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Interfacial Reactions Between Calcium Titanate Investment-Casting Shells and Different Titanium Alloys

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Abstract. The interfacial reactions between calcium titanate investment-casting shells and different titanium alloys were investigated. Shells containing CaTiO_3 as the principal face-coat refractory were used to cast commercially pure titanium (TA1), Ti-6Al-4V (TC4), and Ti-45Al-2Mn-2Nb under vacuum. The shells and castings were characterized by X-ray diffraction (XRD), optical microscopy, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and microhardness testing. After calcination, CaTiO_3 remained the predominant shell phase, accompanied by minor ZrO_2 and CaWO_4 , indicating good high-temperature stability. The metallographically identified transition zones in TA1, TC4, and TiAl were 503.20, 318.24, and 15.15 μm thick, respectively, whereas the corresponding SEM-observed subsurface altered zones were 292.00, 254.88, and 12.48 μm thick. Oxygen enrichment occurred beneath the surfaces of all three castings, but no continuous inward migration of shell-derived cations such as Ca or Zr was detected. The TA1 surface was dominated by α -Ti and Ti-O chemical environments; Ti-O, Ti-V, and Al-O-related species formed on TC4; and Al_2O_3 together with several Ti-O phases formed on TiAl. The markedly thinner altered zone in TiAl is attributed to selective oxidation of Al and the resulting Al-O barrier layer, which restricted further inward diffusion of oxygen.

Keywords: titanium alloys; investment casting; calcium titanate shell; interfacial reaction; oxygen diffusion

Introduction

Titanium and titanium alloys combine low density, high specific strength, and excellent corrosion resistance and are therefore important in aerospace, energy, chemical-processing, and biomedical applications^[1,2]. Molten titanium is, however, extremely reactive and readily interacts with shell-mold materials. The resulting oxygen-enriched α -case is generally hard and brittle and can impair ductility, fatigue performance, and dimensional stability^[3-5]. Suppressing reactions at the mold/titanium-melt interface is consequently a central challenge in investment casting of titanium alloys.

Investment casting is one of the principal processes used for titanium alloys and is particularly suited to complex, thin-walled components requiring high dimensional accuracy and surface quality^[6]. Current face-coat refractories are mainly metal oxides, including Y_2O_3 , ZrO_2 , CaO , and Al_2O_3 . Y_2O_3 is chemically stable against titanium melts but costly and may provide inadequate thermal-shock resistance^[7]. ZrO_2 has a high melting point and good corrosion resistance, but it can release Zr and O into the melt; its phase transformation during calcination also causes volume expansion and shell cracking unless stabilized with Y_2O_3 or CaO ^[8]. CaO is comparatively compatible with Ti but readily absorbs moisture and hydrates, destabilizing shell slurries and limiting its application^[9]. Al_2O_3 has limited high-temperature inertness toward commercially pure titanium and low-Al alloys, although it is widely used for superalloys and titanium aluminides^[10]. Thus, no single oxide simultaneously satisfies the requirements for chemical stability, thermal-shock resistance, processability, and cost, motivating the development of alternative shell systems.

CaZrO_3 is an ABO_3 -type perovskite compound in the CaO - ZrO_2 system. Its high melting point and high-temperature inertness have enabled relatively mature applications in crucibles for melting titanium alloys^[11-14]. Previous studies^[15,16] have also demonstrated its strong potential in titanium investment-casting shells. Silica-free CaZrO_3 shells produce only weak interfacial reactions: cast surfaces show no discernible α -case and contain substantially less oxygen than products cast in silica-based shells. Li et al.^[17,18] compared the interaction of TA15 with CaZrO_3 shells prepared by conventional dipping and stuccoing using different binders. Zirconium-acetate-bonded CaZrO_3 produced the least reaction. Adding Y_2O_3 to the face coat of a silica-based shell also created a physical barrier and reduced reaction severity, although neither approach matched the performance of an Y_2O_3 shell.

Compared with CaZrO_3 , CaTiO_3 offers a simpler synthesis route, widely available raw materials, and good high-temperature phase stability. Mamayeva et al^[19] examined commercially pure titanium in contact with CaZrO_3 crucibles and identified CaTiO_3 as a possible interfacial reaction product and relatively stable transition layer, supporting its direct use as a refractory. Freitag et al^[20] produced an ultrathin functional CaTiO_3 face coat by a replica process. Combined with a silica-free aqueous slurry, it reduced the α -case thickness to 5-12 μm , compared with 60-100 μm for alumina shells. Li et al^[21] prepared $\text{CaAl}_{12}\text{O}_{19}$ - CaTiO_3 composites that exhibited good corrosion resistance against Ti-6Al-4V; apart from limited Fe penetration along pores or grain boundaries, no pronounced interfacial attack was observed. Lu et al^[22] reported that sufficiently high ZrO_2 contents in $\text{ZrO}_2/\text{CaTiO}_3$ composites promoted CaZrO_3 and complex Ca-Zr-Ti-O phases and reduced identifiable reaction products on the titanium-contact side. CaTiO_3 may therefore serve both as a face-coat refractory and as a component that modifies phase constitution and reaction kinetics through interaction with ZrO_2 . High-temperature sessile-drop studies^[23] further showed reactive wetting of liquid titanium on CaTiO_3 -based ceramics, accompanied by oxygen transport and Ti-bearing reaction products. CaTiO_3 is therefore not completely inert, although the interfacial layer may retard subsequent reaction. Refractory screening should also consider more than thermodynamic stability. Because titanium alloys are generally melted and poured under vacuum or low pressure, vapor pressure of alkaline-earth metals and interfacial infiltration kinetics are also important. Kenzhaliyev et al^[24] compared liquid-titanium interactions with BaZrO_3 , SrZrO_3 , and SrTiO_3 under vacuum and atmospheric-pressure argon. Under argon, the principal process was dissolution of Zr and O; under vacuum, volatilization of Sr or Ba shifted the reaction equilibrium and altered refractory corrosion.

Most existing work concerns dense blocks, crucibles, or composite refractories and evaluates macroscopic corrosion, phase stability, or localized elemental penetration. Systematic studies under realistic investment-casting conditions remain scarce, particularly where binder decomposition, face-coat calcination products, rapid mold filling, and alloy chemistry act simultaneously.

In this study, CaTiO_3 was used as the principal face-coat refractory, zirconium acetate as the binder, and ammonium metatungstate as a slurry stabilizer. TA1, TC4, and Ti-45Al-2Mn-2Nb alloys were cast under vacuum. Phase analysis of the shell before and after calcination was combined with cross-sectional optical microscopy and SEM-EDS, surface XRD and XPS, and microhardness profiling. Differences among the alloys in subsurface microstructure, elemental distributions, surface reaction phases, and property gradients were compared to clarify the effect of alloy chemistry on CaTiO_3 /alloy interfacial reactions and to support assessment and stabilization of calcium titanate face coats.

1. Experimental Procedure

Calcium titanate was used as the principal refractory in the shell face coat. The slurry was prepared with a zirconium acetate binder, 10 wt.% ammonium metatungstate (relative to binder mass) to improve stability, and a powder-to-liquid mass ratio of 2:1. Each uniformly applied coat was stuccoed with 100-mesh zirconia; this operation was repeated twice. The backup slurry contained 280-mesh bauxite refractory and zirconium acetate at a powder-to-liquid ratio of 2:1, and successive backup coats were stuccoed with 100-, 60-, and 30-mesh bauxite. The molds were dewaxed in an infrared furnace at 250 °C and then fired in an electric resistance furnace. They were heated at 10 °C/min, held at 350 and 700 °C for 0.5 h at each temperature, heated to 1050 °C and held for 2 h, and finally furnace-cooled to 200 °C for pouring.

TA1, TC4, and Ti-45Al-2Mn-2Nb were melted and poured under vacuum in an 80-kg consumable-electrode skull arc furnace. Their chemical compositions are listed in Table 1. Gravity pouring was performed at a chamber pressure of ≤ 0.1 Pa and pouring temperatures of 1690, 1720, and 1650 °C, respectively. After pouring, the castings were furnace-cooled below 200 °C before removal. The casting geometry and sampling locations are shown in Fig. 1; the specimens are designated TA1, TC4, and TiAl.

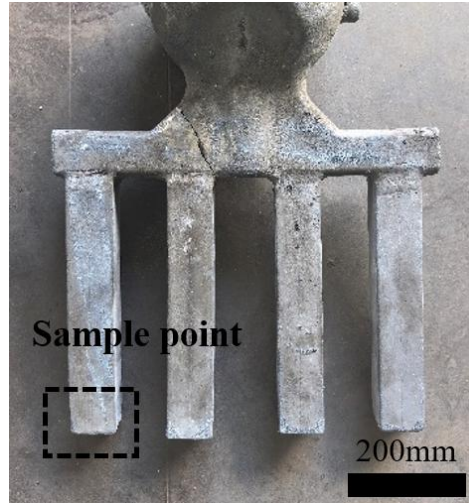


Fig. 1. Casting geometry, sampling positions, and analysis areas.

Table 1. Chemical compositions of the three titanium alloys (wt.%).

No.	Ti	Al	V	Mn	Nb	Fe	Si	C	N	H	O
TA1	Base	-	-	-	-	0.12	0.02	0.008	0.013	0.015	0.06
TC4	Base	6.62	4.26	-	-	0.061	0.006	0.021	0.012	0.001	0.10
TiAl	Base	44.73	-	1.94	2.07	0.043	0.005	0.007	0.009	0.001	0.082

Polished cross sections were examined using a ZEISS Axio Vert.A1 inverted materials microscope after the two-step etching procedures listed in Table 2. Subsurface morphologies were observed with a ZEISS EVO/MA25 scanning electron microscope equipped with an Oxford EDS system for point analysis and line scanning. ImageJ was used to measure the metallographic transition zone and the SEM-observed subsurface altered zone from the casting surface to the boundary with the unaffected matrix. Three interface regions were examined for each specimen, with at least 25 measurements per interface, and mean values were reported.

Table 2. Two-step etching procedures used for metallographic preparation.

No.	Etchant	Step	Method	Time
TA1	4 ml HNO ₃ +1 ml HF+195 ml H ₂ O	1	Swab	2s~5s
	2% NH ₄ HF ₂	2	Immersion	15s~20s
TC4	4 ml HNO ₃ +2 ml HF+94 ml H ₂ O	1	Swab	5s~10s
TiAl	2% NH ₄ HF ₂	2	Immersion	15s~20s

Surface phases were identified using a Rigaku SmartLab X-ray diffractometer with Cu radiation and a graphite monochromator at 9 kW, 45 kV, and 200 mA. Data were collected from 20 to 90 deg at 5 deg/min after ultrasonic cleaning. Surface chemistry was analyzed using a PHI 5000 VersaProbe III scanning XPS microprobe after the specimens had been wiped with ethanol and dried.

Differential scanning calorimetry and thermogravimetry (DSC-TG) were performed on face-coat powder scraped from dewaxed shells. The sample was heated in air at 50 °C/min to 900 °C and then at 10 °C/min from 900 to 1600 °C.

Cross-sectional microhardness was measured with an MH-50 digital tester under a 300-g load (HV0.3). Indentations were made from the casting surface toward the interior at 200- μm intervals. Three measurements at each position were averaged.

2. Results and Analysis

2.1 Phase Constitution of the Shell Before and After Calcination

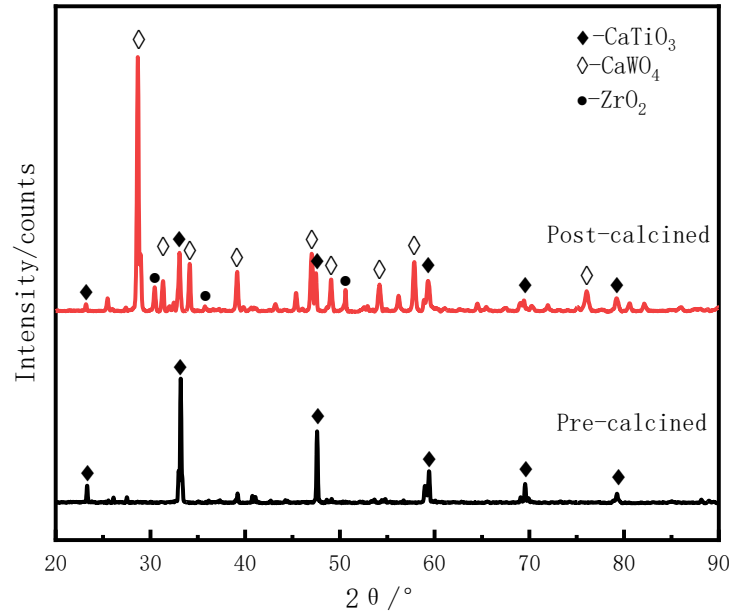
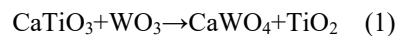


Fig. 2. XRD patterns of the shell face coat before and after calcination.

As shown in Fig. 2, CaTiO_3 was the principal phase in the unfired face coat. After calcination, ZrO_2 and CaWO_4 were also detected, indicating decomposition of zirconium acetate and ammonium metatungstate followed by solid-state reactions.

Zirconium acetate is an acidic binder and is normally stable under mildly acidic conditions. Small amounts of basic impurities in CaTiO_3 powder neutralize the slurry, increase its pH, and can cause destabilization, flocculation, or setting. A small amount of ammonium metatungstate was therefore added to maintain a mildly acidic environment and stable coating behavior.

The fired phases suggest that zirconium acetate and ammonium metatungstate formed ZrO_2 and tungsten-bearing oxides during heating. The latter may react with CaTiO_3 according to Eq. 1 to form CaWO_4 . Thermodynamic calculation gives a standard Gibbs free-energy change of -139.84 kJ/mol at 1050°C , indicating that the reaction is feasible under appropriate conditions.



2.2 Thermal Behavior of the Face Coat

Figure 3 presents the DSC-TG curves of the dewaxed CaTiO_3 face coat. The response was predominantly endothermic and contained no sharp endothermic or exothermic peaks, indicating the absence of abrupt solid-state transformations or other intense thermal reactions over the test range. Maximum mass loss during the full heating cycle was only 0.7%, without a distinct step. The gradual decrease between 200 and 1400°C is attributed to desorption of water and high-temperature decomposition of residual binder. This small change confirms effective dewaxing and indicates that the face coat remained predominantly CaTiO_3 , with only minor binder-derived reactions. Above 1400°C the apparent mass increased slightly by approximately 0.15% of the initial mass. Because post-calcination XRD did not show substantial formation of new phases, this increase was attributed to high-temperature buoyancy effects in air. Thus, the dewaxed CaTiO_3 face coat contained little residual material and exhibited sufficient high-temperature stability for titanium casting.

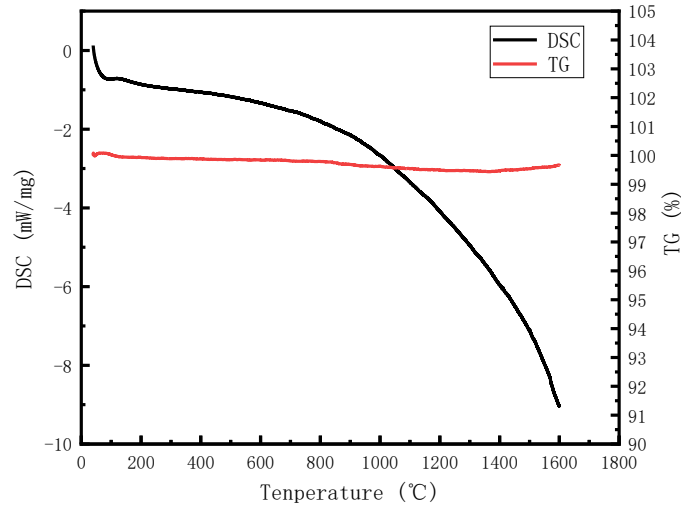


Fig. 3. TG-DSC curves of the dewaxed shell face coat.

2.3 Metallographic Characterization of the Interfacial Zone

Figure 4 shows the cross-sectional microstructures after casting the three alloys against the CaTiO_3 shell. A clear microstructural boundary separated the subsurface region from the matrix in every specimen. TA1 exhibited a fine acicular Widmanstätten α matrix, whereas its subsurface α plates were markedly coarsened and grew approximately normal to the interface. TC4 showed an $\alpha+\beta$ lamellar Widmanstätten matrix with similarly coarsened two-phase lamellae near the interface. TiAl had a fully lamellar microstructure consisting of γ/α_2 colonies of different orientations; near the surface, the original lamellae partially disappeared and were replaced by discontinuous networks and irregular blocks. The transition zones appeared brighter than their respective matrices, reflecting different etching responses and microstructural states. Their measured thicknesses were 503.20, 318.24, and 15.15 μm for TA1, TC4, and TiAl, respectively.

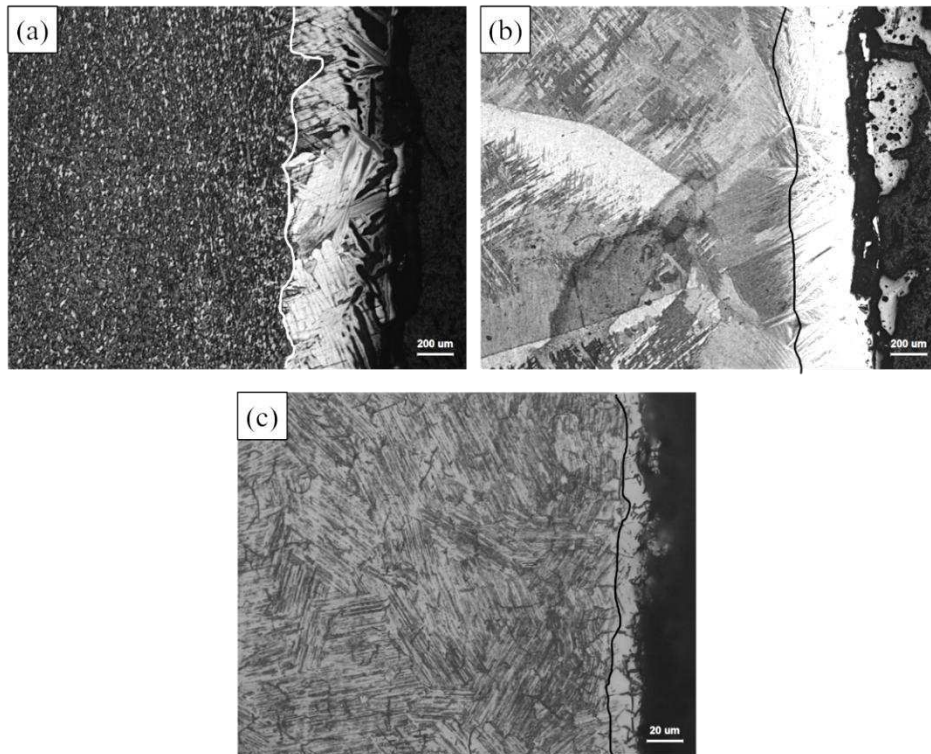


Fig. 4. Microstructures of the interfacial zones: (a) TA1, (b) TC4, and (c) TiAl.

Contact between the hot melt and the cooler shell changes interfacial heat flow and local solidification conditions and may consequently affect subsurface orientation and scale. Simultaneously, interfacial reactions generate

microstructural differences between the affected region and the matrix. Alloy chemistry strongly modified the reaction severity. The highly reactive, nearly pure TA1 exhibited the widest transition zone, whereas increasing alloying complexity and Al content progressively reduced its thickness.

2.4 SEM-EDS Characterization of the Interfacial Zone

Cross-sectional SEM images in Fig. 5 reveal subsurface morphological changes in all specimens. The mean altered-zone thicknesses were 292.00 μm for TA1, 254.88 μm for TC4, and 12.48 μm for TiAl, following the same trend as the metallographic transition zones. EDS point analyses were performed in the subsurface and interior, and line scans were acquired across each section (Figs. 6 and 7).

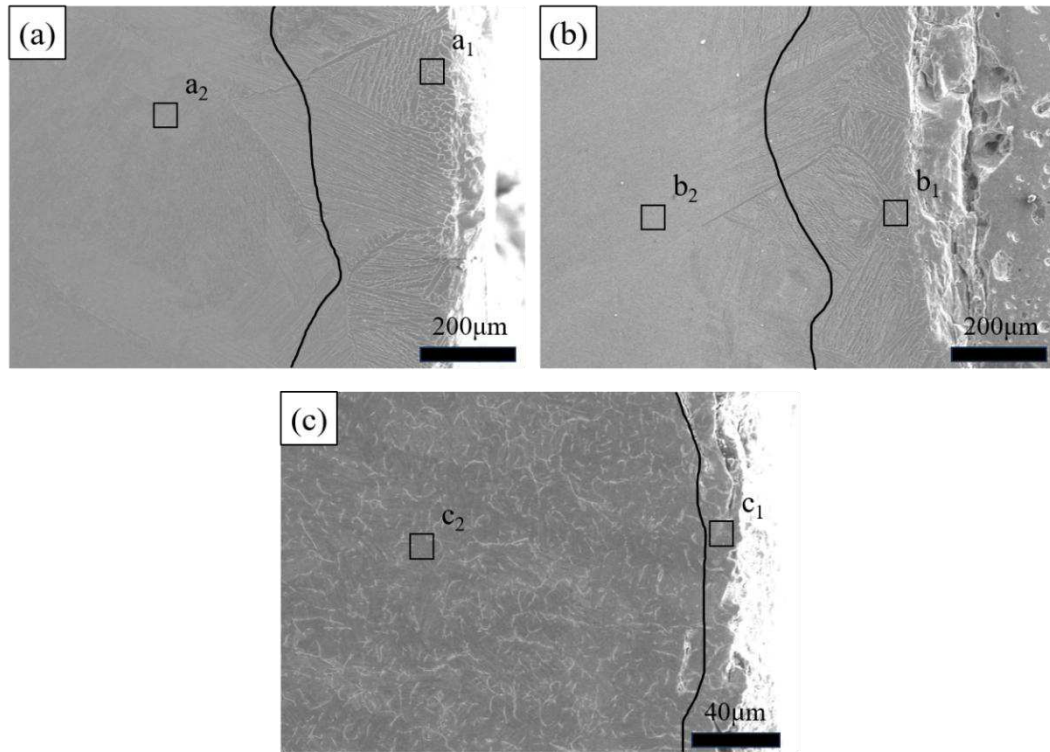


Fig. 5. SEM images of the interfacial zones: (a) TA1, (b) TC4, and (c) TiAl.

As shown in Fig. 6, all three line scans were dominated by signals from the alloy matrices. No appreciable penetration of Ca or Zr was observed in TA1, implying that the shell did not undergo severe reaction accompanied by cation transfer; the principal change was oxygen enrichment to a depth of approximately 303 μm . TC4 likewise showed changes mainly in O and Ti to a depth of approximately 184.7 μm , while Al and V remained nearly constant. In TiAl, variations in Ti, Al, and O were confined to approximately 14.36 μm from the surface, and Mn and Nb showed little change. Oxygen profiles followed the overall microstructural trend. The oxygen-affected depth in TiAl closely matched its altered-zone thickness, whereas the EDS-derived depths in TA1 and TC4 were smaller than the metallographically identified transition zones. This discrepancy may arise from uncertainty in EDS quantification of light elements or oxygen concentrations below the EDS detection limit at greater depths.

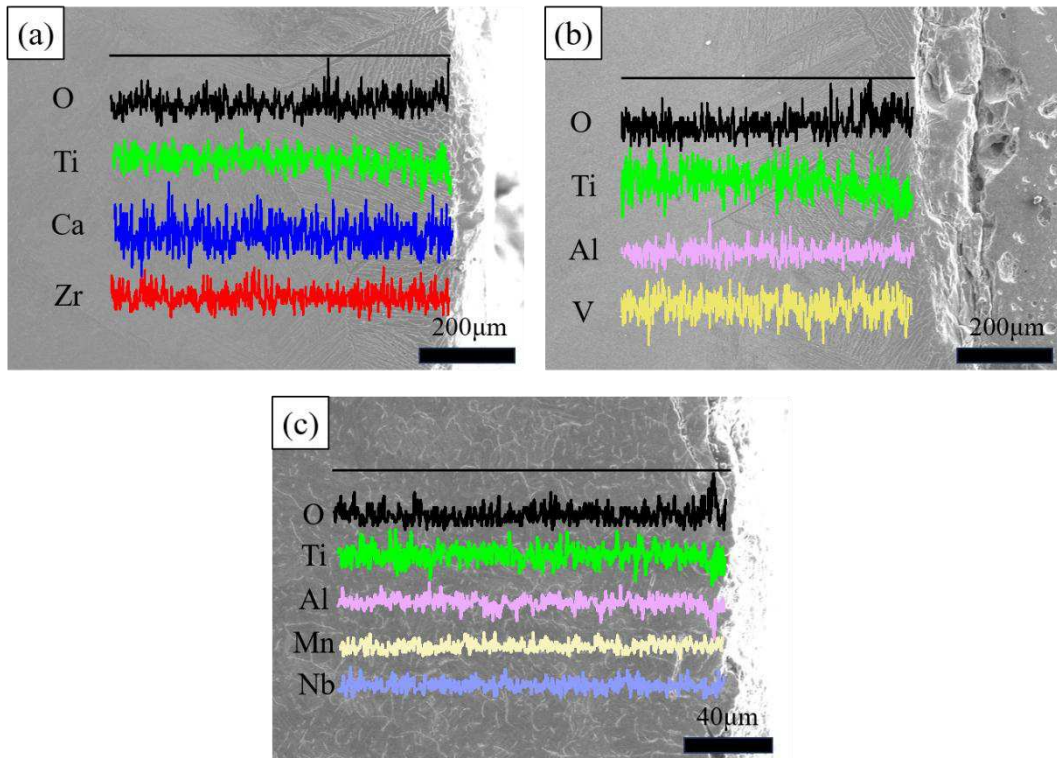
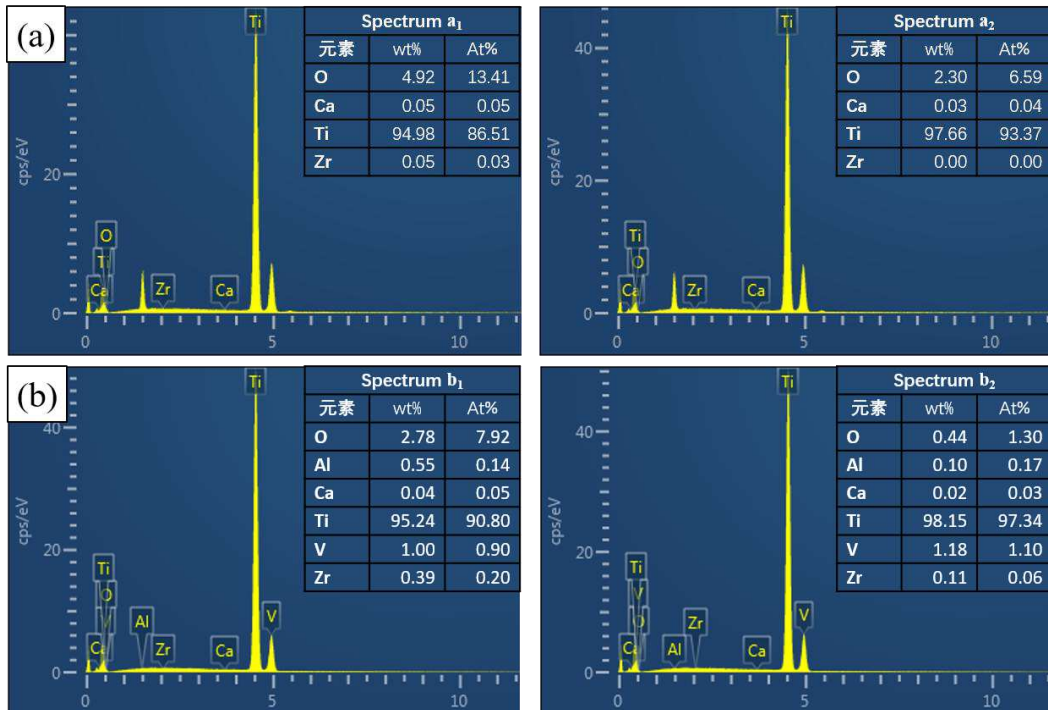


Fig. 6. EDS line scans across the subsurface regions: (a) TA1, (b) TC4, and (c) TiAl.

The point analyses in Fig. 7 likewise show that differences between subsurface and matrix regions were primarily associated with matrix elements and oxygen; no marked enrichment of shell-derived Ca or Zr was detected. In TA1, the subsurface region a_1 contained 4.92 wt.% O (13.41 at.%), compared with 2.30 wt.% (6.59 at.%) in the interior region a_2 . The oxygen signal in region b_1 of TC4 was approximately six times that in b_2 , whereas that in region c_1 of TiAl was approximately three times that in c_2 . Interfacial contamination during casting was therefore governed mainly by oxygen transport, whose penetration depth was constrained by alloy chemistry.



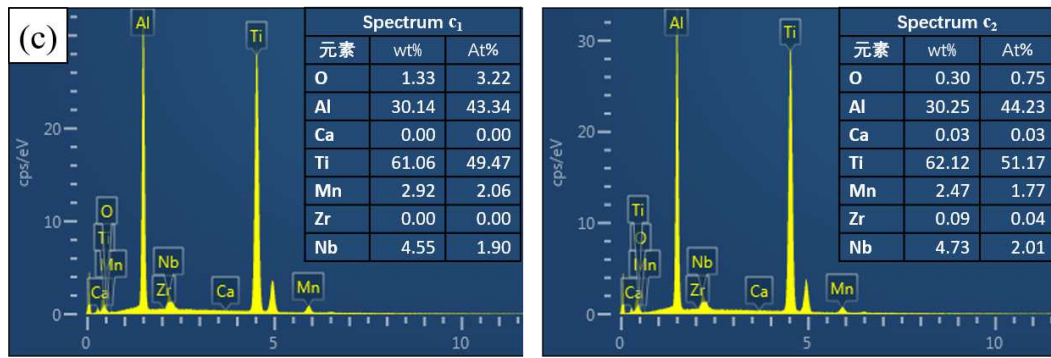


Fig. 7. EDS point analyses of subsurface and matrix regions: (a) TA1, (b) TC4, and (c) TiAl.

2.5 XRD Analysis of the Casting Surfaces

Figure 8 shows the surface XRD patterns. Phase constitution became more complex as the number of alloying elements increased. TA1 was dominated by α -Ti, without peaks from Ca- or Zr-bearing products. Together with EDS, this finding indicates that the interfacial effect was mainly oxygen dissolution in α -Ti, which altered the microstructure without producing a thick reaction-product layer detectable by XRD. In addition to α -Ti, TC4 contained reflections assigned to TiV and Ti₆O, indicating oxygen participation in Ti-bearing phases and stronger surface enrichment. Oxygen enrichment also promoted formation of a metastable TiV phase containing the beta stabilizer V. TiAl exhibited the most complex surface constitution, including α -Ti, AlTi₃, Ti₃Al₂, Al₂O₃, Ti₃O, Ti₆O, and TiO; α -Ti and TiAl-related phases originated from the alloy matrix. At high Al content, preferential oxidation produced stable Al₂O₃, which restricted further oxygen ingress. Several lower-valence or oxygen-deficient titanium oxides were confined to the surface, explaining the smallest contaminated-zone thickness in TiAl.

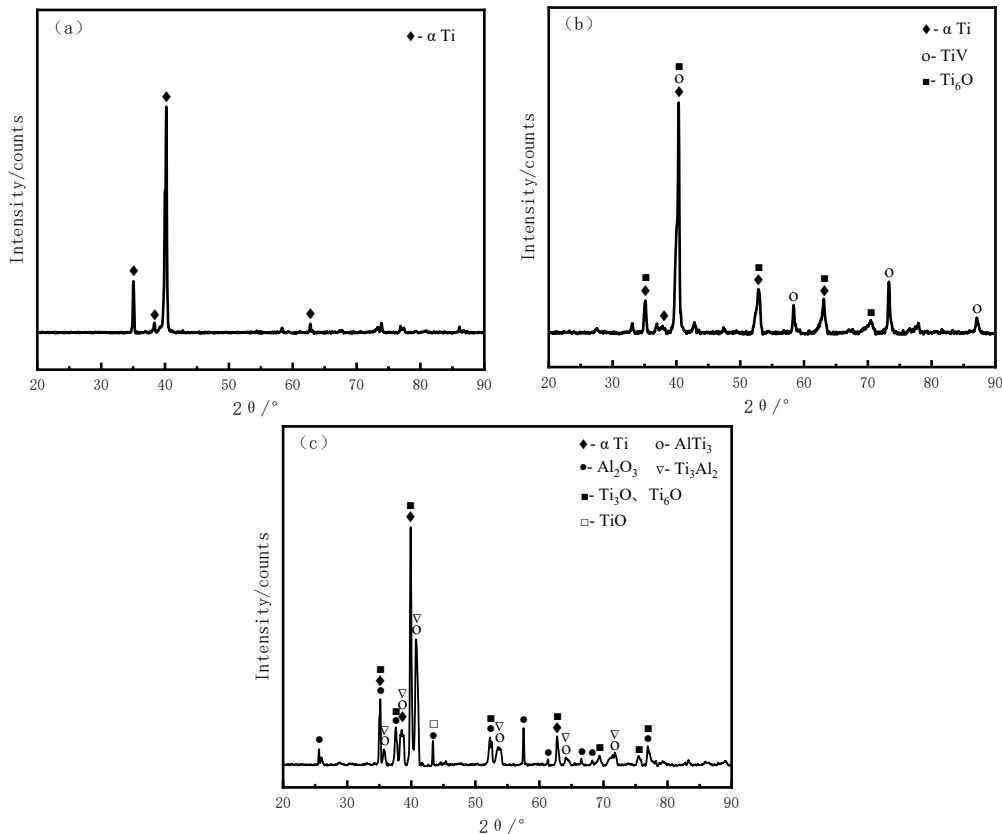


Fig. 8. XRD patterns of casting surfaces: (a) TA1, (b) TC4, and (c) TiAl.

2.6 XPS Analysis of the Casting Surfaces

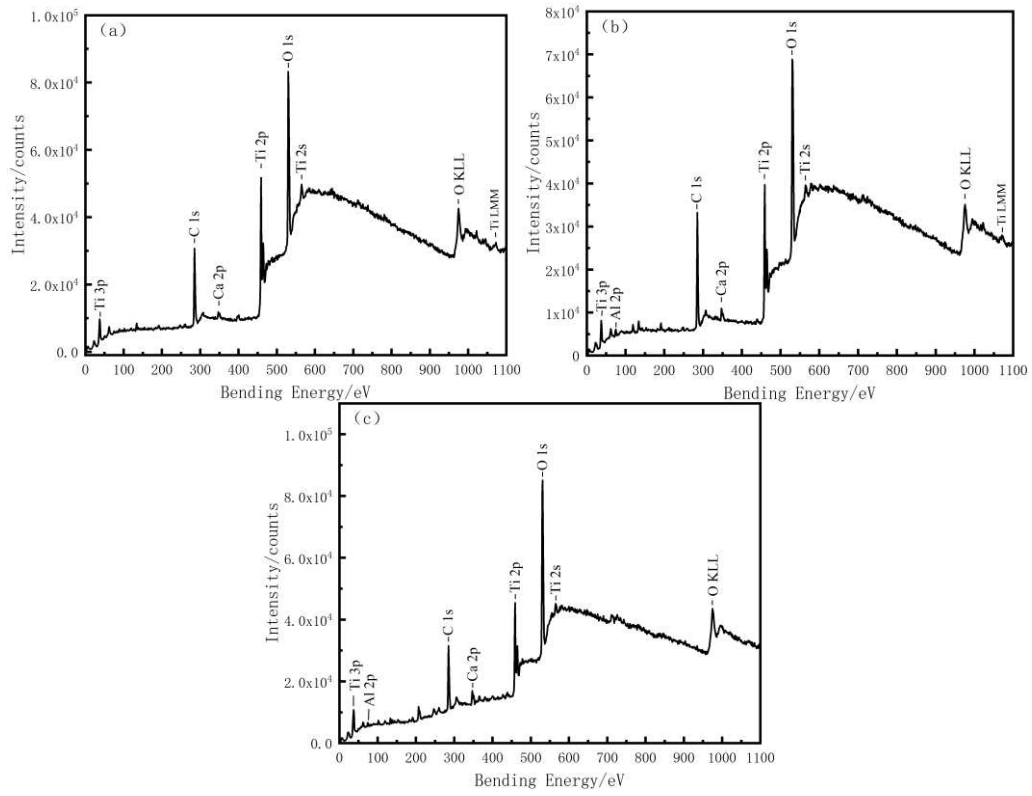
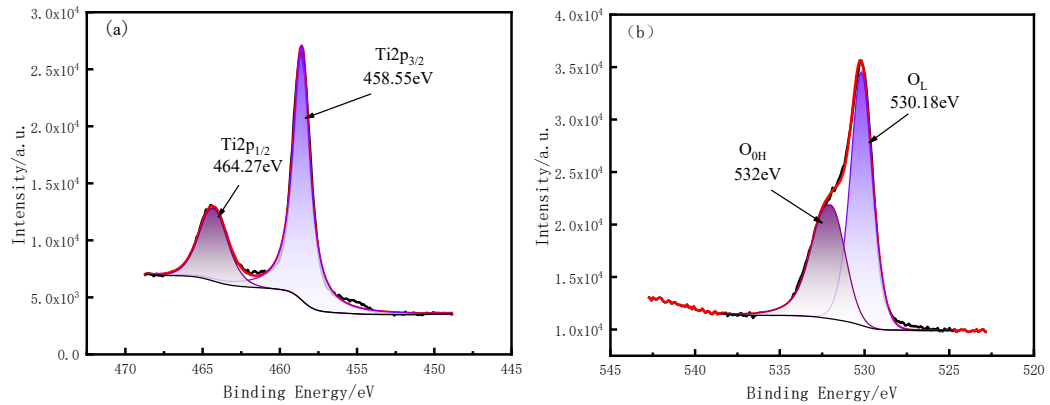


Fig. 9. XPS survey spectra of casting surfaces: (a) TA1, (b) TC4, and (c) TiAl.

The survey spectra in Fig. 9 show pronounced Ti 2p, Ti 2s, Ti 3p, and O 1s signals for all three alloys, a weak Ca 2p signal, adventitious C 1s, and an O KLL Auger feature. Al 2p was also detected on TC4 and TiAl, consistent with their compositions. The outermost contaminated surfaces were therefore dominated by Ti-O chemical environments while retaining signals from the alloying elements.



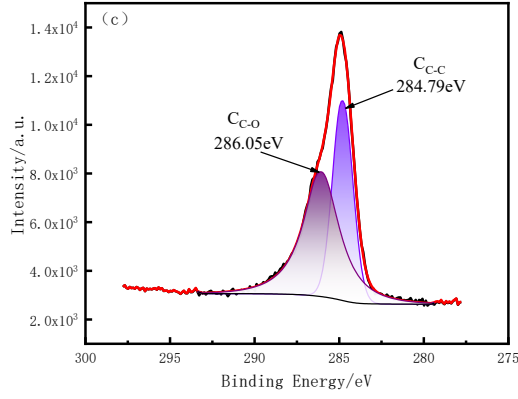


Fig. 10. High-resolution XPS spectra of the TA1 casting surface.

Figure 10 shows the high-resolution spectra from TA1. The Ti 2p peaks at 458.57 and 464.31 eV are assigned to the Ti^{4+} $2p_{3/2}$ and $2p_{1/2}$ components. O 1s components at approximately 530.18 and 532.00 eV correspond to lattice oxygen and higher-binding-energy hydroxyl/adsorbed oxygen species, respectively. The C 1s peaks at 284.79 and 286.06 eV are attributed to C-C/C-H and C-O surface carbon. Thus, a Ti^{4+} -O environment dominated the outermost TA1 surface, consistent with subsurface oxygen enrichment observed by EDS. Because oxygen was diffusely distributed in the commercially pure titanium matrix, no discrete Ti-O phase was identified by XRD.

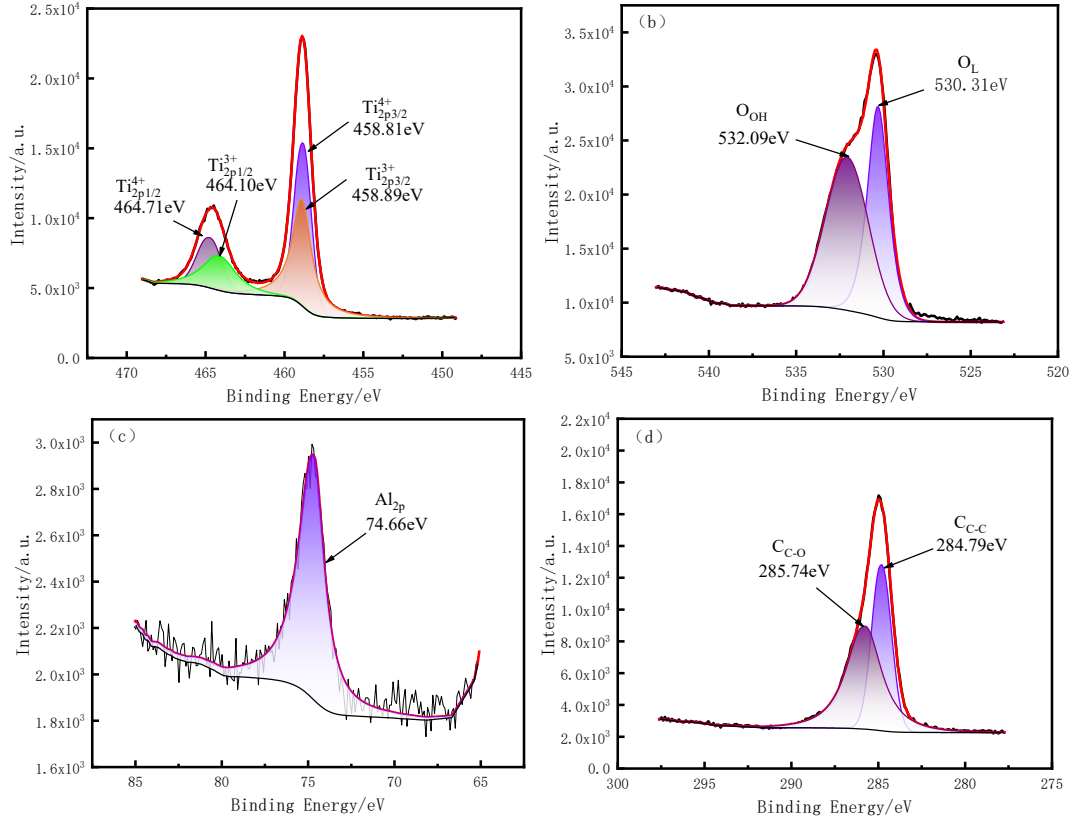


Fig. 11. High-resolution XPS spectra of the TC4 casting surface.

Figure 11 shows the high-resolution spectra from TC4. The fitted Ti 2p components near 458.81, 458.89, 464.10, and 464.71 eV include a Ti^{4+} doublet at 458.81/464.71 eV and a Ti^{3+} doublet at 458.89/464.10 eV, indicating lower titanium oxides at the surface. O 1s components at approximately 530.31 and 532.09 eV are associated with lattice oxygen and hydroxyl/adsorbed oxygen species. C 1s arose mainly from surface carbon, while Al 2p at 74.66 eV indicated oxidized Al. The TC4 surface therefore contained Ti-O and Al-O environments. Because the Al content was low and oxygen continued to diffuse inward, EDS primarily recorded oxygen variation; XRD detected only a minor Ti-O phase and no Al-O phase.

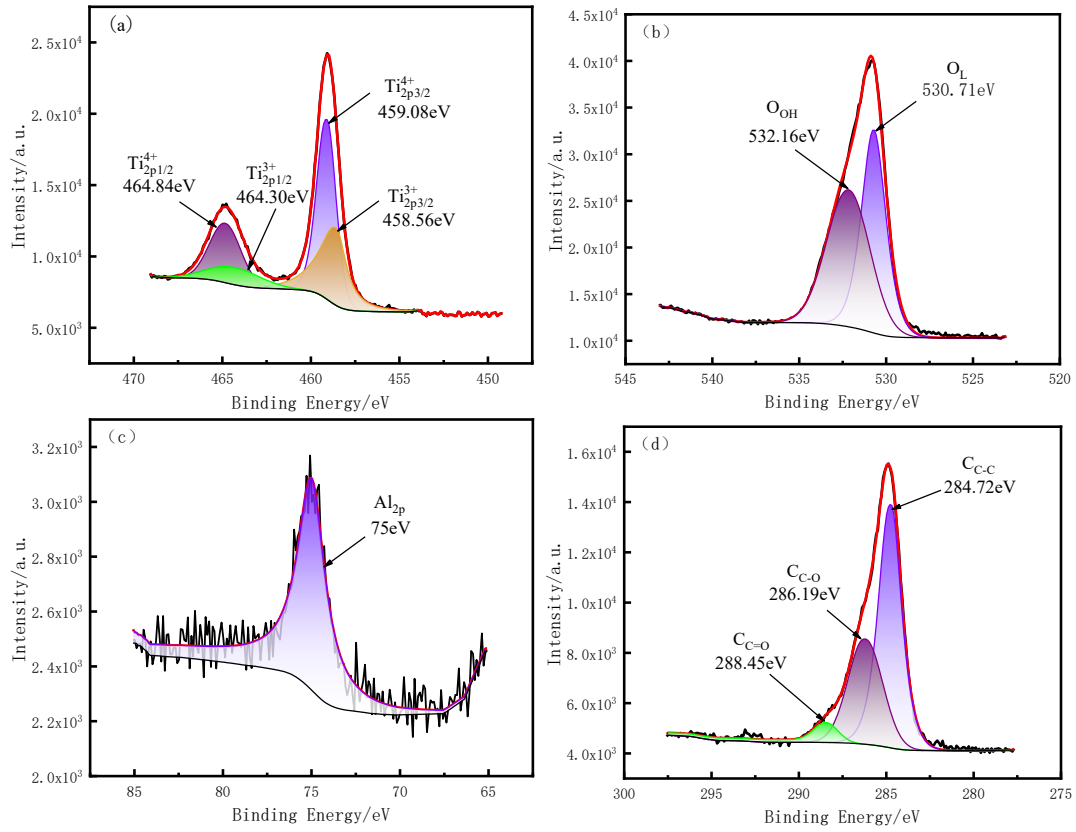


Fig. 12. High-resolution XPS spectra of the TiAl casting surface.

Figure 12 shows the high-resolution spectra from TiAl. Its Ti 2p envelope was dominated by Ti^{4+} with an accompanying Ti^{3+} contribution. O 1s components at approximately 530.71 and 532.16 eV correspond to metal-oxide lattice oxygen and higher-binding-energy hydroxyl/adsorbed oxygen species. Al 2p near 75 eV confirms oxidized Al at the outer surface. C 1s peaks at 284.72, 286.19, and 288.48 eV are assigned to C-C/C-H, C-O, and O-C=O surface carbon, respectively. In conjunction with the Al_2O_3 and multiple Ti-O phases identified by XRD, these results demonstrate a composite Al-O/Ti-O reaction layer on the outermost TiAl surface.

2.7 Microhardness Profiles

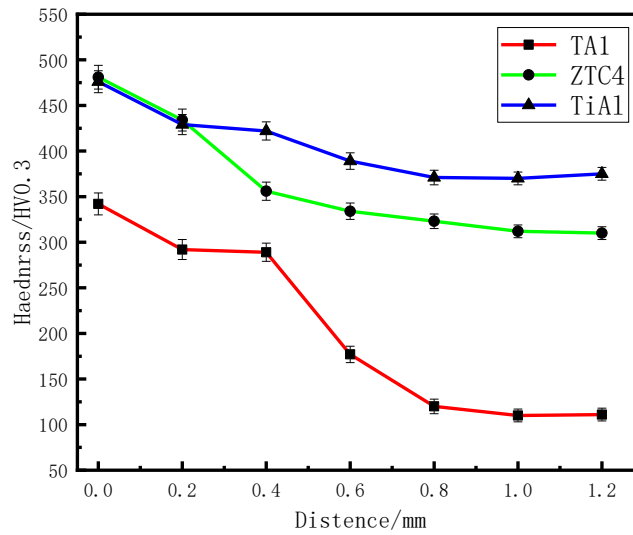


Fig. 13. Microhardness profiles from the casting surfaces toward the interiors.

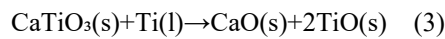
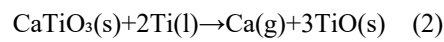
Figure 13 shows microhardness as a function of distance from the casting surface. Hardness generally decreased toward the interior in all three alloys, and the affected depth was less than 1 mm. TA1 decreased from 342 HV0.3

at the surface to approximately 110 HV0.3 at 1.0 mm; TC4 decreased from approximately 481 to 312 HV0.3; and TiAl decreased from approximately 476 to 370 HV0.3. The higher subsurface hardness indicates that the interfacial influence extended beyond the visibly contaminated layer through interstitial oxygen dissolution and microstructural transformation.

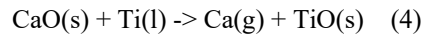
The approximately 0.503-mm metallographic transition zone in TA1 coincided with the sharp hardness decrease between 0.4 and 0.6 mm. In TC4, the transition zone was approximately 0.318 mm thick, whereas hardness continued to change gradually to 0.8 mm, indicating that the visible boundary did not fully define the property-affected region. TiAl had a transition zone of only approximately 0.015 mm, yet hardness varied from 0.2 to 0.8 mm, showing that an extremely thin surface reaction layer can accompany weaker interstitial or microstructural effects at greater depths.

3. Discussion

When molten titanium contacts CaTiO_3 at high temperature, the reduction reactions represented by Eqs. 2 and 3 may occur.



Thermodynamic calculations using HSC Chemistry 6.0 gave ΔG values at 1750 °C of approximately +25 kJ/mol for Eq. 2 and -35 kJ/mol for Eq. 3. Equation 2 is therefore unfavorable under standard-state conditions, whereas Eq. 3 can initially produce CaO and TiO. The resulting CaO may subsequently react with molten Ti according to Eq. 4.



At 1750 °C, the standard-state ΔG for Eq. 4 is approximately +61 kJ/mol. During actual vacuum pouring, however, the high vapor pressure and continuous removal of Ca maintain its partial pressure far below the standard state. From the reaction equilibrium, decreasing Ca partial pressure lowers the actual Gibbs free-energy change and drives Eq. 4 to the right. Previous work^[23] likewise showed that molten titanium can reduce Ca-containing oxide refractories under high-temperature vacuum and produce volatile metallic Ca. This explains why oxygen penetration, but no Ca-bearing phase, was detected in the contaminated layers. A schematic of the proposed mechanism is shown in Fig. 14.

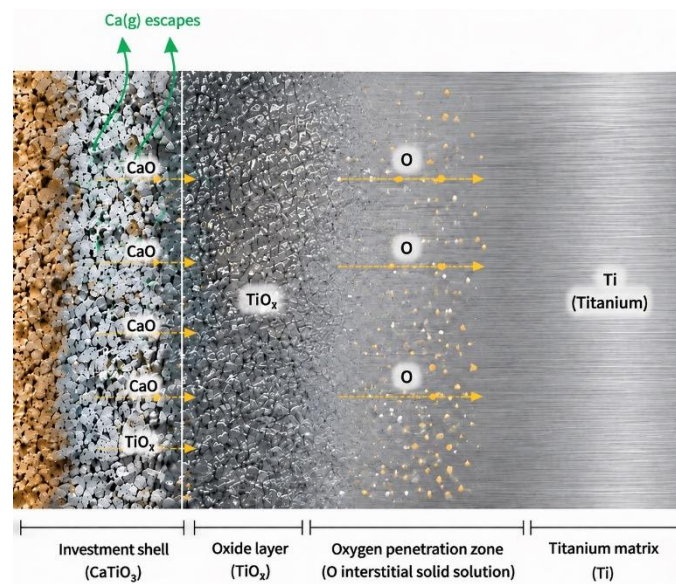


Fig. 14. Schematic illustration of the interfacial reaction between the CaTiO_3 shell and molten titanium.

Differences among TA1, TC4, and TiAl arose principally from alloy chemistry. TA1 consists essentially of α -Ti. Oxygen is both a strong α stabilizer and an effective solid-solution strengthener; its inward diffusion therefore caused extensive coarsening of the acicular structure and increased hardness, producing the widest transition zone. In TC4, partitioning of Al and V and the α/β transformation jointly affected the subsurface microstructure. The TiAl surface contained both Al-O and Ti-O chemical environments, consistent with Al_2O_3 and numerous TiO_x phases identified by XRD. Its thin contaminated layer is attributed to preferential Al oxidation and formation of an Al-O barrier that impeded further oxygen transport. Thermodynamically, increasing Al content can improve the chemical stability of ceramic shells against $\text{Ti}^{[26]}$, which may also contribute to the narrow transition zone in TiAl.

Under the present conditions, the CaTiO_3 shell caused no substantial inward diffusion of Ca, Zr, or other cations, and interfacial contamination was controlled primarily by oxygen transfer. The material therefore displayed useful chemical stability but was not completely inert. Compatibility between CaTiO_3 and the zirconium acetate binder was limited: even with ammonium metatungstate stabilization, long-term slurry stability could not be maintained. More stable binder systems should be explored. Further work should also reduce oxygen transport by lowering CaTiO_3 surface activity or constructing a more stable barrier layer, particularly for TA1 and TC4.

4. Conclusions

- (1) The CaTiO_3 face coat exhibited good high-temperature stability. No intense thermal event occurred during DSC-TG testing, and the maximum mass loss was only 0.7%. CaTiO_3 remained the principal phase after calcination, accompanied by minor ZrO_2 and CaWO_4 .
- (2) The mean metallographic transition-zone thicknesses in TA1, TC4, and TiAl were 503.20, 318.24, and 15.15 μm , respectively; the corresponding SEM-observed altered-zone thicknesses were 292.00, 254.88, and 12.48 μm . Both measures followed the order TA1 > TC4 > TiAl.
- (3) Interfacial contamination in all three castings was dominated by oxygen enrichment and inward diffusion. No continuous inward migration of shell-derived cations such as Ca or Zr was detected. Volatilization of Ca under vacuum can promote the reaction between CaTiO_3 and molten titanium.
- (4) TA1 and TC4 were strongly affected by oxygen diffusion. On TiAl, Al_2O_3 and multiple Ti-O phases formed, and selective Al oxidation created an Al-O barrier that suppressed further oxygen ingress.

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Conflict of interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work in this paper.

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