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THE INFLUENCE OF TiO_2 NANOPARTICLES ON THE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF AA2024 ALUMINIUM ALLOY

PREUČEVANJE VPLIVA DODAJANJA NANO DELCEV TiO_2 NA MEHANSKE LASTNOSTI IN MIKROSTRUKTURO ALUMINIJEVE ZLITINE AA2024

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In this study aluminum alloy 2024 was reinforced with different mass fractions (0 *w*/%, 2.5 *w*/%, 5 *w*/%, and 7.5 *w*/%) of titanium dioxide nanoparticles using the stir-casting method. The main objective was to study an effect of an addition of TiO_2 nanoparticles on the microstructure and the mechanical properties of the 2024 aluminum alloy composite fabricated by stir casting. Scanning electron microscopy, energy-dispersive analysis, as well as X-ray diffraction analysis were implemented to characterize the microstructure, elemental and phase composition of the samples. The tensile and Vickers hardness tests were carried out to evaluate the mechanical properties. The results showed that the addition of 7.5 *w*/% TiO_2 nanoparticles increases the ultimate tensile strength by 37 % and elongation by 71 % while decreases the hardness by 14 % comparing with the initial alloy. The highest hardness was demonstrated in the alloy with 5 *w*/% TiO_2.

Keywords: metal-matrix composites, nanoparticles, aluminum matrix, aging

V študiji smo ojačali aluminijevo zlitino 2024 z različnimi masnimi deleži (0 *w*/%, 2.5 *w*/%, 5 *w*/% in 7.5 *w*/%) nanodelcev titanovega dioksida z metodo mešalnega litja. Glavni cilj je bil preučiti učinek dodatka nanodelcev TiO_2 na mikrostrukturo in mehanske lastnosti kompozita iz aluminijeve zlitine 2024, izdelanega z mešalnim litjem. Za karakterizacijo mikrostrukture, elementarne in fazne sestave vzorcev so bile uporabljene vrstična elektronska mikroskopija, energijsko-disperzijska analiza in analiza rentgenske difrakcije. Za ovrednotenje mehanskih lastnosti so bili izvedeni preskusi natezne trdnosti in Vickersove trdote. Rezultati so pokazali, da dodatek 7.5 *w*/% nanodelcev TiO_2 poveča končno natezno trdnost za 37 % in raztezek za 71 %, medtem ko zmanjša trdoto za 14 % v primerjavi z izhodiščno zlitino. Največjo trdoto je izkazala zlitina s 5 *w*/% TiO_2.

Ključne besede: kovinski matrični kompoziti, nanodelci, aluminijeva matrika, staranje

1 INTRODUCTION

One of the most difficult aspects of producing strong, light, and low-cost engineering materials is getting a high strength-to-weight ratio suitable for vehicles.[1] The global need for such products in the automobile and aerospace industries has attracted the attention of researchers in the field of composite materials.[2,3] Due to the excellent mechanical properties, aluminum-matrix composites (AMCs) are advanced materials that combine the characteristics of a light and tough matrix material with hard ceramic reinforcement.[4] AMCs satisfy the market need for lightweight, durable, and high-performance components.[5,6]

Traditionally, the most common ceramic reinforcements used in AMCs in the last few decades are carbides (SiC, TiC), oxides (Al_2O_3, ZrO_2, TiO_2), and nitrides (TiN, AlN) "e.g.".[7,8] Divagar et al.[9] showed that the addition of 10 *w*/% SiC and 5 *w*/% Al_2O_3 nanoparticles in 7075-T651 aluminum alloy increases the fatigue strength by 13 % compared with the base metal. The presence of ZrO_2 nanoparticles in the aluminum matrix significantly improves the wear resistance and hardness of A356 aluminum alloy.[10] Jaber et al. demonstrated that the 6063-T6 aluminum alloy reinforced by 7 *w*/% TiO_2 nanoparticles had 13 % more fatigue strength than the base metal.[11] An addition of 2 *w*/% TiN nanoparticles in Al2024 followed by aging increases the tensile strength by 38 %, while the yield strength and elongation decrease from 376.5 MPa and 12.7 % to 359.1 MPa and 9.4 %, respectively.[12]

Aluminum alloy 2024 (AA2024) contains Cu, Mg, Mn, and some other minor alloying elements and has an excellent tensile-to-yield strength ratio at elevated temperatures, high ductility, fatigue, and fracture resistance.[13] These properties as well as the capability to form second-phase precipitates for improved strength (age-hardening) determine the high demand of AA2024 in the aerospace and automobile industries. It was demonstrated that the addition of 10 *w*/% TiO_2 nanoparticles

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with an average size of 50 nm in AA2024 matrix by mechanical milling and hot-pressing increases the Vickers hardness by 54 % and the strength by 13 %.[14] Although the properties of the composite are improved compared with the monolithic alloy, the drawback of this technology could be a low elongation value, which might negatively influence the reliability of the alloy when external stresses are applied. Creep resistance is also enhanced by incorporating of 3 φ/% TiO_2 nanoparticles (15 nm in size) in an Al matrix since the creep behavior depends predominantly on the diffusional flows of the matrix that are strictly limited by the nanoparticles.[15] After examining the available resources, it was discovered that there is limited research on the impact of incorporating titanium into Al-Cu-Mg alloys through stir casting. The AA2024 aluminum alloy is a part of the Al-Cu-Mg alloy series that relies on s (Al_2CuMg) and θ (Al_2Cu) precipitates as the primary sources of strength. Introducing titanium into this alloy category can facilitate the development of titanium aluminides with high strength. A challenge with Al-Cu-Mg alloys is their vulnerability to thermal instability at high temperatures. Nevertheless, by creating titanium aluminides that possess excellent thermal stability and ensuring their uniform distribution within the aluminum matrix, the thermal stability of these alloys can be enhanced.

Since AA2024 has promising properties in different fields and Al-Cu-Mg alloys can be hardened by adding hard particles during material production, this study aims to investigate the mechanical properties of an AA2024 alloy fabricated through conventional stir casting with the addition of different mass fractions of TiO_2 nanoparticles.

2 EXPERIMENTAL PART

In this study 2024 aluminum alloy with the composition of 92.8 *w*/% Al, 1.04 *w*/% Mg, 0.78 *w*/% Mn, 5.33 *w*/% Cu, 0.1 *w*/% Zn and 0.2 *w*/% Fe was selected as a matrix material. As a reinforcement material we used nanoparticles of TiO_2 with a purity of 99.8 % and a size of 30 ± 5 nm, as shown in **Figure 1**.

Before adding the TiO_2 nano powder with the different loading fractions of 2.5 *w*/%, 5 *w*/%, and 7.5 *w*/%, the 2024 aluminum alloy was preheated to 700 °C (more than the matrix melting temperature) in a graphite crucible using an electrical furnace to ensure the complete melting of all its components. Using argon as the carrier gas, it was introduced into the molten material as illustrated in **Figure 2**. Subsequently, the resulting molten material was poured into a cylindrical mold measuring 22 mm in diameter and 200 mm in length. The stir casting technique was utilized for 4 minutes at 200 min^{-1} to ensure proper mixing and dispersion of the reinforcement material. The stirring action helps achieve a homogeneous distribution of the reinforcement, reducing the possibility of agglomeration or clustering. The specified time and rotation speed were determined based on previous studies or experimental optimization to achieve the desired level of dispersion and ensure the quality of the resulting composite material.[16] Then the molten material was poured into molds and removed after solidification. The samples were then solution annealed by heating to 500 °C for 4 h in an air-circulated furnace, water quenched at room temperature and precipitation annealed (aged) at 17 °C for 3 h.

Tensile tests were conducted at room temperature using an INSTRON 1125 universal testing machine in accordance with the ASTM standard E8/E8M. The tensile

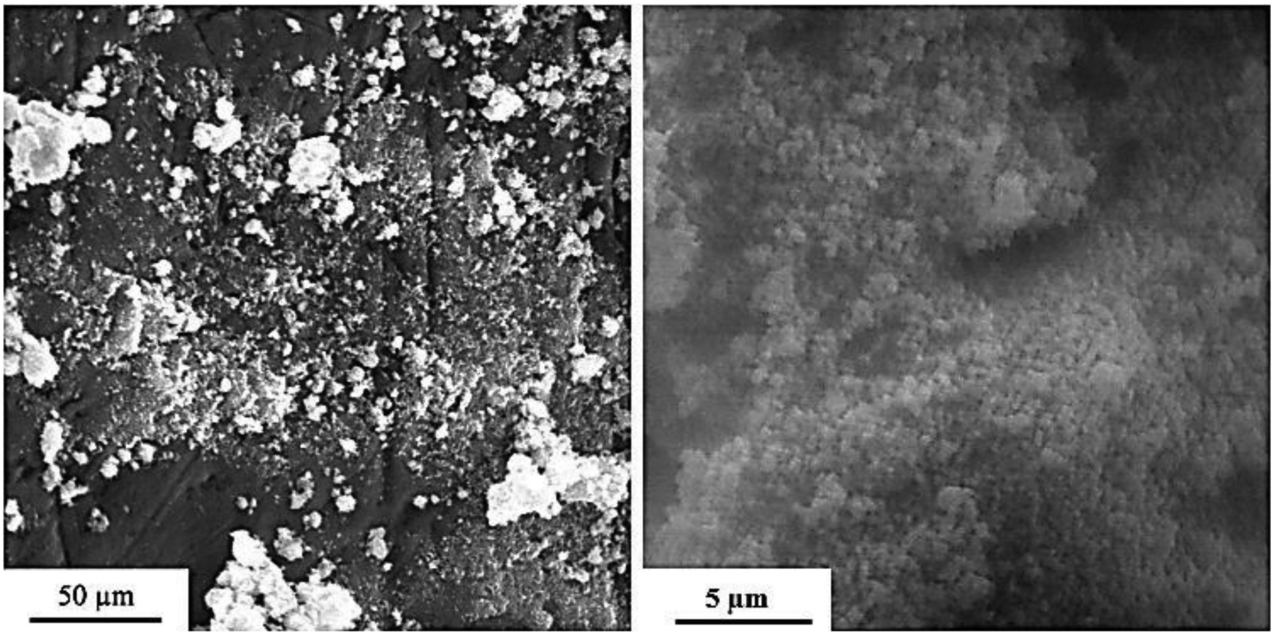

Figure 1: SEM micrographs of TiO_2 nanoparticles

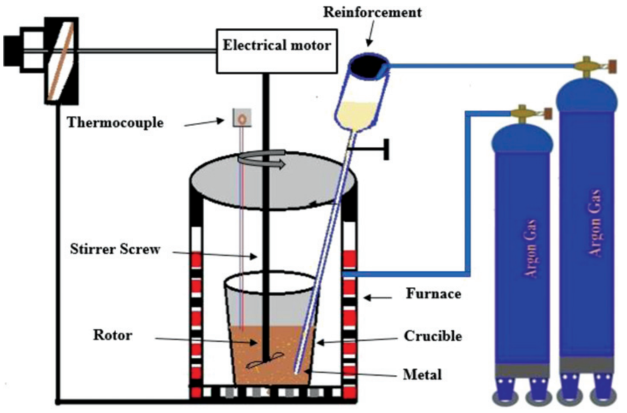

Figure 2: Stir-casting furnace for melting

specimen used was a flat shape, with a load of 5 kN applied at a deformation rate of 2 mm/min. The yield stress of the composites was determined using the offset method at 0.2 % strain from the stress vs. strain curve.

For microstructural characterization the samples were prepared by the standard metallographic procedure and etched for 15 s using Kroll's reagent (H_2O: HNO_3: HF = 92:6:2). Scanning electron microscopy (SEM) (by TESCAN VEGA) and energy disperse spectroscopy (EDS) (by INCA Energy) analyses were carried out to reveal the microstructure and elemental composition distribution of materials.

XRD analysis was performed to examine the structure of the phases and precipitates revealed by SEM. These results were obtained using a DRON-7 instrument (Russia) with Cu-K_α radiation operated at 40 kV, 30 mA and Bragg angles from 20° to 100° with a step size of 0.02° and a scan step time of 5 s.

The Vickers hardness was determined on the polished surface using a HV-1000 tester at a load of 0.025 N for a dwell time of 10 s. At least 10 indentations were made on each sample to obtain the average values.

3 RESULTS AND DISCUSSION

Figure 3 shows the results of tensile and hardness tests of the obtained samples with the various mass fractions of the reinforcing TiO_2 particles. In general, the samples behaved in a brittle manner, as can be deduced from the low values of the elongation at break (not more than 6 %). The initial sample shows the ultimate tensile strength (UTS) of 208 MPa and elongation before fracture of 3.5 %. An addition of 2.5 *w*/% of TiO_2 particles increased the UTS by 43 % to 299 MPa and elongation by 18 % to 4 %. A further increasing of the content of TiO_2 up to 5 *w*/% slightly decreased the UTS from 299 MPa to 273 MPa and an almost unchanged elongation. In terms of balance between the strength and plasticity the alloy obtained by addition of 7.5 *w*/% of TiO_2 showed the optimal properties, compared with the others, due to the relatively high UTS of 286 MPa and elongation of 6 %. The yield stress of the fabricated composites reaches its maximum value of 240 MPa at the 2.5 *w*/% TiO_2, which is higher than in the initial material by 20 %.

Figure 3b illustrates the plotted values of Vickers hardness as a function of TiO_2 mass content. The addition of 2.5 *w*/% and 5 *w*/% of TiO_2 increases the hardness up to 13 % and 40 %, consequently, while at 7.5 *w*/% TiO_2 the value decreases by 14 %. Such an increase can be attributed to the presence of TiO_2 particles in the aluminum matrix that hampers the movement of dislocations.

Comparing with the results of previous research the composites fabricated in this study have less UTS, YS and Vickers hardness, but better elongation before fracture. This might be attributed to the different routes of fabrication of the materials. The route consisted of me-

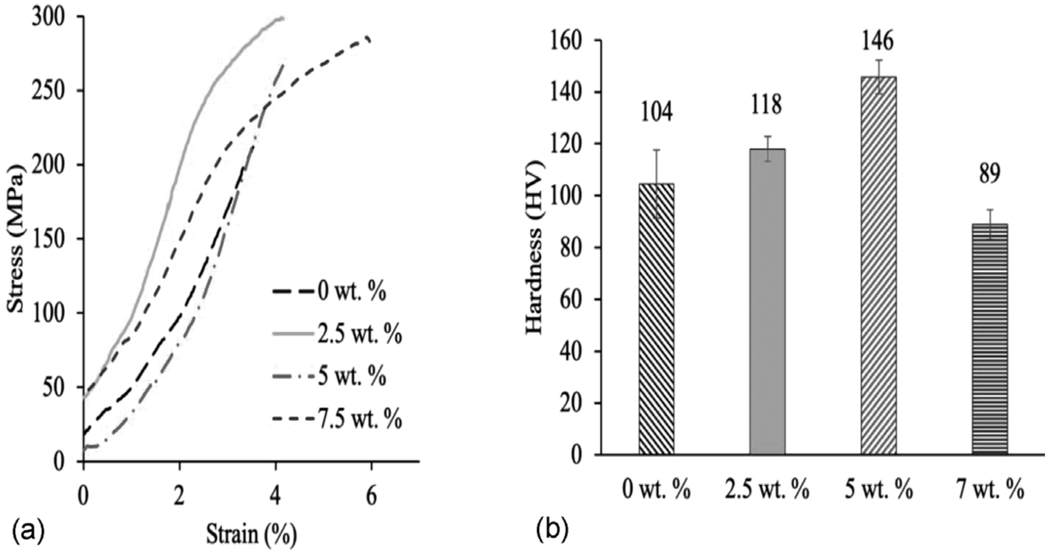

Figure 3: a) Stress-strain curves and b) Vickers hardness of 2024 aluminum alloy with the different mass fractions of TiO_2

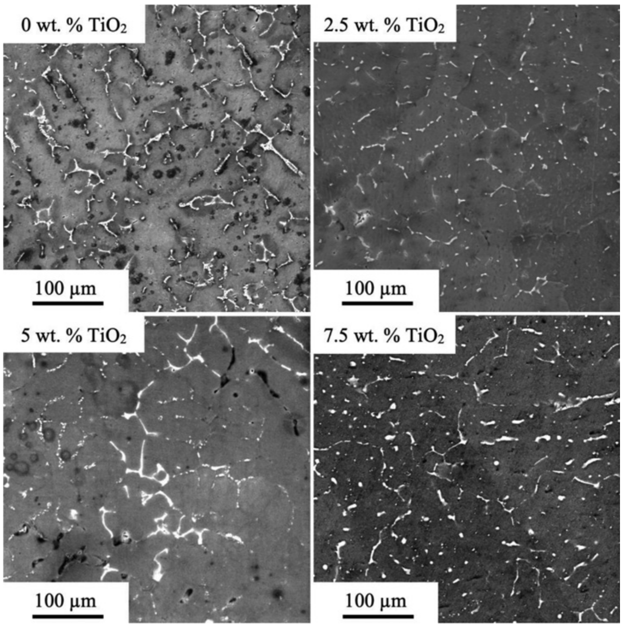

Figure 4: SEM micrographs of 2024 aluminum alloy with the different mass fractions of TiO_2

chanical milling followed by hot-pressing. The external stress during the fabrication led to the higher density of composite (maximum 2.87 g/cm^3 at 10 *w*/% of TiO_2 nanoparticles) and, consequently, the higher hardness values. Stir casting followed by solution aging used in this study probably provided less dense composites but also more mobile dislocations that contribute to plastic deformation.[17] Therefore, the maximum elongation was higher (by 2.5 %).

Figure 4 shows the microstructure of the fabricated samples after casting and heat treatment. The secondary phases composed of the alloying elements are distributed alongside the grain boundaries and as separate particles inside the boundaries. The area fractions of the intermetal ides (white regions) obtained using image analysis software ImageJ revealed the following results: initial sample has 4.4 % of intermetal ides, at 2.5 *w*/% TiO_2 – 7.3 %, at 5 *w*/% TiO_2 – 3.5 %, and at 7.5 *w*/% TiO_2 – 5 %.

Solution annealing and aging of 2024 aluminum alloy result in the formation of $CuAl_2Mg$ and $CuAl_2$ precipitates **Figure 5 and 6.** The addition of TiO_2 particles may increase the number of precipitates after a homogenization and aging treatment.[18] However, **Figure 4** shows that Ti particles are distributed uniformly in the microstructure of the 2024 alloy without the formation of precipitates even alongside the grain boundaries where the accumulation of particles and precipitates usually occurs. This might be related to the high solubility of TiO_2 nanoparticles in the structure of the matrix.[19]

According to the X-ray diffraction patterns for the 2024 aluminum composite presented in **Figure 6**, the intensities of the peaks gradually rise as the amount of

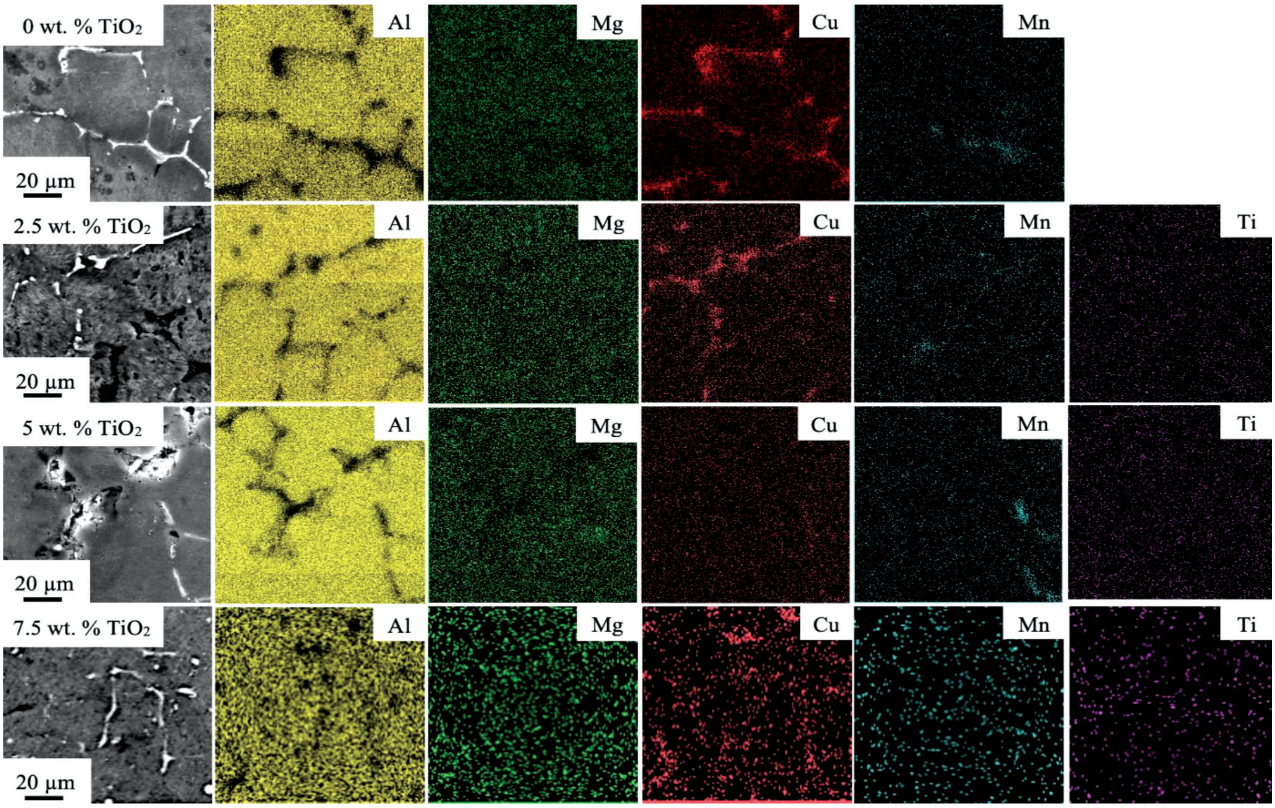

Figure 5: SEM image of AA 2024 alloy with the different loaded TiO_2 fraction. Elemental mapping was utilized to prove the presence of Ti atoms in the microstructure.

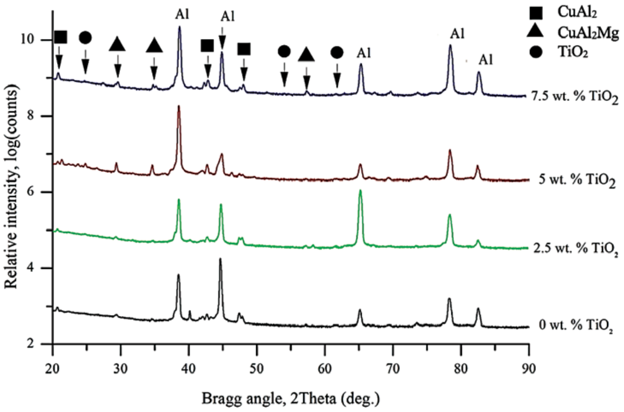

Figure 6: Diffraction pattern of the 2024 with the different loading fractions of TiO_2 nano powder

TiO_2 increases due to the broadening effect.[20] Al peaks are observed at 38.50°, 44.64°, 65.14°, 78.18° and 82.5°. The major peaks of precipitates of the second phases are related to Al_2Cu, $MgCuAl_2$. The peaks related to TiO_2 nanoparticles have low intensities, even with the increasing of the mass fraction. In the literature, there are reports of reactions between Al and TiO_2, which yields Al_3Ti and Al_2O_3 as final results.[21] In this study, however, no obvious reacted product is apparent, which is in good agreement with the results of the SEM-EDS analysis.

To sum up, stir-casting technology is a suitable technology for producing AA2024-TiO_2 composites. The mechanical properties of these composites are slightly lower than those obtained by mechanical milling, but due to the lower cost in some cases this technology might be more economic. A further investigation should be carried out to evaluate other properties of the AA2024-TiO_2 composites fabricated by this method, such as wear and corrosion resistance, fatigue strength, etc.[22]

4 CONCLUSIONS

In this study, AA2024 was reinforced by TiO_2 nanoparticles with different mass fractions using the stir-casting process. Aging was implemented to improve the mechanical properties of the alloys. The following conclusions can be drawn:

1. The strength and plasticity of the composite increases with the increasing mass of TiO_2 nanoparticles. The highest UTC of 299 MPa was obtained in the alloy with 2.5 *w*/% TiO_2. The optimal combination between strength and elongation is obtained at 7.5 *w*/% TiO_2, which showed UTS of 286 MPa and elongation of 6 %.

2. The Vickers hardness was increased by 40 % when 5 % TiO_2 was added, compared with the initial A2024 alloy. This improvement might be related to the solution-hardening mechanism in which TiO_2 particles behave as obstacles and hamper the movement of dislocations.

3. Scanning electron microscopy showed that Ti is uniformly distributed in the microstructure in each sample, independently of the mass fraction of TiO_2. There were no distinguishable precipitates found alongside the grain boundaries.

4. XRD analysis showed no results of reactions between TiO_2 and Al, confirming the SEM results.

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