Microstructures and Characterization of Ti6Al4V Alloy Friction Stir Alloyed with Cu and Al Powders

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Abstract. Friction stir processing (FSP) has been used to prepare composite materials by admixing copper and aluminum powder blends with Cu/Al mass ratios 2:1, 1:1 and 1:2 into Ti6Al4V alloy matrix using a nickel superalloy FSP tool. Structural evolution of a stir zone material was studied as depended on the Cu/Al mass ratio and number of FSP passes. The content of α(α’)-Ti increased in all samples after the first FSP pass but then slowly reduced with the FSP pass number increased to 4. The inverse dependence of β-Ti content on the FSP pass number was demonstrated. Intermetallic compounds Ti₃CuₓAlₓ, TiₓAlₓ and TiₓCuₓ were detected in the stir zone obtained by admixing 2:1, 1:1 and 1:2 powder blends. The maximum tensile strength in the range 1050-1200 MPa was achieved after 4-pass FSP on all samples with ~35% reduction of the ductility as compared to that of the as-received alloy. The stir zones also had increased microhardness numbers as measured across the stir zone section perpendicular to the FSP tool travel direction.

Keywords: friction stir processing, titanium alloy, surface modification, in situ, Ti-Cu-Al composite

1. Introduction

Titanium alloys are widely used in the aerospace, aviation, chemical and biomedical industries because alloying them with β-Ti, or α-Ti supporting elements allows obtaining a set of microstructures and mechanical characteristics suitable for numerous applications [1,2]. The weak point of titanium alloys may be their low wear resistance, fracture toughness and stability under severe weather conditions [3-5]. These characteristics may be improved by adding alloying elements such as Cr, Fe, V, and Cu that allow forming reinforcement intermetallic compounds. For instance, titanium-copper alloys are known that demonstrate reduced friction and improved wear resistance [6] as well as antibacterial properties [7,8] and low corrosion rate in biological fluids [9,10].

Bo Li et al. [11] mentioned that Cr, Al, V and Cu may form anti-combustion dense oxide layers on the titanium alloy surface that block penetration of oxygen deeper into the base metal. Otsuka H. et al. [6] demonstrated the efficiency of Ti/Cu and Ti/Cu/Nb alloys against high-temperature oxidation in hot exhaust systems.

The majority of literature sources devoted to the Ti-Cu-Al alloys deal with their production by casting [6,12], while considerably less number of them are dedicated to standard powder metallurgy approach [13] or high-frequency induction sintering [10], which afford fabricating the Ti-Cu-Al alloys, but come with some drawbacks related with high requirements applied to equipment due to high reactivity of titanium, evaporation of the alloying elements and undesired segregations [15-18].

A new generation of materials and technologies has been developed during the last decades in accordance with a tendency for replacement of conventional metal alloys with composite materials. The latter are more efficient in force transmission, improvement of weight efficiency as well as allow combining functional characteristics such as strength, corrosion and wear resistance, which is important in many applications, including aerospace vehicles, steam and gas turbines, pipelines, etc. [19].

In the last decade, friction stir processing (FSP) [20] has proven to be an effective and promising method for producing high-performance surface composites by admixing powders into metallic matrix. Using powder for in-situ preparation of composites by FSP is a relatively new and widely
used now approach in material sciences. Initially, the FSP method was used to obtain a fine-grained and equiaxed microstructure with a high proportion of high angular boundaries (> 80-90%) in the Ti6Al4V subsurface, which resulted in enhanced superplastic behavior of the processed metal with elongation up to 400-1400 % [21-24].

Admixing chemically stable ceramic particles to the ductile matrix is one of the approaches used for preparing metallic matrix composites by FSP. For instance, the FSP was used for preparation of composites on the Ti6Al4V by admixing ceramic particles such as TiO₂ [25] and B₄C [26], respectively. Those composites possessed higher hardness, elasticity modulus and compression strength as compared to the base metal. Lechun X. et al. [27] studied a Ti-6Al-4V/Ag biocomposite prepared by FSP for fabricating an orthopedic bone fixing device. Another approach may be used when admixing elements that capable of forming reinforcement particles by reacting with the alloying elements during the FSP [28-30]. For instance, aluminum matrix low density composites with excellent strength have been obtained using such an approach [29,30].

Such an in-situ synthesis of mainly intermetallic compounds (IMCs) is the key factor that determines structural and mechanical characteristics of the FSPed composites. The FSP is carried out at temperatures below the melting point of titanium and therefore IMCs are formed by solid state reaction-diffusion facilitated by intensive dynamic shear deformation between powder particles and the titanium alloy matrix, i.e. much alike the what occurs during mechanical alloying. Such an approach allows for obtaining smaller IMC particles dispersed in the ductile matrix instead of large ones obtained in a melted state.

On the other side, it would be desirable to maintain the phase composition of the base alloy, for instance, by adding alloying elements to the copper powder. Controlling IMC and matrix alloy grain size is a way of tailoring the FSP composite for the specific application conditions [31].

Considering the beneficial effect of Cu and Al on the properties of Ti6Al4V when producing composite materials by various methods, the novel study is necessary to demonstrate the feasibility of FSP in-situ production of Ti-Cu-Al composites. To our best knowledge, the effect of admixing Cu/Al powders into Ti6Al4V alloy has never been investigated earlier. Therefore, this would be a productive approach for revealing structure evolution and mechanical characteristics of the Ti-Cu-Al FSP composites.

2. Materials and Methods
Samples in the form of 60×300×2.5 mm³ plates were EDM cut off a Ti6Al4V as-received sheet with element composition as follows: 5.18 wt.% Al, 4.45 wt.% V, 0.228 wt.% Fe, 0.104 wt.% Ni, 0.002 wt.% Zr and balance of Ti. The microstructure of the as-received samples was composed of α-Ti and grain boundary β-Ti grains characterized by their mean sizes 4.5 ± 1.7 μm and 1.4 ± 0.7 μm, respectively (Fig. 1(a)). The content of β-Ti was ~15 vol.%.

Commercial 99.5% and 99.8% purity copper and aluminum powders with mean particle sizes 12.8±5.6 μm and 36.1±18.9 μm, respectively, were used for FSP intermixing with Ti6Al4V (Fig. 1(b, c)).

![Fig. 1 SEM BSE images of Ti6Al4V microstructure (a); Cu (b) and Al (c) powders.](image-url)
The powders were intermixed in a ball mill for 15 min to obtain powder mixtures with contents of both components as those shown in Table 1. Let us remind that Al and Cu are $\alpha$-Ti and $\beta$-Ti stabilizers, respectively. Also both of them may from intermetallic compounds with titanium.

Before FSP (Fig. 2(a)) the Ti6Al4V plates were prepared by drilling $\varnothing$1.2 mm and 2 mm depth holes with 5.4 mm spaces between them as shown in Fig. 2(b), filling the holes with the powder mixtures and compacting them so that the total content of the Cu+Al powders in the subsurface layer of corresponding thickness was ~5 vol.%. A FSP tool with threaded truncated cone 2 mm of height pin and $\varnothing$20 mm shoulder was machined from a nickel-containing heat resistant superalloy. The use of the truncated cone tool was dictated by the necessity for providing uniformity of metal transfer in FSP while the lack of thread allowed reducing its wear by diffusion wear mechanism.

Preliminary FSP experiments with Ti6Al4V allowed obtaining optimal parameters for FSP on Ti6Al4V as those shown in Table 1. Anticlockwise rotation of the tool inclined at an angle of 3° with respect to the vertical axis (Fig. 2(a)) was applied to obtain two parallel FSP tracks with their centerlines coinciding with the lines of powder-filled holes. These tracks included 4 portions sequentially subjected to 4-pass, 3-pass, 2-pass and 1-pass FSP in the left to right order. A water-cooling system and argon shielding were used to reduce heating and oxidizing of the tool and FSPed metal, respectively.

**Table 1. Cu/Al powder mixture compositions and FSP parameters.**

<table>
<thead>
<tr>
<th>Powder mixture</th>
<th>Mass Cu/Al ratio</th>
<th>FSP parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pass number</td>
</tr>
<tr>
<td>Ti/(2Cu+1Al)</td>
<td>2 : 1</td>
<td>4</td>
</tr>
<tr>
<td>Ti/(1Cu+1Al)</td>
<td>1 : 1</td>
<td>4</td>
</tr>
<tr>
<td>Ti/(1Cu+2Al)</td>
<td>1 : 2</td>
<td>4</td>
</tr>
</tbody>
</table>

Samples for microstructural analysis and mechanical characterization were EDM cut off the FSP tracks as shown in Fig. 2(c) so that when secured in a tensile machine UTS-110M-100 their tensile axes would be oriented along the FSP track centerline while metallographic views represented the cross section areas perpendicular to that centerline. The latter were prepared according to a standard grinding, polishing and etching procedure. The etching was performed by holding the polished samples in 40% HNO$_3$ for 2 min and rinsed under water.

Metallographic examination of the samples were carried out using optical microscope Altami Met 1S and scanning electron microscope (SEM) Zeiss LEO EVO 50 attached with an EDS add-on.
Thin foils for TEM were EDM cut and then thinned using the focused ion beam. TEM instrument JEOL-210 was used for detecting phases and microstructures using both bright-field and dark-field methods. The phase analysis was carried out using an XRD diffractometer DRON–7 (Burevestnik, Saint Petersburg, Russia) with Co-Kα radiation (λ = 1.79026 Å) at a current of 24 mA and a voltage of 35 kV. A scan range of 30–100° (2θ) with step size of 0.05° and counting time of 45 s was used. The diffractograms were treated using the software package PDWin. Microhardness profiles were obtained using a microhardness tester Duramin 5 at 100 g load and a dwell time of 10 s. Tensile tests were carried out using a tensile machine UTS-110M and samples oriented with their tensile axes along the FSP track length (Fig. 2c).

3. Results

3.1. Surface temperature and tool travel resistance

Optimal parameters for FSP on a Ti6Al4V plate were determined in previous experiments as follows: plunging force 2300 N, rotation rate 375 rpm (ω=39.25 s⁻¹) and tool travel speed 86.6 mm/min (v = 0.00144 m/s). These parameters provided then heating the track surface to ~800-950°C that was the result of frictional heating. Let us note that temperatures and resistance force dependencies on time were obtained earlier on Ti6Al4V and Ti6Al4V+Cu systems [34]. It was noted that intermixing of copper powder occurred at higher resistance force as compared to those on pure titanium alloy for the first three FSP passes. Also the first passes on Ti and Ti+Cu were characterized by temperatures as high as 1100°C and 1200°C, respectively. Introducing a low-melting element that will intermix with the severely deformed and plasticized Ti6Al4V will allow reducing the force. Aluminum is a component of Ti6Al4V and adding more of it as a powder mixture component will not have a dramatic effect on structures and phases formed in FSP.

Frictional heating intensity during FSP may be determined as mechanical power spent for FSP, \( N_{\text{tot}} = N_1 + N_2 \), where \( N_1 = M \cdot \omega \), \( N_2 = F \cdot v \), where \( M \) is the friction torque measured on the FSW machine spindle, \( \omega \) is the angular velocity, \( F \) is the tool travel resistance force, and \( v \) is the tool travel velocity.

Mean \( N_1 \) and \( N_2 \) values were calculated from in-situ measured time dependencies of the torque and resistance force, respectively, to compare with the similar mean temperature dependencies. It can be seen from the dependencies in Fig. 3(b), that \( N_1 \) values are about two orders of magnitude higher than those of \( N_2 \), i.e. it means that main heat input is from FSP tool rotational friction.

However, since the resistance force is determined by the plasticized metal flow then it can be sensitive to any heat-exchanging or heat generation processes occurring near the tool. Some extra heat-release processes must be involved that may come from diffusion reaction between the components with formation of intermetallic compounds.

\( Ti6Al4V \). FSP on as-received titanium alloys showed that temperature reduced as the number of passes increased (Fig. 3(a)). At the same time \( N_1 \) showed a tendency to increase with the number of passes (Fig. 3b). \( N_2 \) reduced in accordance to the temperature (Fig. 3(c)).

\( Ti/(2Cu+1Al) \). For Ti/(2Cu+1Al) the mean temperature reduced during the second pass and then increased at the third pass. The minimum temperature was shown during the fourth pass. The rotational N1 power (torque) reduced during the second pass and then started increasing with further passes (Fig. 3b). The \( N_2 \) dependence demonstrated reducing the resistance force as the number of passes increased (Fig. 3(c)). The maximum resistance force corresponded to the first pass and then consequently reduced as the pass number increased. Such a behavior of the resistance force is that commonly observed when conducting FSW/FSP over previously FSPed tracks structurally composed of fine recrystallized grains.

\( Ti/(1Cu+1Al) \). Temperature profiles observed on Ti/(1Cu+1Al) system showed maximum surface temperatures obtained during the second pass, namely, 1260-1320 °C, as compared to 1200 °C during the third and fourth passes (Fig. 3(a)). The behavior of \( N_1 \) was almost similar to that of observed above on the Ti/(2Cu+1Al) system (Fig.3b). The \( N_2 \) power (resistance force) dependence showed sharply increasing portion starting from a point corresponded to second pass (Fig. 3(c)).

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Ti-(1Cu+2Al). The mean temperatures on the FSP track varied within the 790 to 850°C range, i.e., it is considerably lower the temperatures obtained on both Ti/(2Cu+1Al) and Ti/(1Cu+1Al) systems (Fig. 3(a)). The specificity of this system was that the first pass allowed achieving the maximum surface temperature ~846°C, while for the next ones the temperature reduced. High friction force power N1 values were obtained during this experiment resulting from those of measured friction torque (Fig. 3(b)). High mechanical resistance was shown against the FSP tool rotation in less heated and plasticized material. The resistance force also increased starting from the minimum at the second pass analogous to that of 1:1 system. (Fig. 3(c)). In accordance with this the maximum resistance was exerted by the stirred metal during the third and fourth passes.

![Graphs showing FSP pass temperatures, torque power, and tool travel resistance force power](image)

Fig. 3 Averaged FSP pass temperatures (a), torque power (b) and tool travel resistance force power (c) for all systems FSPed.

When comparing the N1 and surface temperature behaviors vs. pass number one may say that maximum temperatures achieved on the surfaces of 2:1 ad 1:1 (Fig. 3(a)) that correspond to minimal N1 and N2 power values (Fig. 3(b,c)). At the same time both temperature and N1 dependencies of during FSP on both Ti6Al4V and 1:2 system show the same type of behavior when lower temperatures correspond to high friction torque and therefore high N1 power values. More complicate behavior is observed for N2 power which shows almost linear descending dependence from the pass number for Ti6Al4V and 2:1 samples and increasing one for 1:1 and 1:2 systems (Fig. 3(c)).

Some extra heat sources can have effect on the heating which can be in-situ reaction-diffusion between the alloy and powder components with formation of intermetallic compounds. One formed these IMCs increase the resistance of the stir zone metal to friction and tool travel.

It was shown [32] that Ti2Ni IMC were formed on the superalloy tool in FSP on Ti-(1Cu+1Al) system due to reaction diffusion which is accompanied by exothermic effect. Along with frictional heat such a heating serves to increasing the temperature of the metal layer transferred to the trailing part of the track. This layer is near the tool’s surface and composed of liquid aluminum, plasticized titanium alloy and dissolving Ti2Cu wear particles. From the metallurgical viewpoint there is a solid solution of Ni, Cu and Al in β-Ti, i.e. a composition corresponding to the Ti-rich corner of the Ti-Cu-Ni diagram at temperatures higher the eutectics points [32]. On being transferred behind the tool this layer sticks to the previously deposited one and there starts precipitation of IMCs such as Ti2Cu and Ti2N IMCs as well as β-Ti (Cu, Ni, Al) and α-Ti (Cu, Ni, Al) grains.

Copper content played the main role in the system behavior during FSP. As-received Ti6Al4V and Ti-(1Cu+2Al) system showed their close low temperature behaviors as depended on the pass number. Also their friction torque (N1) dependencies were close in distinction to those belonging to both Ti-(2Cu+1Al) and Ti-(1Cu+1Al).

3.2. Structures and phases in Ti/(2Cu+1Al) stir zone

XRD diffractograms obtained from the polished cross section views of all samples allow observing peaks belonging to HCP α-Ti and BCC β-Ti crystalline planes (Fig. 4). The β-Ti peak height is decreased after the 1-pass FSP which may be evidence of either full or partial β → α transformation. Also the α-Ti peaks change their intensities after the FSP which is usually due to texturing in the stir...
zone. Examining the angular position of an $\alpha$-Ti peak at 41.0-41.5° (Fig. 4(b-f)) one can see that the peak is broadened and shifted to the left after 1-pass and 2-pass FSP, i.e. its interplanar distance increased, plausibly due to $\alpha \rightarrow \alpha'$ transformation [33].

Fig. 4 X-ray diffractograms of as-received Ti6Al4V and FSPed composites Ti/(2Cu+1Al) (a), Ti/(1Cu+1Al) (b), Ti/(1Cu+2Al) (c) in the 20 ranges 35-100° (a, c, e) and 40-43° (b, d, f).

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The 1-pass FSP reduces the content of β-Ti with simultaneous increasing the content of α-Ti for all samples (Fig. 5). Further FSP passes show a monotonous inverse tendency for increasing the content of β-Ti and reducing that of the α-Ti. These dependencies allow suggesting that the full transformation cycle in FSP on the as-received alloy would be α→β during intermixing and then β→β+α/α’ in cooling. Further cycles allow some moderate stabilizing of the β-Ti due to increasingly more efficient intermixing and diffusion of copper into recrystallized titanium alloy grains.

Let us note that increasing the volume content of α-Ti after 1-pass FSP was inherent also with base Ti6Al4V FSPed without admixing any metals (Fig.5(d)) [33]. Furthermore, β→α/α’+β transformation had not been suppressed even in the stir zone of TiAl64V admixed with β-supporting copper [32]. However, slight increasing of the β-Ti content was observed with increasing the FSP pass number for all composites as well as for the FSPed Ti6Al4V.

Macrosopic optical images of stir zone (SZ) cross section views obtained after 1-pass, 2-pass, 3-pass and 4-pass FSP intermixing (2Cu+1Al) powder mixture into Ti6Al4V substrate allow observing that the degree of intermixing is increasing with the number of passes applied (Fig. 6(a,c,e,g)). The EDS profiles (Fig. 6(b,d,f,h)) obtained along the lines in (Fig. 6(a,c,e,g)) can be evidence in favor of such a conclusion. The 1-pass FSP stir zone in Fig. 6(a) shows at least two thin layers containing the powders. One of them that is characterized by tree-like structures has been formed in the pin-driven part of the stir zone while the other in the shoulder-driven part. EDS profile in Fig. 6(b) allows suggesting formation of high-titanium Ti-Al-Cu intermetallic compounds (IMC) in the bottom part while IMC found in the top part of the stir zone show less titanium containing

Fig. 5 Percentages of β-Ti and α(α’)-Ti phases in Ti/(2Cu+1Al) (a), Ti/(1Cu+1Al) (b) and Ti/(1Cu+2Al) (c) as depended on the FSP pass numbers.
IMCs. The content of the IMCs is increased with the number of passes thus forming thick composite structure subzones (Fig. 6(c,e,g)) in the bottom and top parts of the SZ.
Fig. 6 Macrostructures (a, c, e, g) and EDS linear distributions of elements across the stir zone in Ti/(2Cu+1Al) for different numbers of FSP passes (b, d, f, h).

Area A in Fig.6(a) was examined using TEM to show that α’-Ti grains with grain boundary α-Ti and lamellar α/β structures appeared after 1-pass FSP on Ti-(2Cu+1Al) (Fig.7(a,b)). In addition, Ti₃Cu₆Al₂, Ti₃Al₁ and Ti₃Cu₁y IMC grains were in-situ formed in the stir zone judging by EDS (Fig.7(c,d), Table 2). EDS profiles (Fig. 8(d)) and SAED patterns (Fig. 8(b,c)) obtained from area in Fig.8(a) allowed identifying TiCu₂Al and TiCuAl IMCs with neighboring β-Ti and recrystallized α-Ti enriched with both Cu and Al (Fig.7(c), Table 2). Isolated Ti₃Al(Cu) particles may grow between Ti₆Al₄V(Cu) and TiCuAl/TiCu₂Al grains (Fig.8(a,d)). Another type of IMCs formed in FSP is Ti₂Cu₃ enriched with ~17 at.% of Al (Fig.7(d), Table 2, lines 6-8).

![TEM images](image)

**Table 2.** EDS element concentrations in points indicated on the Ti-(2Cu+1Al) sample after 1-pass FSP (Figure 7(c)).

<table>
<thead>
<tr>
<th>Probe spot</th>
<th>Al</th>
<th>Ti</th>
<th>V</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.74</td>
<td>38.98</td>
<td>1.86</td>
<td>48.42</td>
</tr>
<tr>
<td>2</td>
<td>12.67</td>
<td>39.50</td>
<td>1.79</td>
<td>45.60</td>
</tr>
<tr>
<td>3</td>
<td>7.72</td>
<td>74.78</td>
<td>4.24</td>
<td>11.72</td>
</tr>
<tr>
<td>4</td>
<td>10.92</td>
<td>69.88</td>
<td>4.96</td>
<td>12.71</td>
</tr>
<tr>
<td>5</td>
<td>7.07</td>
<td>73.53</td>
<td>2.79</td>
<td>13.52</td>
</tr>
<tr>
<td>6</td>
<td>17.28</td>
<td>29.74</td>
<td>–</td>
<td>52.98</td>
</tr>
<tr>
<td>7</td>
<td>17.00</td>
<td>29.77</td>
<td>–</td>
<td>52.95</td>
</tr>
<tr>
<td>8</td>
<td>16.88</td>
<td>28.38</td>
<td>–</td>
<td>54.74</td>
</tr>
</tbody>
</table>

Fig. 7 Bright-field TEM images of α/β lamellar (a), grain boundary α-Ti and acicular α’-Ti (b). Intermetallic precipitates (c,d) in zone A located near the top surface of the stir zone in Ti-(2Cu+1Al) after 1-pass FSP.
Area B in Fig. 6(g) represents microstructures produced in the stir zone after 4-pass FSP on Ti/(2Cu+1Al) with better intermixing. Phases detected in this zone include $\alpha''$-Ti grains with grain boundary $\alpha$-Ti containing up to 15 at.% Al and 3.9 at.% Cu as well as Ti$_3$Al(Cu) IMCs (Fig. 9(a,b)).

The crystalline lattice of Ti$_3$Al is close to that of the h.c.p. $\alpha$-Ti, which is decomposed into Ti$_3$Al and TiAl at containing 39-46 at.% Al. The fact that Ti$_3$Al precipitates from $\alpha$-Ti in cooling after 4-pass FSP testifies in favor of suggestion that some effective intermixing is achieved. The temperature at which the Ti$_3$Al is usually formed is 1200 °C, therefore this phase was not found in the Ti/(1Cu+2Al) sample with the maximum used content of aluminum.

In addition on the above-described well-formed IMC grains there are ~30 μm in size core/multishell particulates inside the Ti6Al4V matrix (Fig. 10(a)), which were suspected to consist of Ti$_3$Al$_4$ and Ti$_6$Cu$_5$Al$_2$ IMC shells nested around a core. EDS element distribution profile (Fig. 10(b,c)) allowed confirming this suggestion that the unreacted Ti6Al4V core was covered by successively nesting TiCuAl, Ti$_2$CuAl$_5$, and Ti$_3$Al(Cu) shells. These particulates might be formed by slow diffusion reaction between Ti6Al4V matrix and Cu/Al powder agglomerates.
Fig. 10. SEM BSE micrographs of microstrictures in the Ti/(2Cu+1Al) stir zone parts: (a) top part, (b) medium part and (c) EDS element distributions.

No TiCu2Al IMCs were detected within the B area and therefore a suggestion was made that it could be transformed into TiCuAl or Ti2CuAl3 by means of enriching with both Ti and Al as a result of more intense stirring after 4-pass FSP. At least, no Ti2CuAl3 IMCs were found in the A area after 1-pass FSP.

3.3. Structures and phases in Ti/(1Cu+1Al) stir zone
Macroscopic images of Ti/(1Cu+1Al) show the FSP intermixing patterns similar to those observed above for Ti/(2Cu+1Al) (Fig. 11(a,c,e,g)). EDS profiles were obtained for all stir zones that demonstrated formations of Ti$_x$Cu$_y$Al$_z$ and Ti$_x$Al$_y$Ni$_z$ IMCs (Fig. 11(b,d,f,h)). Intense diffusion reaction occurred close to the surface at the distance 1000-1200 μm during the second pass (Fig. 11(d)).
Fig. 11 Macrostructures (a, c, e, g) and EDS linear distributions of elements across the stir zone in Ti/(1Cu+1Al) for different numbers of FSP passes (b, d, f, h).

SEM BSE images in Fig. 12 demonstrate the presence of Ti6Al4V (pos. 1, 5) and Al (Cu, Ti, Fe) (pos. 2-4) grains.

Grain boundary α-Ti, lamellar α/β, martensitic α’-Ti phases detected in the SZ after 4-pass FSP (Fig. 13(a-c)). The lamellar and grain boundary α-Ti are enriches with both aluminum and copper, i.e. contain ~15 at.% Al and ~1 at.% Cu (Fig. 13(a,c)).
Large multi-shell particles were also found in the Ti/(1Cu+1Al) FSPed (Fig. 14) samples that formed from agglomerated powder particulates. EDS element profiles across such a core-shell particle allows observing the core composed of Ti$_2$Al$_2$Cu IMCs and Ti$_x$Al$_y$Cu$_z$ (Ti$_3$Al, TiAl) shells with 14-27 at.% Al and 62-78 at.% Ti (Fig. 14(b)). Around the shells there are Cu-enriched Ti6Al4V.

3.4. Structures and phases in Ti/(1Cu+2Al) stir zone

The minimal 1:2 Cu/Al powder concentration ratio resulted in minimal surface temperatures during the FSP as compared to those of above discussed 2:1 and 1:1 powder mixtures (Fig. 3(a)). Even less
IMCs were formed in this case (Fig. 14) so that most of them were found in the core-shell particles (Fig. 15).
Fig. 15 Macrostructures (a, c, e, g) and EDS linear distributions of elements across the stir zone in Ti/(1Cu+2Al) for different numbers of FSP passes (b, d, f, h).

According to EDS, the core was composed of Ti$_2$Al$_5$Cu IMC with Ti (Al, Cu) shells (Fig. 16).

![EDS line scan](image1.png)

**Fig. 16 SEM BSE micrographs of microstructires in the Ti/(1Cu+2Al) stir zone parts**: (a) top part, (b) – medium part and EDS element distributions (c)

TEM shows the presence of grain boundary α-Ti, lamellar α/β and martensitic α’-Ti (Fig. 17).

![TEM images](image2.png)

**Fig. 17 TEM bright-field images of grain boundary α-Ti (a,b) and lamellar α/β-Ti (b) in the stir zone of Ti-(1Cu-2Al) after 4-pass FSP (a, b), SAED pattern (c) from image (b) and dark-field images (d-f) obtained using α reflection.**

3.5. **Mechanical characteristics of in-situ FSP Ti-Cu-Al composites**

The tensile test results obtained on the samples cut off the FSPed stir zones are shown in Figure 18 in comparison with as-received Ti6Al4V characteristics such as ultimate tensile strength (UTS) 1000 MPa and elongation-to-failure (ETF) 14.9%.

Ti/(2Cu+1Al) samples obtained after 1 to 3 pass FSP show both UTS and ETF lower than those of as-received Ti6Al4V, namely 888-974 MPa and 4.6-5%, respectively (Fig. 18(a)). The 4-pass FSP gives higher UTS=1177 MPa and ETF=6.1% (Fig. 18(b)).

Ti/(1Cu+1Al). The FSP provides UTS in the range 912-1032 MPa, i.e. somewhat higher than that of as-received Ti6Al4V while ETF is reduced from 5.5% to 4.2 (Fig. 18(b)).
**Ti-(1Cu+2Al).** The 1-pass FSP shows UTS=990 MPa and ETF=4.9%, however both characteristics improve with the number of FSP passes to achieve mean UTS 1126 MPa and ETF 5 to 7%.

The UTS behaviors as depended on the number of passes do not allow making unambiguous conclusions and can be explained by inhomogeneity of IMC distribution over the stir zone.

The maximum UTS value was for the Ti/(2Cu+1Al) composite. It may be suggested then that in-situ formed Ti<sub>1</sub>Al<sub>1</sub> shells provide some transition zone between Ti6Al4V matrix and core Ti<sub>2</sub>CuAl<sub>3</sub> + Ti<sub>2</sub>CuAl<sub>5</sub>/TiCuAl IMCs, thus additionally enhancing the effect of dispersion hardening. Generally, the relative elongation in these in-situ composites Ti/(2Cu+1Al), Ti/(1Cu+1Al) and Ti/(1Cu+2Al) reduced to 5-6%.

Sharp fall in ETF on all samples was observed after the 1-pass FSP (Fig.18(b)) may be related to increased volume fraction of α'-Ti that was observed on all composites as well as on FSPed Ti6Al4V [33] rather that to the effect if in-situ formed IMCs.

The microhardness profiles were obtained along the lines as shown in Fig. 19. The specifics of microhardness number distribution across the Ti/(2Cu+1Al) and Ti/(1Cu+1Al) stir zones may be that their microhardness maximums are located close to advancing and retreating sides, respectively. Such a difference means that the most hard IMCs were localized in different parts of the SZ, i.e. zone behind the FSP tool. For Ti/(1Cu+2Al) stir zone the corresponding profile shows almost uniform distribution of the microhardness numbers, i.e. IMCs.

It may be suggested that metal transfer in FSP is determined by the specificity of the metal flow in these systems. Uniform distribution of IMCs is achieved in Al-rich system when all powder aluminum melts and thus reduce the plasticized metal viscosity.

Figure 19 shows the microhardness distribution profiles in the in stir zones of the Ti/(2Cu+1Al), Ti/(1Cu+1Al) and Ti/(1Cu+2Al) composites. Microhardness measurements were carried out along and across the SZ, as shown in Figure 19(a). From Figure 19(b,c) it can be seen also that all microhardness distribution profiles show the highest values in the stirring zone compared to the base Ti6Al4V. The Ti/(1Cu+2Al) sample has a relatively uniform microhardness distribution profile, which is related to a uniform distribution of intermetallic particles in the SZ (Fig. 19(b)). The microhardness values for the Ti/(1Cu+2Al) composite are on average 20% higher compared to those of the base Ti6Al4V. The Ti/(2Cu+1Al) and Ti/(1Cu+1Al) composites have uneven microhardness distribution profiles in the horizontal direction and their microhardness numbers vary from 4.2 to 5.8 GPa. The study of microhardness in the vertical direction demonstrates a more abrupt distribution of profiles, which is associated with in-situ formed intermetallic particles falling into the region. It is worth noting that the microhardness values decrease as the distance below the surface, that is, the
composites have higher microhardness from 4 to 5.7 GPa near the surface. For samples with high Cu content, i.e. for Ti-(2Cu+1Al), Ti-(1Cu+1Al), the highest microhardness numbers (~7 GPa) are observed along line 2 at the beginning of the distribution, which is associated with intermetallic particles formed in the composite layer under the tool shoulder during the FSP process. The increased values of strength and microhardness of the resulting composites are associated with the formation of fine grains in the SZ during FSP, as well as due to the formation of martensite and intermetallic particles.

Fig. 19 Microhardness profile measurement lines (a) and microhardness profiles along horizontal (1) (b) and vertical (2, 3) directions (c).

4. Discussion
The rotating FSP tool generates local heat and involves the plasticized material in stirring, i.e. severe plastic deformation. It is unavoidable that strong adhesion is developed between the material and FSP tool at that high-temperatures and contact pressure, so that diffusion-reactions occur with the following formation of IMCs. In this case, the FSP tool was made from the nickel superalloy and reaction diffusion between nickel and titanium may have occurred as reported earlier [34]. In fact more reactions are possible including exothermic one between Cu and Al, and the additional heat
generated during the reaction also helps to accelerate the reaction between the Cu, Al powders and the Ti6Al4V matrix. The fact that the reaction between Cu and Al releases additional heat is clearly seen from Figure 3(a,c), where the temperature profiles show higher temperatures (by 20%) during the FSP process, for samples with a high Cu content (Cu:Al ratio = 2:1, 1:1) than when processing Ti6Al4V without powders and at a low Cu:Al ratio = 1:2 (Fig. 3(e)). It is obvious that the Cu:Al ratio plays an important role in formation of the structural and phase composition during the FSP process. This effect leads to the fact that, under the influence of a higher temperature, a more intense process of diffusion of a mixture of powders (Cu + Al) into the Ti6Al4V matrix occurs with the formation of Ti_xCu_yAl_z and Ti_xAl_y in situ composites of different sizes, shapes and concentrations.

According to Ti-Cu-Al phase diagrams [35] there are three equilibrium phases such as TiCuAl, TiCu_2Al and Ti_2CuAl_3 with large regions of primary crystallization (Fig. 20(a)). It is worth noting here that the FSP is an extremely inequilibrium process that depends on local heat generation and sink that govern the inter-diffusion of Ti, Al, and Cu. Intensive heat generation allows in-situ formation of localized Ti_2CuAl_3/TiCuAl/TiCu_2Al IMCs with varied concentrations of elements and IMC/matrix interfaces composed of Ti_3Al(Cu) and TiAl(Cu) particles as observed from SEM, TEM and EDS results. These data are consistent with the results shown on the isothermal section of the Ti-Cu-Al phase diagram at 500°C (Fig. 20(b)), which gives a row of phases such as γ-TiAl, α_2-Ti_3Al, Ti_2CuAl_5, TiCuAl and TiCu_2Al.

At the same time the region containing the TiCu_2Al phase is neighboring with Ti_xCu_y phases at 500°C (Fig. 20(b)). It was shown by Shmorgun et al. [36] that IMCs of the types TiCu, TiCu_2, and Ti_3Cu_4 appear along with TiCu_2Al in contact melting between Ti6Al4V and copper plates after their explosion welding. Laser-assisted deposition of Al10Cu90 powder o a pure titanium also resulted in forming TiCu_2Al, Ti_3Cu, TiCu_3 and Ti_3Al [37]. The presence of Ti_2Cu_3 was also shown in Fig. 6(d) so that there might be also non-stoichiometric Ti_xCu_y ones.

The probability of formation of IMCs is determined by their formation enthalpy changes (Table 3). The IMCs whose formation in the systems presented in this work is most expected are shown in Table 3 with their highest negative ΔH.

Table 3. Enthalpies of formation for Ti-Ni, Ti-Cu Ti-Al-Cu and Ti-Al-Ni IMCs calculated according to [38].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Phase stability</th>
<th>Enthalpy of formation ΔH, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti_xNi_y</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 20 Ti-Cu-Al phase diagram sections: (a) Liquidus surface; (b) Isothermal section at 500 °C.

The probability of formation of IMCs is determined by their formation enthalpy changes (Table 3). The IMCs whose formation in the systems presented in this work is most expected are shown in Table 3 with their highest negative ΔH.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Phase</th>
<th>Stability</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti + Ni → TiNi</td>
<td>metastable</td>
<td>-30</td>
<td></td>
</tr>
<tr>
<td>2Ti + Ni → Ti₂Ni</td>
<td>stable</td>
<td>-80</td>
<td></td>
</tr>
<tr>
<td>Ti + Ni → TiNi</td>
<td>stable</td>
<td>-76</td>
<td></td>
</tr>
<tr>
<td>2Ti + Cu → Ti₂Cu</td>
<td>Stable</td>
<td>-34</td>
<td></td>
</tr>
<tr>
<td>3Ti + Cu → Ti₃Cu</td>
<td>Stable</td>
<td>-8</td>
<td></td>
</tr>
<tr>
<td>2Ti + 3Cu → Ti₂Cu₃</td>
<td>Instable</td>
<td>-58</td>
<td></td>
</tr>
<tr>
<td>3Ti + 4Cu → Ti₃Cu₄</td>
<td>Instable</td>
<td>-85</td>
<td></td>
</tr>
<tr>
<td>5Ti + 2Cu → Ti₅Cu₂</td>
<td>Instable</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>Ti + Cu → TiCu</td>
<td>Stable</td>
<td>-26</td>
<td></td>
</tr>
<tr>
<td>8Ti + 3Cu + Ni → Ti₈Cu₃Ni</td>
<td>Stable</td>
<td>-186</td>
<td></td>
</tr>
<tr>
<td>Ti + Cu + Ni → TiCuNi</td>
<td>Stable</td>
<td>-90</td>
<td></td>
</tr>
<tr>
<td>2Ti + Cu + Ni → Ti₂CuNi</td>
<td>Instable</td>
<td>-81</td>
<td></td>
</tr>
<tr>
<td>Ti + Cu + 2Ni → Ti₃CuNi²</td>
<td>Instable</td>
<td>-134</td>
<td></td>
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<tr>
<td>Ti + Al + 2Ni → TiAlNi₂</td>
<td>Stable</td>
<td>-240</td>
<td></td>
</tr>
<tr>
<td>Ti + Al + 6Ni → TiAlNi₆</td>
<td>Stable</td>
<td>-366</td>
<td></td>
</tr>
<tr>
<td>2Ti + 3Al + Ni → Ti₂Al₃Ni</td>
<td>Instable</td>
<td>-278</td>
<td></td>
</tr>
<tr>
<td>Ti + Al + Ni → TiAlNi</td>
<td>Instable</td>
<td>-141</td>
<td></td>
</tr>
<tr>
<td>2Ti + Al + Ni → Ti₂AlNi</td>
<td>Instable</td>
<td>-105</td>
<td></td>
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<tr>
<td>Ti + 2Cu + Al → TiAlCu₂</td>
<td>Stable</td>
<td>-118</td>
<td></td>
</tr>
<tr>
<td>Ti + Cu + Al → TiAlCu</td>
<td>Stable</td>
<td>-85</td>
<td></td>
</tr>
<tr>
<td>2Ti + Cu + 5Al → Ti₂CuAl₃</td>
<td>Stable</td>
<td>-22</td>
<td></td>
</tr>
</tbody>
</table>

Ti/Ni system was included in this analysis because of using the FSP tools made from heat-resistant and high-temperature nickel superalloy. The intensive adhesion of the plasticized Ti₆Al₄V to the tool results in formation of Ti₂Ni IMCs, which then detach from the tool and intermix with the plasticized metal to form IMC streaks [34] IMCs when contacting the composites. The Ti/Al/Ni IMCs are distinguished by high negative ΔHs and therefore were found in the stir zones of all three composites.

These and other IMC particles, however, are not to much deleterious for the SZ metal strength, especially in case of tensile testing on Ti/(1Cu+2Al) samples (Fig. 18(a)) whose mean microhardness was lower than those of two other ones (Fig. 19(b)). All samples are characterized by sharp fall in their plasticity which was only 35-40% of the as-received Ti₆Al₄V sample plasticity and did not depended on the FSP pass number (Fig. 18(b)).

Similar effects were observed, for example, after addition of copper into Ti₆Al₄V that resulted in precipitation of Ti₂Cu and greatly affected the alloy ductility [32, 39-41]. It was shown , however, that adding 1-4 mass % of Cu may provide acceptable mechanical characteristics [42].

According to semiquantitative XRD analysis, concentration of β-Ti is reduced after the 1-pass FSP in all cases including the FSPed Ti₆Al₄V with simultaneous increase in the concentration of α-Ti. Such a behavior may be explained by transformation that occur in cooling from the recrystallized β-Ti that yet contain no copper or extra aluminum. On reaching the β-transus temperature the α-Ti grains start growing on the β-Ti grain boundaries and form a grain boundary α-Ti and lamellar α/β structures inside the formed β-Ti grains (Fig.7a), however, some of the residual β-Ti grains might experience martensitic transformation and thus form α'-Ti grains.

Further FSP passes provide that β-Ti and α-Ti concentrations that slightly grow and fall with the number of FSP passes, respectively (Fig.5). This behavior is typical for all samples FSPEd
irrespective of the additives. It seems that multipass FSP serves to enhance the stability of β-Ti while admixing Cu and Al has no effect of these phases because of reacting with other to from IMCs.

FSP on the Ti/(1Cu+2Al) system demonstrates the lowest temperature during the 1-pass FSP (Fig.3a), i.e. almost no exothermic reaction occurred while the FSP tool torque value was highest (Fig.3b). The tool travel resistance force was also minimum because extra plasticized aluminum might provide some lubrication effect as compared to FSP on the pure Ti6Al4V.

The presence of α'-Ti in Ti-(2Cu+1Al), Ti/(1Cu+1Al) and Ti-(1Cu-2Al) is a main factor contributing to their increased tensile strength, reduced ductility and enhanced hardness [43-45].

It was shown earlier and in this study that intensive deformation and temperature in the stir zone are factors that accelerate diffusion and formation of IMCs. Commonly these IMCs are brittle and hard phases but, nevertheless, it is not inconceivable that some of them, such as for example Ti2Cu may be decomposed β-Ti and α-Ti using the corresponding heat treatment [46], which, however, affects also the mechanical strength. Finding an optimum between strength and ductility is always a problem in materials sciences [47] and therefore our next goal will be development of Ti-Al-Cu in-situ FSP composites possessing both strength and ductility that results from decomposition of brittle phases such as α' and Ti2Cu and formation of α + α" structures [48].

5. Conclusion
Friction stir processing by the tool made from nickel superalloy was performed on Ti6Al4V alloy for intermixing it with powder blends composed of copper and aluminum powders in mass ratio 2:1, 1:1 and 1:2. The microstructures of stir zones obtained after 1 to 4 FSP passes have been examined and demonstrated improved with the FSP pass number homogeneity of the IMC distribution across the stir zone. Intermetallic compounds such as TiCu2Al, TiCuAl, Ti2Cu3 have been detected in the T(2Cu+1Al) in-situ composite while Ti(1Cu+1Al) contained Ti2Al2Cu, Ti3Al, and TiAl ones. The Ti/(1Cu+2Al) composite demonstrated the presence of Ti2Al3Cu IMC. All samples were contaminated with Ti2Ni(Al, Cu) particles that detached off the nickel superalloy FSP tool. The FSP intermixing the Ti6Al4V alloy with powder blends resulted in reduction of the alloy plasticity while the tensile strengths of 4-pass FSPed composites were close or even higher that that of the as-received hot rolled sample. The minimal mean microhardness was achieved on the Ti/(1Cu+2Al) sample whose tensile strength was as high as 1126 MPa.

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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

References


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