

Article

Effect of Zr Content on the Ignition Conditions and Flame Propagation of $\text{Ti}_{100-x}\text{Zr}_x$ Alloys

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Abstract

Zr is a common element in titanium alloys to enhance their mechanical properties; however, its role in combustion remains unknown. This study aimed to elucidate the effects of Zr on the ignition conditions and flame propagation of $\text{Ti}_{100-x}\text{Zr}_x$ alloys via promoted ignition-combustion (PIC) tests. Results indicated that increasing Zr content (from 30 at% to 70 at%) decreased the critical oxygen pressure, ignition temperature, and burning velocity of $\text{Ti}_{100-x}\text{Zr}_x$ alloys. The reduction in ignition conditions was attributed to a decrease in ignition activation energy (from 108.37 kJ/mol to 94.26 kJ/mol) and an increase in combustion heat (from 986.34 kJ/mol to 1049.84 kJ/mol) with Zr addition. Additionally, microstructural analysis indicated that the suppression of flame propagation was attributed to Zr promoting the formation of a dense oxide layer. This hindered oxygen diffusion, thereby suppressing the heat release of oxidation reactions in the oxide zone and the peritectic reaction in the melting zone. These findings provided new insights into optimizing the composition of burn-resistant titanium alloys to inhibit combustion kinetics.

Keywords: $\text{Ti}_{100-x}\text{Zr}_x$ alloy; titanium fire; oxygen-enriched combustion; flame propagation; ignition condition



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1. Introduction

Aeroengines are critical to aircraft flight performance and safety. To withstand the high-temperature and high-pressure conditions inside high-pressure compressors and achieve higher thrust-to-weight ratios, titanium alloys are widely used in manufacturing the internal components of high-pressure compressors due to their light weight and high strength [1,2]. However, titanium alloys have high combustion heat and low thermal conductivity. In emergency situations, such as surge events or blade fractures during flight, these properties can lead to “titanium fires”. Consequently, such fires pose a serious threat to flight safety [3,4]. The combustion behavior of titanium alloys is influenced by numerous factors, including gas flow velocity [5], initial temperature [6], oxygen concentration [7], droplet size [8], etc. For instance, in friction ignition tests [5], it has been demonstrated that altering the gas flow velocity can modify ignition conditions by changing oxygen diffusion and convective heat dissipation rates. Molten droplet experiments indicate that titanium alloy sheets gradually extinguish after ignition when the initial temperature ranges between 573 and 673 K [6]. However, at higher initial temperatures, combustion persists.

Among numerous influencing factors, composition is currently regarded as a significant and extensively researched factor.

Existing research indicates that the combustion characteristics of titanium alloys vary significantly with composition. The ignition conditions of alloys such as Ti14 [9], Ti40 [10], and TiAl [11] vary accordingly. Mi et al. [12] proposed that mixtures of oxides (e.g., Cr_2O_3 and V_2O_5) on the frictional surfaces of titanium alloys could improve lubrication conditions during friction, thereby enhancing combustion resistance. Chen Y. et al. [13] proposed that Cr has a smaller ionic radius compared to those of Ti and V in Ti40 alloy, diffuses faster within the oxide layer, and forms Cr_2O_3 . This Cr_2O_3 layer hinders oxygen transport. The effect of Cr content in $\text{Ti}_{100-x}\text{Cr}_x$ alloys and Cu content in $\text{Ti}_{100-x}\text{Cu}_x$ alloys has been specifically studied, with Cr and Cu contents showing a significant correlation with the burning velocity of these alloys [14,15]. The effect of Cr is attributed to its lower combustion heat compared to that of Ti, resulting in titanium alloys with high Cr content releasing less heat and burning at a slower rate [16]. The effect of Cu is attributed to its promotion of the formation of the Ti2Cu phase, which impedes oxygen diffusion. Additionally, studies have been conducted on elements such as V and Mo [17,18]. However, research involving Zr remains relatively scarce. In certain studies examining the combustion of Zr-containing titanium alloys such as TC11 and TC17, the role of Zr has not been noted [19–21]. Sui et al. [22] observed that an O-rich Zr solid solution was formed in the sintered zone after the combustion of TA19 and TA15. They proposed that this solid solution, together with other phases, constitutes a dense layered structure that impedes oxygen diffusion inward and Ti diffusion outward. Liu [23] and Shao [24] independently observed enrichment of Zr along with other elements at the solid–liquid interface in TC25 and TC11 alloys, respectively. They proposed that this enrichment alters the interface melting point and impedes the diffusion of Ti and O.

Compared to Cr and Cu, which have been extensively studied in commercial alloys and specifically investigated in $\text{Ti}_{100-x}\text{Cr}_x$ and $\text{Ti}_{100-x}\text{Cu}_x$ alloys, research on Zr remains insufficient. The limited studies conducted are rather cursory in commercial titanium alloys, and these studies cannot rule out interference from other elements. Zr, as a commonly used dopant in titanium alloys [25,26], has been extensively studied for its role in phase composition regulation and mechanical properties optimization [27–30]. However, research gaps in the combustion field hinder the further clarification of the “titanium fire” mechanism and the optimization of burn-resistant titanium alloy compositions.

This study aims to elucidate the influence of individual zirconium on the ignition conditions and flame propagation mechanisms in titanium alloys to address this issue. Therefore, $\text{Ti}_{100-x}\text{Zr}_x$ alloys were selected to avoid interference from elements such as Al and Mo. Moreover, a wide range of compositions was designed to highlight the variation patterns. This study prepared $\text{Ti}_{100-x}\text{Zr}_x$ alloys with different $\text{Ti}_{100-x}\text{Zr}_x$ atomic ratios (i.e., $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, $\text{Ti}_{30}\text{Zr}_{70}$). Their critical oxygen pressure, ignition temperature, and burning velocity were determined through Promoted Ignition-Combustion (PIC) tests, and their post-combustion microstructures were characterized. Based on ignition thermodynamics and combustion kinetics, through comprehensive analysis of combustion phenomena, microstructures, and element distributions, the ignition boundaries of titanium alloys with different Zr contents were identified, and the influence of Zr content on the combustion behavior and mechanisms of $\text{Ti}_{100-x}\text{Zr}_x$ alloys was analyzed.

2. Materials and Methods

2.1. Experimental Materials

This study employed high-purity Ti (99.95%) and high-purity Zr (99.95 wt.%) as raw materials and melted them three times using vacuum suspension melting to ensure a

uniform chemical composition. The materials were then annealed at 1000 °C for 4–6 h in a vacuum tube furnace under an argon atmosphere and cooled with the furnace. A cylindrical, water-cooled copper crucible was used as the mold. The resulting ingots of the three $\text{Ti}_{100-x}\text{Zr}_x$ alloys were cylindrical, measuring approximately 150 mm in diameter and 75 mm in height. Their nominal compositions are listed in Table 1, and the alloys were denoted as $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$, respectively. The original metallographic morphologies are shown in Figure 1. Due to the formation of an infinite solid solution between Ti and Zr, the β phase transforms into the α phase during cooling, resulting in all three $\text{Ti}_{100-x}\text{Zr}_x$ alloys exhibiting a typical basketweave structure. The as-cast ingots were machined into rod-shaped samples with a length of 70 mm and diameters of 3.2 mm, 5 mm, 8 mm, 10 mm, and 12 mm. All samples were ground with abrasive paper from 240 to 1500 grit to obtain uniform and smooth surfaces.

Table 1. Measured composition of the as-received sample determined by OES analysis (at%).

	Ti	Zr
$\text{Ti}_{70}\text{Zr}_{30}$	70.53	29.47
$\text{Ti}_{50}\text{Zr}_{50}$	50.96	49.04
$\text{Ti}_{30}\text{Zr}_{70}$	31.07	68.93

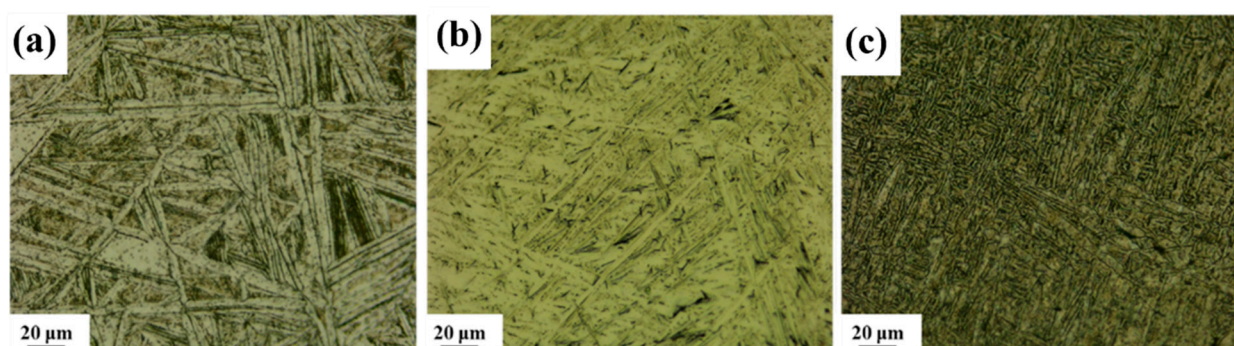


Figure 1. Metallographic structure of the as-received sample: (a) $\text{Ti}_{70}\text{Zr}_{30}$, (b) $\text{Ti}_{50}\text{Zr}_{50}$, and (c) $\text{Ti}_{30}\text{Zr}_{70}$.

2.2. Promoted Ignition-Combustion (PIC) Tests

In this experiment, the combustion behavior of $\text{Ti}_{100-x}\text{Zr}_x$ alloy rods was investigated under oxygen-enriched conditions using PIC tests. The apparatus, designed in accordance with the ASTM G124 standard [31], is schematically illustrated in Figure 2. During the test, the sample was first fixed between two electrodes using a copper wire. The chamber was then sealed and evacuated. After the desired vacuum level was achieved, oxygen was introduced and then evacuated, with this process repeated three times to ensure the removal of residual impurity gases from the chamber as thoroughly as possible. After re-evacuation, oxygen was introduced to reach the specified pressure, ensuring that the oxygen concentration inside the chamber was approximately 100%. The sample was ignited by Joule heating of the copper wire via the electrodes. The critical oxygen pressure is defined as the maximum pressure at which ignition did not occur in five consecutive tests. The ignition temperature is determined as the point of initial sharp rise in the temperature curve. Temperature profiles were measured using an infrared thermal camera (MCS640, Lumasense Technologies, Milpitas, CA, USA), with a temperature measurement accuracy of 2% of the reading and an emissivity setting of 0.8. The burning velocity is calculated based on the burning time and the length of the sample, which were recorded by a high-speed camera (PCO.DIMAX S4, PCO AG, Kelheim, Germany) with the frame rate set to 1000 frames per second, and the average value was obtained from three repeated tests.

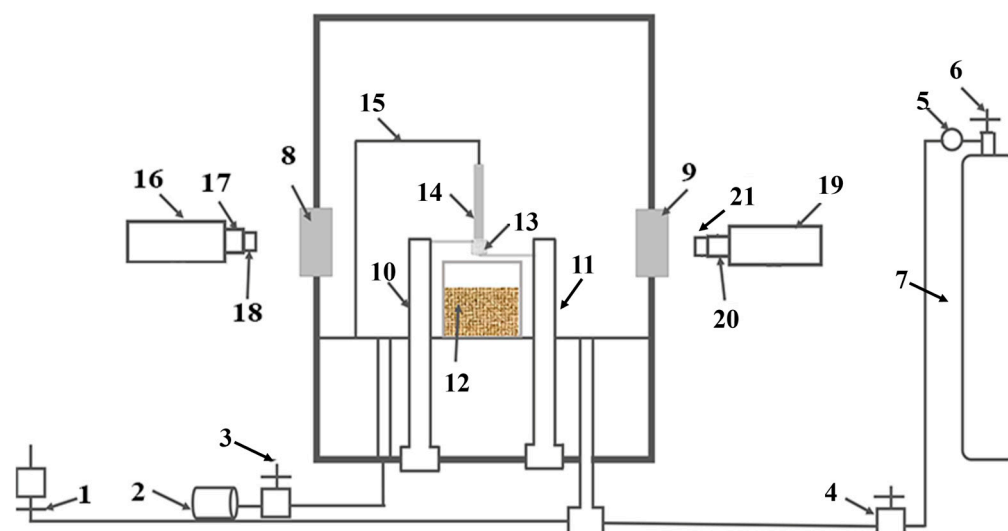


Figure 2. Schematic diagram of the promoting ignition device: (1) vent valve; (2) vacuum pump; (3) vacuum valve; (4) inlet valve; (5) gas pressure reducing valve; (6) cylinder valve; (7) oxygen cylinder; (8,9) observation window; (10,11) pressure regulator; (12) quartz crucible; (13) copper wire; (14) sample; (15) bracket; (16) high-speed camera; (17,20) focus knob; (18,21) lens; and (19) infrared thermal camera. This figure reprinted from Ref. [32].

2.3. Microstructure Characterization

The combustion process was forcibly terminated by introducing argon gas. The unburned sample was sectioned longitudinally to obtain a sample exhibiting the morphological characteristics of steady-state combustion. The cut samples were cold-embedded in epoxy resin, ground using 240–3000 grit sandpaper, polished with diamond polishing compounds with particle sizes of 2.5 μm and 0.5 μm (Hengyu Instruments Co., Ltd., Jinhua, Zhejiang, China), and then with a 0.04 μm colloidal silica suspension (Lab testing technology Co., Ltd., Shanghai, China). The polished surface of the sample was thoroughly rinsed and then immersed in a solution with a volume ratio of 1:3:6 (HF, HNO₃, and H₂O) for 3–5 s at room temperature, followed by rinsing again. The microscopic morphology and chemical composition were characterized using a laser confocal optical microscope (LSCM, VK-X200, Keyence K.K., Osaka, Japan) and a field-emission scanning electron microscope (FESEM, SUPRA 55, Zeiss GmbH, Oberkochen, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS, Aztec X-Max 80, Oxford Instruments PLC, Abingdon, UK). The SEM was operated at an accelerating voltage of 15 kV. Microstructural examination of various regions was conducted in back-scattered electron imaging (BEI) mode. The EDS detection limit is 0.1 wt%. Raw data were corrected using the XPP method (exponential model of Pouchou and Pichoir matrix correction) in the Aztec 6.1 software for quantitative elemental analysis.

3. Results

3.1. Combustion Behavior

The infrared thermal camera was employed to document the combustion processes of Ti₇₀Zr₃₀, Ti₅₀Zr₅₀, and Ti₃₀Zr₇₀ alloys under a pressure of 0.45 MPa. All three alloys underwent four distinct stages: thermal oxidation, ignition, flame propagation, and steady combustion, as illustrated in Figure 3. The copper wire, serving as the resistance-heating filament, was first heated to its melting point. The sample heated by the resistance wire underwent a gradual temperature rise until a violent deflagration occurred, characterized by a steep temperature jump, intense light emission, copious smoke, and splattering droplets. The heat released from the sample's intense combustion propelled the flame

upward, causing the sample to melt and form a molten pool. The molten pool grew and dripped under the influence of gravity. This process was repeated until the sample was completely consumed.

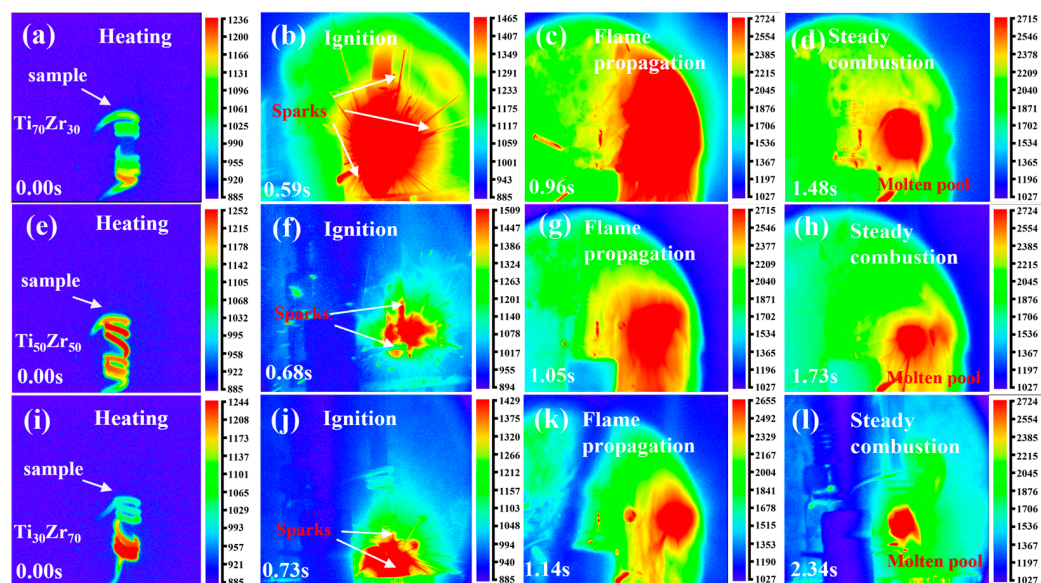


Figure 3. Time points and thermal images of $\text{Ti}_{100-x}\text{Zr}_x$ alloys during the heating, ignition, flame propagation, and steady combustion stages: (a–d) $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (e–h) $\text{Ti}_{50}\text{Zr}_{50}$ alloy, and (i–l) $\text{Ti}_{30}\text{Zr}_{70}$ alloy.

High-speed photography was employed to document the combustion process of $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ alloys under 0.45 MPa (as shown in Figure 4). All three alloys were in a solid state upon ignition, with an explosive spark emission event occurring at ignition. Subsequently, the flame rapidly propagated until a molten pool formed and began to drip periodically. Notably, $\text{Ti}_{70}\text{Zr}_{30}$ exhibited the most intense sparking behavior during ignition among the three alloys. As indicated by the time stamps in the lower-right corner of the images, the times required for molten pool formation in $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ were 0.21 s, 0.26 s, and 0.32 s, respectively, and those for achieving steady combustion were 1.36 s, 1.92 s, and 2.69 s, respectively. This indicates that increasing Zr content slows the combustion reaction rate.

Combustion tests were conducted on three different compositions of $\text{Ti}_{100-x}\text{Zr}_x$ alloys to determine the critical oxygen pressure for samples of varying diameters, as well as the ignition temperature and burning velocity under different oxygen pressures for 3.2 mm diameter samples, as shown in Figure 5. It was observed that as the sample diameter increased from 3.2 mm to 12 mm, the critical oxygen pressure of $\text{Ti}_{70}\text{Zr}_{30}$ increased from 0.11 MPa to 0.53 MPa; that of $\text{Ti}_{50}\text{Zr}_{50}$ increased from 0.07 MPa to 0.43 MPa; and that of $\text{Ti}_{30}\text{Zr}_{70}$ increased from 0.05 MPa to 0.33 MPa. Comparisons of the three alloys revealed that, at the same diameter, the critical oxygen pressure consistently followed the order: $\text{Ti}_{70}\text{Zr}_{30} > \text{Ti}_{50}\text{Zr}_{50} > \text{Ti}_{30}\text{Zr}_{70}$. When the oxygen pressure increased from 0.21 MPa to 1.01 MPa, the ignition temperature of $\text{Ti}_{70}\text{Zr}_{30}$ decreased from 1199.6 K to 990.6 K; that of $\text{Ti}_{50}\text{Zr}_{50}$ decreased from 1181.1 K to 977.2 K; and that of $\text{Ti}_{30}\text{Zr}_{70}$ decreased from 1153.3 K to 970.9 K. Among the three alloys, under the same oxygen pressure, the ignition temperature consistently followed the order: $\text{Ti}_{70}\text{Zr}_{30} > \text{Ti}_{50}\text{Zr}_{50} > \text{Ti}_{30}\text{Zr}_{70}$. When the oxygen pressure increased from 0.21 MPa to 0.81 MPa, the burning velocity of $\text{Ti}_{70}\text{Zr}_{30}$ increased from 9.76 mm/s to 18.62 mm/s; that of $\text{Ti}_{50}\text{Zr}_{50}$ increased from 9.49 mm/s to 17.94 mm/s; and that of $\text{Ti}_{30}\text{Zr}_{70}$ increased from 8.89 mm/s to 16.44 mm/s. Comparisons of the three alloys

revealed that, under the same oxygen pressure, the burning velocity consistently followed the order: $\text{Ti}_{70}\text{Zr}_{30} > \text{Ti}_{50}\text{Zr}_{50} > \text{Ti}_{30}\text{Zr}_{70}$.

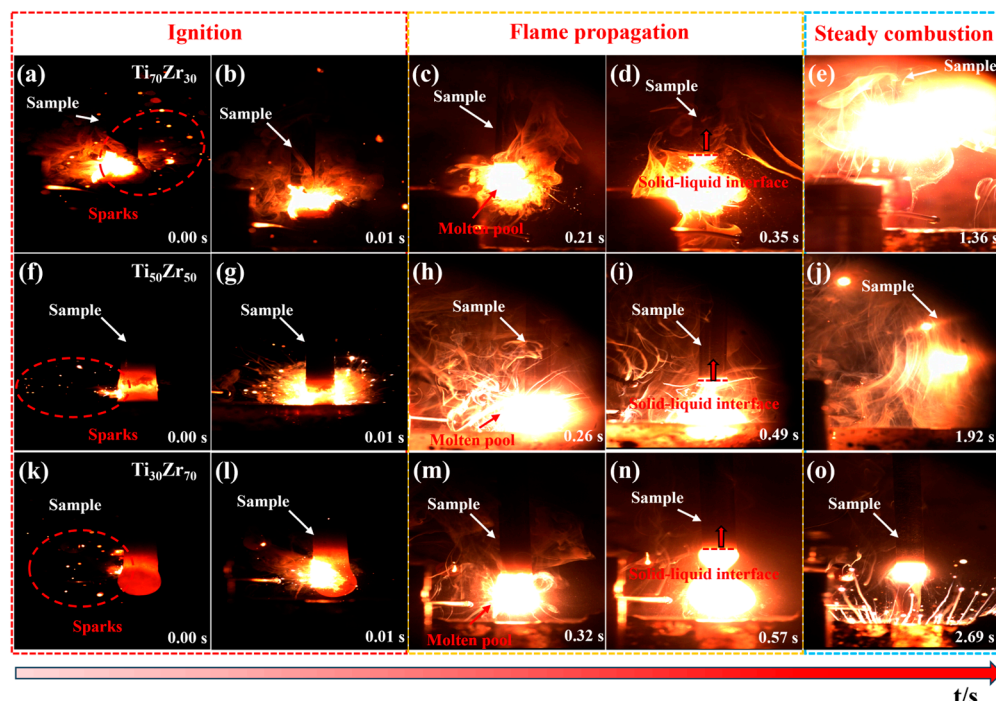


Figure 4. Time points and high-speed photography images of $\text{Ti}_{100-x}\text{Zr}_x$ alloys during the ignition, flame propagation, and steady combustion stages: (a–e) $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (f–j) $\text{Ti}_{50}\text{Zr}_{50}$ alloy, and (k–o) $\text{Ti}_{30}\text{Zr}_{70}$ alloy.

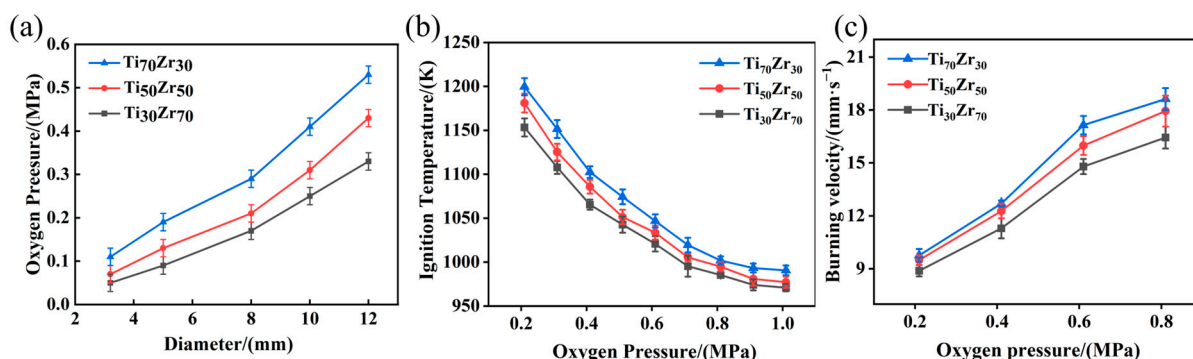


Figure 5. Combustion characteristic parameters of three $\text{Ti}_{100-x}\text{Zr}_x$ alloys: (a) diameter vs. critical oxygen pressure, (b) oxygen pressure vs. ignition temperature, and (c) oxygen pressure vs. burning velocity.

3.2. Microstructural Characteristics After Combustion

The overall morphology of the three $\text{Ti}_{100-x}\text{Zr}_x$ alloy samples post-combustion is shown in Figure 6. It can be observed that the solidified molten droplets exhibit a hemispherical shape suspended at the bottom of the samples. Based on morphological differences, the structures can be divided into four regions: the oxide zone, the melting zone, the heat-affected zone, and the matrix zone. With increasing Zr content, the area of the oxide zone exhibits a noticeable decrease, while that of the melting zone increases. A detailed comparative analysis of the microstructural morphology in each region is provided below.



Figure 6. SEM BSE micrograph showing morphology of $\text{Ti}_{100-x}\text{Zr}_x$ alloy post-combustion: (a) $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (b) $\text{Ti}_{50}\text{Zr}_{50}$ alloy, and (c) $\text{Ti}_{70}\text{Zr}_{30}$ alloy.

The microstructure of the post-combustion oxide zone in the three $\text{Ti}_{100-x}\text{Zr}_x$ alloys is shown in Figure 7. The regions marked with red dots were analyzed for composition using EDS, with the results listed in Table 2. The post-combustion oxide zone of the three $\text{Ti}_{100-x}\text{Zr}_x$ alloys primarily consists of a continuous white layer, dark phases, light phases, and white dendritic structures. EDS results indicate that the white layer (points 11, 16) is enriched in Zr and O, primarily consisting of ZrO_2 . The dark phases (points 2, 4, 5, 8, 10, 14, 15) are predominantly enriched in Ti and O, primarily consisting of TiO_2 or Ti-Zr composite oxides. The light phases are enriched in Zr (points 3, 6, 9), mainly comprising Zr oxides. The dendritic structures are enriched in Zr and O (points 1, 7, 12, 13), primarily consisting of ZrO_2 . From a microstructural perspective, as Zr content increases, the proportion of Zr-rich phases rises, significantly reducing the area of the oxide zone (from approximately 1000–1300 μm to 200–300 μm). Additionally, more continuous (Figure 7a,d,e) and denser (Figure 7c,f,i) Zr oxide layers form on the outer periphery of the oxide zone.

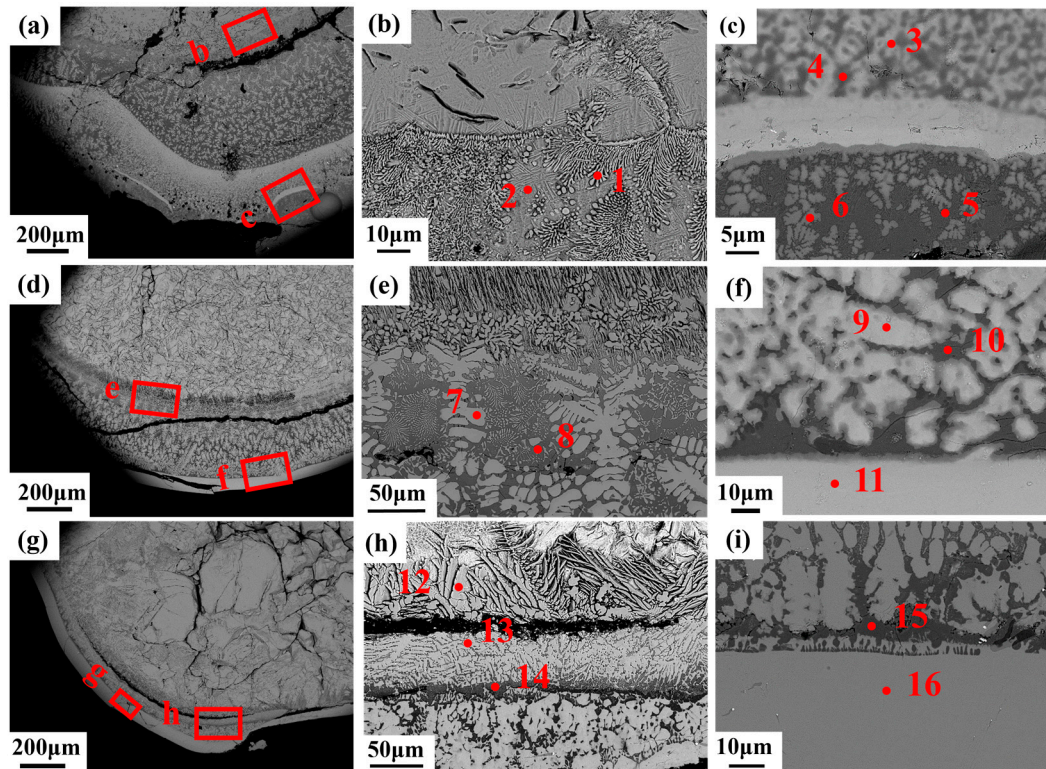
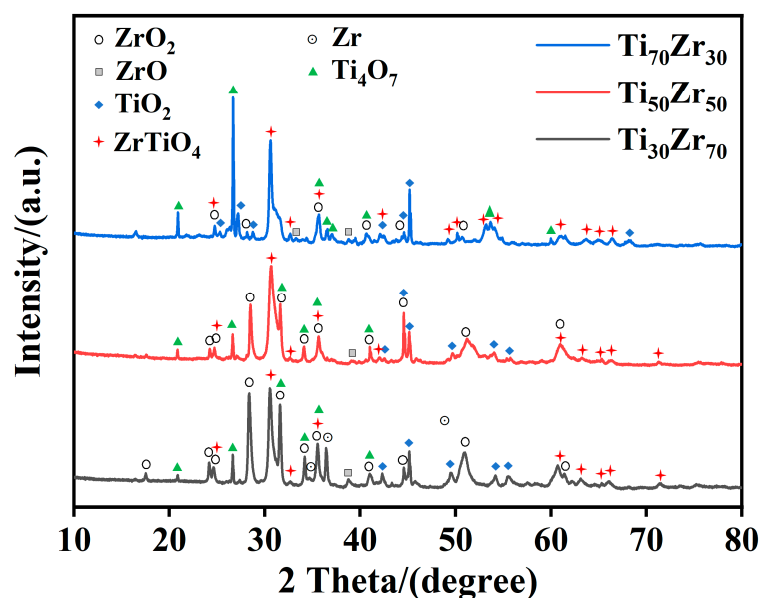


Figure 7. SEM BSE micrograph showing the morphology of $\text{Ti}_{100-x}\text{Zr}_x$ alloy oxide zones post-combustion: (a) overall morphology of $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (b,c) local magnification of $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (d) overall morphology of $\text{Ti}_{50}\text{Zr}_{50}$ alloy, (e,f) local magnification of $\text{Ti}_{50}\text{Zr}_{50}$ alloy, (g) overall morphology of $\text{Ti}_{30}\text{Zr}_{70}$ alloy, and (h,i) local magnification of $\text{Ti}_{30}\text{Zr}_{70}$ alloy.

Table 2. Chemical composition at different positions in the oxide zone of Ti₇₀Zr₃₀, Ti₅₀Zr₅₀, and Ti₃₀Zr₇₀ alloys (at%).

	Ti	Zr	O
Point 1	2.6	31.4	65.9
Point 2	54.1	15.4	30.4
Point 3	8.3	35.0	56.7
Point 4	50.3	0.0	49.7
Point 5	32.0	9.3	58.7
Point 6	30.1	15.6	54.3
Point 7	0.8	35.4	63.7
Point 8	41.6	10.7	47.5
Point 9	16.0	58.0	25.9
Point 10	42.0	4.0	54.0
Point 11	4.9	38.7	56.4
Point 12	0.0	36.6	63.3
Point 13	1.3	35.1	63.6
Point 14	45.0	11.0	43.9
Point 15	47.7	0.3	52.0
Point 16	3.6	43.1	53.4

Figure 8 shows the XRD results for the combustion product, formed by the natural dripping and solidification of molten droplets produced when the titanium alloy was burned. Its primary composition is ZrO₂, TiO₂, ZrTiO₄, and Ti₄O₇, with trace amounts of ZrO, which is consistent with the EDS results from the oxide zone. Additionally, a small quantity of unoxidized Zr was identified in the Ti₃₀Zr₇₀ alloy, whereas no unoxidized elements were detected in the Ti₇₀Zr₃₀ or Ti₅₀Zr₅₀ alloys.

**Figure 8.** The XRD results of the ignition sample products.

The microstructures of the post-combustion melting zones of the three Ti_{100-x}Zr_x alloys are shown in Figure 9, with the compositions of the melting zones listed in Table 3. The post-combustion melting zones of the three Ti_{100-x}Zr_x alloys exhibit a uniform single-phase microstructure, with visible internal cracks. Upon comparison of the compositions of the melting zones of Ti₇₀Zr₃₀, Ti₅₀Zr₅₀, and Ti₃₀Zr₇₀ alloys, the primary difference lies in the oxygen contents: the oxygen contents of Ti₇₀Zr₃₀, Ti₅₀Zr₅₀, and Ti₃₀Zr₇₀ are 32.9 at%,

26.3 at%, and 23.0 at%, respectively. The oxygen content in the melting zones decreases with increasing Zr content.

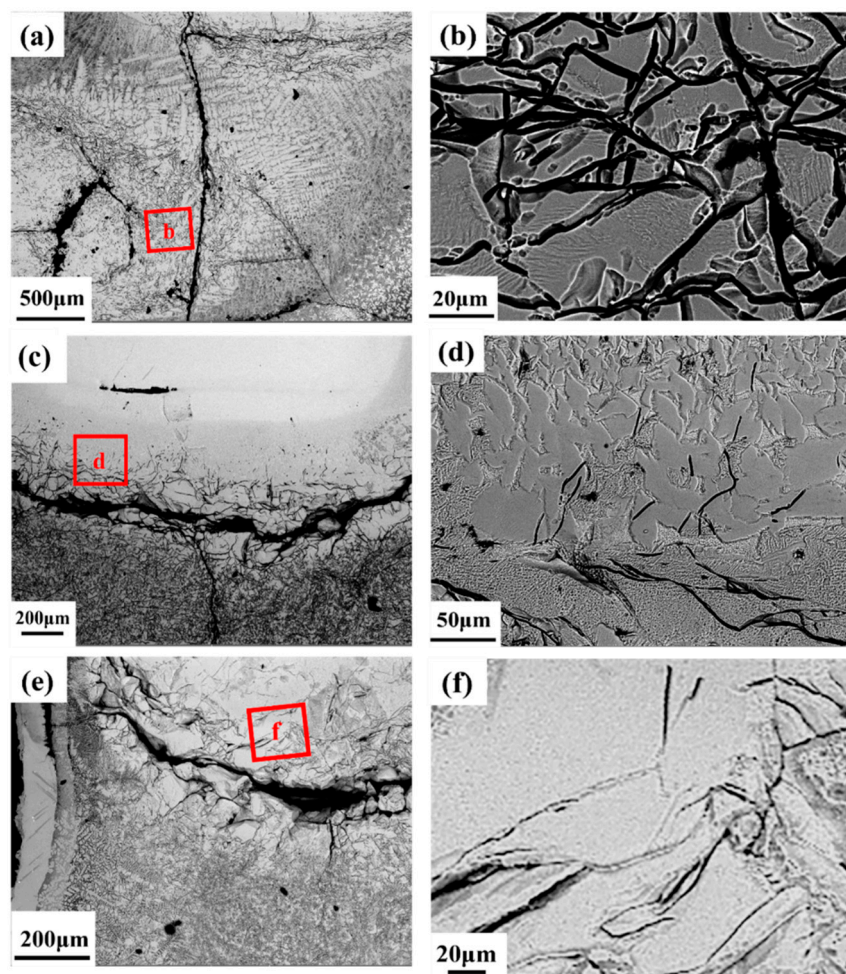


Figure 9. SEM BSE micrograph showing the morphology of $\text{Ti}_{100-x}\text{Zr}_x$ alloy melting zones post-combustion: (a) overall morphology of $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (b) local magnification of $\text{Ti}_{70}\text{Zr}_{30}$ alloy, (c) overall morphology of $\text{Ti}_{50}\text{Zr}_{50}$ alloy, (d) local magnification of $\text{Ti}_{50}\text{Zr}_{50}$ alloy, (e) overall morphology of $\text{Ti}_{30}\text{Zr}_{70}$ alloy, and (f) local magnification of $\text{Ti}_{30}\text{Zr}_{70}$ alloy.

Table 3. Chemical composition of the melting zone of $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ alloys (at%).

Melting Zone	Ti	Zr	O
$\text{Ti}_{70}\text{Zr}_{30}$	46.8	18.2	32.9
$\text{Ti}_{50}\text{Zr}_{50}$	40.4	33.3	26.3
$\text{Ti}_{30}\text{Zr}_{70}$	21.5	55.4	23.0

The microstructures of the post-combustion heat-affected zones of the three $\text{Ti}_{100-x}\text{Zr}_x$ alloys are shown in Figure 10, with EDS results presented in Table 4. The heat-affected zones of the three $\text{Ti}_{100-x}\text{Zr}_x$ alloys primarily consist of a matrix and a honeycomb-like structure, but EDS results indicate no compositional differences between the two. Upon comparison of the matrix compositions in the heat-affected zones of $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$, the primary difference lies in the oxygen contents: 22.77 at%, 15.65 at%, and 8.10 at% for $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$, respectively. As the Zr content increases, the oxygen content in the heat-affected zones decreases significantly.

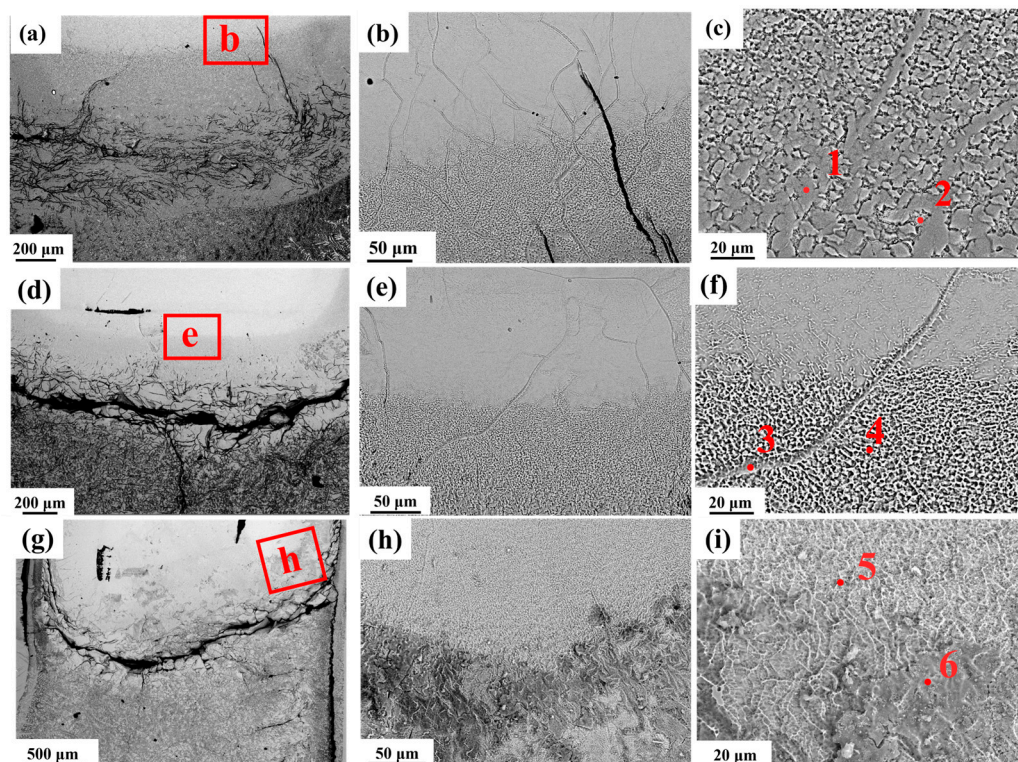


Figure 10. SEM BSE micrograph showing the morphology of $Ti_{100-x}Zr_x$ alloy heat-affected zones post-combustion: (a) overall morphology of $Ti_{70}Zr_{30}$ alloy, (b,c) local magnification of $Ti_{70}Zr_{30}$ alloy, (d) overall morphology of $Ti_{50}Zr_{50}$ alloy, (e,f) local magnification of $Ti_{50}Zr_{50}$ alloy, (g) overall morphology of $Ti_{30}Zr_{70}$ alloy, and (h,i) local magnification of $Ti_{30}Zr_{70}$ alloy.

Table 4. Chemical composition at different positions in the heat-affected zone of $Ti_{70}Zr_{30}$, $Ti_{50}Zr_{50}$, and $Ti_{30}Zr_{70}$ alloys (at%).

Heat-Affected Zone	Ti	Zr	O
Point 1	54.4	22.7	22.7
Point 2	58.7	24.2	17.0
Point 3	45.2	39.0	15.6
Point 4	43.6	37.4	18.9
Point 5	27.1	64.8	8.1
Point 6	26.8	62.8	10.4

4. Discussion

4.1. Comparison of Thermodynamic Parameters for Ignition of $Ti_{100-x}Zr_x$

Based on the metal ignition model established using the Frank-Kamenetskii theory, the expression is given by Equation (1) [33]:

$$\delta = \frac{El_m^2 k q_r}{\lambda RT^2} \frac{\left(C_i \frac{P}{P_a}\right)^n}{1 + \alpha(1 - C_i)^n P^n} \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where k ($\text{kJ}/\text{m}^2 \cdot \text{s}$) and E (kJ/mol) represent the pre-exponential factor and activation energy, respectively; R ($\text{J}/\text{mol} \cdot \text{K}$) is the universal gas constant; λ ($\text{W}/\text{m} \cdot \text{K}$) denotes the thermal conductivity of the sample material; l_m (m) is the length of the sample; q_r (MJ/kg) is the heat generation rate of the sample material during ignition; n and α (MPa^{-n}) are the reaction order and adsorption coefficient, respectively; C_i is the oxygen concentration; P

(MPa) is the critical pressure; and P_a (MPa) is the atmospheric pressure. In Equation (1), ignition occurs when $\delta > \delta_c$, where δ_c is a constant dependent solely on the sample's shape and dimensions, and may be expressed by the following empirical formula:

$$\delta_c = 0.84 \left[2 + 1 \left(\frac{c}{a} \right)^2 \right] \quad (2)$$

where a (m) denotes the sample diameter and c (m) denotes the reaction zone length. Considering oxygen-enriched conditions and assuming the temperature change rate is constant, the relationship between sample diameter and critical oxygen pressure can be derived as follows:

$$\ln \frac{P}{P_a} = \frac{1}{n} \ln(a^2 + A) + \frac{1}{n} \ln B \quad (3)$$

where $A = \frac{1.68}{0.84} c^2$, $B = \frac{Eq_r l_m^2}{\lambda RT^2} k c^2 \exp\left(-\frac{E}{RT}\right)$, both of which are generally regarded as constants. The relationship between oxygen pressure and ignition temperature can be further expressed as follows:

$$\ln \frac{P}{P_a} = \frac{2}{n} \ln T + \frac{Y}{T} + Z \quad (4)$$

where $Y = \frac{E}{RT}$, and $Z = \frac{1}{n} \ln\left(\frac{\delta_c \lambda R}{El_m^2 k q_r}\right)$ can be considered constants. According to Equations (2) and (4), for a given material, as the size increases, the oxygen pressure and ignition temperature gradually increase, which is consistent with the trend in Figure 5a. In addition, when the sample size is constant, there is a negative correlation between pressure and temperature; that is, as the environmental pressure increases, the ignition temperature gradually decreases, consistent with the trend in Figure 5b.

Based on the relationship between sample size and critical pressure (Equation (3)), the combustion characteristic data for the three alloys were fitted using the least squares method, and the results are shown in Figure 11a. Each reaction order was fitted using five data points. The results indicate that, under oxygen-enriched conditions, the behavior of all three $\text{Ti}_{100-x}\text{Zr}_x$ alloys is intermediate between first- and second-order reactions. The values are 1.58, 1.32, and 1.23 for the $\text{Ti}_{70}\text{Zr}_{30}$ alloy, $\text{Ti}_{50}\text{Zr}_{50}$ alloy, and $\text{Ti}_{30}\text{Zr}_{70}$ alloy, respectively. According to Equation (1), a higher n value under oxygen-enriched conditions should enhance ignition resistance. Based on the relationship between oxygen pressure and ignition temperature (Equation (4)), the data were fitted using the least squares method, and the results are shown in Figure 10b. Each activation energy was fitted using nine data points. The activation energies for $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ alloys were 108.37 kJ/mol, 96.55 kJ/mol, and 94.26 kJ/mol, respectively. The results indicate that the ignition activation energy decreases with increasing Zr content.

According to thermodynamic handbooks, the enthalpy of combustion of Ti to TiO_2 is approximately 938.72 kJ/mol, while that for Zr to ZrO_2 is about 1097.46 kJ/mol [34]. Previous studies indicate that the formation enthalpies of $\text{Ti}_{100-x}\text{Zr}_x$ alloys with varying compositions exhibit minimal variation and differ by orders of magnitude from those of TiO_2 and ZrO_2 . Therefore, assuming linear mixing of Ti and Zr, an approximate calculation is performed using the weighted average of the enthalpies of each component [35,36]. The heat release for $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ alloys is approximately 986.34 kJ/mol, 1018.09 kJ/mol, and 1049.84 kJ/mol, respectively, as listed in Table 5. With increasing Zr content, the heat release of the alloys gradually increases. According to Equation (1), both the critical pressure and ignition temperature decrease when the heat release q_r° of the alloys increases and the ignition activation energy decreases. This indicates that, thermodynamically, the addition of Zr reduces the combustion resistance of $\text{Ti}_{100-x}\text{Zr}_x$ alloys.

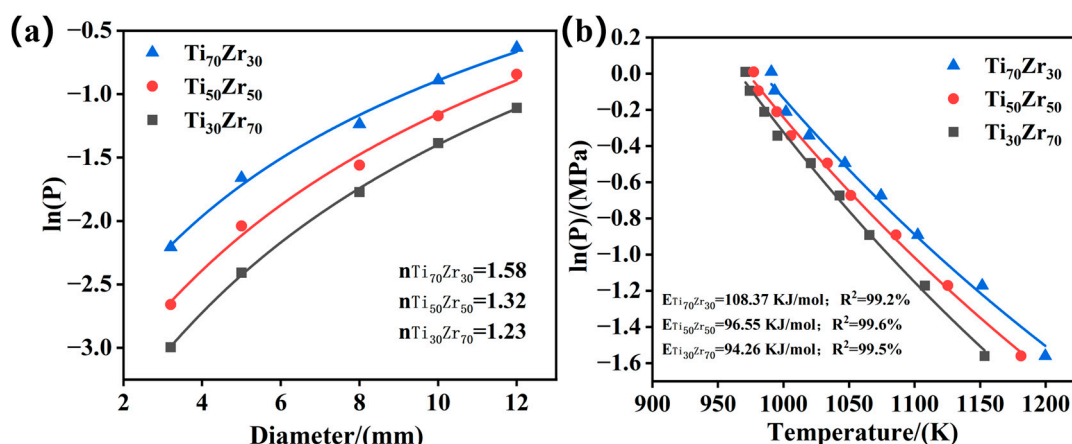


Figure 11. Data fitting curves for the three Ti_{100-x}Zr_x alloy: (a) reaction order, (b) ignition activation energy.

Table 5. Thermodynamic parameters of Ti₇₀Zr₃₀, Ti₅₀Zr₅₀, and Ti₃₀Zr₇₀ alloys.

	Heat Release q_r° (kJ/mol)	Reaction Order n	Activation Energy E (kJ/mol)
Ti ₃₀ Zr ₇₀	1049.84	1.23	94.26
Ti ₅₀ Zr ₅₀	1018.09	1.32	96.55
Ti ₇₀ Zr ₃₀	986.34	1.58	108.37

4.2. Flame Propagation Mechanism of Ti_{100-x}Zr_x Alloy

With the increase in Zr content, the burning velocity of Ti_{100-x}Zr_x alloys gradually decreases. According to existing research, the migration rate of the solid–liquid interface can be described by the following equation [22]:

$$v = \frac{\bar{q}}{\{\rho[c(T_m - T_0) + \lambda_m]\}} \cdot \frac{\bar{A}}{S} \quad (5)$$

In the equation, $\bar{q}$ (W/m²) denotes the heat flux out of the molten pool, $\bar{A}$ (m²) represents the solid–liquid interfacial area related to the grain size, ρ (kg/m³) and c (J/kg·K) are the density and specific heat of the molten pool, respectively, T_0 (K) is the initial temperature of the sample, S (m²) is the cross-sectional area of the sample, which depends solely on its diameter, and T_m (K) is the melting point at the solid–liquid interface.

The heat required for solid–liquid interface melting primarily originates from the exothermic reaction within the molten pool. Characterization results indicate that increasing Zr content from 30 at% to 70 at% is accompanied by the following phenomena: a significant decrease in oxygen content within the melting zone/heat-affected zone; a substantial reduction in the area of the oxide zone; formation of continuous and densified Zr oxide layers on the outer periphery of the oxide zone; and a marked increase in the proportion of Zr-rich phases. This indicates that oxygen diffusion from the external environment toward the heat-affected zone is impeded, suppressing oxidation reactions within the oxide zone. Consequently, the exothermic oxidation during combustion is reduced, thereby lowering the burning velocity. Furthermore, the reduced oxygen content in the melting zone alters the peritectic reaction mechanism within that zone. According to the Ti–O phase diagram in Figure 12a [37], the oxygen content in the melting zone of Ti₇₀Zr₃₀ is 32.9 at%. At this oxygen content, the melting zone undergoes two peritectic reactions: $L + \alpha\text{-Ti} \rightarrow \beta\text{-Ti}$ and $L + \alpha\text{-Ti} \rightarrow \text{TiO}$, leading to increased heat release. In contrast, the oxygen contents in the melting zones of the Ti₅₀Zr₅₀ and Ti₃₀Zr₇₀ alloys are 26.3 at% and 23.0 at%, respectively, at which only one peritectic reaction occurs ($L + \alpha\text{-Ti} \rightarrow \beta\text{-Ti}$ or

$L + \alpha\text{-Zr} \rightarrow \beta\text{-Zr}$). Therefore, the $\text{Ti}_{70}\text{Zr}_{30}$ alloy releases more heat, promoting combustion propagation. Additionally, further analysis of phase transitions in each region shows that when the oxygen content is approximately 20–30 at%, the melting zones of $\text{Ti}_{50}\text{Zr}_{50}$ and $\text{Ti}_{30}\text{Zr}_{70}$ consist solely of α and β phases. Subsequent cooling induces the $\beta \rightarrow \alpha$ transformation, resulting in a single α phase across the melting zone of $\text{Ti}_{100-x}\text{Zr}_x$ alloys. As the oxygen content increases to 50–60 at%, α phase, TiO , and ZrO_2 are formed in $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$, which matches the phase assemblage observed in the oxide zones of $\text{Ti}_{100-x}\text{Zr}_x$ alloys. The distribution morphology is primarily influenced by zirconium content, as Zr reacts preferentially over Ti [38]. Moreover, ZrO_2 possesses a higher melting point and undergoes earlier nucleation. Consequently, a small amount of Ti becomes enriched in interdendritic regions, forming TiO , consistent with the morphology shown in Figure 6. Finally, when the oxygen content approaches approximately 66 at%, as shown in Figure 12c, only $\text{Ti}_{70}\text{Zr}_{30}$ forms TiO_2 , whereas $\text{Ti}_{50}\text{Zr}_{50}$ and $\text{Ti}_{30}\text{Zr}_{70}$ form ZrO_2 . This is consistent with the EDS results.

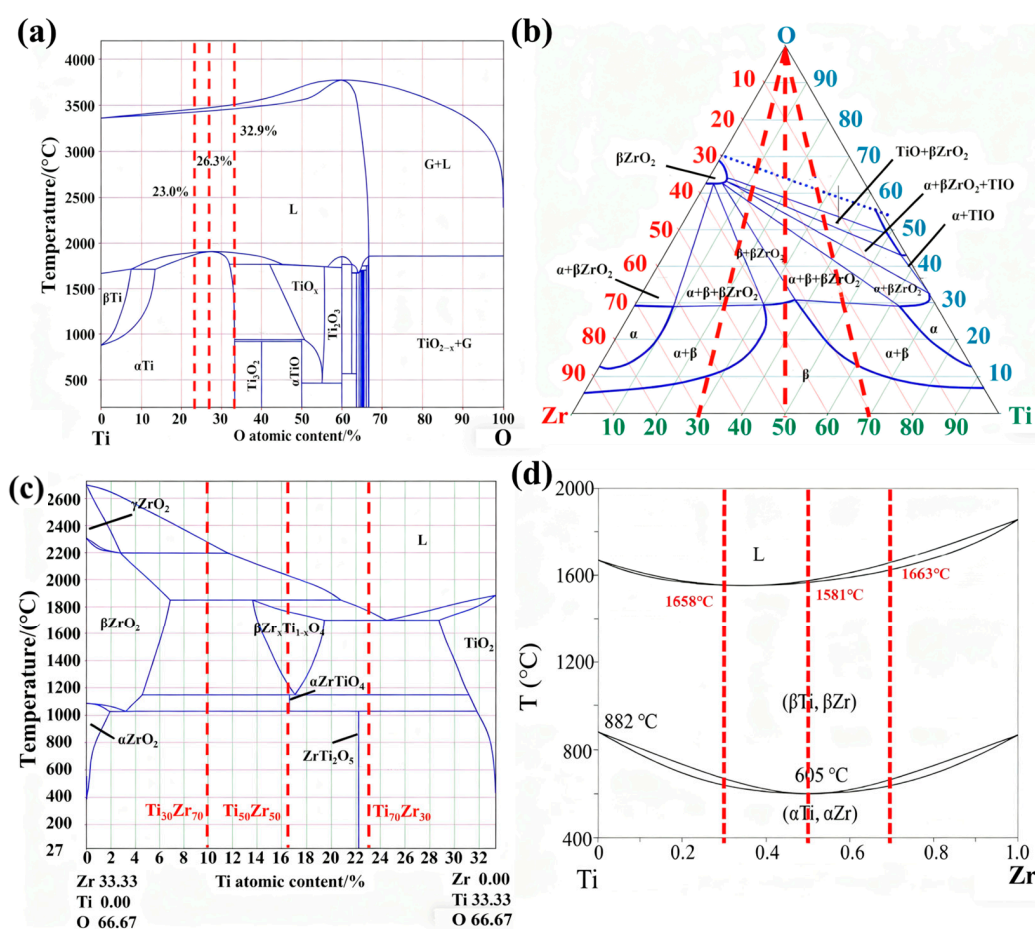


Figure 12. Phase diagram: (a) Ti-O binary phase diagram adapted from Ref. [37], (b) partial isothermal section of Ti-Zr-O phase diagram at 1450 °C, (c) phase diagram for the quasibinary ZrO_2 - TiO_2 system, and (d) Ti-Zr binary phase diagram reprinted with permission from ref. [39]. Copyright 2025 Copyright Elsevier.

The melting point (T_m) at the solid–liquid interface also significantly affects the combustion rate, and T_m is influenced by the elemental composition of the solid–liquid interface. The atomic ratios of Ti to Zr at the solid–liquid interface of $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ remain consistent with their respective original proportions. Thus, the melting points of the three alloys are used as references for T_m during combustion. According to Figure 12d [39], the melting points of $\text{Ti}_{70}\text{Zr}_{30}$, $\text{Ti}_{50}\text{Zr}_{50}$, and $\text{Ti}_{30}\text{Zr}_{70}$ are approximately

1558 °C, 1581 °C, and 1663 °C, respectively. Hence, the melting points gradually increase with increasing Zr content. According to Equation (5), the burning velocities follow the order: $v_{Ti_{70}Zr_{30}} > v_{Ti_{50}Zr_{50}} > v_{Ti_{30}Zr_{70}}$, which is consistent with experimental results.

In summary, increasing Zr content forms a dense Zr oxide layer that impedes oxygen diffusion. This reduces heat release by suppressing oxidation reactions in the oxide zone and altering peritectic reactions in the melting zone. Simultaneously, higher Zr content elevates the alloy's melting point. The combined effects of reduced reaction heat release and increased melting point lead to a decrease in burning velocity. Research demonstrates that the addition of Zr increases the ignition sensitivity of titanium alloys yet suppresses the combustion process. Thus, for Zr-containing burn-resistant titanium alloys, it is necessary to evaluate whether their ignition resistance meets service requirements or whether other low-heat-release elements should be added to reduce ignition sensitivity. It should be noted that the investigation was performed only under oxygen-enriched conditions on $Ti_{100-x}Zr_x$ alloy samples by PIC tests. As a result, the synergistic effects between Zr and other elements remain unclear, and the influence of Zr on the combustion behavior of titanium alloys under conditions such as large components, complex flow fields, and friction/impact cannot be determined. Hence, future work can further investigate the synergy between Zr and common alloying elements (e.g., Cr, V) in titanium alloys during combustion under complex flow fields and friction/impact conditions.

5. Conclusions

This study investigated the influence of Zr content on the combustion behavior and mechanisms of $Ti_{100-x}Zr_x$ alloys. Combustion characteristic parameters for $Ti_{70}Zr_{30}$, $Ti_{50}Zr_{50}$, and $Ti_{30}Zr_{70}$ were obtained through ignition promotion tests. The combustion mechanisms were analyzed based on thermodynamic and kinetic models. The specific results are as follows:

- (1) An increase in zirconium content leads to decreases in critical oxygen pressure, ignition temperature, and burning velocity under identical conditions.
- (2) The thermodynamic parameters of $Ti_{100-x}Zr_x$ alloys were obtained based on the ignition thermodynamic model. Increased Zr content lowers the activation energy (from 108.37 kJ/mol to 94.26 kJ/mol) for ignition and increases the heat release (from 986.34 kJ/mol to 1049.84 kJ/mol), thereby decreasing the ignition conditions.
- (3) Increasing Zr promotes the formation of a dense Zr oxide layer in the oxide zone, impeding oxygen diffusion into the matrix. This reduces the oxidation zone area and lowers oxygen content in the melting zone (from 32.9 at% to 23.0 at%). The decreased oxygen content inhibits reactions in the oxide zone, alters the peritectic reaction mechanism in the melting zone, reduces heat release, and ultimately leads to a lower burning velocity.

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