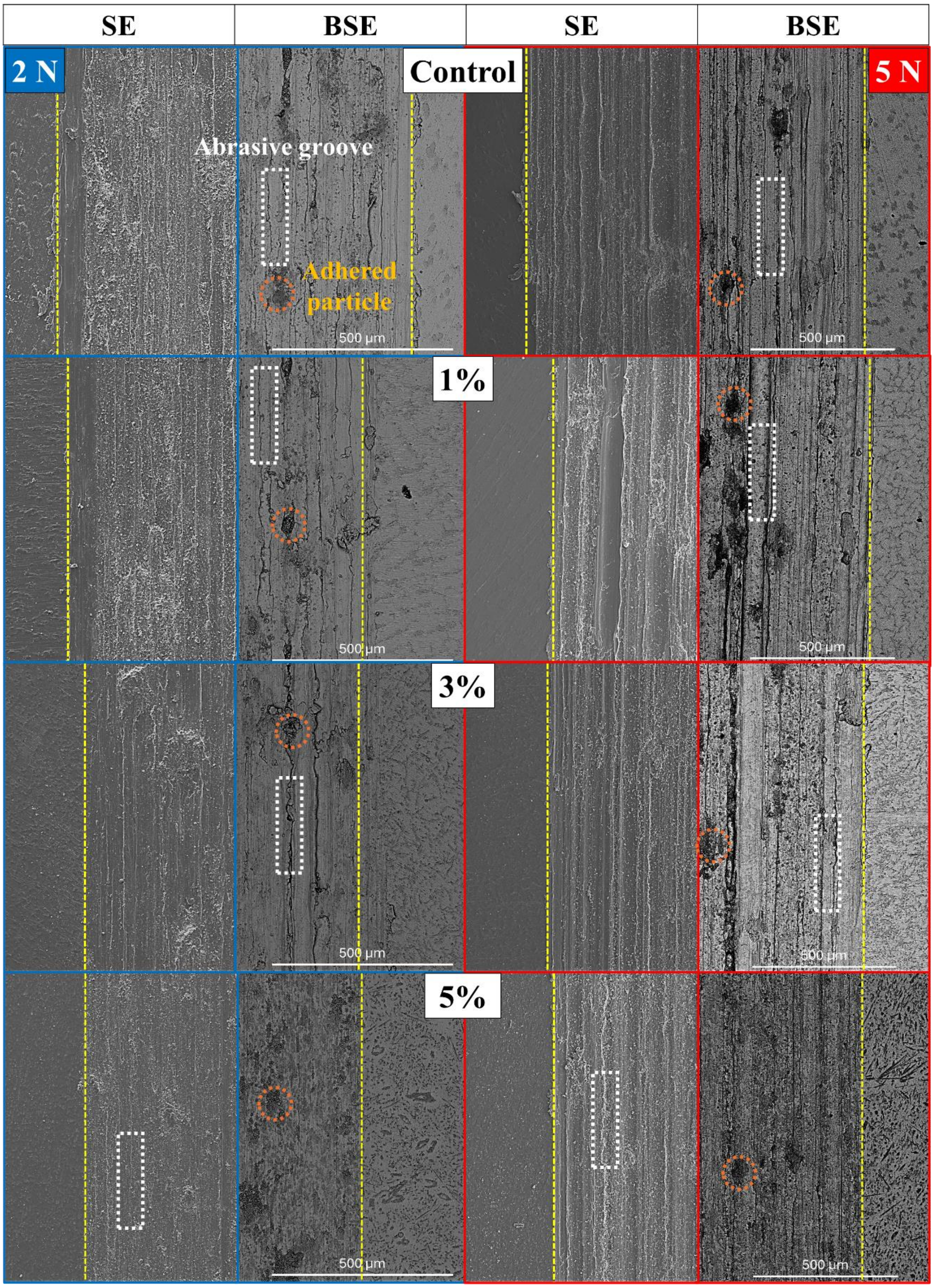


Fig. 6: SEM images of the wear tracks in the TMC samples.

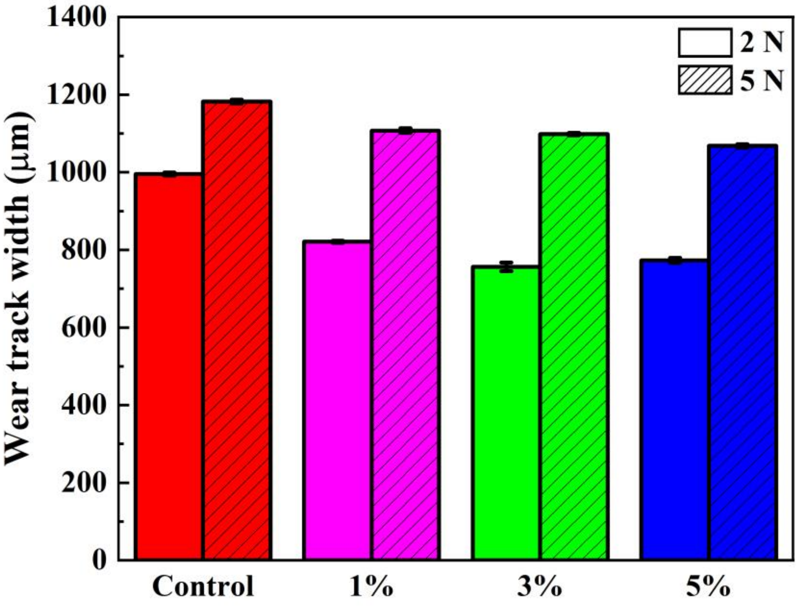


Fig. 7: Average width values of the wear tracks in the TMC samples.

Semi-quantitative chemical analyses of the wear tracks are presented in **Fig. 8**, which shows the evaluated zones and the corresponding elemental proportions of interest. Overall, oxygen (O) atoms were detected in all regions, indicating that oxidation reactions were induced by heating during wear sliding. Furthermore, the presence of aluminum (Al) indicates that debris of the counter body remained adhered to the surface after the wear sliding. The slight increase in the Nb content can be attributed to the depletion of Ti atoms in the solid solution during oxidation, given the higher affinity of Ti for bonding with O. Lastly, the amount of B and C remained above those of the nominal values indicated previously. Thus, it can be inferred that the TiB and TiC particles removed during wear sliding could be redeposited on the surface, enriching the wear track. A similar finding was reported by Liu *et al.* [27], who tested the wear resistance of Ti-(TiC+TiB) composites produced by laser powder bed fusion. The authors detected debris aggregation throughout the worn surface, which served as a protective layer.

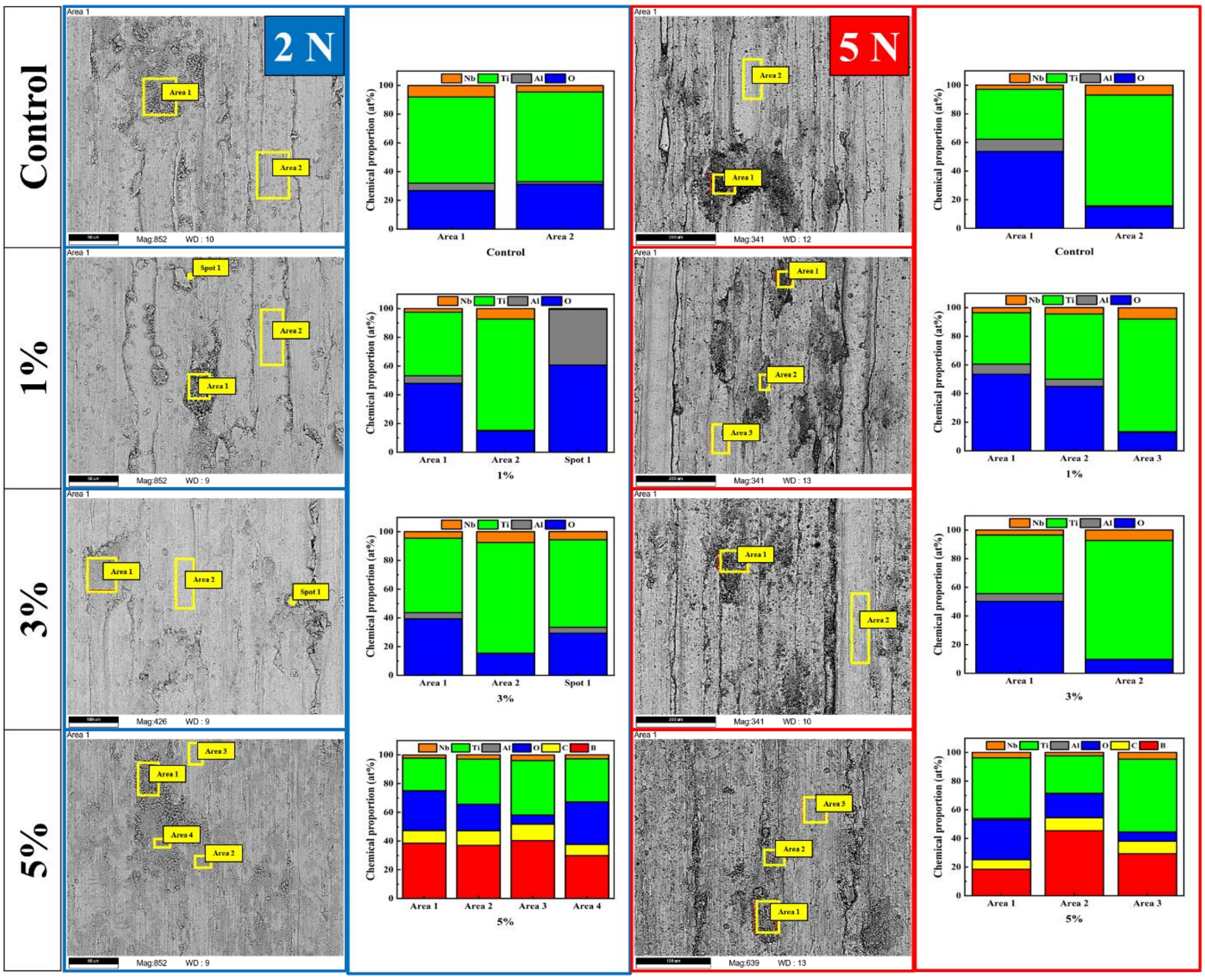


Fig. 8: Semi-quantitative EDS analysis of selected regions of the wear tracks in the TMC samples.

Fig. 9 describes the wear rate and the wear track profiles of the samples under the distinct applied loads. Overall, at the 2 N load, the wear rate increased compared to the unreinforced alloy; however, the sample with 1% TiB/TiC reinforcement showed a smaller degradation compared to the others. For the 5 N load, the 1% reinforced sample exhibited less material loss compared to the others, since the 3% and 5% samples generally presented a value comparable to the Control sample. Qi *et al.* [28], who investigated the wear and corrosion properties of Ni-TiB_2-TiC composites, noted that the presence of hard particles trapped between the surface and the counterbody can significantly affect the material's wear mechanisms.

In addition to the particles adhering to the counterbody surface, another factor that can impact the wear rate is the ω phase that may be present in the alloy. The study carried out by Song B. *et al.* [29] shows that the ω phase can directly interfere with the microstructure and consequently with the overall behavior of the wear tests. Thus, the presence of this phase can lead to the embrittlement of the alloy.

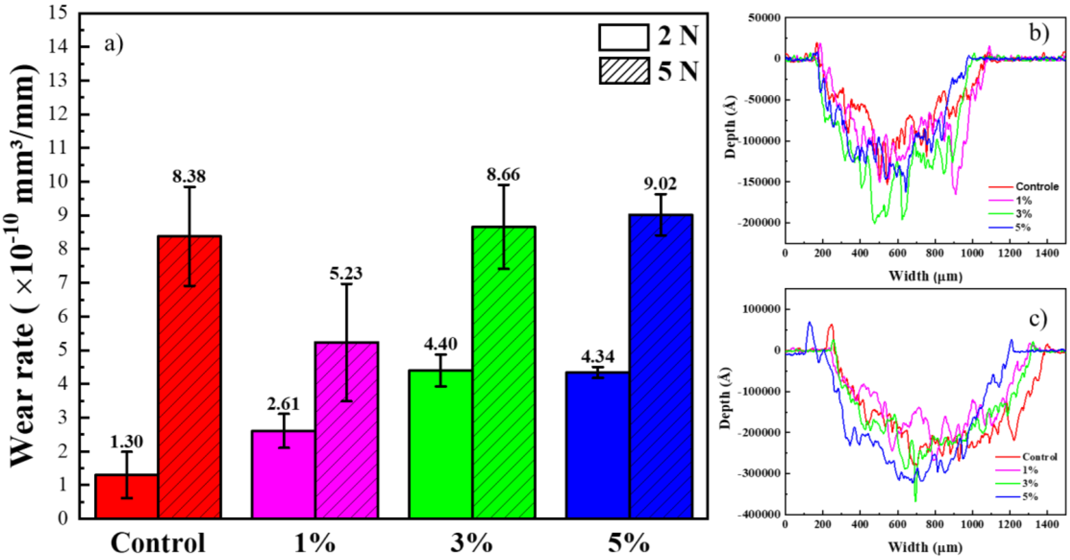


Fig. 9: a) Wear rate of the TMC samples on each applied load and wear track profiles at b) 2 N and c) 5 N loads

Fig. 10 presents the results of the in vitro cytotoxic tests acquired with MTT and CV colorimetric assays. For the MTT test, at both 24 and 72 hours, all samples possessed values above those of the reference, indicating proper cell viability. Regarding the CV test at 24 hours, the values were equal to or higher than those of the reference, especially for the 1% TMC sample, which had a statistically significant difference, indicating proper cell adhesion. Thus, the results highlight that the presence of TiB and TiC precipitates benefits cell activity when in contact with the samples. Gonçalves *et al.* [30] reported higher cell viability in the Ti-40Nb (wt%) alloy melted with B_4C than in the bare alloy or in those reinforced with NbC and NbB_2, shedding light on the benefits of TiB and TiC for cell biocompatibility.

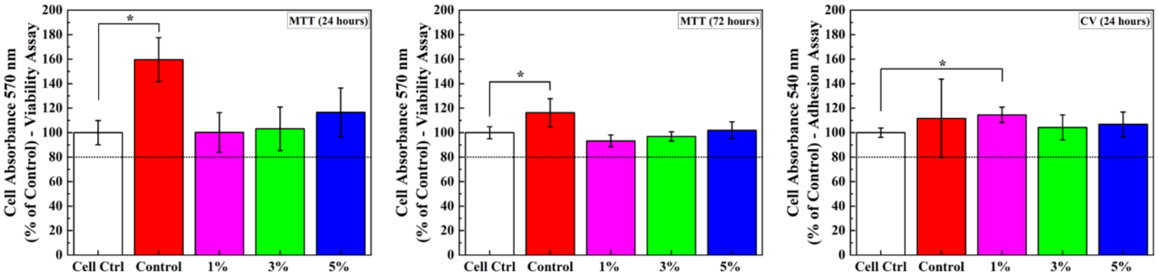


Fig. 10: Cytotoxicity tests of the TMC samples acquired by MTT and CV assays (*$p < 0.05$).

3.3.3. Considerations about the *in situ* reactions between B_4C and the matrix

During the arc-melting, the Ti-15Nb alloy reacts with B_4C particles, forming TiC and TiB precipitates. Higher TiB amounts are expected, given the chemical stoichiometry of B_4C. According to Nartu *et al.* [31], at high temperatures, the decomposition reaction $B_4C \rightarrow 4B + C$ takes place, then followed by $Ti + B \rightarrow TiB$ and $Ti + C \rightarrow TiC$. Later, the remaining metallic matrix solidifies with the precipitates forming a composite microstructure. It is worth noting that excessive Ti atoms favor TiB precipitates over TiB_2, as found in the current study. As shown in **Fig. 11**, the elemental mapping of the precipitate indicates complete decomposition of the B_4C particle into TiB and TiC precipitates, confirming the previous assumption. Furthermore, considering the depletion of Ti in the Ti-Nb solid solution, it is possible to expect phase transitions induced by the increased Nb content, such as α’ → α” and α’ → β. The presence of TiC and TiB precipitates can directly affect the properties, as cited by Hua *et al.* [32], who investigated the mechanical properties of Ti-6Al-4V alloy reinforced with TiC and TiB. The results indicated that the precipitates affected mechanical properties by providing grain refinement and load-transfer mechanisms.

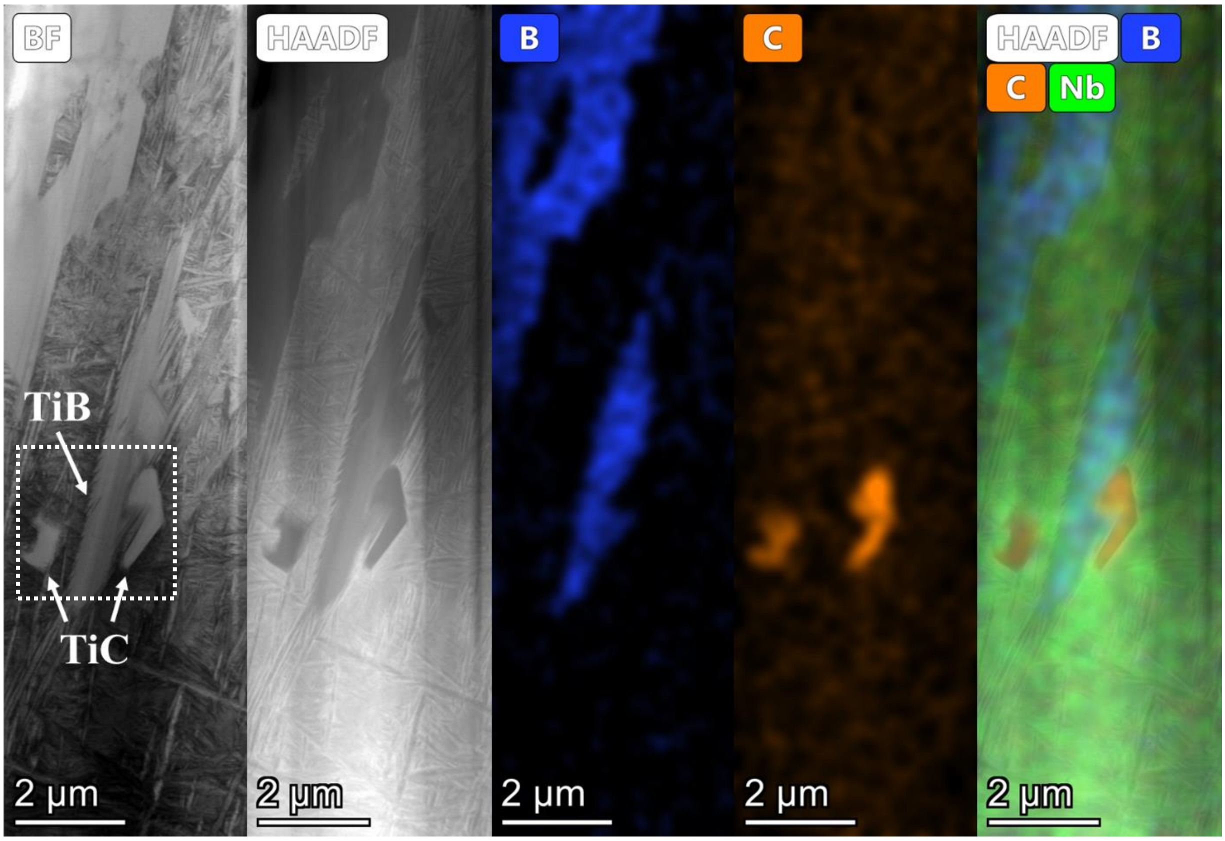


Fig. 11: Chemical elemental mapping of the FIBed 5% lamella acquired STEM-BF and STEM-HAADF modes (from left to right), and showing STEM-EDS X-ray mapping of elements: B-K (blue) representing TiB borides, C-K (orange) representing TiC carbides, and color image combining STEM-HAADF + B-K (borides) + C-K (carbides) + Nb-K (green) from the Ti-15Nb matrix of the alloy.

Fig. 12 presents the automatic crystallographic orientation mapping (ACOM) of the FIBed Ti-15Nb alloy matrix with 5% B_4C addition. The anayzed region refers to the white dotted line of **Fig. 11** (STEM-BF image) and the results obtained by ASTAR are: virtual bright field (VBF) image (**Fig. 12a**), inverse pole figure in X direction, IPF-X image (**Fig. 12b**), inverse pole figure in Z direction, IPF-Z image (**Fig. 12c**), and finally Phases map combined with Index image image (**Fig. 12d**), showing combination of β-Ti phase (in red), nanoscale α′-Ti martensite needles (light blue) in the Ti-15Nb alloy matrix [33], besides TiB boride particle (in yellow), and TiC carbide particles (black regions), respectively

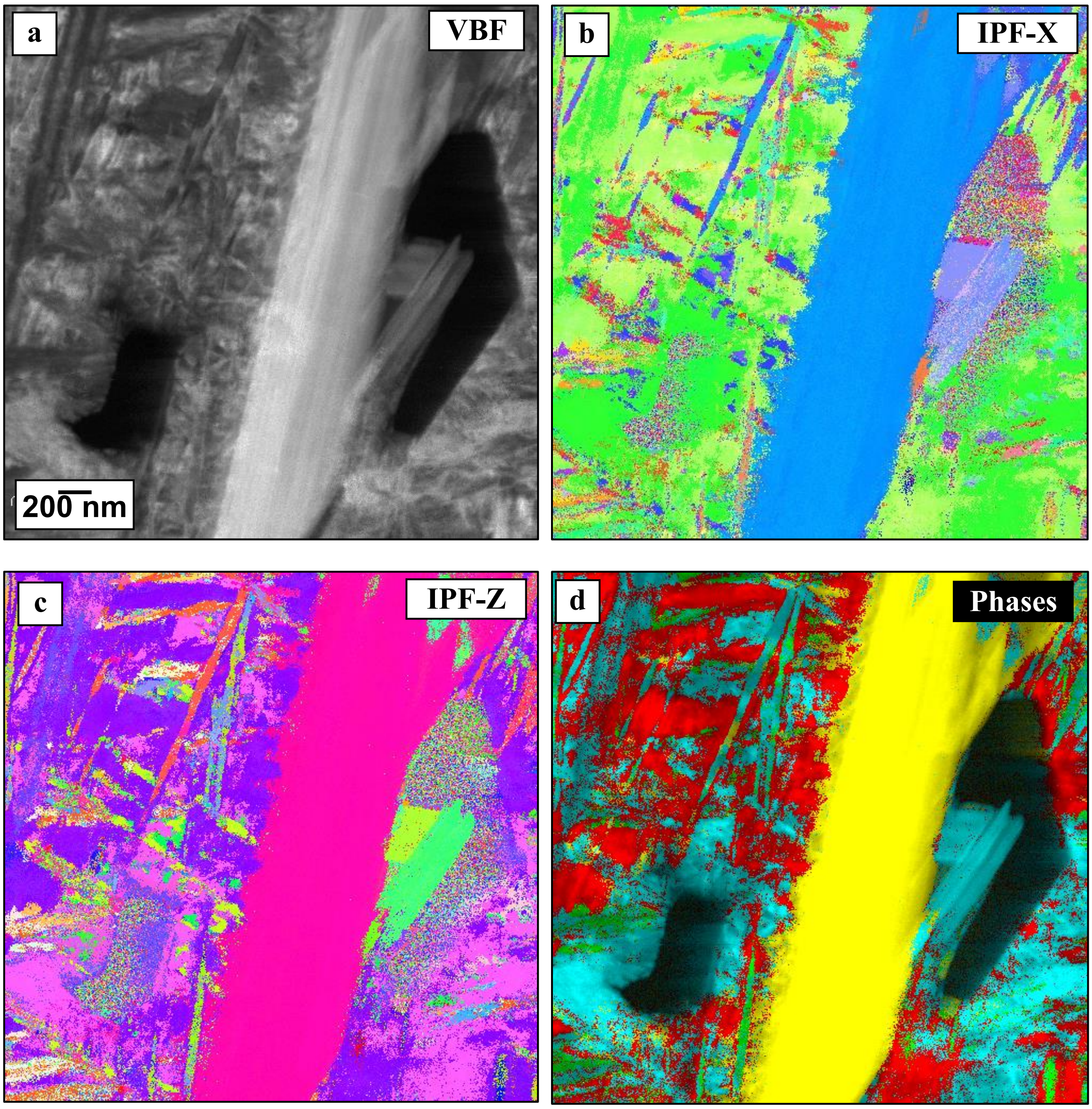


Fig. 12: TEM-ASTAR analysis of TMC samples of Ti-15Nb alloy matrix with 5% B_4C addition, resulting in TiB borides and TiC carbides presenting different results of white dotted line of **Fig. 11** (STEM-BF image) region as **(a)** virtual bright field (VBF) image, **(b)** inverse pole figure in X direction (IPF-X), **(c)** inverse pole figure in Z direction (IPF-Z) and, **(d)** Phases map combined with Index image showing β-Ti bcc phase matriz (in red), nanoscale α΄-Ti martensite needles hcp phase (light blue), TiB boride particle (in yellow), and TiC carbide particles (black regions), respectively.

3.4. Conclusions

The present study developed a new TMC by combining Ti-15Nb alloy with varying amounts of B_4C powders during argon arc melting. From the results obtained so far, it is possible to wrap up:

- XRD profiles indicated the occurrence of in situ reactions between the B_4C particles and Ti atoms in the solid solution, forming TiB and TiC precipitates. The corresponding Ti depletion in the matrix resulted in phase transitions, changing from $\alpha' + \beta$ to $\alpha'' + \beta$ phase composition;
- The microstructural analysis, including advanced characterization techniques, such as TEM, STEM-EDS, and TEM-ASTAR, confirmed the presence of microscaled precipitates, with a whisker and particle shapes, where the EDS results showed to be TiB and TiC, respectively. The number and size of the precipitates increased according to the amount of B_4C;
- Elastic modulus exhibited a gradual increase with the number of precipitates, resulting from the reduced dislocation movement in the matrix. While the hardness depicted an increase caused by solid solution and phase precipitation hardening effects from the reinforcements and the bulk phases;
- Dry sliding wear revealed a direct impact of the TiB and TiC precipitates on the wear track, especially the wear rate, which was highlighted under high applied loads. Furthermore, chemical analysis indicated the presence of oxidative reactions on the surface, forming mainly Ti oxide;
- *In vitro* biological tests indicated satisfactory preliminary results of the TMC samples, indicating proper cell viability, proliferation, and adhesion;
- The results show that it is possible to control the mechanical, tribological, and biological properties of the Ti-15Nb alloys by adjusting the formation of TiB and TiC precipitates during arc-melting. Thus, the production of these metal-matrix composites can be promising for the next generation of biomedical implants intended for long-term use.

Data availability

The raw-processed data required to reproduce these findings can be shared upon request.

CRediT authorship contribution statement

C.E. Silva: Investigation, Methodology, Data curation, Formal analysis, Writing – original draft. **V.R.M. Gonçalves**: Conceptualization, Investigation, Data curation, Validation, Supervision, Writing – Review & Editing. **C.R. Grandini**: Writing - review & editing, Funding acquisition. **C.R.M. Afonso**: Investigation, Data curation, Writing – Review & Editing. **S.A. Tsipas**: Investigation, Data curation, Writing – Review & Editing. **G.S. Almeida**: Investigation, Data curation, Writing – Review & Editing. **W.F. Zambuzzi**: Investigation, Data curation, Writing – Review & Editing. **D.R.N. Correa**: Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

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

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4. Considerações finais

O presente trabalho teve como objetivo produzir e caracterizar novos TMCs *in situ* com fusão a arco voltaico com diferentes concentrações de B_4C, a qual foi feita com sucesso.

De modo geral, a difração de raios X (DRX) indicou que ocorreram reações *in situ* do B_4C com o titânio, levando à formação de TiC e TiB. As imagens de Microscopia Eletrônica de Varredura/Espectroscopia por Dispersão de Energia (MEV/EDS) revelaram a morfologia dos precipitados, sendo as partículas mais arredondadas identificadas como TiC e os whiskers (microfilamentos) mais alongados como TiB.

Os testes de dureza demonstraram que a adição do material cerâmico aumentou a microdureza. A dureza subiu de 298,8 HV para 489,8 HV sob uma força de 0,025 kgf e também de 276 HV para 388 HV sob uma força de 2 kgf. Os testes do módulo de elasticidade também mostraram aumento com a adição de B_4C, variando de 66,57 GPa para 107,32 GPa. É importante notar que esses valores permaneceram inferiores ou semelhantes aos do titânio comercialmente puro (cp-Ti) e aos da liga Ti-6Al-4V.

Em relação aos testes de desgaste, o material apresentou boa resistência, conforme as imagens de MEV, que mostram trilhas de desgaste de menor tamanho. No entanto, em termos de quantidade de material perdido, a resistência não foi tão alta, o que provavelmente se deve à adesão de algumas partículas ao contracorpo, removendo, assim, mais material da amostra. Por fim, os testes biológicos apresentaram resultados satisfatórios, com todas as amostras apresentando valores acima do grupo controle, o que sugere boa viabilidade e adesão celular.

Ou seja, o TMC de Ti-15Nb com reforços de TiC e TiB apresentou boa avaliação mecânica e resistência ao desgaste, além de não ser citotóxico. Dessa forma, seu uso pode ser considerado para a avaliação de implantes biomédicos.

Por fim, é necessário investigar como essa liga se comportaria com a adição de um tratamento de superfície através do método de oxidação por micro-arco. Outras perspectivas seria variar o reforço utilizado, ou também mudar a forma em que os compósitos foram feitos, como por exemplo por manufatura aditiva.

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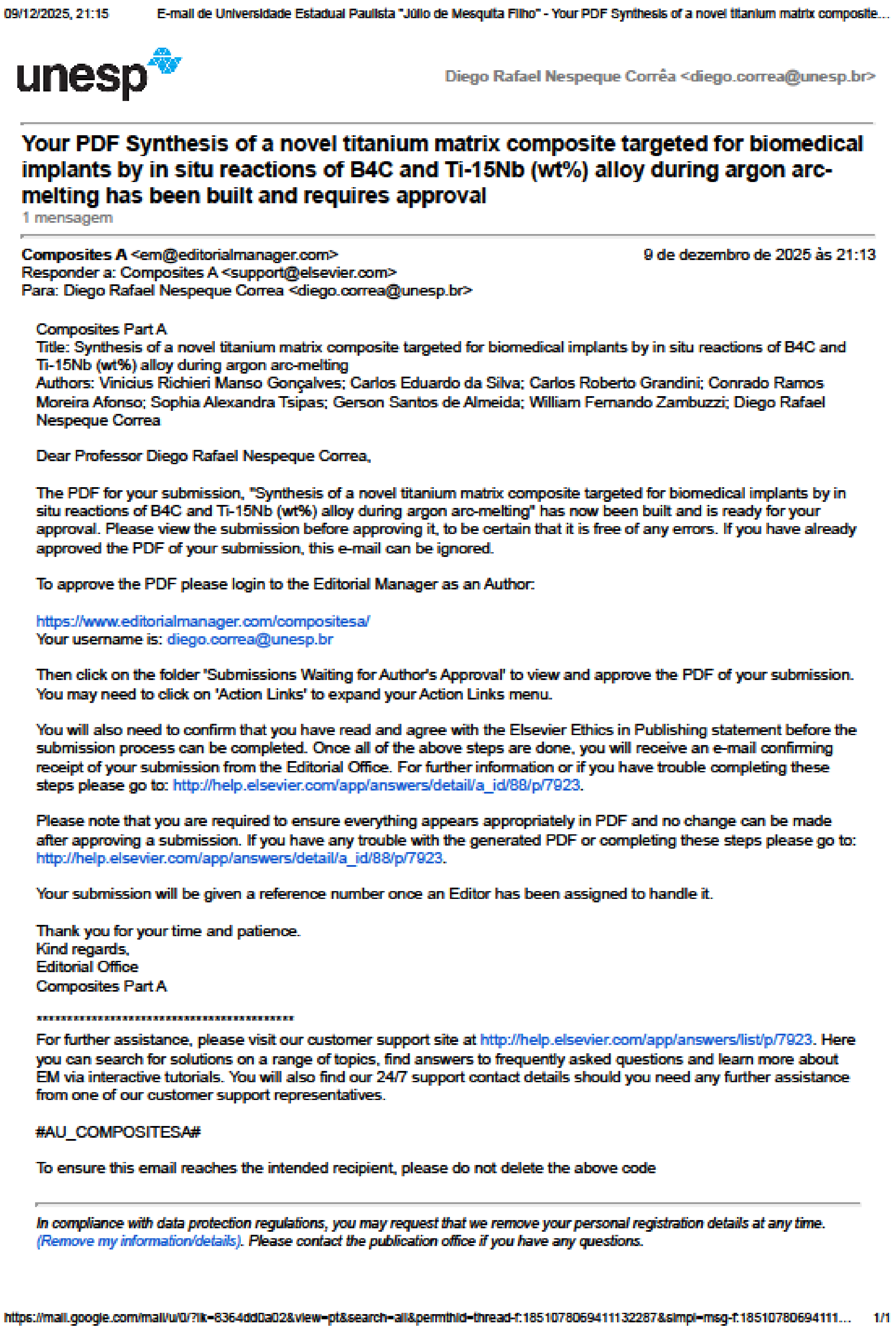

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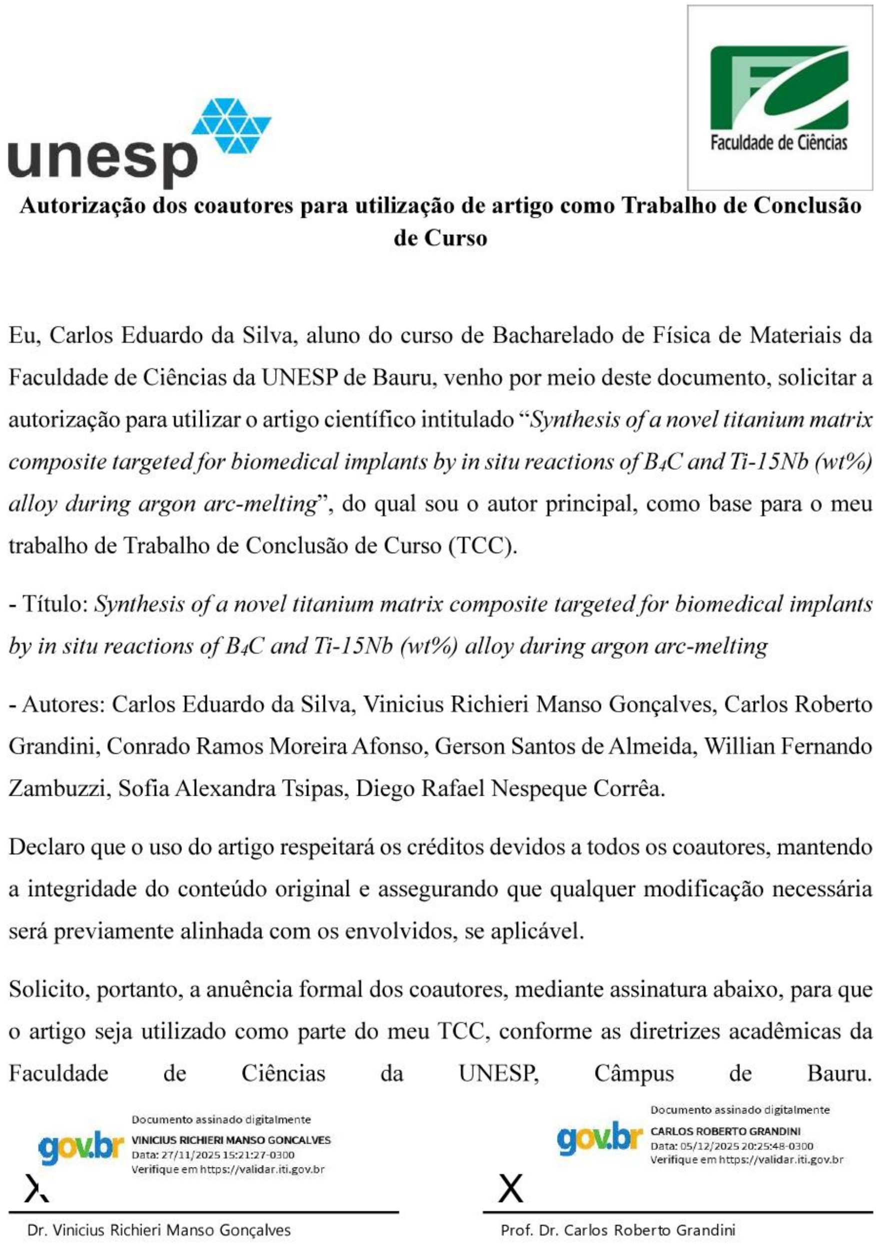

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