Arch. Metall. Mater. **71** (2026), 3, 751-763

DOI: https://doi.org/10.24425/amm.2026.1964

S. TERLICKA[1*], K. JANUS[2*], A. JARZĘBSKA[1], J.J. SOBCZAK[2], N. SOBCZAK[1]

HIGH-TEMPERATURE INTERACTIONS BETWEEN MOLTEN Mg-10Ca ALLOY AND Ti SUBSTRATE UNDER DIFFERENT ATMOSPHERIC CONDITIONS

This work investigates the combined effects of atmosphere and alloying with calcium on the high-temperature interaction between a molten Mg-10Ca alloy and a polished titanium substrate. The sessile drop method was employed with non-contact heating and capillary purification, enabling the generation of an oxide-free Mg-10Ca drop. Experiments were conducted isothermally at 700°C under two flowing atmospheres: (i) pure Ar and (ii) Ar + 5 wt.% H_2.

In pure Ar, the evolution of the average contact angle results from both evaporation of the oxide-free Mg-10Ca alloy and chemical interaction between Mg-Ca vapor and the oxidized Ti surface. Initially, non-wetting behavior ($\theta > 90°$) was observed. A non-wetting-to-wetting transition occurred at ~200 s ($\theta = 90°$), followed by progressive improvement in wettability, reaching an average final contact angle of ~70° at 300 s.

SEM/BSE/EDS analysis of the Mg-10Ca/Ti couple formed in pure Ar revealed interfacial discontinuities, absence of permanent bonding, and pronounced triple-line pinning, which led to an asymmetric drop geometry arising from the inhomogeneous structure and chemistry of the Ti surface. In contrast, excellent wettability and bonding were obtained under the Ar + 5 wt.% H_2 atmosphere. Under identical testing conditions, the contact angle decreased rapidly from 19° to 11° within ~50 s and remained nearly constant during holding at 700 °C up to 300 s, with a final contact angle of ~9° at the end of the test. The results of structural characterization suggest that the remarkable improvement in wettability arises from the synergistic effect of several factors: (1) alloying magnesium with calcium, (2) presence of hydrogen in the surrounding atmosphere, (3) the evaporation of both Mg and Ca from the drop and (4) the enhanced chemical interaction between the Mg-Ca alloy and the Ti substrate in the presence of hydrogen.

Keywords: Wettability; Mg-Ca alloy; Titanium; Interface; Sessile drop method

Highlights

- The wettability of molten Mg-10Ca alloy on Ti at 700°C was examined under two atmospheres (pure Ar and Ar + 5 wt.% H_2) using the sessile drop method combined with non-contact heating to eliminate heating-history effects, and capillary purification to produce an oxide-free Mg-10Ca drop ensuring reliable contact-angle measurements.
- In pure Ar, the contact angle evolution is governed by evaporation of the oxide-free Mg-10Ca alloy and subsequent chemical interaction between Mg-Ca vapor and the oxidized Ti surface.
- Two distinct wetting stages were identified in pure Ar: an initial non-wetting regime ($\theta > 90°$), followed by a non-wetting-to-wetting transition at ~200 s ($\theta = 90°$), and progressive improvement to an average final contact angle of ~70° at 300 s.
- Adding 5 wt.% H_2 to Ar dramatically enhances wetting, reducing the contact angle from 19° to 11° within ~50 s and maintaining excellent wettability at 700°C with a final contact angle of 9° at the end of the test.
- Synergistic effects markedly improved wetting of Mg-Ca alloy on titanium.

1. Introduction

Metallic biomaterials play a fundamental role in modern orthopedic and dental surgery owing to their excellent mechanical performance, corrosion resistance, and biocompatibility. Among currently available metallic implant materials, titanium and its alloys are considered the benchmark for long-term load-bearing applications because of their high specific strength, excellent corrosion resistance, and outstanding biological response. Nevertheless, their elastic modulus remains significantly higher

[1] INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 25 REYMONTA STR., 30-059, KRAKOW, POLAND
[2] AGH UNIVERSITY OF KRAKOW, FACULTY OF FOUNDRY ENGINEERING, 23 REYMONTA STR., 30-059, KRAKÓW, POLAND

* Corresponding authors: s.terlicka@imim.pl, kjanus@agh.edu.pl

than that of natural bone, which may lead to stress shielding and progressive bone resorption. Although β-type titanium alloys containing Nb, Ta, Zr, Mo, or Sn have been developed to reduce the elastic modulus, their production generally requires expensive alloying elements and complex thermomechanical processing routes, limiting their broader application [1-7].

In contrast, magnesium and its alloys have attracted considerable attention as biodegradable biomaterials because their density and elastic modulus are much closer to those of human bone than those of conventional implant metals. Furthermore, magnesium gradually dissolves under physiological conditions, eliminating the need for secondary implant-removal surgery. Among biodegradable magnesium alloys, Mg-Ca alloys are regarded as particularly promising because calcium is an essential constituent of the human body and improves both the mechanical properties and corrosion behavior of magnesium alloys. Depending on calcium content, Mg-Ca alloys exhibit elastic moduli approaching those of cortical bone while maintaining excellent biocompatibility [8-14]. However, their relatively rapid degradation and accompanying hydrogen evolution remain important challenges that limit their use as stand-alone structural implant materials [14].

Rather than replacing one biomaterial with another, increasing attention has recently been devoted to the development of hybrid materials, such as Mg-Ti**,** designed to combine the long-term mechanical stability and corrosion resistance of titanium with the favorable biomechanical compatibility and controlled biodegradability of magnesium alloys [15]. Such hybrid concepts may enable the design of implants exhibiting improved mechanical compatibility with bone while simultaneously providing localized biodegradation and enhanced biological performance. The successful fabrication of these hybrid systems, however, requires the formation of a reliable metallurgical interface between titanium and magnesium-based materials.

Currently, most attempts to synthesize Mg-Ti materials have been based on solid-state processing techniques, including powder metallurgy, mechanical alloying, and related consolidation methods [16,17]. Liang and Schulz [16] demonstrated that mechanical alloying can produce nanocrystalline Mg-Ti alloys exhibiting an extended solid solubility of titanium in magnesium beyond equilibrium conditions. Similarly, Zhou et al. [17] reported the successful synthesis of nanocrystalline Mg-based composite powders reinforced with finely dispersed titanium particles through mechanical milling. These studies, primarily focused on phase formation and microstructural evolution, confirmed that Mg-Ti materials can be successfully fabricated using solid-state routes. However, available literature data provide limited information regarding the mechanisms governing liquid-assisted synthesis, where bonding is controlled by wetting, spreading, and interfacial reactions occurring between molten magnesium alloys and titanium substrates.

Compared with solid-state processing, investigations of liquid-phase interactions between magnesium alloys and titanium remain limited, despite their direct relevance to liquid-assisted manufacturing technologies, coating processes, infiltration, brazing and reactive joining. In such processes, the formation of a stable interface depends primarily on the wetting behavior of the liquid metal, the kinetics of spreading and the physicochemical reactions occurring at the liquid/solid interface [18-21]. Previous studies have shown that these phenomena are strongly affected by alloy composition, substrate chemistry, surface condition and processing atmosphere [18-20]. Understanding the interplay between these factors is therefore essential for the design of reliable liquid-assisted routes for manufacturing Mg-Ti hybrid materials.

Despite the increasing interest in liquid-assisted synthesis of Mg-Ti materials, wetting of molten magnesium on titanium remains inherently poor. Our previous systematic studies with pure Mg have shown that, under identical testing conditions, oxide-free liquid Mg exhibits non-wetting behavior not only on commercially pure Ti and Ti-26Nb biomedical alloys [21,22], but also on several refractory metals, including W, Mo, Ta and Nb, as well as on stainless steel and cast iron [22-25]. These observations indicate that, for applied conditions, metals exhibiting negligible chemical affinity toward magnesium generally do not promote spontaneous spreading and metallurgical bonding. Consequently, improving the wettability of magnesium on titanium requires modification of the interfacial chemistry rather than optimization of processing conditions alone.

Various approaches have been proposed to overcome the poor wettability of Mg-based alloys, including alloying additions, surface modification, and atmosphere control. Among the alloying elements used in biodegradable magnesium alloys, calcium is particularly attractive. Besides its well-established biological compatibility [9-13], calcium modifies the surface tension and thermodynamic activity of magnesium, influences oxidation processes, and affects the formation of interfacial reaction products [26-30]. Moreover, previous studies have demonstrated that the processing atmosphere may strongly influence the stability of oxide films, hydrogen evolution, and the chemical reactions occurring during high-temperature interaction of Mg-Ca alloys with metallic substrates (e.g., steel [31]). These observations suggest that calcium alloying combined with appropriate atmosphere control may provide an effective strategy for improving the wetting and bonding behavior of magnesium on titanium. Nevertheless, despite the growing interest in Mg-Ti materials, systematic investigations of the wetting behavior and interfacial reactions of Mg-Ca alloys on titanium under different atmospheres are still missing**.**

Therefore, the present work investigates, for the first time, the high-temperature interaction between a molten Mg-10Ca alloy and commercially pure titanium under different processing atmospheres during isothermal exposure at 700°C. Real-time sessile-drop experiments were complemented by detailed microstructural characterization to understand the mechanisms governing spreading, interfacial reactions and metallurgical bonding. Particular attention was devoted to understanding the synergistic effects of calcium alloying, titanium reactivity and atmosphere on the formation and evolution of the Mg-10Ca/Ti interface.

2. Materials and experimental procedure

The Mg-10Ca alloy with 10 wt.% Ca used in the high-temperature study has been previously characterized by Terlicka et al. [31]. The commercial bulk titanium grade 2 ASTM was used as the substrate. Before the wettability experiments, the Mg-10Ca cylinder was machined, and the Ti substrate was ground and polished with the nano-SiO_2 suspension. Subsequently, both the Mg-10Ca alloy cylinder and Ti substrate were ultrasonically cleaned several times in isopropanol (STANLAB, p.a.) to remove contaminants. In addition, the surface roughness (R_a) of the polished Ti substrate was measured to be 250 nm using a 3D surface analyzer (KEYENCE VHX-7000N series digital optical microscope, Japan).

The sessile drop method with non-contact heating and capillarity purification (CP) procedure has been used to study the high-temperature interactions between molten Mg-10Ca alloy and a Ti substrate. This procedure significantly reduces the effect of the heating history of the samples and removes the native oxide film from the Mg-10Ca alloy surface to obtain a clean and symmetrical drop [18,20,23]. The experiments were performed using a unique device described in detail in the previous work [23]. Before the wettability tests, the Mg-10Ca alloy cylinder was placed inside a graphite capillary in the measurement chamber. At the same time, a Ti substrate was put on a holder inside a storage chamber of the device [23], which had the same controlled atmosphere as the experimental chamber but remained at approximately room temperature throughout the test. Titanium chips and sponge pieces were placed near the substrate to function as oxygen getters during the experiment. It should be emphasized that under the testing conditions applied in this study, neither Mg nor Ca exhibits any measurable reactivity toward graphite [29].

The apparatus preparation and purification procedure were identical to those described in detail in our previous study [31]. After assembling the experimental setup, the chamber was evacuated to approximately 10^{-6} mbar and heated to 400°C. This temperature was maintained for 10 min to outgas the chamber and remove contaminants adsorbed on the graphite capillary and the internal surfaces of the apparatus. Subsequently, the chamber was filled with the selected protective atmosphere: (i) pure Ar (99.9999 wt.%) or (ii) a mixture of Ar + 5 wt.% H_2, to a pressure of 1.10×10^3 mbar and heated to the experimental temperature of 700°C. After the temperature and gas atmosphere had stabilized, the Ti substrate was introduced into the measurement chamber. Once isothermal conditions were re-established, the wettability test was initiated.

Apart from metallographic polishing to a mirror-like finish, no further cleaning of the Ti substrate was carried out before the wettability test. Nevertheless, titanium is well-known to oxidize rapidly even at room temperature and under very low oxygen partial pressures, leading to the formation of a nanometer-scale oxide film whose thickness depends on local temperature and oxygen availability [32]. According to literature data [33], titanium can dissolve a substantial amount of oxygen to form a solid solution even at room temperature. Therefore, despite its bright, metallic appearance before testing, the Ti substrate was expected to contain oxygen and to be partially oxidized before the wettability experiments.

Once the temperature stabilized at 700 °C, the liquid Mg-10Ca alloy was extruded from the capillary and deposited onto the surface of the Ti substrate. In sessile drop tests, the images of Mg-10Ca alloy/Ti couples were recorded using two perpendicularly oriented CCD cameras [23] at a speed of 60 frames per second from the two directions of the quartz glass observation window for 300 s. After completion of the wettability tests, the left (θ_l), right (θ_r), and average (θ_{av}) contact angles were determined from the recorded images using the DROP software [34].

Microstructural observations and chemical composition analyses of the sessile drop couples were performed using an FEI E-SEM XL30 scanning electron microscope (SEM) equipped with an EDAX GEMINI 4000 energy dispersive X-ray spectrometer (EDS) and an FEI Quanta 3D 200i FEG-SEM microscope equipped with an EDAX OIM TSL EBSD system ver. 7.0. For the top-view and cross-sectional observations, secondary electron (SE) and backscatter electron (BSE) detectors were used in Z-contrast with an accelerating voltage of 15 kV. For detailed cross-sectional SEM observations of the Mg-Ca/Ti couples, the specimens were embedded in an epoxy resin and cut perpendicular to the interface using an electric cut-off wheel with a diamond disk and polished with a diamond and silica suspension similar to previous work [31].

3. Results

3.1. Mg-10Ca alloy characterization

As was previously observed in our study of the wettability of steel by the same hypoeutectic Mg-10Ca alloy [31], the as-cast microstructure is composed of primary dendrites of the α(Mg) phase and a eutectic mixture containing the intermetallic Mg_2Ca phase and the α(Mg) phase in the interdendritic channels. In addition, the α(Mg) dendrites and the eutectic mixture exhibit a relatively fragmented structure.

3.2. Contact angle measurements

Fig. 1 and Fig. 2 show the wetting kinetics curves of the molten Mg-10Ca alloy on the polished Ti substrate at 700°C under two different atmospheric conditions. The first experiment was performed in pure argon (Fig. 1a) and the second one in a gas mixture of Ar + 5 wt.% H_2 (Fig. 1b). Real-time videos of the sessile drop tests using the CP procedure were recorded and made available via the QR codes provided in Fig. 1a and Fig. 1b. In addition, Fig. 2 presents a comparison of θ_{av} between Mg-10Ca/Ti couples exposed to 700°C under both atmospheric conditions. Contact angle calculations using the DROP software [34] were performed at 2-second intervals.

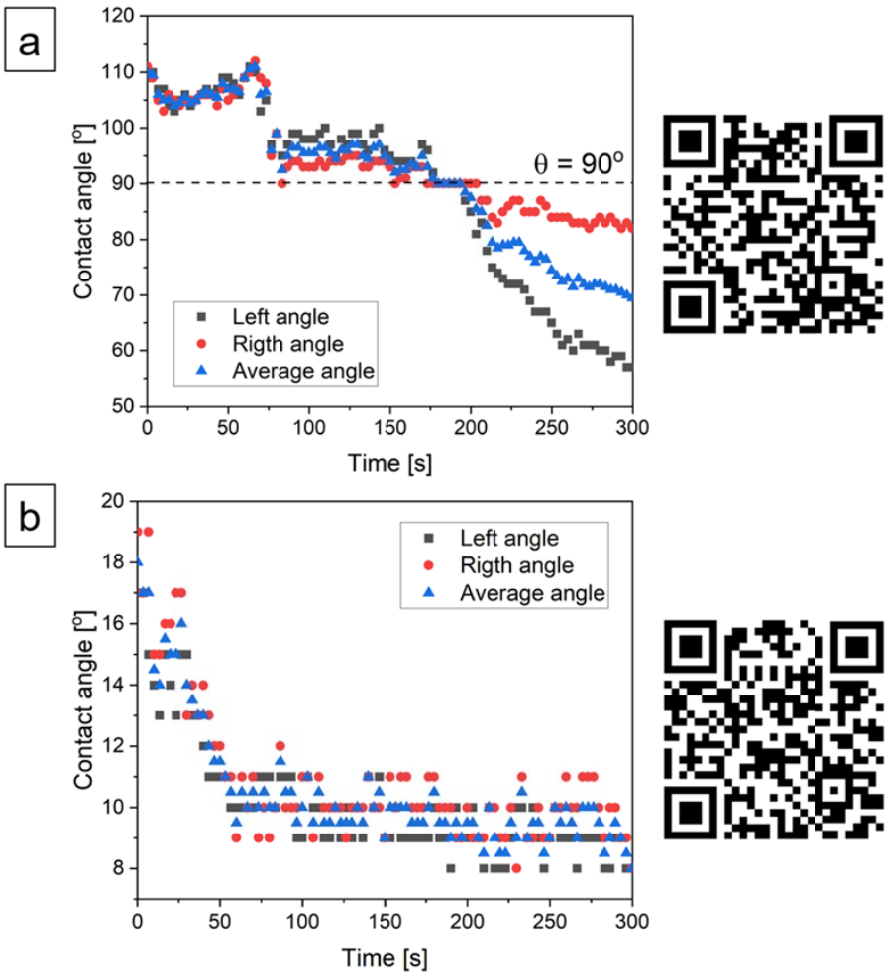

Fig. 1. The wetting kinetics observed during sessile drop tests of Mg-10Ca/Ti couples using the CP procedure at 700°C for 300 s under different atmospheres: a) in pure Ar, and b) in Ar + 5 wt.% H_2 mixture, along with QR codes linking to real-time videos recorded during the wettability tests

The variation in contact angle values over time reveals two different wetting behaviors as shown in Fig. 2.

During the examination of the Mg-10Ca/Ti couple under a pure Ar atmosphere, the initial contact angle measured immediately after drop deposition (θ_0 at t = 0 s) was approximately 110°, indicating non-wetting behavior. As the interaction progressed, a non-monotonic decrease in the contact angle was observed, and after ~200 s a non-wetting-to-wetting transition occurred (θ < 90°), followed by a further gradual decrease in the contact angle to a final value of about θ_f ~ 70° at the end of the test.

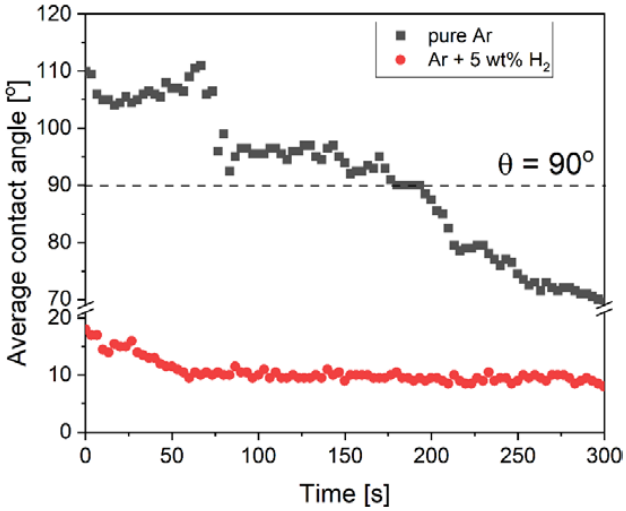

Fig. 2. Comparison of the average contact angle values (θ_{av}) recorded between Mg-10Ca alloy and Ti substrates in the sessile drop test at 700°C under pure Ar vs Ar + 5 wt.% H_2 mixture

In contrast, excellent wettability and bonding were obtained under the Ar + 5 wt.% H_2 atmosphere. Under identical testing conditions, the contact angle decreased rapidly from θ_0 ~19° to 11° within ~50 s and remained almost unchanged during holding at 700°C up to 300 s (θ_f ~9°).

3.3. Microstructure characterization

Fig. 3 shows top-view photos of the Ti substrates before and after wettability tests, along with images of the Mg-10Ca/Ti couples after experiments conducted under both Ar (Fig. 3a,b) and Ar + 5 wt.% H_2 (Fig. 3c,d) atmospheres. These photos evidence that, before the high-temperature tests, the polished surfaces of both Ti substrates appeared bright and metallic, with no visible oxide films, despite the fact that the substrates

were expected to contain oxygen and be partially oxidized, as discussed above. Examining the Mg-10Ca/Ti couple after the wettability test in the Ar atmosphere (Fig. 3b), it is observed that the surface of the Mg-10Ca drop is not perfectly shiny, and its secondary surface oxidation is evident. This phenomenon may occur during the wettability test conducted in pure Ar, arising from the reaction of Mg or Ca with trace oxygen-bearing species (O_2, H_2O, CO_2) unavoidably present in the gas stream or released from the chamber walls, which were not completely removed or reduced.

In contrast, during the wettability test performed in the Ar + 5 wt.% H_2 atmosphere, the Mg-10Ca drop spreads much more effectively, covering a significantly larger area of the Ti substrate. In fact, partial runoff of the molten alloy onto the side wall of the substrate, as shown in Fig. 3d, most likely occurs during transfer of the couple to the colder region of the storage chamber. This behavior further indicates a markedly enhanced spreading tendency of the Mg-10Ca alloy under reducing conditions.

It should be highlighted that under testing conditions applied in this study, the Ti surface can also react with residual oxygen present in the chamber. This effect is visible in Fig. 3b and Fig. 3d, where the oxidized regions of the Ti surface exhibit a characteristic brown to dark-blue coloration. Notably, after the wettability test in pure Ar, the Ti surface is fully oxidized. In contrast, after the test in a reducing Ar + 5 wt.% H_2 atmosphere, the Ti substrate is only partially oxidized (dark blue area), leaving the large portion of the Ti substrate (white area) unoxidized. This substantial reduction in secondary oxidation of the Ti substrate is attributed to the presence of hydrogen in the experimental atmosphere, which continuously lowers the oxygen partial pressure in the chamber and acts as a reducing agent [18,20,23,31].

Top-view SEM/BSE observations provide additional information on the reactivity of the Mg-10Ca alloy in both Ar (Fig. 4) and Ar + 5 wt.% H_2 (Fig. 5) atmospheres. After testing

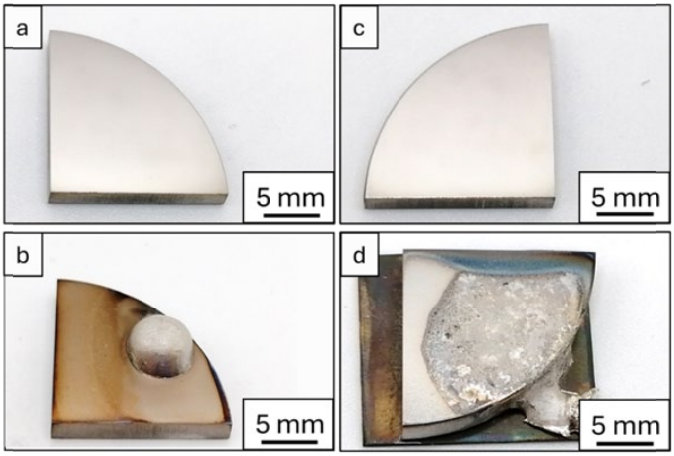

Fig. 3. Top-view photos of Ti substrates (a, c), along with photos of the Mg-10Ca/Ti couples (b, d) before and after wettability tests at 700°C, respectively, in the pure Ar (a, b) and Ar + 5 wt.% H_2 (c, d) atmospheres

in pure Ar, the surface of the solidified drop is relatively clean and smooth. However, detailed microstructural characterization (Fig. 4b and Fig. 4c) reveals bright or light gray precipitates forming a continuous film on the surface of the Mg-10Ca drop. This film was also observed in Fig. 3. It appears that these precipitates likely originate from pure Mg or the Mg_2Ca eutectic phase, which may have undergone partial oxidation after the wetting tests, once the sample was removed from the vacuum chamber and exposed to air.

After testing in Ar + 5 wt.% H_2, the solidified Mg-10Ca drop exhibits extensive spreading, covering a large area of the Ti substrate (Fig. 5a). Light-gray precipitates, several micrometers in size, are visible on the drop surface (Fig. 5b and Fig. 5c). These precipitates may correspond to Mg_2Ca eutectic phase, similar to those observed in the Mg-10Ca/Ti couple after testing in pure Ar. However, according to the detailed study by Terlicka et al. [31], high-temperature interaction of molten Mg-10Ca alloy with

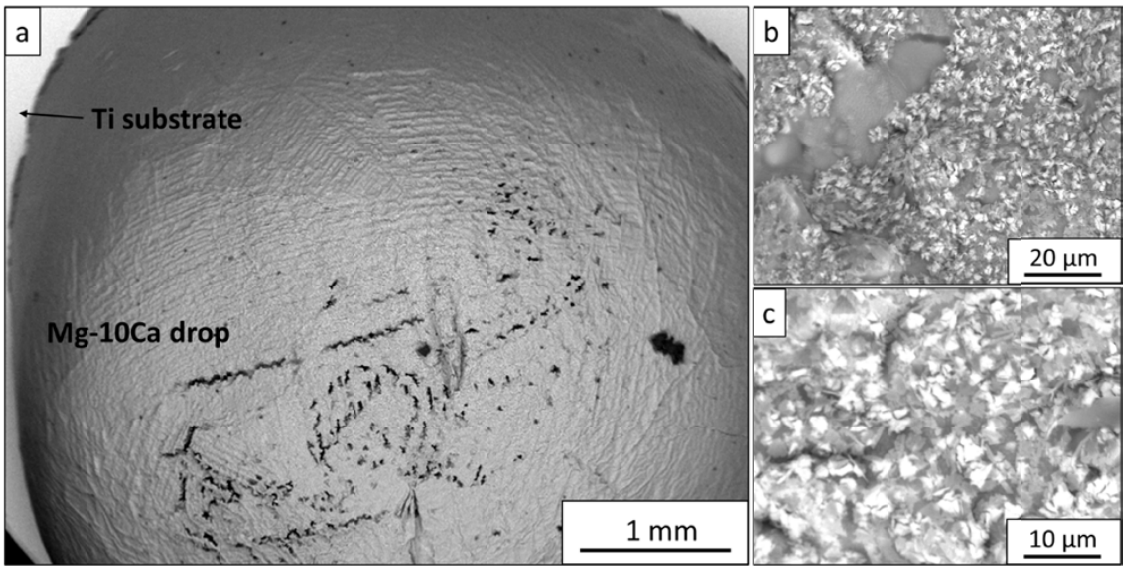

Fig. 4. The top-view SEM/BSE images show the surface of the Mg-10Ca/Ti couple after the wettability test at 700°C in a pure Ar atmosphere. The images were taken at different magnifications: a) 50×, b) 2000×, and c) 5000×

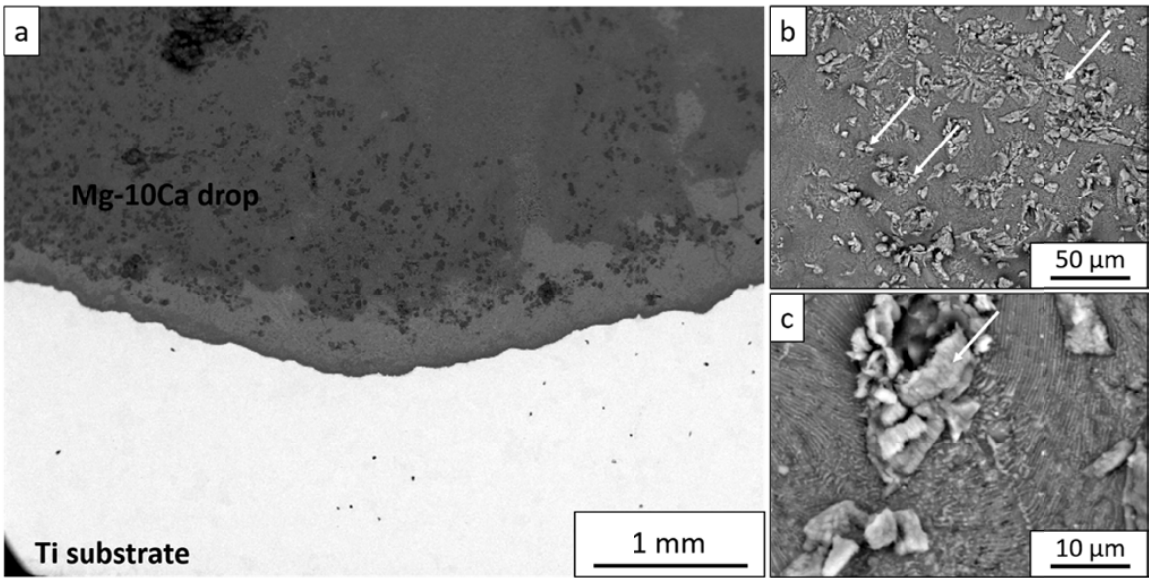

Fig. 5. The top-view SEM/BSE images show the surface of the Mg-10Ca/Ti couple after the wettability test at 700°C in Ar + 5 wt.% H_2 atmosphere. The arrow indicates light-gray precipitates of $Ca(OH)_2$. The images were taken at different magnifications: a) 50×, b) 1000×, and c) 5000×

a steel substrate under identical measurement conditions revealed that such light-gray precipitates can be identified as $Ca(OH)_2$ based on X-ray diffraction analysis.

In the present work, the XRD pattern obtained from the top region of the Mg-10Ca/Ti couple tested in Ar + 5 wt.% H_2 (Fig. 6) confirms that, following the high-temperature wettability experiment, $Ca(OH)_2$, Mg, Mg_2Ca, and CaO are present on the surface of the Mg-10Ca drop, as well as within the subsurface region extending a few micrometers below it. These findings indicate that $Ca(OH)_2$ forms through a two-stage process involving the Ar + H_2 atmosphere during testing and subsequent exposure to air. First, during high-temperature contact of the Mg-Ca alloy with both steel [31] and Ti [this work] substrates, Ca reacts with H_2 from from surrounding mixture of Ar + H_2 to produce CaH_2. Subsequently, CaH_2 reacts with residual water vapor present in

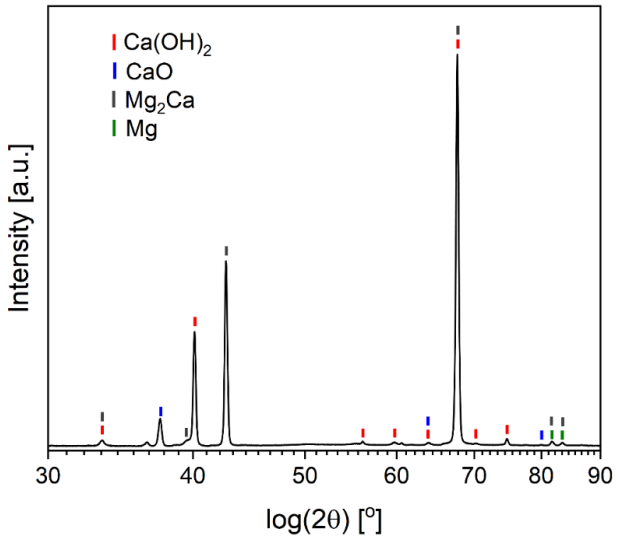

Fig. 6. The XRD diffraction pattern from the Mg-10Ca drop surface after wettability test at 700°C in Ar + 5 wt.% H_2 atmosphere

the chamber, generating a thin $Ca(OH)_2$ film on the surface of the Mg-10Ca drop. After removal of the couple from the chamber, this film further thickens due to immediate interaction with water vapor in ambient air. In the present study, the light-gray $Ca(OH)_2$ precipitates appear fragmented because of the extensive spreading of the Mg-10Ca drop on the Ti substrate during the high-temperature wettability test.

Detailed SEM/BSE observations of the cross-sectioned Mg-10Ca/Ti couples reveal clear differences in the high-temperature interaction of the alloy with the Ti substrate depending on the testing atmosphere. In pure Ar (Fig. 7a-e), the solidified couple exhibited extensive debonding along the drop/substrate interface at low magnification (Fig. 7a). However, high magnification images (Fig. 7c-d) show that the debonding has a mixed character, as residual fragments of the drop with varying thickness remain well bonded to the substrate surface, indicating that local separation occurred within the metal drop itself, in the vicinity of the drop/substrate interface. These observations suggest that debonding occurred during sectioning of the solidified couple and was facilitated by the inherently weak bonding between the Mg-10Ca alloy and titanium. These findings are consistent with analyses of the Mg-Ti and Ca-Ti phase diagrams [35], which indicate a weak physicochemical interaction of Ti with both Mg and Ca, arising from the lack of mutual dissolution and the absence of reactively formed phases between them.

In contrast, the solidified and cross-sectioned couple produced in the Ar atmosphere containing hydrogen was free of structural defects (cracks, voids, or discontinuities at the interface) and consequently exhibited the formation of a permanent metallurgical bond (Fig. 8a,c-e). The excellent interfacial integrity agrees with the wetting kinetics (Figs. 1 and 2) and the top-view SEM observations (Fig. 5), which showed enhanced spreading of the molten Mg-10Ca alloy on the Ti substrate under the hydrogen-containing atmosphere. Moreover, in this couple,

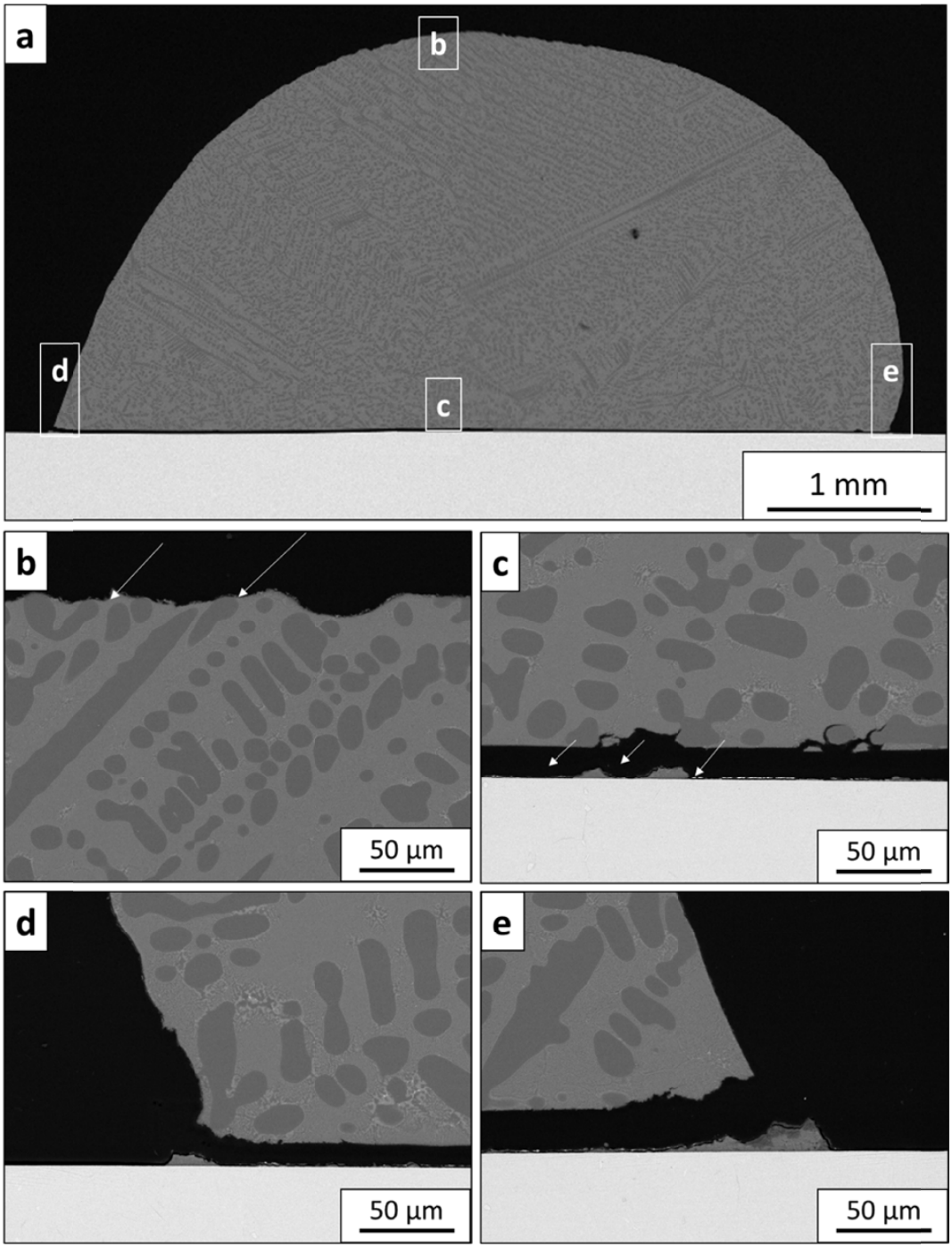

Fig. 7. SEM/BSE images of the cross-sectioned Mg-Ca/Ti couple after wettability test at 700°C in the pure Ar atmosphere: (a) the general view (magnification 50×), (b) the top of the drop surface, (c) the drop/substrate interface, (d, e) left and right drop edges (triple line), respectively; (b-e) magnification 1000×

nucleation of the α(Mg) phase occurred directly at the Ti substrate surface, followed by the growth of α(Mg) dendrites perpendicular to the substrate, consistent with the direction of heat transfer. This specific microstructure, characterized by directionally solidified α(Mg) precipitates reinforcing the Mg-10Ca alloy in the vicinity of the drop/substrate interface, additionally contributes to the higher mechanical strength of the couple compared with that produced in pure Ar.

In both atmospheres, a thin dark-grey film was observed on the upper surface of the solidified drop (white arrows in Figs. 7b and 8b). Similar surface films were previously reported for the Mg-10Ca/steel system [31] and were tentatively identified as $Ca(OH)_2$. However, only the sample tested in the Ar + 5 wt.% H_2 atmosphere exhibited an additional continuous dark-grey subsurface layer approximately 23 µm thick beneath the drop surface (Fig. 8b). Its composition was investigated by detailed SEM/BSE observations combined with EDS line-scan analysis (Fig. 9). The line profiles showed that the drop core was dominated by Mg and Ca, while oxygen was practically absent up to a distance of approximately 4 µm from the surface. Beyond

this point, oxygen concentration increased rapidly, accompanied by a corresponding decrease in the Mg content, whereas the Ca concentration remained nearly constant throughout the analyzed region. These results suggest that the subsurface layer consists of a mixture of α(Mg), Mg_2Ca, and CaO formed as a consequence of secondary oxidation of the Ca-containing alloy.

A similar oxygen-rich layer was also detected at the Mg-10Ca/Ti interface (Fig. 10a). Elemental mapping (Fig. 10c-f) confirmed that this interfacial layer is enriched in oxygen and depleted in magnesium while maintaining a relatively uniform calcium distribution, indicating the presence of a continuous CaO layer approximately 5 μm thick. Furthermore, isolated Ti-rich particles were observed within the Mg-10Ca alloy adjacent to the interface (Fig. 10b,d), although no continuous reaction layer or measurable interdiffusion between the alloy and the substrate was detected. An additional noteworthy observation is the increased oxygen concentration within the titanium substrate immediately beneath the interface (Fig. 10e), suggesting that oxygen transport toward the substrate occurred during the high-temperature test in the hydrogen-containing atmosphere.

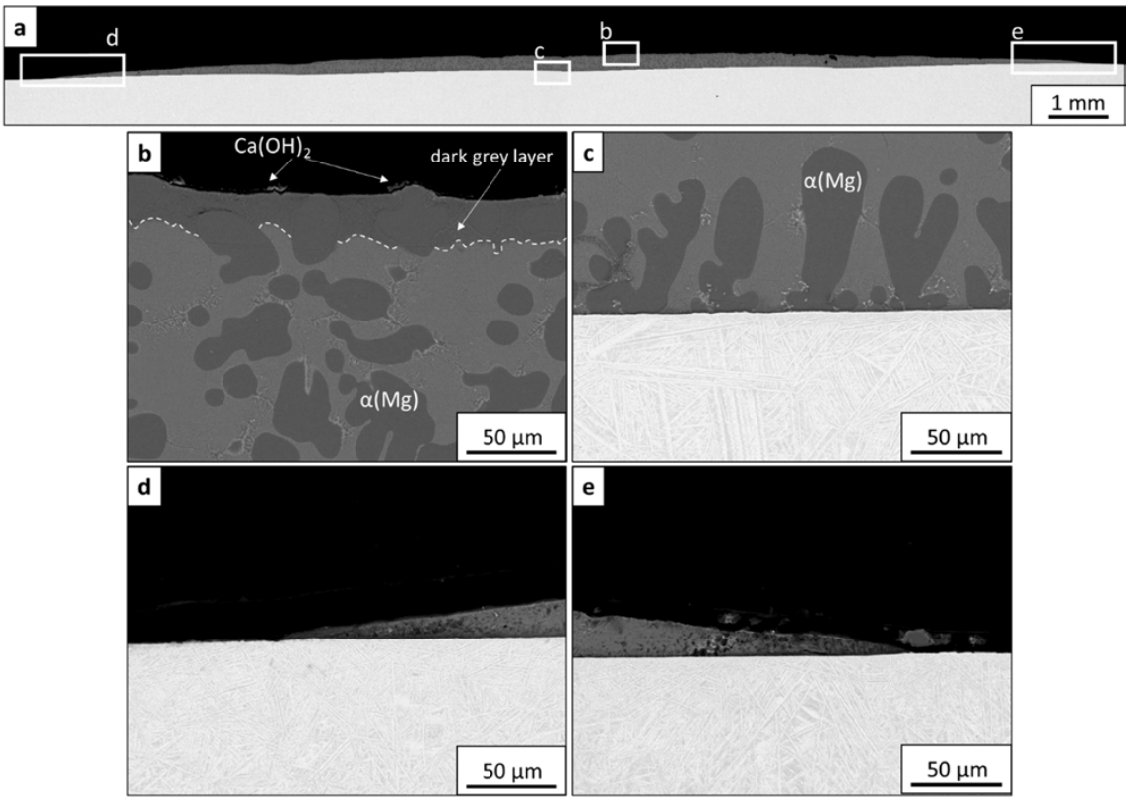

Fig. 8. SEM/BSE images of the cross-sectioned Mg-Ca/Ti couple after wettability test at 700°C in Ar + 5 wt.% H_2 atmosphere: (a) the general view (magnification 50×), (b) the top of the drop surface, (c) the drop/substrate interface, (d, e) left and right drop edges (triple line), respectively; (b-e) magnification 1000×

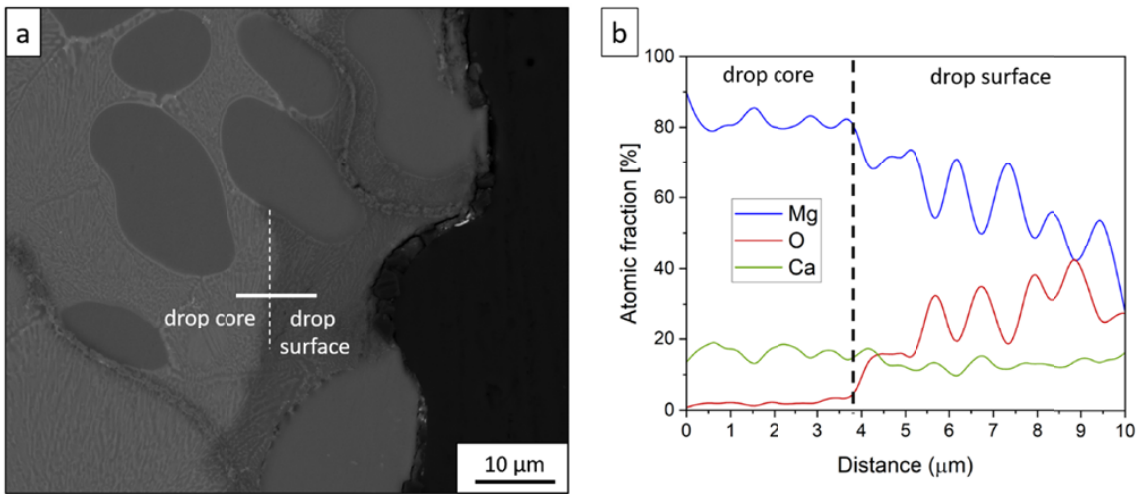

Fig. 9. (a) SEM cross-sectional microphotograph of the interface of the Mg-10Ca/Ti couple after the wettability test at 700°C in Ar + 5 wt.% H_2 atmosphere, and (b) EDS line scan results obtained from analysis marked as the white solid line of the cross-section

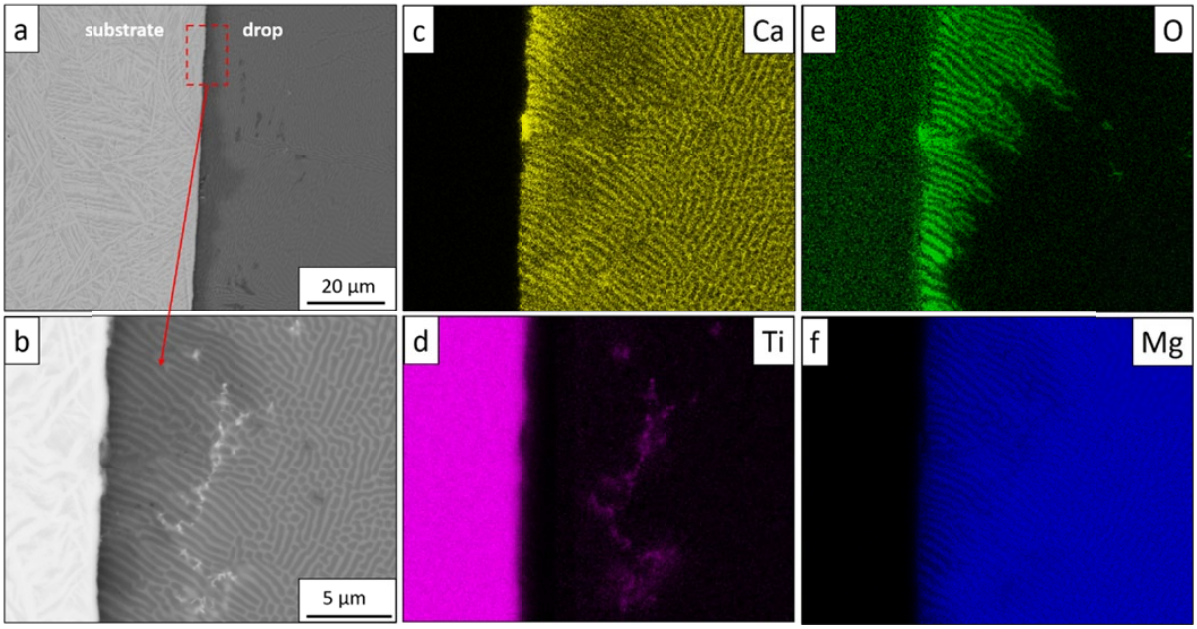

Fig. 10. (a, b) SEM/BSE cross-sectional microphotograph of the Mg-10Ca/Ti interface after wettability test in Ar +5 wt.% H_2 atmosphere, as well as the EDS maps from Fig. 10b showing distribution of Ca (c), Ti (d), O (e) and Mg (f)

Overall, the results demonstrate that the addition of hydrogen to the protective atmosphere fundamentally changes the interfacial behavior of the Mg-10Ca/Ti system. While no new reaction products between Mg-10Ca and Ti were identified in this study, the hydrogen-containing atmosphere promoted excellent wetting, permanent bonding, directional solidification of the Mg-rich phase at the interface, and the development of oxygen-rich CaO layers on both the free surface of the drop and at the Mg-10Ca/Ti interface. These microstructural changes are consistent with the significantly improved integrity of the bonded couple compared with that produced in pure argon.

4. Discussion

4.1. Wetting behavior and interfacial reaction

The wetting kinetics of the Mg-10Ca/Ti couple carried out in a pure Ar atmosphere at a temperature of 700°C are shown in Fig. 1. Based on these results, the left (θ_l), right (θ_r) and average (θ_{av}) contact angles after 200 seconds of the wettability test indicated that the Mg-10Ca/Ti system is wetted, as these values were below 90°. The wetting behavior during the wettability test of the Mg-10Ca/Ti couple was also captured using two different high-speed CCD cameras: one positioned parallel (camera (i) – Fig. 11) and the other perpendicular (camera (ii) – Fig. 12) to the cross-section of the apparatus. These cameras were crucial for capturing the dynamic wetting behavior of the Mg-10Ca/Ti system as described in [23]. Selected images from the high-temperature observations with camera (i) at four different stages of the sessile drop test (1 s, 50 s, 150 s and 300 s after deposition) confirmed that the average contact angle (θ_{av}) changes from a non-wetting to a wetting system (Fig. 11a-d). At the end of the test, both the left and right contact angles were less than 90°. However, when analyzing the selected images at the same intervals using camera (ii), it is clearly visible that at the end of the sessile drop test, the left, right, and average contact angles are higher than 90°. Thus, from this perspective, the Mg-10Ca/Ti system is apparently not wetted after the wettability test performed in a pure Ar atmosphere at 700°C. It is also important to note the dynamic effects, such as the evaporation of the Mg-10Ca alloy (Fig. 12b-d). This evaporation leads to a decrease in the contact angle (Fig. 1), consistent with the observations in Fig. 12, and a decrease in the height of the liquid Mg-10Ca drop ($H > H^*$) (Fig. 12a and d). Furthermore, in pure Ar, the drop progressively loses its symmetry, resulting in noticeable differences between the left and right contact angles. Such asymmetric spreading indicates that the drop encounters locally different wetting conditions along the triple line. During the high-temperature experiment, the chemical environment is continuously evolving because of the evaporation of liquid alloy. Magnesium evaporation under close experimental conditions has been directly visualized previously using improved illumination of the object under examination (Fig. 13), where a dense vapor cloud surrounding the liquid Mg drop is observed before contact with the substrate. Although this visualization was obtained for a pure Mg drop during its deposition on a pure Al substrate, it demonstrates that significant evaporation occurs throughout the experiment. In the Mg-10Ca alloy, both Mg and Ca are expected to contribute to the vapor phase because of their relatively high vapor pressures at 700°C. Consequently, the titanium surface is exposed to reactive metallic vapors before and during liquid contact, meaning that the chemistry and roughness of the substrate can be continuously modified rather than remaining identical to its initial state. Under a neutral pure Ar atmosphere, local variations in oxygen partial pressure together with transport of metal vapors by the flowing

gas may produce spatially non-uniform heterogeneous surface conditions. Since wetting is extremely sensitive to even minor variations in surface chemistry and roughness, such heterogeneity provides a plausible explanation for the preferential spreading observed in one direction and the resulting differences between the left and right contact angles. In contrast, the Ar + 5 wt.% H_2 atmosphere promotes a more uniform reducing environment over the entire substrate surface, resulting in nearly symmetric spreading and considerably lower contact angles.

Another piece of evidence for the role of the atmosphere is provided by the compression trial performed on the couple after the wettability test before its removal from the experimental chamber (Fig. 14). Immediately after capillary purification (Fig. 11a and Fig. 12a), the liquid alloy exhibited a bright metallic surface characteristic of an oxide-free melt. During isothermal holding in pure Ar, however, the drop gradually lost its metallic appearance and became matte (Fig. 11c,d). Mechanical compression of the drop, shown in Fig. 14a,b, caused fracture of the surface film, indicating that a visually continuous surface film had developed during the experiment. In contrast, no comparable behavior was observed in the Ar + 5 wt.% H_2 atmosphere, where the drop spread immediately after extrusion without evidence of surface film fracture. These observations indicate that secondary oxidation of the liquid surface is substantially suppressed under reducing conditions of a hydrogen-containing atmosphere, allowing the liquid alloy to preserve its high spreading ability throughout the experiment. Together, the observations demonstrate that wetting of the Mg-10Ca/Ti couple is governed by continuously evolving physicochemical processes involving evaporation from the drop, gas-surface interactions, and atmosphere-dependent modification of both the liquid alloy and the titanium substrate, rather than by the initial surface condition alone.

What is more, under conditions used in our previous and this study, pure Mg, even when oxide-free, does not wet Ti or steel at 700°C [22,24] because both substrates remain covered by stable native oxides which maintain high interfacial energies. Alloying Mg with Ca fundamentally changes the interfacial behavior: Ca lowers the surface tension [29,30] of the melt and simultaneously deoxidizes TiO_x through formation and decomposition of Ca-Ti-O and CaO, progressively exposing metallic Ti. In pure Ar, this leads to delayed wetting, whereas in Ar + 5 wt.% H_2, the Ca-driven deoxidation is strongly accelerated and stabilized by hydrogen, producing an immediate and very low contact angle. Thus, for the Mg-10Ca/Ti couple, wetting of Ti is not an intrinsic property of Mg, but a synergistic effect arising only when Ca is present and operates under reducing conditions.

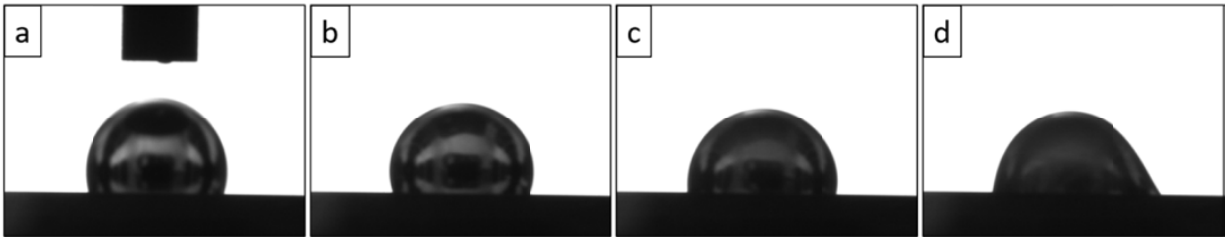

Fig. 11. Images recorded with the camera (i) with external LED lighting during the CP sessile drop test of the Mg-10Ca/Ti couple at 700°C under flowing Ar atmosphere after different times from drop deposition: a) 1 s, b) 50 s, c) 150 s, d) 300 s

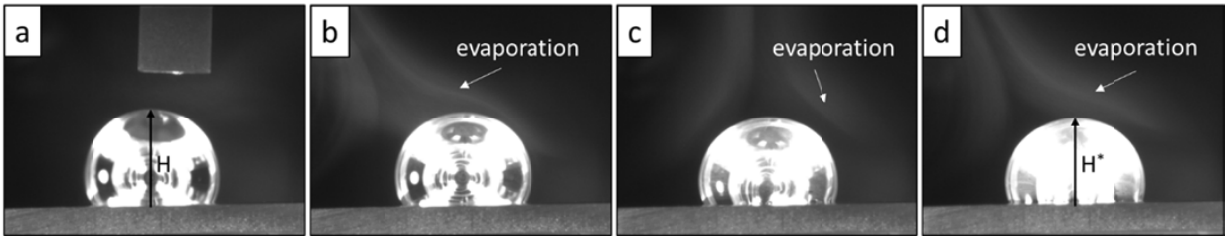

Fig. 12. Images recorded with the camera (ii) without external LED lighting during the CP sessile drop test of the Mg-10Ca/Ti couple at 700°C under flowing Ar atmosphere after different times from drop deposition: a) 1 s, b) 50 s, c) 150 s, d) 300 s

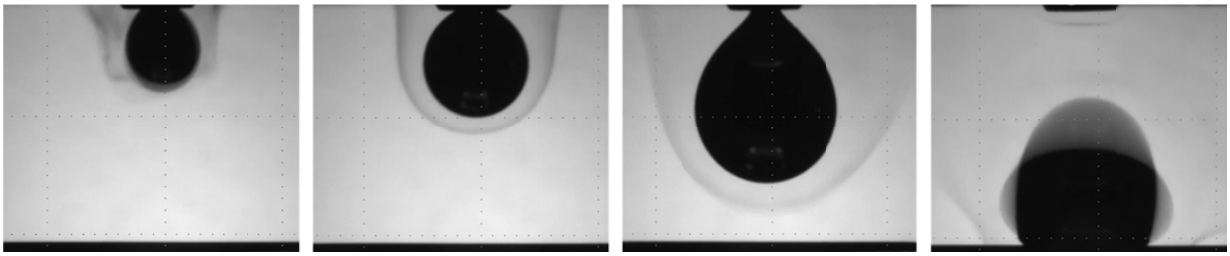

Fig. 13. The phenomenon shows the transport of metal vapors from the droplet and atmospheric constituents into the Al 1050 substrate during high-temperature testing at 700°C under a reactive atmosphere.

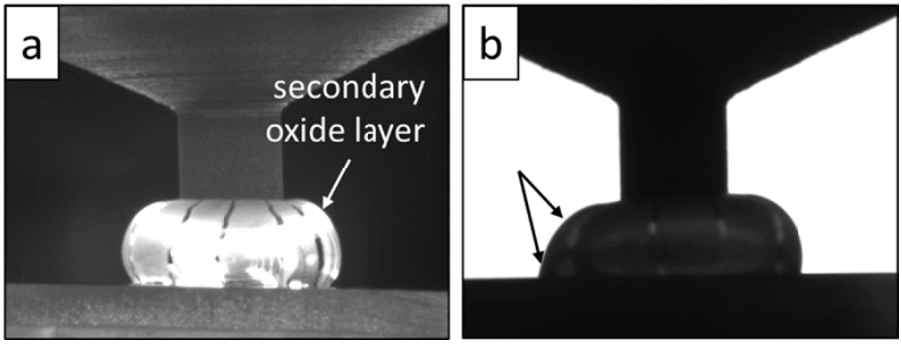

Fig. 14. Images recorded with: a) the camera (ii), and b) the camera (i) with external LED lighting during the CP sessile drop tests of the Mg-10Ca/Ti couple at 700°C under Ar atmosphere after 300 s of the high-temperature wettability test

In the case of Ar + 5 wt.% H_2, the fragmented $Ca(OH)_2$ and the dark gray CaO layer were observed on the surface of the Mg-10Ca drop after the high-temperature wettability test (Fig. 8 and Fig. 9). As mentioned in our previous work [31], the surface reaction product of $Ca(OH)_2$ on the Mg-10Ca drop is most likely formed by the reaction of CaH_2 with residual water vapor from the chamber atmosphere during cooling, forming a thin film of $Ca(OH)_2$. The $Ca(OH)_2$ fragments were detected and shown in Fig. 8b and confirmed by XRD measurements in Fig. 6. In addition, oxygen was identified in the dark gray layer a few micrometers into the drop surface (Fig. 9). The dark gray layer is most likely composed of CaO, α(Mg), and a Ca-depleted eutectic mixture. CaO, as a component of the eutectic mixture, can form both during and after the high-temperature test. Initially, during the high-temperature test at 700°C, considering the presence of residual oxides in the chamber or oxides originating from the Ti substrate, and with 10 wt.% Ca in Mg-10Ca, liquid Mg-10Ca and CaO coexist at this temperature [27,28]. On cooling after the high-temperature test, α(Mg), Mg_2Ca, and CaO are formed from the liquid Mg-10Ca and CaO. This phenomenon was observed in our study, as confirmed by the results shown in Fig. 9. Consequently, $Ca(OH)_2$ and the layer containing the eutectic mixture of CaO, α(Mg), and Mg_2Ca were detected on the drop surface under an Ar + 5 wt.% H_2 atmosphere after the high-temperature wettability test. Based on literature data [38], the formation of $Ca(OH)_2$ on the drop surface is most likely associated with post-experimental reactions occurring during cooling and subsequent exposure of the sample to residual moisture. In particular, CaH_2 formed under the hydrogen-containing atmosphere may react with residual water vapor during cooling after the wettability test, resulting in the formation of $Ca(OH)_2$. Therefore, $Ca(OH)_2$ is not considered to be a primary high-temperature reaction product formed at 700°C, but rather a secondary product generated after testing

To better understand the wetting behavior of the Mg-10Ca/Ti system at a temperature of 700°C in an atmosphere consisting of a mixture of Ar + 5 wt.% H_2, the adsorption kinetics described by the Dezellus model were applied to explain the rapid spreading stage visible in Fig. 2b during the first 70 seconds of the wettability test. This model can be described with the following equation [19,37]:

$$\cos\theta_e - \cos\theta_d = (\cos\theta_e - \cos\theta_0)\exp(-kt) \qquad (1)$$

where θ_e, θ_d and θ_0 are the equilibrium, dynamic, and initial (after deposition of drop on the substrate) contact angles, respectively, k is the kinetic constant and t is the time in seconds. Following to the above equation, the time is linearly related to the Napierian logarithm ($\cos\theta_e - \cos\theta_d$), and the slope is equal to $-k$. The $\ln(\cos\theta_e - \cos\theta_d)$ in the function of time was established, and the fitting results are shown in Fig. 15. The good fit for the contact angle marked by the red line ($R^2 = 0.90$) is visible during the initially rapid spreading stage lasting through 73 s. However, the small value of k equal to 0.03 in the Dezellus model suggests that the physical or chemical processes occurring during the spreading of the liquid drop of Mg-10Ca alloy on the Ti surface are slow since the change in the dependent value (contact angle) is very small as a function of the independent value (time). Considering the results of the microstructure observations shown in Fig. 10, which highlight a CaO layer with 5 µm width separations of Ti configurations at the Mg-10Ca/Ti interface, it can be concluded that the displacement of the contact angle (spreading kinetics during the first 73s) is controlled

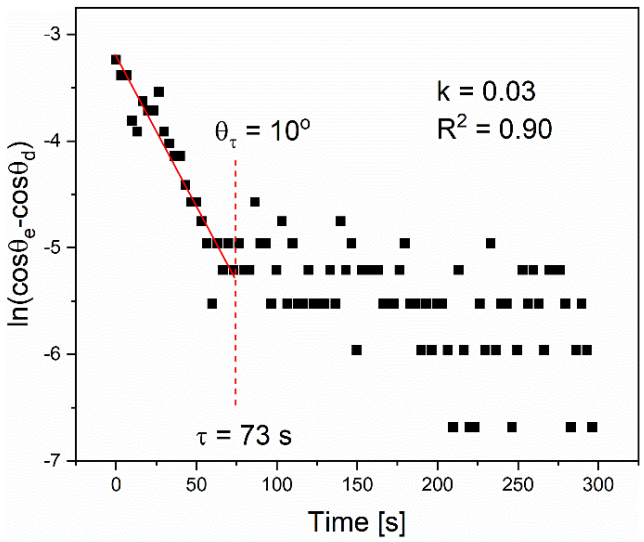

Fig. 15. Napierian logarithm of ($\cos\theta_e - \cos\theta_d$) in the function of time experiment for the Mg-10Ca/Ti couple obtained under an atmosphere consisting of a mixture of Ar and 5 wt.% H_2.

by the physicochemical reaction at the drop/surface interface, which is emphasized by Eustathopoulos [37]. This layer is similar to that observed at the drop surface, so it can be argued that it is a eutectic mixture consisting of CaO, α(Mg), and Mg_2Ca intermetallic phases. However, it should be noted that inside the Mg-10Ca drop near the Mg-10Ca/Ti interface, Ti segregations were observed, as confirmed with elemental distribution mapping (Fig. 10). In the under-discussed consideration, where a reactive atmosphere was used, significant chemical reactions can be recognized.

Further systematic studies combining detailed structural characterization of the interfaces with advanced thermodynamic modelling that accounts for the various factors influencing chemical reactions in the Mg-Ca-Ti-O-H system, particularly under dynamic conditions involving flowing gas, are required to fully elucidate the complex phenomena occurring during the sessile drop test of the Mg-10Ca/Ti couple in a hydrogen-containing atmosphere. Although the exact mechanisms remain to be clarified, the present results suggest that the remarkable improvement in wettability arises from the synergistic effect of several factors: (1) alloying magnesium with calcium, (2) the presence of hydrogen in the surrounding atmosphere, (3) evaporation of both Mg and Ca from the drop, and (4) enhanced chemical interaction between the Mg-Ca alloy and the titanium substrate.

5. Conclusions

The wetting behaviors and interface characteristics of the Mg-10Ca/Ti couples by the sessile drop method combined with non-contact and a capillarity purification procedure at 700°C were studied in two different atmospheres: (i) pure Ar and (ii) a mixture of Ar + 5 wt.% H_2. The following conclusions were obtained:

1. The atmosphere has a decisive influence on the wetting behavior and interfacial bonding of the Mg-10Ca/Ti system. Under pure Ar, the liquid alloy spread asymmetrically while the contact angle gradually decreased to values below 90° up to a final average value of 70°. In contrast, testing under an Ar + 5 wt.% H_2 atmosphere resulted in immediate good wetting ($\theta_0 \sim 19°$), rapid spreading to a final contact angle of ~9°, accompanied by the formation of a continuous, defect-free interface and good bonding.
2. Microstructural and chemical characterization revealed distinct oxygen-containing reaction products under the two atmospheres. The improved wettability and interfacial bonding obtained under the hydrogen-containing atmosphere are attributed to the synergistic combination of calcium alloying, the reducing atmosphere, and high-temperature interfacial interactions. Although the precise reaction mechanism requires further investigation, the present results demonstrate that controlling both alloy composition and processing atmosphere provides an effective strategy for promoting wetting and metallurgical bonding between magnesium alloys and titanium.

Acknowledgments

This research was supported by the National Science Centre of Poland within the OPUS 21 program under Project No. 2021/41/B/ST5/02787.

REFERENCES

[1] D. Zhu, S. Hu, Y. Fu, N. Zhao, D. Liu, A review of preparation methods, friction and wear, corrosion, and biocompatibility of biomedical high-entropy alloys. Journal of Materials Science **59** (4), 1153-1183 (2024). DOI: https://doi.org/10.1007/s10853-023-09314-5

[2] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, Ti based biomaterials, the ultimate choice for orthopaedic implants – a review. Progress in Materials Science **54** (3), 397-425 (2009). DOI: https://doi.org/10.1016/j.pmatsci.2008.06.004

[3] M. Abdel-Hady Gepreel, M. Niinomi, Biocompatibility of Ti-alloys for long-term implantation. Journal of the Mechanical Behavior of Biomedical Materials **20**, 407-415 (2013). DOI: https://doi.org/10.1016/j.jmbbm.2012.11.014

[4] Q. Chen, G.A. Thouas, Metallic implant biomaterials. Materials Science and Engineering R: Reports **87**, 1-57 (2015). DOI: https://doi.org/10.1016/j.mser.2014.10.001

[5] L.C. Zhang, L.Y. Chen. A review on biomedical titanium alloys: recent progress and prospect. Advanced Engineering Materials **21** (4), 1801215 (2019). DOI: https://doi.org/10.1002/adem.201801215

[6] M Niinomi, M Nakai, Titanium-based biomaterials for preventing stress shielding between implant devices and bone. International Journal of Biomaterials 836587 (2011). DOI: https://doi.org/10.1155/2011/836587

[7] Y.L. Hao, S.J. Li, S.Y. Sun, C.Y. Zheng, R. Yang, Elastic deformation behaviour of Ti–24Nb–4Zr–7.9 Sn for biomedical applications. Acta Biomaterialia **3** (2), 277-286 (2007). DOI: https://doi.org/10.1016/j.actbio.2006.11.002

[8] M.P. Staigera, A.M. Pietaka, J. Huadmaia, G. Dias, Magnesium and its alloys as orthopedic biomaterials: a review. Biomaterials **27** (9), 1728-1734 (2006). DOI: https://doi.org/10.1016/j.biomaterials.2005.10.003

[9] Z. Li, X. Gu, S. Lou, Y. Zheng, The development of binary Mg–Ca alloys for use as biodegradable materials within bone. Biomaterials **29**, 1329-1344 (2008). DOI: https://doi.org/10.1016/j.biomaterials.2007.12.021

[10] P. Makkar, S.K. Sarkar, A.R. Padalhin, B.G. Moon, Y.S. Lee, B.T. Lee, In vitro and in vivo assessment of biomedical Mg–Ca alloys for bone implant applications. Journal of Applied Biomaterials and Functional Materials **16** (13), 126-136 (2018). DOI: https://doi.org/10.1177/2280800017750359

[11] U. Riaz, I. Shabib, W. Haider, The current trends of Mg alloys in biomedical applications – A review. Journal of Biomedical Materials Research – Part B Applied Biomaterials **107** (6), 1970-1996 (2019). DOI: https://doi.org/10.1002/jbm.b.34290

[12] S.N. Nayab, F.H. Jones, I. Olsen, Modulation of the human bone cell cycle by calcium ion-implantation of titanium. Biomaterials **28** (1), 38-44 (2007).
DOI: https://doi.org/10.1016/j.biomaterials.2006.08.032

[13] Y. Li, P.D. Hodgson, C. Wen. The effects of calcium and yttrium additions on the microstructure, mechanical properties and biocompatibility of biodegradable magnesium alloys. Journal of Materials Science **46** (2), 365-371 (2011).
DOI: https://doi.org/ 10.1007/s10853-010-4843-3

[14] K. Kumar, R.S. Gill, U. Batra. Challenges and opportunities for biodegradable magnesium alloy implants. Materials Technology **33** (2), 153-172 (2018). DOI: 10.1080/10667857.2017.1377973

[15] L. Tian, Y. Sheng, L. Huang, D. H.-K. Chow, W. H. Chau, N. Tang, T. Ngai, C. Wu, J. Lu, L. Qin, An innovative Mg/Ti hybrid fixation system developed for fracture fixation and healing enhancement at load-bearing skeletal site. Biomaterials **180**, 173-183 (2018).
DOI: https://doi.org/10.1016/j.biomaterials.2018.07.018

[16] G. Liang, R. Schulz. Synthesis of Mg-Ti alloy by mechanical alloying. Journal of Materials Science **38** (6), 1179-1184 (2003).
DOI: https://doi.org/10.1023/A:1022889100360

[17] H. Zhou, L. Hu, H. Sun, X. Chen, Synthesis of nanocrystalline Mg-based Mg–Ti composite powders by mechanical milling. Materials Characterization **106**, 382-390 (2015).
DOI: https://doi.org/10.1016/j.matchar.2015.05.021

[18] N. Sobczak, J. Sobczak, R. Asthana, R. Purgert, The mystery of molten metals. China Foundry **7** (4), 425-37 (2005)

[19] N. Eustathopoulos, M.G. Nicholas, B. Drevet, Wettability at High Temperatures, Elsevier, Oxford, 1999.

[20] N. Sobczak, M. Singh, R. Asthana, High-temperature wettability measurements in metal/ceramic systems – Some methodological issues. Current Opinion in Solid State and Materials Science **9** (4-5), 241-253 (2005).
DOI: https://doi.org/10.1016/j.cossms.2006.07.007

[21] K. Kondoh, M. Kawakami, H. Imai, J. Umeda, H. Fujii, Wettability of pure Ti by molten pure Mg droplets. Acta Materialia **58** (2), 606-614 (2010).
DOI: https://doi.org/10.1016/j.actamat.2009.09.039

[22] S. Terlicka, K. Janus, N. Sobczak, J.J. Sobczak, Comparative study of high-temperature interaction of Nb, Ti-Nb, and Ti substrates with liquid Mg. International Journal of Refractory Metals and Hard Materials **132**, 107245 (2025).
DOI: https://doi.org/10.1016/j.ijrmhm.2025.107245

[23] S. Terlicka, P. Darłak, N. Sobczak, J.J. Sobczak, Non-wetting and non-reactive behavior of liquid pure magnesium on pure tungsten substrates. Materials **15** (24), 9024 (2022).
DOI: https://doi.org/10.3390/ma15249024

[24] S. Terlicka, N. Sobczak, K. Janus, J.J. Sobczak, Wetting behavior of Mo, Ta, and stainless steel substrates in contact with molten Mg. Journal of Magnesium and Alloys **13** (3), 1149-1159 (2025).
DOI: https://doi.org/10.1016/j.jma.2025.02.012

[25] S. Terlicka, N. Sobczak, Y. Vronska, A. Korneva, K. Janus, M. Górny, J.J. Sobczak, Influence of atmosphere and surface heterogeneity on high-temperature interaction between liquid magnesium and different types of cast irons. Archives of Civil and Mechanical Engineering **26**, 35 (2026).
DOI: https://doi.org/10.1007/s43452-025-01413-1

[26] B.-S .You, W.-W Park, I.-S Chung, The effect of calcium additions on the oxidation behavior in magnesium alloys. Scripta Materialia **42**, 1089-1094 (2000).
DOI: https://doi.org/10.1016/S1359-6462(00)00344-4

[27] A. Halwax, D. Sergeev, M. Müller, et al., Enthalpy of Formation of Calcium and Magnesium Oxide Obtained by Knudsen Effusion Mass Spectrometry. Metallurgical and Materials Transactions B **55**, 821-835 (2024).
DOI: https://doi.org/10.1007/s11663-024-02995-6

[28] S.M. Liang, A. Kozlov, R. Schmid-Fetzer, The Mg–Ca–O system: Thermodynamic analysis of oxide data and melting/solidification of Mg alloys with added CaO. International Journal of Materials Research (2018). DOI: https://doi.org/10.3139/146.111596

[29] B.J. Keene, Review of data for the surface tension of pure metals, International Materials Reviews **38**, 157-192 (1993).
DOI: https://doi.org/10.1179/imr.1993.38.4.157

[30] J. Bohdansky, H.E.J. Schins, Surface tension and density of the liquid earth alkaline metals Mg, Ca, Sr, Ba. Journal of Inorganic and Nuclear Chemistry **30**, 2331-2337 (1968).
DOI: https://doi.org/10.1016/0022-1902(68)80241-6

[31] S. Terlicka, K. Janus, N. Sobczak, J.J. Sobczak, Effect of atmosphere on the high-temperature interaction of molten Mg-10Ca alloy with steel substrates. Archives of Civil and Mechanical Engineering **24**, 160 (2024).
DOI: https://doi.org/10.1007/s43452-024-00975-w

[32] T. Smith, Oxidation of titanium between 25°C and 400°C. Surface Science **38** (2), 292-312 (1973).
DOI: https://doi.org/10.1016/0039-6028(73)90163-5

[33] H. Okamoto, O-Ti (Oxygen-Titanium). Journal of Phase Equilibria and Diffusion **32**, 473-474 (2011).
DOI: https://doi.org/10.1007/s11669-011-9935-5

[34] E. Ziółkowski, J.J. Sobczak, P. Fima, N. Sobczak, Implementation of a methodology for determining the density and surface tension of liquid metal during high-temperature tests. Metalurgia (2020). ISBN 978-83- 63605-51-3, 519-530 (in Polish).

[35] FactSage Version 8.2, with FTlite Database. Available online: https://w:ww.crct.polymtl.ca/fact. Accessed 10 June 2023.

[36] E. Saiz, A.P. Tomsia, R.M. Cannon, Triple line ridging and attachment in high-temperature wetting. Scripta Materialia **44** (1), 159-164 (2001).
DOI: https://doi.org/10.1016/S1359-6462(00)00549-2

[37] N. Eustathopoulos, Progress in understanding and modeling reactive wetting of metals on ceramics. Current Opinion in Solid State and Materials Science **9** (4-5), 0-160 (2005).
DOI: https://doi.org/10.1016/j.cossms.2006.04.004

[38] T. Kim, G.-H. Cho, J.-W. Lim, Surface reaction and deoxidation mechanism of titanium powder deoxidized by calcium in atmospheric pressure argon. Advanced Powder Technology **33**, 103729 (2022).
DOI: https://doi.org/10.1016/j.apt.2022.103729