



Article

The Influence of Mixing Modes on Structure Formation and Mechanical Properties of Ti-Al-Fe-O-C Powder Materials During Vacuum Sintering

Elena N. Korosteleva, Kirill O. Akimov and Andrey I. Dmitriev *

Laboratory of Physics of Powder Materials Consolidation, Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademicheskii Av., Tomsk 634055, Russia; elenak@ispms.tsc.ru (E.N.K.); akimov_ko@ispms.ru (K.O.A.)

* Correspondence: dmitr@ispms.ru

Abstract

One of the possible ways to increase the functional properties of titanium-based composites is the use of additional components in the form of solid inclusions of oxides, carbides, etc. The key task in this case is to achieve a uniform distribution of such inclusions in the structure of the material. This study demonstrates that this problem can be more effectively solved at the stage of preparing the powder mixture from which a titanium matrix composite is subsequently obtained. The paper presents the results of a study of the structure and mechanical properties of sintered powder materials of the Ti-Al-Fe-O-C system using two procedures for mixing the initial components. In the first case, traditional mixing of titanium, aluminum, soot and iron oxide Fe_2O_3 powders was used, and in the second case, a two-stage procedure was used with preliminary mechanical activation of the powder composition $\text{Al} + \text{Fe}_2\text{O}_3$ and the subsequent addition of titanium and soot powders to the product of this treatment. Analysis of the structure formation and mechanical properties of sintered compacts from the studied powder mixtures showed the advantage of the two-stage option in terms of the formation of a denser structure in the samples with minimal residual porosity and higher values of compressive strength.

Keywords: metal matrix composites; mechanical processing; synthesis; vacuum sintering; phase formation; structure; mechanical properties

1. Introduction

Due to the optimal combination of relatively low density, high strength and corrosion resistance, titanium-based composites are widely used across a broad range of industries, including mechanical engineering, transport, aerospace engineering, energy, chemical and biotechnology, including medical materials science [1–8]. However, despite the high-performance characteristics of composites based on titanium and its alloys, their relatively low hardness and wear resistance are noted, which can significantly reduce the service life of components, parts and assemblies. One of the most effective approaches to solving such problems is the creation of titanium-based metal matrix composites (TMCs) with ceramic inclusions formed by both *ex situ* and *in situ* methods. In particular, ceramic inclusions based on TiB, TiC, TiN and Al_2O_3 significantly increase the elastic modulus, hardness and wear resistance, while maintaining a sufficient level of ductility and tough-

Academic Editor: Steven Y. Liang

Received: 8 June 2026

Revised: 10 July 2026

Accepted: 11 July 2026

Published: 13 July 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\) license](https://creativecommons.org/licenses/by/4.0/).

ness [4,5,7,9–16]. Among such components, oxide compounds are of particular interest, capable of preventing metal creep at high temperatures, thus expanding the operating range of parts, which is important for aircraft engines [7,10–12,14,17]. The presence of solid oxide inclusions, for example, Al_2O_3 , contributes to the strengthening of the fine-grained structure while improving corrosion resistance at elevated temperatures [7,10]. Corundum has high hardness (19–22 GPa Vickers), thermochemical stability and good compatibility with the titanium matrix. It is known that the introduction of dispersed Al_2O_3 particles in an amount of 5–15 vol.% provides an increase in tensile strength by 20–40% compared to unalloyed titanium with a moderate decrease in ductility [10,18]. The addition of Al_2O_3 to multicomponent titanium-based alloys further increases the resistance to high-temperature oxidation [7]. From the point of view of functional properties, Al_2O_3 reinforcement in combination with Ti-Al intermetallic compounds significantly improves the corrosion resistance and tribocorrosion behavior of TMCs in physiological environments, which is of fundamental importance for biomedical applications [19]. On the other hand, it should be taken into account that, along with corundum, in the Ti-Al-O system, with insufficient reduction of TiO_2 , titanium suboxides— Ti_2O and TiO —can form. These phases arise under conditions of reducing agent deficiency or specific thermal conditions and change the local stress distribution at the matrix–inclusion interface, affecting fracture toughness [18,20].

Despite the advantages of titanium matrix composites with oxide inclusions, in contrast to titanium carbides, there is a problem with the use of oxide powders in mixtures with other components, which is caused by wettability and adhesion between the oxide particle and the titanium matrix against the background of significant heterogeneity of particle distribution [11].

To overcome these difficulties, they resort to the use of additional technologies for producing metal-matrix composites with an oxide phase, which are based on combined or multi-stage operations of synthesis and molding of the final material [14,18,21–24]. In this regard, an alternative direction for producing titanium matrix composites with synthesized in situ oxide phases is dynamically developing [13–15,22]. The fundamentally important component of the multicomponent systems under study is iron oxide (Fe_2O_3). In Ti-Al- Fe_2O_3 -C mixtures, hematite enters into a thermite-like reaction with aluminum ($2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$, $\Delta H = -851$ kJ/mol), as a result of which dispersed Al_2O_3 is formed and metallic iron is reduced. In the TiO_2 -Al-C-Fe systems, three-phase TiC- Al_2O_3 -Fe₃Al composites were obtained by the SHS method (self-propagating high-temperature synthesis); it has been shown that Fe additives fundamentally change the combustion rate, temperature and phase composition of the synthesis products [14]. A similar concept was implemented in the synthesis of Fe- Al_2O_3 nanocomposites in the wave combustion mode with uniformly distributed oxide particles, demonstrating high chemical stability [25]. The studies presented in [14,15,22,23,26–28] show that it is important to study the mutual influence of oxygen and carbon in the formation of the structure of metal matrix composites. The presence of aluminum further complicates the reaction–diffusion process during heating, as a result of which predicting the final structural-phase state becomes more difficult [25,29–31]. Powders of inexpensive components of hematite Fe_2O_3 , ilmenite FeTiO_3 and carbon in the form of soot are considered as interacting components [23,26,27,29]. For example, the authors of studies [22,29] consider the use of Fe_2O_3 oxides (or ilmenite FeTiO_3) in reactions with aluminum and carbon for the synthesis of composites containing intermetallic compounds and ceramic phases TiC and Al_2O_3 .

Notwithstanding the large number of studies of composites based on the combination of Ti-Al-Fe-O-C elements, many questions of the formation of the structure and the formation of functional properties, however, remain open. Obviously, if we consider compositions of titanium, aluminum, iron, carbon powders with their compounds TiO_2 or

Fe_2O_3 and TiC under vacuum heating conditions, the problem arises of assessing possible reactions not only quantitatively, but even qualitatively. In this case, reference to traditional phase diagrams does not work, and in fact, experimentally, after reaction sintering, an unpredictable group of phases and their quantitative combination can be observed in the composite of a multicomponent Ti-Al-Fe-O-C system. The mechanisms of such complex reactions include the formation of intermediate phases (for example, iron aluminides Fe_2Al_5) and their subsequent interaction [28,29]. Despite existing studies of vacuum sintering of Ti-Al-TiO₂/ Fe_2O_3 -C systems [14,22], at the moment it is important to study the mechanisms of structure formation in such systems and their influence on various properties in order to understand the fundamental processes of phase formation and the formation of the microstructure that determines these properties. The new knowledge obtained is the key to the development of new titanium-based composite materials with a given set of properties. These points are especially important in the development of modern technologies, including those associated with powder metallurgy, additive manufacturing, etc., [14,15,22–24,29]. In the Ti-Al- Fe_2O_3 -C system, the key problem with traditional mixing is the almost simultaneous activation of several highly exothermic processes, namely the melting of aluminum followed by interaction with titanium and iron oxide, as well as aluminothermic reduction. The energy released in this case leads to local temperature surges, promoting the formation of an excess amount of liquid phase (based on Al and Ti-Fe eutectic), which is a difficult-to-control process and ultimately affects the nature of the formed composite structure. Therefore, the task arises of leveling out this uncontrolled energy input at a certain stage in order to form a more controlled structure of the titanium matrix composite at the next stage.

Despite significant progress in TMC research, the in situ synthesis of Ti-Al₂O₃-TiO_x composites from a multicomponent Ti-Al- Fe_2O_3 -C powder system by vacuum sintering remains poorly understood. The effect of small additions of iron oxides on the microstructure and mechanical properties of pure titanium was revealed only for simplified Ti-Fe-O systems [17]. The role of preliminary mechanical activation (MA) of the aluminothermic mixture in order to suppress undesirable exothermic reactions, the nature of the formed suboxide phases Ti₂O and TiO and the mechanism of their influence on the matrix at a given composition and sintering mode are still not established [20].

In connection with the above, a detailed study of the influence of certain technological parameters on the final characteristics of composites based on multicomponent Ti-Al-Fe-O-C compositions is relevant, which determines the purpose of this work. In particular, when analyzing the formative structure of a powder material with interacting components, a special role is given to the mutual distribution of particles in the powder mixture, their chemical composition and structural state, depending on the pretreatment. Further research in this area, especially with the use of vacuum sintering for the consolidation of reactive powder mixtures such as Ti-Al- Fe_2O_3 -C, is necessary to fully unlock the potential of these materials, since it is currently difficult to predict the final structure of the composite if several reaction–diffusion processes are realized during heating.

2. Material and Experimental Procedure

The system Ti-Fe-Al-O-C, where oxygen is present in the oxide Fe_2O_3 , was considered as an object of study. Mixtures of titanium powders (grade TPP-8, purity ≥ 96.3 wt.%, CAS: 7440-32-6, particle size < 125 – 160 μm , AVISMA, Berezniki, Russia), aluminum (grade PA-4, purity ≥ 98.0 wt.%, CAS: 7429-90-5, particle size < 100 μm , RUSAL Shelekhov, Russia), carbon black (grade P-803, purity ≥ 99.0 wt.%, CAS: 1333-86-4, particle size < 3 μm , Ivanovo Carbon Black, Ivanovo, Russia) and iron oxide (Fe_2O_3 , analytical grade, purity ≥ 98.7 wt.%, CAS: 1309-37-1, particle size < 120 μm , LenReaktiv, Saint Petersburg, Russia) were prepared. The ratio of the components was chosen in such a way as to facilitate the

formation of the specified calculated phases according to the possible reactions occurring in the studied systems of elements, including accompanying metallothermic reactions. Since powder mixtures contain oxides, when calculating the compositions, we took into account the molar ratios of the components that ensure the reduction reaction: $\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + \text{Al}_2\text{O}_3$. As is known, such reactions are often used to obtain a wide range of composites based on Fe-Al₂O₃ [24,25,32]. To fully implement the reduction reaction, the following quantitative ratio of reagents (mol.) is required: $2/3\text{Fe}_2\text{O}_3 + 4/3\text{Al} = 2/3\text{Al}_2\text{O}_3 + 4/3\text{Fe}$. The total amount of these reagents in the total mass of the powder mixture corresponded to the possibility of forming an oxide phase of no more than 10 vol.%. Another condition for calculating the components was to focus on the ratio of titanium and iron close to their eutectic ratio Ti:Fe = 68:32 (wt.%) according to the equilibrium phase diagram of the Ti-Fe system. Based on preliminary calculations, the ratio of components (wt.%) in the mixtures under study corresponds to the values presented in Table 1.

Table 1. Composition of powder mixtures.

Target phase compositions expected after sintering	Powder components, weight. %			
	Ti	Al	Fe ₂ O ₃	C
(Ti-Fe) + Al ₂ O ₃ + TiC	78.2	5.3	15.7	0.8
	Powder components, vol. %			
	76.6	8.7	13.2	1.5

Powder mixing was carried out via two different routes. In the first route (hereinafter referred to as mixture 1), the components were directly blended using a low-energy mode in a laboratory drum tumble mixer (axial mixer) equipped with a 1 L stainless steel drum rotating at 30 RPM for 4 h. Steel balls up to 10 mm in diameter were added strictly as blending aids to ensure uniform mixing and prevent agglomeration, without causing any grinding or particle deformation. Since no mechanical activation or fresh surface generation occurred, this low-energy blending was performed in air at room temperature. In the second option, the mixing mode was divided into two stages: (a) preliminary mechanical activation of iron oxide with aluminum, (b) subsequent addition of titanium and carbon black to this mixture and mixing in an axial mixer (hereinafter referred to as mixture 2). For mechanical activation, a high-speed planetary mill “Activator-2S” (NTK Activator, Novosibirsk, Russia) was used. The activation of the aluminum and iron oxide mixture was performed in two sealed stainless steel vials (250 mL volume) using steel balls (6 mm diameter) with a ball-to-powder weight ratio of 20:1 under an argon atmosphere. For the high-energy mechanical activation step, a protective argon atmosphere was mandatory. The powder charge was loaded into sealed steel vials inside an argon-filled glove box. The argon gas pressure inside the vials was monitored throughout milling. After completion, the vials were unloaded and the activated mixture was stored and handled exclusively inside the glove box to prevent oxidation prior to compaction. The rotation speed of the basis plate was 700 RPM, and the milling duration was 20 min (divided into 10 min cycles with cooling breaks). This regime ensures complete solid-state aluminothermic reduction of hematite by aluminum, while the steel milling tools avoid contamination with foreign chemical species since iron is a target alloying element in the composite. No process control agent was used during mechanical activation. The purpose of high-energy milling was the in situ solid-state aluminothermic reaction between Al and Fe₂O₃, not particle size reduction; therefore, preventing cold welding was not a concern in this experiment.

The distribution of powder particles in the mixture depending on the mixing option is shown schematically in Figure 1. Samples from the resulting powder mixtures were compacted by uniaxial pressing in a hardened cylindrical steel die (10 mm diameter) with a double-action floating punch configuration (upper and lower punches) using a hydrau-

lic press MS-500 (Tehmash, Neftekamsk, Russia). A compaction pressure of 440 MPa was applied for all specimens, yielding cylindrical green compacts with a height of 10–15 mm and a residual porosity of 23–37%. The initial (green) porosity φ of the compacts was calculated according to the following formula:

$$\varphi = \left(1 - \frac{\rho_{\text{sample}}}{\rho_{\text{theor}}}\right) \times 100\%, \quad (1)$$

where ρ_{sample} is the bulk density of the green compact (g/cm^3), determined as:

$$\rho_{\text{sample}} = \frac{M}{V}, \quad (2)$$

where M is the mass of the compact measured by analytical balance (g), and V is the geometric volume calculated from the dimensions measured by digital micrometer (cm^3). The theoretical density ρ_{theor} was determined by the additive rule of mixtures:

$$\rho_{\text{theor}} = \frac{1}{\frac{a_1}{\rho_1} + \frac{a_2}{\rho_2} + \frac{a_3}{\rho_3} + \dots}, \quad (3)$$

where $a_1, a_2, a_3, \dots$ are the weight fractions of the components in the mixture, and $\rho_1, \rho_2, \rho_3, \dots$ are the theoretical densities of the respective components (g/cm^3).

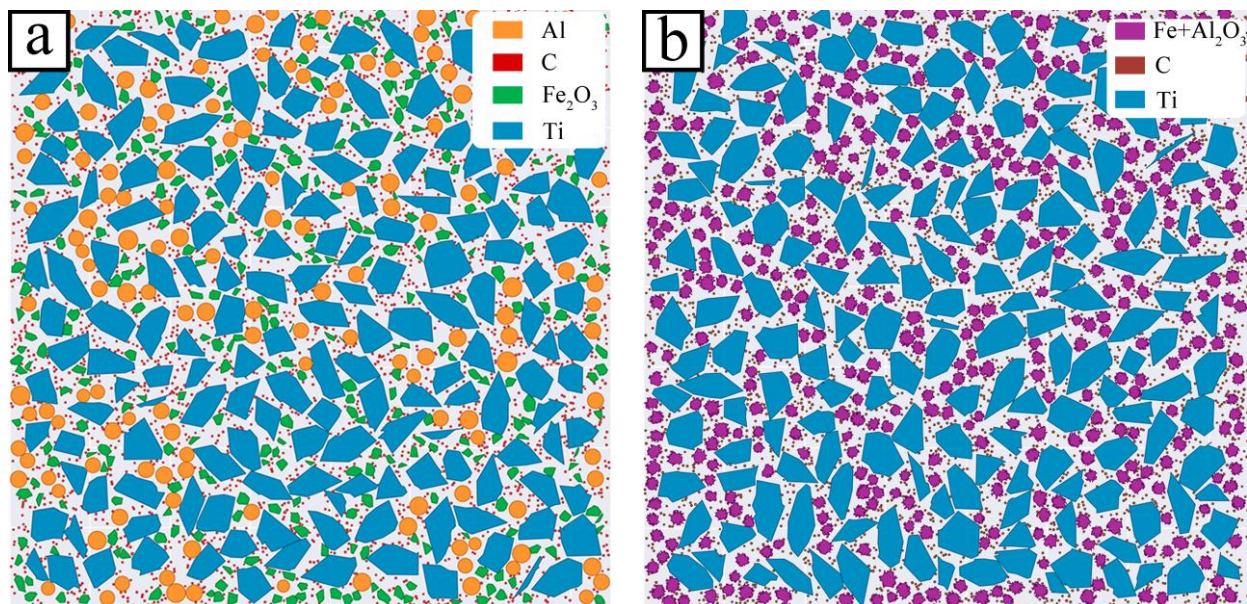


Figure 1. Schemes of possible configurations of powder components for different mixing options: (a) traditional mixing of all powder components (Ti + Al + Fe₂O₃ + C); (b) two-stage mixing with preliminary MA of the powder mixture (Al + Fe₂O₃) → (Fe + Al₂O₃) and subsequent addition of Ti and C.

For each mixing condition, batches of 10–15 specimens were fabricated. Part of the specimens was used to optimize the compaction pressure and sintering parameters. From each optimized batch, 8 specimens per condition were selected for structural characterization (XRD, SEM/EDX) and mechanical testing (uniaxial compression) to ensure the statistical validity of the reported results. Higher compaction pressures were not used, as the significant oxide content in the mixtures would cause damage to the steel tooling.

The samples were sintered in a vacuum furnace SNVE-1.3.1/16 (MEEP, Moscow, Russia) under controlled heating conditions using automated thermocouple monitoring at a rate of 3–5°/min to 1200 °C, followed by holding for 60 min. The nominal heating rate was programmed at 5 °C/min; due to inherent voltage fluctuations and the thermal inertia of the vacuum chamber, the actual heating rate ranged between 3 and 5 °C/min throughout the sintering cycle. The density of the sintered specimens was determined by the Archi-

medes method. Specimens were pre-coated with Zapon lacquer (NOVBYTKHIM, Saint Petersburg, Russia) to seal open surface pores.

The schematic diagram in Figure 1 represents a model of the spatial distribution of the powder components. It was constructed based on the volume fractions, particle morphology (spherical Ti and Al particles; angular Fe₂O₃ and carbon particles), and conditional maximum packing arrangement observed experimentally by SEM. The model illustrates the possible inter-particle contact zones between the components, which serve as the primary pathways for reaction–diffusion processes during subsequent sintering and govern the phase composition of the resulting composites.

X-ray phase analysis was carried out using a DRON-8 diffractometer ((Innovation Center Burevestnik, Saint Petersburg, Russia) (CuK α , λ = 1.54186 Å) in the 2 θ angle range from 30 to 100°. Identification of phases and selection of initial structural models was carried out using the open crystallographic database Materials Project. The reference IDs used are: α -Ti: mp-46; Ti₃Al: mp-1823; TiAl: mp-1953; Al₂O₃: mp-1143; TiC: mp-631; TiO: mp-1071163; Ti₂O₃: mp-458; TiFe: mp-305; TiFe₂: mp-2454; Ti₂AlFe: mp-999069; TiAlFe₂: mp-31187. Processing of diffraction patterns was carried out in Origin Pro 2018 (SR1) software. The background line was subtracted using the asymmetric weighted least squares method. Due to the multiphase nature of the synthesis products and the strong mutual overlap of diffraction reflections, the profile was processed by the method of deconvolution of overlapping peaks. The approximation and separation of complex overlapping peaks into individual components was performed using the pseudo-Voigt profile function. Quantitative phase analysis (QPA) was carried out by the corundum number method (reference intensity ratio, RIR). The calculation of the mass fractions of the phases was carried out on the basis of the integrated intensities of the separated peaks using standard RIR factors (I/I_c) for each of the identified phases.

(a) For each potential phase from the database, the theoretical positions of Bragg reflections $2\theta_{\text{theor},j}$ were calculated based on the corresponding crystal structure using a wavelength λ = 1.54186 Å. To assess the reliability of the qualitative identification and quantitative phase composition of the obtained composites, a combined statistical approach was used, based on the analysis of angular deviations of reflections and spectral similarity. The local reliability of the coincidence of individual Bragg maxima was determined by the normalized δ -criterion of agreement with a decision threshold $\delta_j < 3$:

$$\delta_j = \frac{2\theta_{\text{exp},j} - 2\theta_{\text{theor},j}}{\sigma}, \quad (4)$$

where $2\theta_{\text{exp},j}$ is the experimental angular position of the maximum of the j th peak, $2\theta_{\text{theor},j}$ is the theoretical position of the Bragg reflection of the j th phase according to the Materials Project database, σ = 0.02 is the instrumental error of the DRON-8 diffractometer (Innovation Center Burevestnik, Saint Petersburg, Russia).

(b) The integral reliability of the presence of phases was assessed through the FOM (figure of merit) indicator as the product of the spectrum completeness coefficient (the proportion of peaks found), the angular proximity of the peaks, the similarity of relative intensities using the de Gelder cosine measure method [33] and a penalty factor for the number of lines less than three. In this case, the average angular deviation of the peak positions $\Delta 2\theta_{\text{avg}}$ is related to the classical Smith–Snyder criterion (F_N) [34] by the expression

$$\Delta 2\theta_{\text{avg}} = \frac{N}{N_{\text{poss}} \times F_N}, \quad (5)$$

where N is the number of registered coincident reflections, N_{poss} is the theoretically possible number of reflections for a given system in the studied angular interval. The latter made it possible to express the average normalized angular deviation of the position of the phase peaks (δ_{avg}) as

$$\delta_{\text{avg}} = \frac{N}{N_{\text{pos}} \times \sigma \times F_N} \quad (6)$$

and relate the instrument scanning error to the overall reliability of the phase analysis.

To assess the formed structural-phase state of sintered compacts from the mixtures under study, structural studies were carried out using the equipment of the Center for Collective Use “Nanotech” of the Institute of Physics and Mathematics of Problems of the Siberian Branch of the Russian Academy of Sciences. Investigation of the surface microstructure of the samples and energy dispersive X-ray spectroscopy (EDX) were carried out using a Carl Zeiss EVO-50 scanning electron microscope (Carl Zeiss, Oberkochen, Germany). Using INCA V. 4.11 software, the elemental composition of the samples was calculated based on the obtained spectra. The change in porosity and volume depending on the configuration of the powder compositions under different mixing conditions was analyzed and the mechanical properties during compression of the sintered composites were assessed using INSTRON 5582 (Instron, Norwood, MA, USA).

3. Results and Discussion

Figure 2 shows a general view of sintered compacts from the mixtures under study, obtained by different methods. The options used for mixing four-component mixtures Ti + Al + Fe₂O₃ + C had different effects on the sintering ability and the formed structure of the compacts from them, which subsequently affected the mechanical properties.

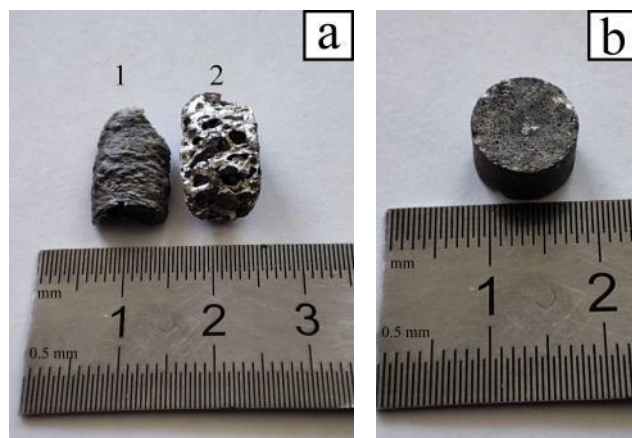


Figure 2. General view of sintered compacts from mixtures (Ti + Al + Fe₂O₃ + C), obtained in different ways: (a) compact from mixture 1 (1—outside view; 2—inside view); (b) pressing from mixture 2.

3.1. Phase Composition and Microstructure: Direct Mixing

Figure 3 shows an experimental diffraction pattern of a sintered composite material from a simple mixture of components with a nominal composition of 76.6Ti + 13.2Fe₂O₃ + 8.7Al + 1.5C (vol.%).

Qualitative phase analysis showed the formation of a complex multiphase state. The complete absence of diffraction maxima of the original hematite (Fe₂O₃) was established, which indicates the complete occurrence of the reducing aluminothermic reaction during the vacuum sintering process. Due to the strong overlap of peaks from various intermetallic, carbide and oxide phases, many of which have similar crystal lattice parameters, it is difficult to unambiguously attribute the majority of experimental peaks in the diffraction pattern to one specific phase. For a detailed interpretation of the diffraction spectrum, a comparison was made of the positions of the experimental maxima (taking into account the calibration of the zero shift 2θ by $+0.06^\circ$) with the theoretical reflection angles for the candidate phases. Table 2 shows the results of this comparison for 27 characteristic angular positions of peaks in the diffraction pattern.

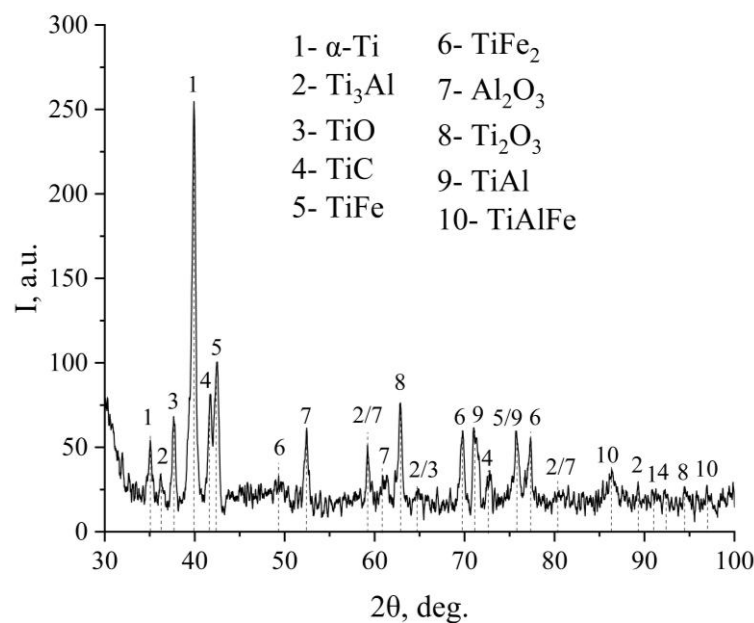


Figure 3. X-ray diffraction pattern of a sintered compact from mixture 1.

Table 2. Comparison of experimental 2θ angles of the diffraction pattern with theoretical peaks of candidate phases.

No.	$2\theta_{\text{exp}}$, deg.	$2\theta_{\text{caliber}}$, deg.	Coincident Phases (hkl)	$2\theta_{\text{theor}}$, deg.	I_{rel} , %	$\delta_{2\theta}$, deg.
1	31.941	31.881	TiAl (1 0 0)	31.84	6.8	0.04
			Ti ₃ Al (1 1 $\bar{2}$ 0)	31.12	2.2	0.76
2	36.200	36.140	TiAlFe (1 $\bar{2}$ 1 0)	36.19	31.5	0.05
			Ti ₃ Al (0 2 $\bar{2}$ 0)	36.09	24.8	0.05
			TiO (111)	36.28	49.7	0.14
3	37.600	37.540	TiO (1 0 $\bar{1}$ 1)	37.59	100.0	0.05
			Al ₂ O ₃ (1 0 $\bar{1}$ 1)	37.43	42.6	0.11
4	39.820	39.760	TiAlFe (1 $\bar{1}$ 0 3)	39.82	84.5	0.06
			α -Ti (2 $\bar{1}$ $\bar{1}$ 0)	39.46	73.4	0.30
5	41.700	41.640	Ti ₂ AlFe (2 1 1)	41.71	100.0	0.07
			TiC (1 1 0)	41.71	100.0	0.07
6	42.490	42.430	TiAlFe (0 2 $\bar{2}$ 0)	42.24	17.8	0.19
			TiO (200)	42.13	100.0	0.53
7	44.970	44.910	TiFe ₂ (2 0 $\bar{2}$ 1)	44.71	92.0	0.20
			TiAl (0 0 2)	44.56	16.6	0.35
			TiFe ₂ Al (2 1 1)	44.24	100.0	0.67
8	49.300	49.240	TiFe ₂ (2 0 $\bar{2}$ 2)	49.26	26.0	0.02
			Ti ₂ O ₃ (2 2 0)	48.95	40.0	0.29
9	52.400	52.340	TiAlFe ₂ (2 0 $\bar{2}$ 2)	49.26	26.0	0.02
			Al ₂ O ₃ (2 2 0)	52.06	49.1	0.28
10	59.100	59.040	Al ₂ O ₃ (1 0 $\bar{2}$)	59.16	1.3	0.12
			Ti ₃ Al (3 $\bar{3}$ 0 1)	59.15	0.2	0.11
11	60.800	60.740	Al ₂ O ₃ (3 3 2)	60.72	7.5	0.02
			Al ₂ O ₃ (2 $\bar{1}$ 1)	60.54	1.7	0.20
12	61.300	61.240	Ti ₂ O ₃ (1 3 0)	61.68	16.7	0.44
			TiAlFe (2 1 $\bar{3}$ 2)	62.57	2.9	0.17
			Ti ₂ O ₃ (1 1 $\bar{2}$)	63.06	38.1	0.32
13	62.800	62.740	TiFe (2 0 0)	63.29	14.8	0.55

14	65.000	64.940	TiO (2 0 $\bar{2}$ 0)	64.91	13.2	0.03
			Ti ₃ Al (2 2 $\bar{4}$ 0)	64.89	15.3	0.05
			TiFe ₂ Al (2 2 0)	64.35	29.8	0.59
15	66.970	66.910	TiFe ₂ (3 0 $\bar{3}$ 0)	66.89	3.2	0.02
			TiAl (2 0 0)	66.54	9.2	0.37
16	69.780	69.720	TiFe ₂ (3 $\bar{2}$ $\bar{1}$ 3)	69.31	9.6	0.41
			Al ₂ O ₃ (3 0 2)	69.71	0.7	0.01
			TiAlFe ₂ (3 1 1)	70.94	0.2	0.05
17	70.950	70.890	TiAl (2 0 1)	70.96	0.8	0.07
			TiAl (3 $\bar{1}$ $\bar{2}$ 1)	71.38	19.0	0.49
			α -Ti (1 0 $\bar{1}$ 3)	71.38	19.0	0.06
18	71.380	71.320	TiFe ₂ (3 0 $\bar{3}$ 2)	71.63	20.3	0.31
			TiFe ₂ (0 0 0 6)	72.33	4.5	0.01
19	72.400	72.340	TiC (1 2 2)	72.36	10.2	0.02
20	72.850	72.790	TiFe ₂ (0 0 0 6)	72.33	4.5	0.46
21	75.700	75.640	TiAl (2 1 0)	75.66	0.7	0.02
			TiFe ₂ (2 0 $\bar{2}$ 5)	75.74	26.2	0.10
22	76.660	76.600	Ti ₃ Al (0 4 $\bar{4}$ 0)	76.56	2.3	0.04
			TiO (2 1 $\bar{3}$ $\bar{2}$)	76.52	15.2	0.08
23	77.350	77.290	TiFe ₂ (2 1 $\bar{3}$ 4)	77.41	2.0	0.12
24	86.350	86.290	TiAlFe (2 0 $\bar{2}$ 6)	86.28	9.7	0.01
			Ti ₃ Al (1 0 $\bar{1}$ 4)	86.27	0.1	0.02
25	89.300	89.240	Ti ₃ Al (4 $\bar{4}$ 0 2)	89.39	3.0	0.15
			Al ₂ O ₃ (4 4 4)	89.71	3.3	0.47
26	94.400	94.340	Ti ₂ O ₃ (4 0 0)	94.16	1.1	0.18
			Al ₂ O ₃ (4 0 2)	94.16	5.3	0.18
27	96.900	96.840	TiAlFe (1 $\bar{3}$ 2 6)	96.84	0.5	0.00
			TiFe ₂ (4 $\bar{2}$ $\bar{2}$ 4)	96.87	8.0	0.03

Analysis of the data in Table 2 shows that almost all the key diffraction maxima in the experimental curve are the result of a superposition of reflections of several phases. For example, in the areas of angles 31.94°, 36.20°, 37.60°, 41.70° and 72.40°, reflections of titanium oxides, intermetallic compounds of the Ti-Al, Ti-Fe systems and titanium carbide are located within tenths of a degree from each other, merging into single peaks. Such strong mutual overlap of reflections, combined with shifts due to distortions of solid solution lattices, makes qualitative visual analysis insufficient. To reliably separate the partial contributions of individual phases and carry out more accurate quantitative analysis, deconvolution of peak clusters was performed by approximation using the pseudo-Voigt function. As representative examples of deconvolution results, Figure 4 shows approximated profiles of characteristic peak clusters in the angle ranges 36.5°–38.5° and 42.0°–45°. The choice of these areas is due to the need to separate the overlapping diffraction maxima of the oxide and intermetallic phases: aluminum and titanium oxides in the range of 36.5°–38.5° for the first cluster and key products of reaction sintering (binary and ternary phases of the Ti-Al-Fe system) in the range of 42.0°–45° for the second cluster, the reflections of which undergo the most intense mutual overlap.

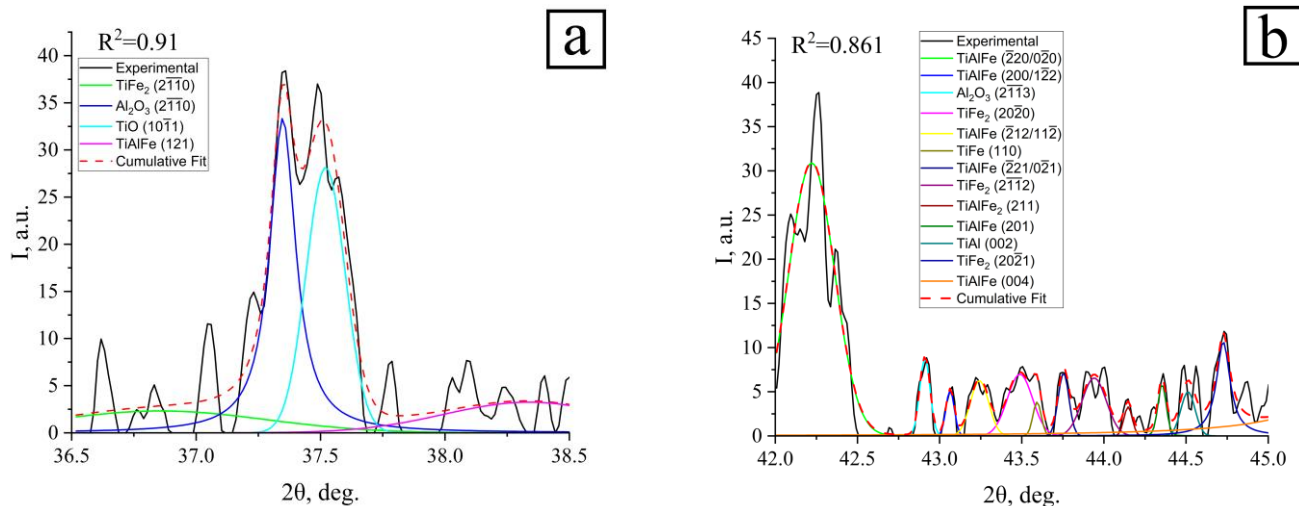


Figure 4. Results of mathematical deconvolution of overlapping diffraction maxima of sample 1 in characteristic angular ranges: (a) 36.5°–38.5°, (b) 42.0°–45°.

In Figure 4a, as a result of deconvolution of the complex peak profile, it was found that it was formed by close superposition of reflections of oxide phases: corundum Al_2O_3 ($2\bar{1}\bar{1}0$) at 37.35° and TiO monoxide ($10\bar{1}1$) at 37.52°, with an additional contribution from the ternary phase TiAlFe ($1\bar{2}1$) at 38.34° and Laves phase TiFe_2 ($2\bar{1}\bar{1}0$) at 36.86°.

The results of deconvolution of peaks in the range of 42.0°–45° (Figure 4) showed that in this region the presence of three intermetallic components is most likely: the reflection of the Laves phase TiFe_2 ($20\bar{2}1$) at 44.73°, the reflection of binary aluminide TiAl (002) at 44.52° and the reflection of the triple Heusler phase TiAlFe_2 (211) at 44.15°. Numerical separation of these contributions made it possible to correctly distribute iron reduced from hematite between competing phases and avoid false overestimation of the content of the binary intermetallic TiFe_2 . Data on the phase composition for the sample obtained from mixture 1 are presented in Figure 5.

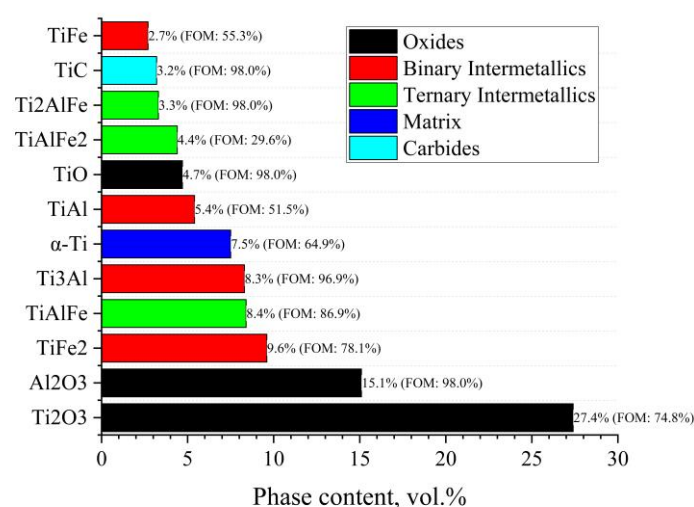


Figure 5. Volume fractions of phases in sample 1 in comparison with indicators of the reliability of their identification (FOM, figure of merit).

Analysis of quantitative data shows that as a result of sintering, a heterophase composite is formed, in which the largest volume fraction is titanium (III) oxide Ti_2O_3 (27.4 vol.%), which, along with corundum Al_2O_3 (15.1 vol.%), is the main strengthening oxide component. The predominance of oxide phases by volume (total 47.2 vol.%) is due to both thermodynamic factors and a significant difference in the densities of the formed phases. From a thermodynamic point of view, the Gibbs free energy of formation of aluminum and titanium oxides at a sintering temperature of 1200 °C (1473 K) per 1 mol O_2 (calculated from the NIST-JANAF tables [35]) is $dG^\circ(\text{Al}_2\text{O}_3) \approx -804$ kJ and $dG^\circ(\text{Ti}_2\text{O}_3) \approx -750$ kJ, which is significantly lower than for the original hematite $dG^\circ(\text{Fe}_2\text{O}_3) \approx -370$ kJ. This ensures complete recovery of iron. However, since part of the aluminum is bound into intermetallic phases (Ti_3Al , TiAl) and ternary compounds, the oxygen released from hematite is actively absorbed by the excess titanium matrix with the formation of suboxides Ti_2O_3 and TiO . From a physical point of view, the volume fraction of phases is inversely proportional to their density. The densities of oxides ($\text{Al}_2\text{O}_3 = 3.87$ g/cm³, $\text{Ti}_2\text{O}_3 = 4.60$ g/cm³) are significantly lower than the densities of intermetallic phases (for example, for the Laves phase $\text{TiFe}_2 = 6.65$ g/cm³). As a result, with the same mass, the oxides occupy a significantly larger volume, which explains the large volume fraction of the oxide framework in the structure of the composite.

It has been established that reduced iron and aluminum take an active part in the formation of both binary and ternary intermetallic phases of the Ti–Al–Fe system. Iron recovered from hematite is distributed between the hexagonal Laves phase TiFe_2 (9.6 vol.%), the cubic phase TiFe (2.7 vol.%) and a family of ternary phases: TiAlFe (8.4 vol.%), TiAlFe_2 (4.4 vol.%) and the inverse Heusler phase Ti_2AlFe (3.3 vol. %). The total volume content of ternary intermetallic compounds reaches 16.1 vol.%, which indicates the large role of in situ ternary phases in the binding of alloying components and the formation of the composite matrix. The titanium (α -Ti) solid solution matrix is 7.5 vol.% for which there is a weak intensity and blurriness of reflections, as well as a virtual absence of its isolated peaks. The main reflection ($1\ 0\ \bar{1}\ 1$) of the α -Ti matrix (theoretical angle 40.46°) is not recorded as an independent peak on the experimental curve, since its intensity is overlapped by powerful reflections of the ternary TiAlFe intermetallic compound and Ti_2O_3 oxide. The only relatively clear reflection of α -Ti is the reflection ($1\ 0\ \bar{1}\ 3$) at the experimental angle of 71.32°. Oxygen released during the reduction of hematite was distributed mainly into the corundum phase Al_2O_3 (15.1 vol.%), titanium oxide (III) Ti_2O_3 (27.4 vol.%) and titanium monoxide TiO (4.7 vol.%). The high reliability of identification of these phases (FOM from 74.84% to 98.00%) confirms their presence in the sintered composite. The volume content of titanium carbide TiC is 3.2 vol.%, which is consistent with the low initial proportion of carbon in the charge (0.8 wt.%). Despite the low mass fraction, the TiC phase is reliably identified (FOM 98.00%) due to the presence of a characteristic reflection (200) at 41.71° (shift of only 0.07°). This phase is in a highly dispersed state and distributed in the form of submicron precipitates, which makes it difficult to visually detect using SEM up to magnifications of $\times 40,000$.

Despite the fact that the content of a number of identified phases (TiFe , TiC , Ti_2AlFe , TiAlFe_2) is in the range of 2.7–4.4 vol.%, that is, near the detection limit of phase X-ray diffraction analysis (3–5%), their presence can be considered verified. Phase identification was carried out by the coincidence of several independent reflections throughout the diffraction pattern, and highly symmetric phases have high scattering ability, giving clear reflections even at low volume fractions. The use of the FOM indicator made it possible to separate reliably identified phases from trace compounds with strong mutual overlap (such as TiAlFe_2 , FOM 29.60%), for which the quantitative assessment is predominantly of an evaluative nature.

To verify the spatial distribution of elements of the detected phases, assess their morphology and analyze the microstructure of the metal matrix composite formed in situ, further studies were carried out using scanning electron microscopy (SEM). Figure 6 shows an SEM micrograph of the cross section of a sintered composite material from mixture 1 (without preliminary MA).

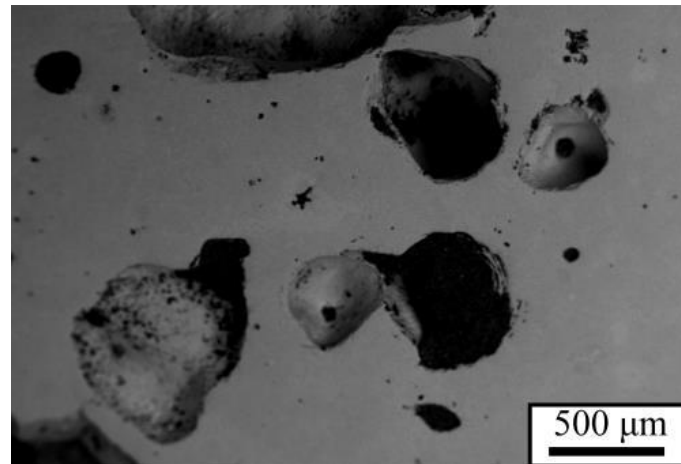
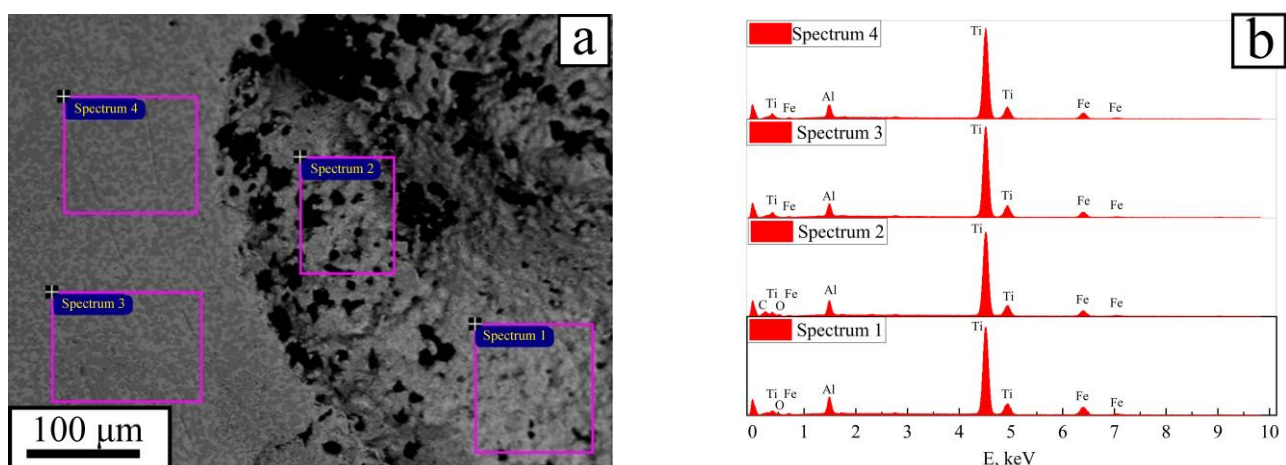


Figure 6. SEM image of the surface of a sintered sample from mixture 1.

A characteristic feature of the microstructure of samples from mixture 1 is its high porosity. The structure contains large rounded macropores ranging in size from 200 to 500 μm , unevenly distributed over the cross section of the sample. The formation of such large pores is due to the lack of preliminary mechanochemical treatment of the initial charge, which is why reduction and diffusion processes during sintering are localized in the volumes of individual large particles of reagents. The course of the reactions is accompanied by the formation of a local liquid melt (in particular, the low-melting Ti–Fe eutectic at a temperature of 1085 $^{\circ}\text{C}$) and its uneven capillary flow, which, in combination with the difference in the rates of mutual diffusion of the components, leads to the formation of macropores in place of the original particles. The internal structure is presented in more detail in Figure 7 with accompanying EDX analysis of element distribution.



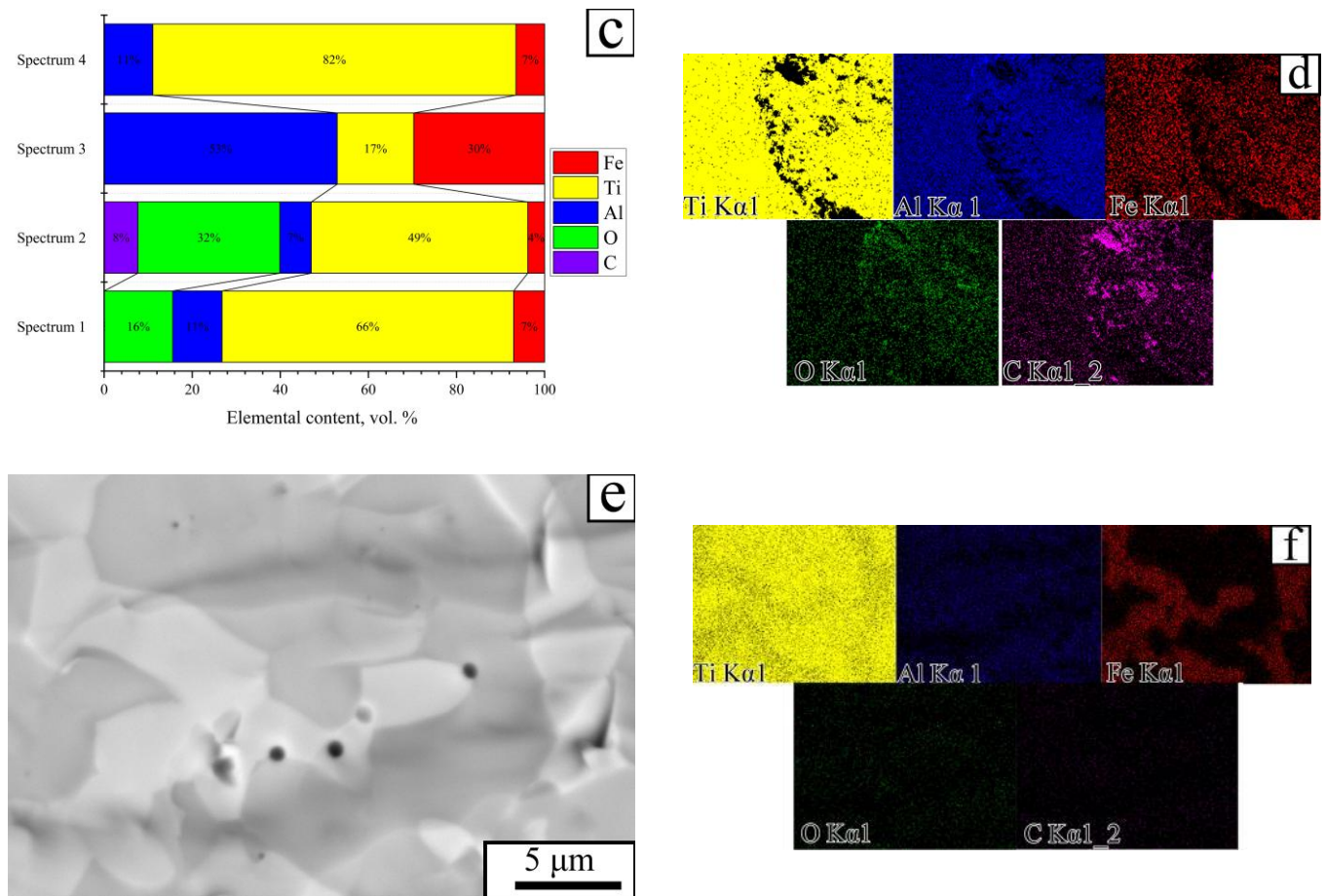


Figure 7. SEM image of a general view of the porous structure of a sintered sample from mixture 1 indicating the areas of EDX analysis (a); EDX spectra of different regions of sample 1 (b); graphs of phase content in different areas of the sample from mixture 1 (c); maps of the distribution of elements in the characteristic radiation of titanium, iron, aluminum, oxygen and carbon (d); image at $\times 10,000$ magnification (e) and corresponding element distribution maps (f).

Analysis of the local chemical composition in different areas of the sintered compact from mixture 1 (Figure 7b) confirms the results of qualitative and quantitative XRD. Spectrum 4 corresponds to a relatively homogeneous titanium metal matrix with dissolved elements (82 vol.% Ti, 11 vol.% Al, 7 vol.% Fe), which indicates the formation of an interstitial-substitution solid solution α -Ti(Al, Fe). Spectrum 3 indicates a higher content of aluminum (53 vol.%) and iron (30 vol.%) with a relatively low titanium content (17 vol.%). This indicates the formation of zones of intermetallic phases (such as the ternary intermetallic compound TiAlFe_2 and binary aluminides of the Ti-Al system) along the path of diffusion flows between the reduced iron and the titanium matrix. Spectra 1 and 2 are localized in dark regions enriched in oxygen (32 and 16 vol.%, respectively) and carbon (up to 8 vol.% in Spectrum 2). This indicates that dark inclusions may represent accumulations of dispersed titanium oxides (Ti_2O_3 , TiO) and corundum (Al_2O_3), as well as submicron precipitates of titanium carbide (TiC). Elemental distribution maps at various scales (Figure 7d,f) show pronounced phase segregation in the material. At an increase of $\times 10,000$ (Figure 7e,f), features of the phase distribution are revealed. Iron (Fe) is localized in the form of continuous tortuous intergranular channels (red color on the maps), corresponding to intermetallic compounds of the Ti-Al-Fe system.

3.2. Phase Composition and Microstructure: Two-Stage Mixing with Mechanical Activation

(a) Formation of a precursor structure from a mixture ($\text{Fe}_2\text{O}_3 + \text{Al}$) using MA

To understand the features of the formation of the phase structure of a sintered compact from mixture 2, it is advisable to consider the phase and structural evolution of the reaction oxide-reduction mixture $\text{Fe}_2\text{O}_3 + \text{Al}$, selected as a precursor, at the stage of preliminary mechanical activation. XRD and SEM studies of the initial mixture (before MA) and the activated powder (after MA) made it possible to verify the occurrence of solid-phase reduction in situ (Figure 8).

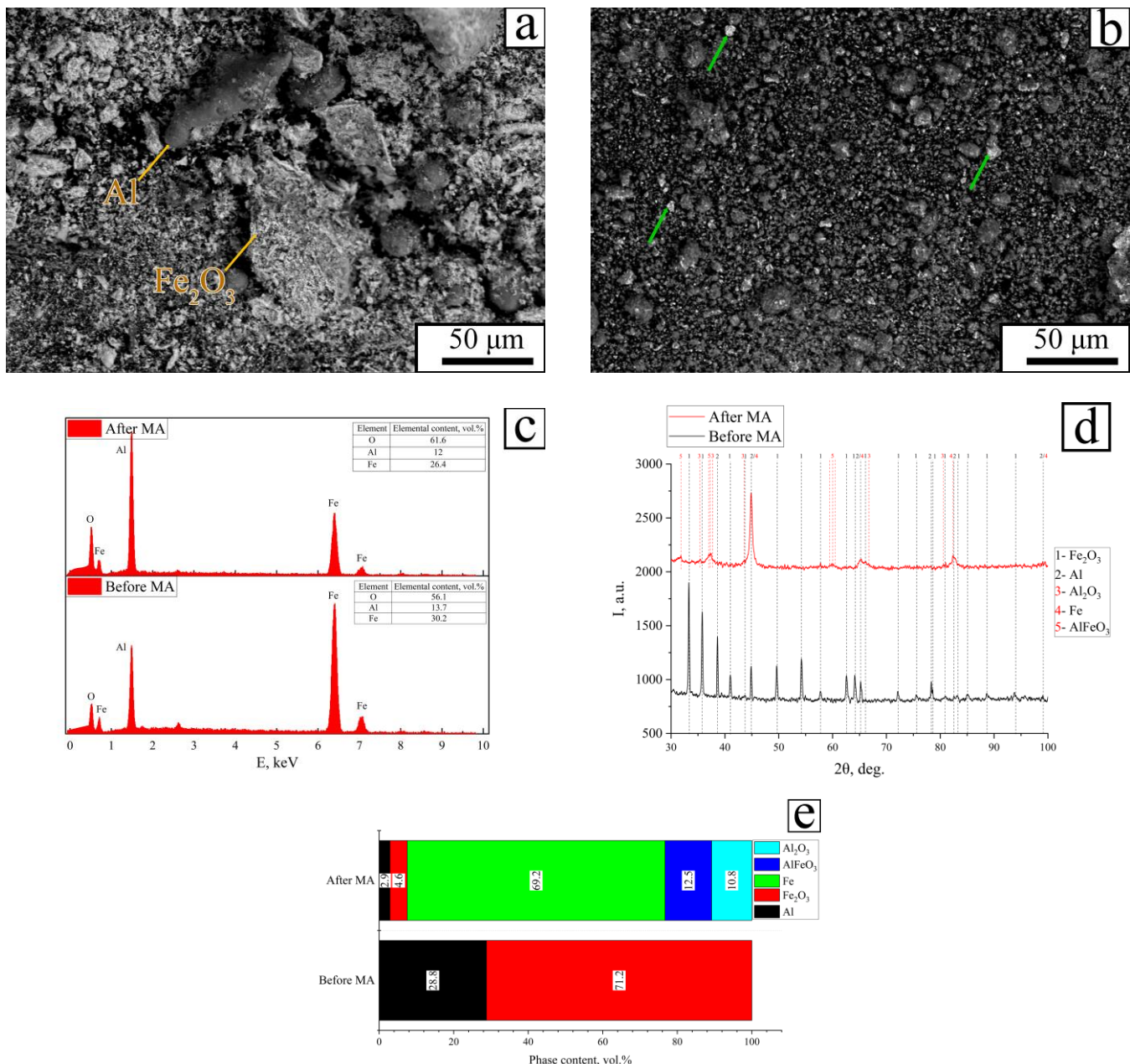


Figure 8. Microstructure of the reaction mixture of $\text{Fe}_2\text{O}_3 + \text{Al}$ powders before (a) and after MA (b), their elemental composition (c), X-ray diffraction patterns (d), and phase composition (e).

In the SEM image of the initial powder mixture before MA (Figure 8a), round aluminum Al with a size of 20–70 μm alternates with clusters of much smaller particles of hematite Fe_2O_3 with a size of 1–10 μm and its agglomerates reaching a size of more than 100 μm . Both components are clearly distinguishable by contrast; Fe_2O_3 particles are lighter than Al particles due to the higher average atomic number of iron. The local EDX spectrum of the initial mixture (Figure 8c, “Before MA” spectrum) records 56.1 vol.% O, 13.7 vol.% Al and 30.2 vol.% Fe, which corresponds to the calculated composition of the charge and confirms the absence of any interaction between the components at the mixing stage. After 20 min of high-energy grinding in a planetary mill, the morphology of the mixture changes significantly. As a result, dense, quasi-spherical conglomerate particles ranging in size from submicron sizes to tens of microns are formed, within which the components are mixed on a submicron scale. A notable feature of the powder after MA is the pronounced heterogeneous contrast of the particles. In the gray matrix, bright white inclusions of submicron size corresponding to Fe are clearly observed, marked in Figure 8b with green arrows. Thus, already at the stage of SEM analysis at low magnification, it can be stated that the powder after MA is a heterophase nanocomposite with pronounced inclusions of reduced iron.

The energy spectra clearly demonstrate the difference in elemental composition. The initial mixture is dominated by oxygen and iron, characteristic of hematite. The composition after MA (61.6 vol.% O, 12.0 vol.% Al and 26.4 vol.% Fe) in comparison with the initial one (56.1/13.7/30.2 vol.%, respectively) records a noticeable decrease in the proportion of iron in the recorded signal, which is explained by its partial transition to the ultrafine and amorphized state Al_2O_3 and AlFeO_3 , which make an increased contribution to the oxygen signal.

X-ray diffraction analysis quantitatively confirms the findings of electron microscopy. The diffraction pattern of the initial mixture contains only narrow high-intensity reflections of the initial reagents: hematite Fe_2O_3 (71.2 vol.%) and aluminum Al (28.8 vol.%). After MA, significant changes are observed: the intensities of the peaks of the initial phases drop sharply (Fe_2O_3 to 4.6 vol.%, Al to 2.9 vol.%), and their reflections greatly broaden, which indicates a decrease in the CSR (coherent scattering region) to the nanometer scale and the accumulation of defects. At the same time, peaks of new phases of metallic iron Fe (69.2 vol.%), complex oxide AlFeO_3 (12.5 vol.%) and corundum Al_2O_3 (10.8 vol.%) appear. The total residual content of unreacted reagents is $4.6 + 2.9 = 7.5$ vol.%, which corresponds to the degree of completeness of the reaction ~92.5% in crystalline phases. Taking into account the fact that part of the synthesized Al_2O_3 is in an amorphized state and is not detected by the RIR method, the actual degree of completeness of the aluminothermic reaction is higher. The formation of the intermediate oxide AlFeO_3 is determined by the total stoichiometry of the charge. The mixture $\text{Fe}_2\text{O}_3 + 2\text{Al}$ corresponds to the composition $\text{Fe}_2\text{Al}_2\text{O}_6$, i.e., exactly two formula units AlFeO_3 .

To confirm that the bright white areas in Figure 8b represent reduced iron and not the heavier oxide phase, detailed examinations of individual conglomerate particles were carried out at higher magnification using linear EDX scanning. The results of these studies are presented in Figure 9.

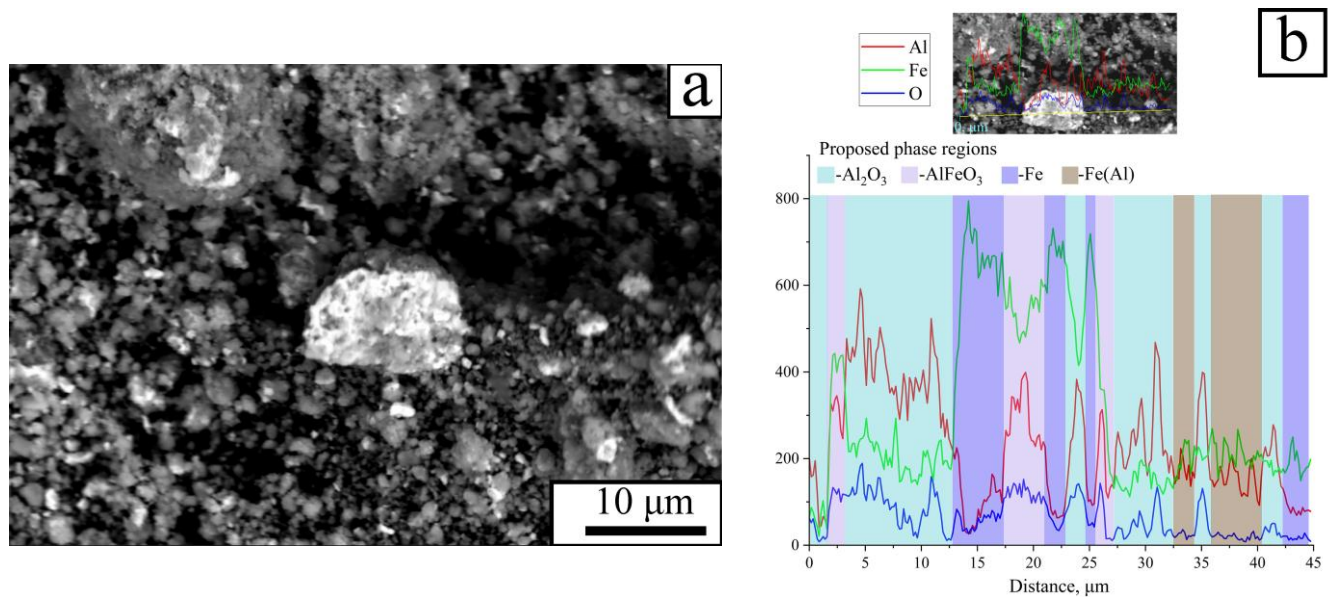


Figure 9. Microstructure of composite powder particles after mechanical activation at a magnification of $\times 5000$ (a) and linear distribution of chemical elements (b).

In the SEM image of composite particles at high magnification (Figure 9a), a large (about $10\ \mu\text{m}$ in size) round particle with a large proportion of Fe, surrounded by smaller particles of various compositions, is clearly visible in the center of the frame. The line EDX scan profile (Figure 9b) taken along a path intersecting this inclusion (yellow line in inset) shows the intensity distribution of Al, Fe and O. In the intervals $0\text{--}12\ \mu\text{m}$ and $27\text{--}32.5\ \mu\text{m}$, signals of aluminum and oxygen predominate with low intensity of iron, which may correspond to the alumina phase Al_2O_3 . When crossing the bright inclusion boundary, the intervals $13\text{--}17\ \mu\text{m}$ and $21\text{--}23\ \mu\text{m}$, the intensity of the iron signal increases sharply, while the aluminum and oxygen signals drop to almost zero. The minimum level of the oxygen signal in these zones is indirect evidence of the presence of reduced iron and excludes the presence of its oxides. In transition regions at the interfaces, for example $17\text{--}21\ \mu\text{m}$, the combined presence of Al, Fe and O is observed, characteristic of the intermediate complex oxide AlFeO_3 . In the right part of the profile, after $32.5\ \mu\text{m}$, an extended region of the joint presence of Fe and Al is recorded at an extremely low intensity of the oxygen signal. This indicates the formation of a solid solution of aluminum in Fe(Al) iron (shown in brown on the graph) or nano-sized Fe-Al intermetallic compounds during the process of mechanical synthesis. Inside this region, a local oxide island is detected near $35.1\ \mu\text{m}$, on which the Al and O signals increase synchronously, indicating the presence of a dispersed inclusion of Al_2O_3 .

Thus, the results of a comprehensive analysis of the activated powder mixture confirm the successful occurrence of the aluminothermic reaction of iron reduction directly during the grinding process with the formation of nanostructured Fe- Al_2O_3 conglomerates. This activated mixture containing metallic iron and nanodispersed alumina was further used as a reaction additive to create titanium-based metal matrix composites.

(b) Structure of sintered composites from a mixture with MA precursors

To study the effect of pre-grinding on the phase structure and mechanisms of interaction between the components of the sintered composite, first of all, XRD analysis of the obtained samples was carried out (Figure 10).

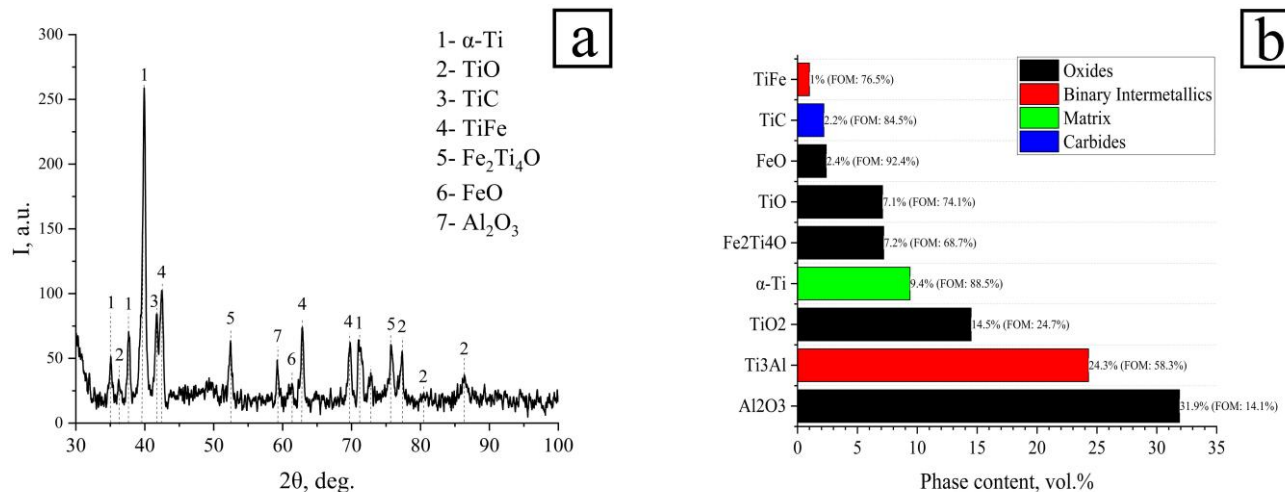


Figure 10. Diffraction pattern of a sintered sample from mixture 2 (a) and the corresponding phase composition (b).

The basis of the diffraction pattern is formed by reflections of a hexagonal close-packed α -Ti lattice. In addition, reflections of strengthening oxide, carbide and intermetallic phases are recorded on the diffraction pattern. Similar to the first sample, the diffraction pattern of the sample from mixture 2 shows a significant number of overlapping peaks from different phases close in angular positions 2θ . Due to the similarity of the lattice parameters of cubic and hexagonal structures, the Bragg reflections of highly dispersed phases FeO, TiC, TiO, as well as the TiFe intermetallic compound, almost completely overlap the intense reflections of the α -Ti matrix. Similar to the sample from mixture 1, deconvolution of the overlapping peaks was performed using the pseudo-Voigt function.

For the sample from mixture 2 and for the sample from mixture 1, the consumption of the α -Ti matrix is observed for the formation of various compounds. However, the phase transformation paths and the final phase composition are different. In the case of a sample from mixture 2, preliminary mechanical activation leads to the solid-phase reaction of aluminothermic reduction $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$ directly at the grinding stage. This eliminates the melting of free aluminum at 660 °C and the development of an uncontrolled thermal explosion during the sintering process. However, the high defectiveness of the crystal structure and the nano-sized state of the reduction products accelerate solid-phase diffusion during vacuum sintering at 1200 °C. Aluminum oxide interacts with the titanium matrix. Thermodynamically and kinetically, this leads to the reduction of corundum with titanium and intensive exchange reactions with the formation of intermetallic titanium aluminide Ti_3Al (24.7 vol.%) and titanium dioxide TiO_2 -rutile (14.5 vol.%). In this case, iron reduced during MA actively diffuses into titanium at temperatures above 1000 °C through the controlled formation of the eutectic liquid Ti-Fe phase at 1085 °C. Iron is bound predominantly into the phase of complex cubic oxide $\text{Fe}_2\text{Ti}_4\text{O}$ (7.2 vol.%), iron (II) oxide FeO (2.6 vol.%) and intermetallic compound TiFe (1.1 vol.%). Due to the absence of additional heat release from the aluminothermic reduction reaction, the formation of the brittle Laves phase TiFe_2 and complex ternary intermetallic compounds of the Ti–Al–Fe system is suppressed. Highly dispersed aluminum oxide Al_2O_3 (31.1 vol.%) gives strongly broadened peaks in the diffraction pattern with a low FOM value (14.10%), which is due to the nanometer size of the coherent scattering regions. The weak visibility of the Al_2O_3 reflections in the sintered composite is due to severe peak overlap, where the primary peak of corundum at $2\theta \approx 43^\circ$ is masked by the dominant reflections of TiFe, Ti_3Al , and TiC. It should be noted that due to the intensive in situ reactions during sintering, a

significant portion of the starting titanium matrix (originally 76.6 vol.%) was consumed to form Ti_3Al intermetallic and reinforcing oxide/carbide phases. Consequently, the final sintered material structurally transforms from a classic titanium-matrix composite into a complex dispersion-strengthened intermetallic–ceramic composite, where the metallic α -Ti phase occupies only 9.4 vol.%.

Thus, preliminary mechanical activation of the $\text{Fe}_2\text{O}_3 + \text{Al}$ mixture significantly changes the reaction mechanism during sintering. The reduction reaction is transferred to the stage of solid-phase grinding, and subsequent vacuum sintering is accompanied by intense interaction of titanium with highly active reduction products. This leads to the formation of a heterophase metal matrix composite with a predominance of strengthening titanium aluminide Ti_3Al and oxide phases (Al_2O_3 , TiO_2 -rutile) while suppressing the formation of undesirable ternary intermetallic compounds. The results of XRD analysis of the sample from mixture 2 are in good agreement with the SEM and local EDX data presented in Figure 11.

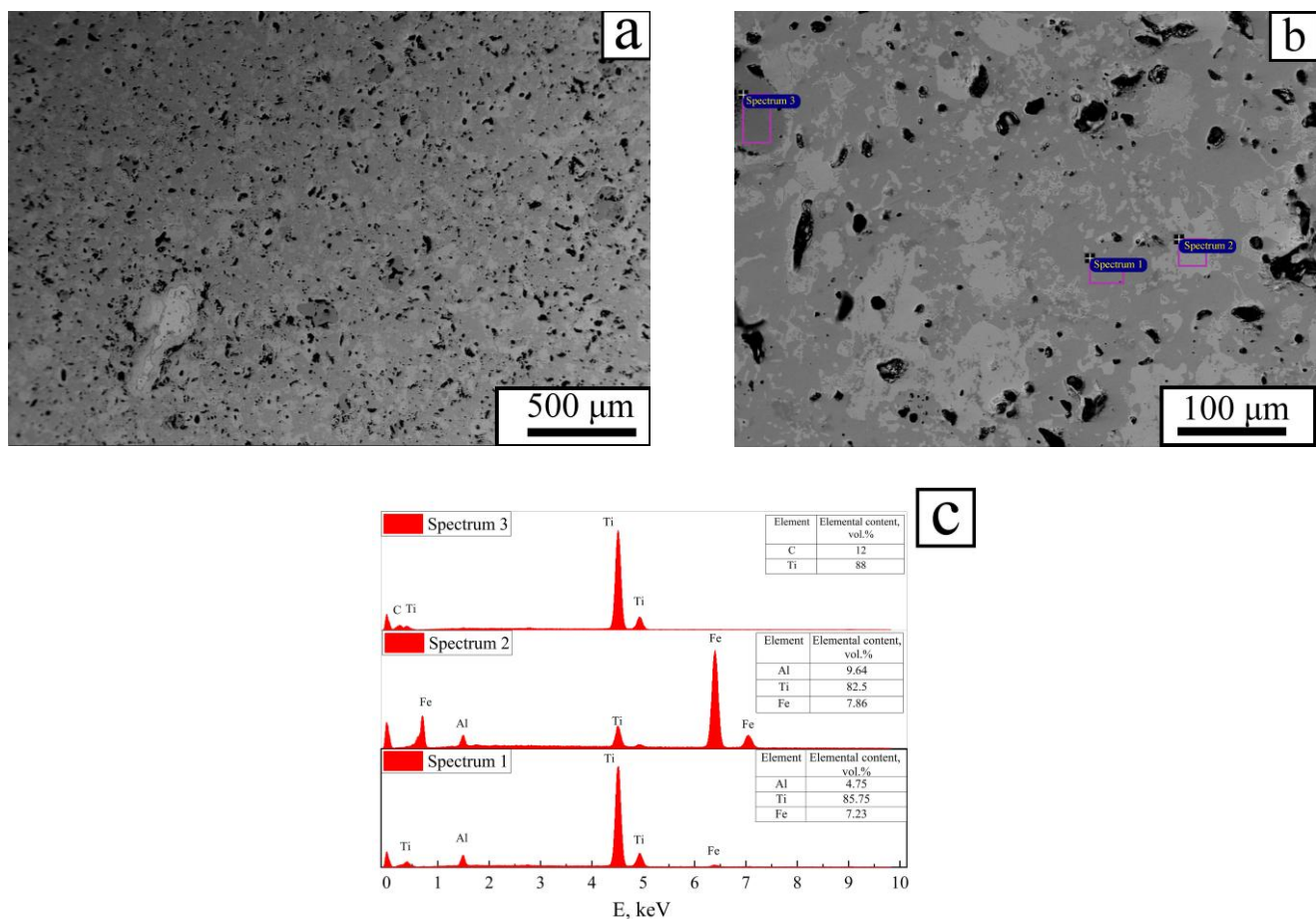


Figure 11. SEM image of the structure of a sample from mixture 2 at magnifications of $\times 100$ (a), $\times 500$ (b) and EDX spectra (c) of the areas marked in (b).

In the SEM image of the general view of a sample from mixture 2 at a magnification of $\times 100$ (Figure 11a), large round macropores (200–500 μm) are not observed, and the residual porosity is represented mainly by small, isolated pores ranging in size from 5 to 30 μm , evenly distributed over the cross section of the compact. This confirms that the transfer of the main exothermic reactions to the pre-grinding stage eliminates local thermal runaway and melting of free aluminum, transferring consolidation to the regime of controlled solid-phase sintering with uniform volumetric shrinkage. At a higher magnifica-

tion of $\times 500$ (Figure 11b), a heterophase structure of the matrix is revealed with a characteristic contrast of regions of different chemical compositions, which is confirmed by the results of local EDX analysis (Figure 11c). Spectrum 1, obtained in the typical gray region of the matrix, records 85.75 vol.% Ti, 4.75 vol.% Al and 7.23 vol.% Fe. This elemental composition corresponds to a solid solution based on α -Ti(Al, Fe), in which alloying components are dissolved. Spectrum 2, localized in lighter areas of the structure, is characterized by an increased concentration of aluminum (9.64 vol.%) and iron (7.86 vol.%) with a decrease in the titanium content to 82.50 vol.%. The accumulation of Al and Fe in these microregions indicates the formation of zones of diffusion interaction of reagents and the formation of intermetallic phases (such as Ti_3Al and TiFe), which is in good agreement with quantitative XRD data. Spectrum 3, taken in dark dispersed inclusions on the matrix, reveals the presence of 12.00 vol.% carbon (C) and 88.00 vol.% titanium (Ti). This confirms the in situ formation of highly dispersed non-stoichiometric titanium carbide (TiC), formed due to the reaction of titanium with soot during sintering. The presence of oxide phases (Al_2O_3 and TiO_2 -rutile), identified by XRD, is not observed due to their high dispersion. Their presence in the sintered composite can be judged by the formed fine-grained structure, which was influenced by submicron particles that physically restrict grain boundary migration during sintering.

3.3. Mechanical Properties and Deformation Behavior

The formed features of the macro- and microstructure, as well as the phase composition of the sintered samples had a significant impact on their mechanical behavior under compression. Figure 12 shows the experimental stress–strain diagrams.

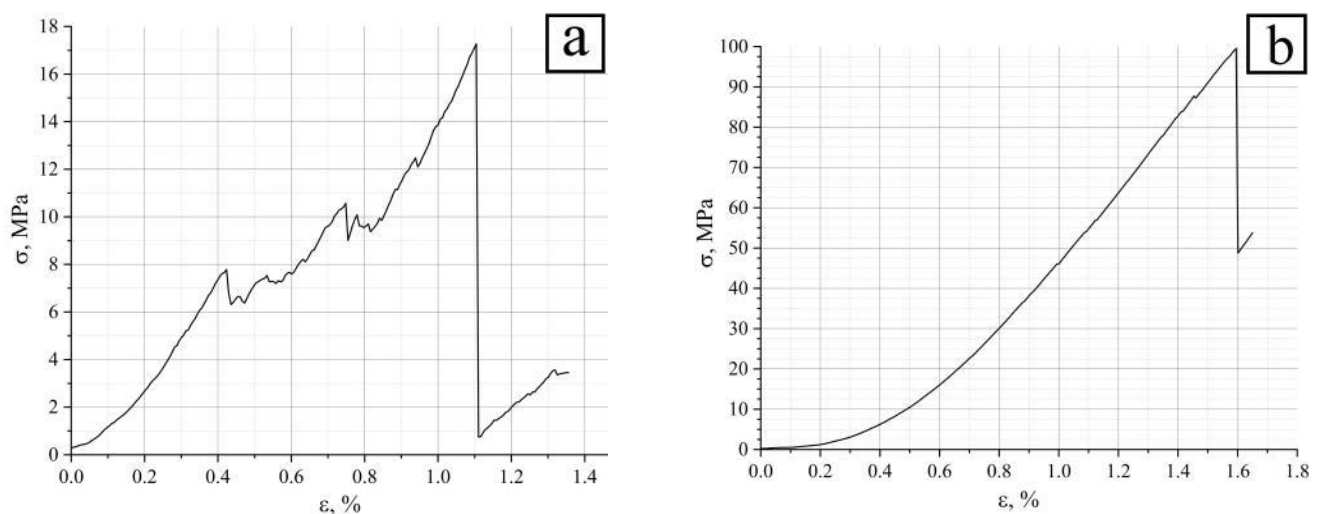


Figure 12. Compression diagrams for samples from mixtures 1 (a) and 2 (b).

Analysis of the behavior of the compression curve of a sample from mixture 1 (Figure 12a) reveals a low level of strength, the ultimate strength before failure is only about 17 MPa (with a mean ultimate compressive strength of 17.44 ± 1.78 MPa based on eight tested specimens) with an ultimate deformation of about 1.1%. A characteristic feature of this curve is its pronounced “step” shape with alternating local peaks and voltage drops. The first drop in load is recorded at a stress of ~ 8 MPa (strain 0.42%), after which the stress drops to ~ 6 MPa. A similar load release followed by subsequent loading is observed at a stress of 10.5 MPa (strain 0.75%). This specific stepwise nature of the deformation of the sample from mixture 1 is due to its high porosity and the presence of large isolated macropores. When loaded, critical stresses are consistently reached in the bridges between individual pores, which leads to their local brittle destruction and “collapse.” Each such

microfracture is accompanied by local relaxation of the total load on the diagram and an abrupt increase in deformation. After compaction of the damaged zone, the resistance of the material increases, and the load increases again until the next act of local destruction, up to the complete macrofracture of the sample.

In contrast to the sample from mixture 1, the sample from mixture 2 shows a different mechanical behavior (Figure 12b). The compression diagram has a smooth, classic appearance without any jumps or deformation steps. At the initial stage (at deformations up to 0.4%), a slight nonlinearity is observed (grinding in of the sample and closing of small pores), which turns into a straight elastic section, which ends in brittle fracture when the ultimate strength reaches about 100 MPa (with a mean ultimate compressive strength of 99.53 ± 3.64 MPa based on eight tested specimens) and a deformation of 1.6%. The low macroscopic plasticity (less than 2%) of the sintered composites under compressive load is primarily explained by the distribution of oxygen and the resulting structural embrittlement. During vacuum sintering, oxygen is predominantly distributed within submicron and nanoscale structural elements, forming thin, semi-amorphous or nanocrystalline oxide films along the grain boundaries and interparticle interfaces. This network of grain boundary oxides, combined with the interstitial dissolution of oxygen and carbon into the hcp α -Ti matrix, distorts the crystal lattice and blocks dislocation motion. Consequently, these boundary films act as active pathways for rapid crack initiation and propagation under stress, leading to premature brittle cleavage fracture before macroscopic plastic yielding can occur. To gain a detailed understanding of the fracture mechanisms, SEM images of the fracture surfaces of the samples after compression tests were analyzed (Figure 13).

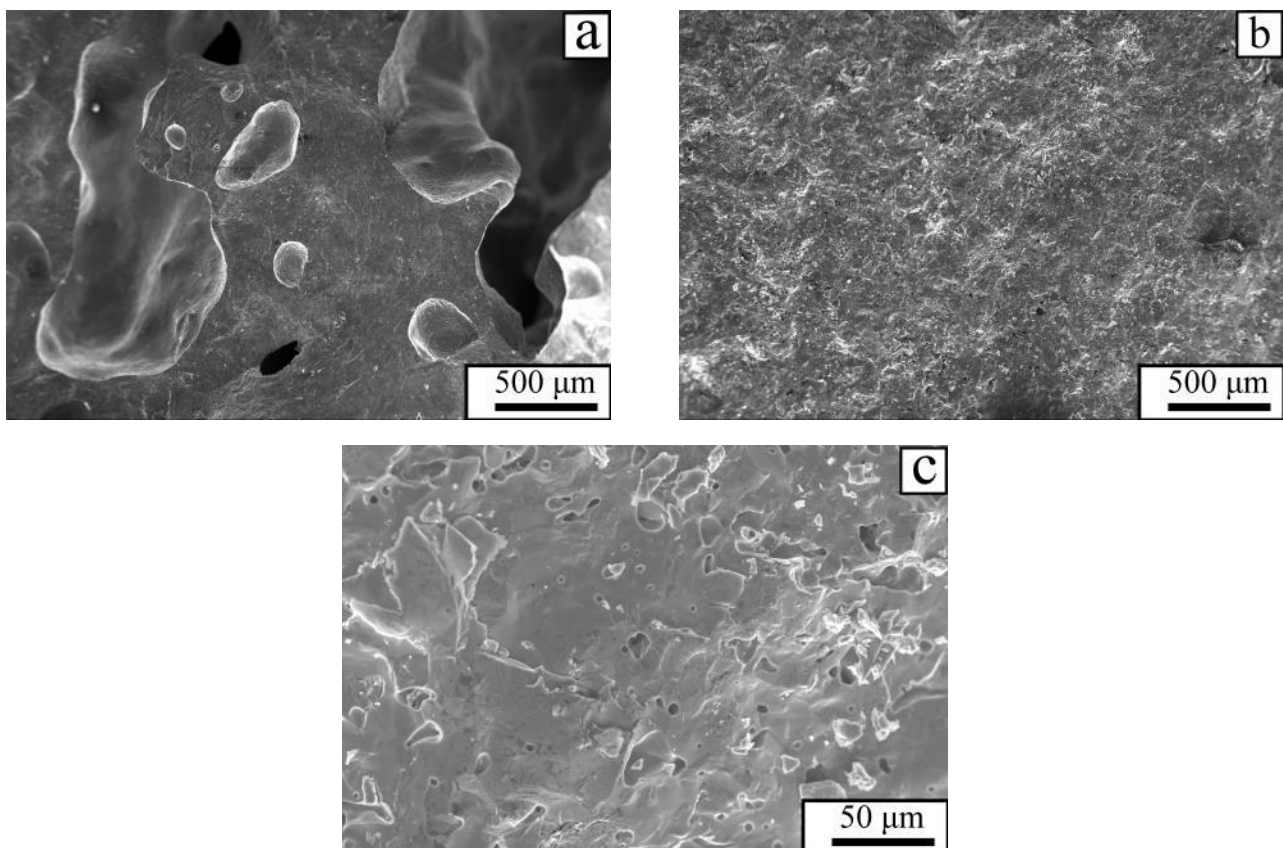


Figure 13. SEM image of fracture after compression of samples from mixture 1 (a) and from mixture 2 ((b), $\times 100$; (c), $\times 1000$).

Fractograms of the fracture surface of a sample from mixture 1 (Figure 13a) are characterized by pronounced heterogeneity of the relief. Large macropores and rounded smoothed surfaces of the original powder particles that did not form strong sintered contacts are clearly visible at the fracture. The presence of such free surfaces indicates weak interparticle adhesion during the sintering process. Due to the lack of pretreatment, the diffusion interaction was localized in the volumes of individual contacts, and the resulting liquid phase did not ensure the formation of a continuous strong frame.

In turn, the fracture surface of a sample from mixture 2 (Figure 13b) demonstrates a uniform fracture with a developed rough relief. The fracture is completely free of large macropores and free rounded boundaries of the original particles, which confirms the formation of a strong consolidated structure during the sintering process. A more detailed analysis of the fracture surface of the sample from mixture 2 at a higher magnification of $\times 1000$ (Figure 13c) reveals a mixed nature of fracture. Smooth flat facets of a transgranular fracture are visible on the surface. These brittle areas are bordered by ridges of plastic shearing and rupture, forming a rough topography. Small quasi-spherical pores ranging in size from 2 to 10 μm are also observed on the fracture surface. The round shape of these pores and the absence of sharp corners indicate a low stress concentration at their boundaries during plastic flow of the matrix. This prevents their transformation into sites of premature destruction and allows the composite to achieve a high level of strength (up to 100 MPa).

A comparison of the results of qualitative and quantitative phase analysis, electron microscopy, mechanical tests and fracture fractography allows us to establish a direct relationship between the method of preliminary preparation of the powder mixture and the nature of the behavior of materials during heating and subsequent loading. The use of a two-stage scheme with preliminary mechanochemical synthesis of the reaction pair $\text{Al} + \text{Fe}_2\text{O}_3$ completely changes the kinetic scenario of sintering, preventing a thermal explosion and transferring the system to controlled solid-phase diffusion. This ensures the formation of a dense composite with a uniform distribution of strengthening phases and defect-free interparticle contacts, which is reflected in a sixfold increase in compressive strength.

4. Conclusions

Thus, the presented research results show that the procedure for mixing certain types of components of the same elemental composition is of significant importance in the process of forming the structure and phase composition during vacuum sintering. The sequence of stages of the reaction–diffusion interaction of the components strongly depends on the nature of the distribution of their elements in the total volume of the mixture. Analysis of the behavior of such powder systems during sintering makes it possible to determine the possible priority of one or another reaction between components while limiting other processes. The excess thermal contribution during the interaction of the reacting powder components can be leveled through the preliminary mechanical synthesis of the thermite mixture ($\text{Al} + \text{Fe}_2\text{O}_3$). As a result, during vacuum sintering of $\text{Ti} + \text{Al} + \text{Fe}_2\text{O}_3 + \text{C}$ compositions, a fairly dense composite structure with solid inclusions can be formed, which is reflected in the level of compressive strength.

Based on the research conducted, the following conclusions can be drawn:

- (1) Mechanical activation of the reaction mixture of $\text{Al} + \text{Fe}_2\text{O}_3$ powders in a planetary mill ensures the solid-phase occurrence of the aluminothermic reaction directly during the grinding process (the degree of completeness of the reaction is about 92.5%). This eliminates the presence of free aluminum in the charge and prevents the occurrence of an uncontrolled liquid-phase thermal explosion during the heating stage to 1200 °C during subsequent vacuum sintering of the multicomponent system.

- (2) With traditional mixing of components without preliminary mechanical activation, the energy released during thermal acceleration contributes to the formation of the brittle Laves phase TiFe_2 (9.6 vol.%) and a family of complex ternary intermetallic compounds of the Ti-Al-Fe system (totaling up to 16.1 vol.%). Preliminary solid-phase mechanosynthesis completely suppresses the formation of the brittle Laves phase and ternary intermetallic compounds; iron binds into the phases $\text{Fe}_2\text{Ti}_4\text{O}$ (7.2 vol.%) and FeO (2.6 vol.%), and the ordered phase Ti_3Al (24.7 vol.%) becomes the main intermetallic hardener.
- (3) The elimination of uncontrolled liquid-phase thermal runaway in the activated material prevents the formation of large pores in place of the original reagent particles. The residual porosity of the sample from mixture 2 decreases from the initial 26% to 5–8%, and the pores become small (2–10 μm), isolated in nature with rounded boundaries. At the same time, the non-activated sample from mixture 1 retains high porosity with macropores hundreds of microns in size.
- (4) Differences in phase composition and pore morphology determine the mechanical behavior of materials under compression. Due to the sequential collapse of the walls of macropores, the sample from mixture 1 is deformed stepwise and fails by the interparticle mechanism (by exfoliation along the particle boundaries) at a low stress level (17 MPa). A sample from mixture 2 deforms stably without load surges, undergoing transgranular cleavage with local plastic ridges of matrix shear, and demonstrates a compressive strength of about 100 MPa, which is almost six times higher than that of the non-activated analog.

Author Contributions: Conceptualization, E.N.K.; methodology, E.N.K.; formal analysis, A.I.D.; investigation, K.O.A.; data curation, K.O.A.; writing—original draft, E.N.K. and K.O.A.; writing—review and editing, A.I.D.; visualization, K.O.A.; supervision, A.I.D.; project administration, A.I.D. All authors have read and agreed to the published version of the manuscript.

Funding: The work was performed according to the Government research assignment for ISPMS SB RAS, project FWRW-2026-0009.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Saurabh, A.; Meghana, C.M.; Singh, P.K.; Verma, P.C. Titanium-based materials: Synthesis, properties, and applications. *Mater. Today Proc.* **2022**, *56*, 412–419. <https://doi.org/10.1016/j.matpr.2022.01.268>.
- Ammisetti, D.K.; Kruthiventi, S.S.H.; Vinjavarapu, S.; Babu, N.N.; Gandepudi, J.R.; Battula, S.K. A review on reinforcements, fabrication methods, and mechanical and wear properties of titanium metal matrix composites. *J. Eng. Appl. Sci.* **2024**, *71*, 60. <https://doi.org/10.1186/s44147-024-00392-z>.
- Falodun, O.E.; Obadele, B.A.; Oke, S.R.; Okoro, A.M.; Olubambi, P.A. Titanium-based matrix composites reinforced with particulate, microstructure, and mechanical properties using spark plasma sintering technique: A review. *Int. J. Adv. Manuf. Technol.* **2019**, *102*, 1689–1701. <https://doi.org/10.1007/s00170-018-03281-x>.
- Hayat, M.D.; Singh, H.; He, Z.; Cao, P. Titanium metal matrix composites: An overview. *Compos. Part A Appl. Sci. Manuf.* **2019**, *121*, 418–438. <https://doi.org/10.1016/j.compositesa.2019.04.005>.
- Abakay, E.; Armağan, M.; Yıldırım Avcu, Y.; Güney, M.; Yousif, B.F.; Avcu, E. Advances in improving tribological performance of titanium alloys and titanium matrix composites for biomedical applications: A critical review. *Front. Mater.* **2024**, *11*, 1452288. <https://doi.org/10.3389/fmats.2024.1452288>.
- Attar, H.; Ehtemam-Haghighi, S.; Soro, N.; Kent, D.; Dargusch, M.S. Additive manufacturing of low-cost porous titanium-based composites for biomedical applications: Advantages, challenges and opinion for future development. *J. Alloys Compd.* **2020**, *827*, 154263. <https://doi.org/10.1016/j.jallcom.2020.154263>.

7. Chen, X.; Xu, C.; Fang, L.; Xu, G.; Yang, L.; Tang, H.; Ouyang, Y.; Tao, X. Enhanced mechanical properties and oxidation resistance in Ti-rich medium entropy alloy via Al₂O₃ addition. *Vacuum* **2025**, *233*, 113928. <https://doi.org/10.1016/j.vacuum.2024.113928>.
8. Fang, J.; Tan, Y.C.; Tai, V.C.; Janasekaran, S.; Kee, C.C.; Wang, D.; Yang, Y. Selective laser melting of titanium matrix composites: An in-depth analysis of materials, microstructures, defects, and mechanical properties. *Heliyon* **2024**, *10*, e40200. <https://doi.org/10.1016/j.heliyon.2024.e40200>.
9. Traxel, K.D.; Bandyopadhyay, A. Influence of in situ ceramic reinforcement towards tailoring titanium matrix composites using laser-based additive manufacturing. *Addit. Manuf.* **2020**, *31*, 101004. <https://doi.org/10.1016/j.addma.2019.101004>.
10. Kaykilarli, C.; Uzunsoy, D.; Yeprem, H.A. Role of process control agent in the production of Al₂O₃-reinforced titanium matrix composites. *Ceram. Int.* **2024**, *50*, 16452–16462. <https://doi.org/10.1016/j.ceramint.2024.02.130>.
11. Luo, Y.-F.; Lu, R.-Y.; Wang, Y.; Liu, B.; Yang, H.-T.; Liu, Y. Interfacial reaction in Al₂O₃ fiber reinforced TiAl matrix composite. *Trans. Nonferrous Met. Soc. China* **2023**, *33*, 2054–2063. [https://doi.org/10.1016/S1003-6326\(23\)66234-X](https://doi.org/10.1016/S1003-6326(23)66234-X).
12. He, B.; Yan, Z.; Liu, T.; Wei, Z.; Yan, Q.; Chen, Z.; Pan, J.; Liu, Z.; Wang, J.; Chen, F. Preparation and characterization of highly catalytic and corrosion resistant Fe–Ti–O magnetorheological composite powders. *J. Mater. Res. Technol.* **2024**, *32*, 2063–2075. <https://doi.org/10.1016/j.jmrt.2024.08.073>.
13. Yeh, C.-L.; Ke, C.-Y. Combustion synthesis of FeAl–Al₂O₃ composites with TiB₂ and TiC additions via metallothermal reduction of Fe₂O₃ and TiO₂. *Trans. Nonferrous Met. Soc. China* **2020**, *30*, 2510–2517. [https://doi.org/10.1016/S1003-6326\(20\)65397-3](https://doi.org/10.1016/S1003-6326(20)65397-3).
14. Sharifitabar, M.; Vahdati Khaki, J.; Haddad Sabzevar, M. Formation mechanism of TiC–Al₂O₃–Fe₃Al composites during self-propagating high-temperature synthesis of TiO₂–Al–C–Fe system. *Ceram. Int.* **2016**, *42*, 12361–12370. <https://doi.org/10.1016/j.ceramint.2016.05.009>.
15. Mahmoodian, R.; Hassan, M.A.; Rahbari, R.G.; Yahya, R.; Hamdi, M. A novel fabrication method for TiC–Al₂O₃–Fe functional material under centrifugal acceleration. *Compos. Part B Eng.* **2013**, *50*, 187–192. <https://doi.org/10.1016/j.compositesb.2013.02.016>.
16. Manes, A.; Giglio, M. Microstructural numerical modeling of Al₂O₃/Ti composite. *Procedia Struct. Integr.* **2018**, *8*, 24–32. <https://doi.org/10.1016/j.prostr.2017.12.004>.
17. Li, X.X.; Zhang, H.M.; Cheng, X.W.; Mu, X.N.; Yang, L.Z.; Duan, H.Q. Superior mechanical property of Ti–Fe–O material via doping low content iron oxide in pure Ti. *Mater. Charact.* **2025**, *222*, 114819. <https://doi.org/10.1016/j.matchar.2025.114819>.
18. Cai, Z.; Zhang, D. Sintering behaviour and microstructures of Ti(Al,O)/Al₂O₃, Ti₃Al(O)/Al₂O₃ and TiAl(O)/Al₂O₃= in situ composites. *Mater. Sci. Eng. A* **2006**, *419*, 310–317. <https://doi.org/10.1016/j.msea.2006.01.030>.
19. Sousa, L.; Antunes, R.D.; Fernandes, J.C.; Alves, A.C.; Toptan, F. Influence of Al₂O₃= reinforcements and Ti–Al intermetallics on corrosion and tribocorrosion behavior of titanium. *Surf. Coat. Technol.* **2023**, *471*, 129835. <https://doi.org/10.1016/j.surf-coat.2023.129835>.
20. Zheng, Z.; Kong, F.; Wang, X.; Chen, Y. Microstructure evolution, mechanical properties and strengthening mechanism of titanium matrix composite sheets. *Mater. Sci. Eng. A* **2022**, *860*, 144256. <https://doi.org/10.1016/j.msea.2022.144256>.
21. Wang, R.; Bai, S.; Chen, X.; Xie, L.; Yu, Z.; Kang, Y.; Li, Y.; Hu, Y.; Shi, Z.; Yan, Z. Effect of titanium on the wettability between Fe–P–Ti alloy and Al₂O₃ substrate. *Prog. Nat. Sci. Mater. Int.* **2024**, *34*, 555–561. <https://doi.org/10.1016/j.pnsc.2024.05.003>.
22. Musa, C.; Licheri, R.; Locci, A.M.; Orru, R.; Cao, G.; Rodriguez, M.A.; Jaworska, L. Energy efficiency during conventional and novel sintering processes: The case of Ti–Al₂O₃–TiC composites. *J. Clean. Prod.* **2009**, *17*, 877–882. <https://doi.org/10.1016/j.jclepro.2009.01.012>.
23. Khoshhal, R.; Soltanieh, M.; Boutorabi, M.A. Formation mechanism and synthesis of Fe–TiC/Al₂O₃ composite by ilmenite, aluminum and graphite. *Int. J. Refract. Met. Hard Mater.* **2014**, *45*, 53–57. <https://doi.org/10.1016/j.jirmhm.2014.03.002>.
24. Rafiei, M.; Enayati, M.H.; Karimzadeh, F. Mechanochemical synthesis of (Fe,Ti)₃Al–Al₂O₃ nanocomposite. *J. Alloys Compd.* **2010**, *488*, 144–147. <https://doi.org/10.1016/j.jallcom.2009.09.007>.
25. Zhang, D.; Zhang, J.; Wu, Y.; Lu, T.; Wu, H.; Jia, B.; Qin, M.; Qu, X. Microstructure and magnetic properties of Fe–Al₂O₃ nanocomposites prepared by a versatile facile combustion-based route. *Ceram. Int.* **2025**, *51*, 4780–4785. <https://doi.org/10.1016/j.ceramint.2024.11.452>.
26. Tang, A.; Liu, S.; Pan, F. Novel approaches to produce Al₂O₃–TiC/TiCN–Fe composite powders directly from ilmenite. *Prog. Nat. Sci. Mater. Int.* **2013**, *23*, 501–507. <https://doi.org/10.1016/j.pnsc.2013.08.006>.
27. Zou, Z.; Wu, Y.; Yin, C.; Li, X. Preparation of Fe–Al intermetallic/TiC–Al₂O₃ ceramic composites from ilmenite by SHS. *J. Wuhan Univ. Technol.-Mat. Sci. Edit.* **2007**, *22*, 706–709. <https://doi.org/10.1007/s11595-006-4706-6>.
28. Khoshhal, R.; Soltanieh, M.; Boutorabi, M.A. The effect of Fe₂Al₃ as reducing agent in intermediate steps of Al₂O₃/TiC–Fe composite production process. *Int. J. Refract. Met. Hard Mater.* **2015**, *52*, 17–20. <https://doi.org/10.1016/j.jirmhm.2015.05.002>.

29. Khoshhal, R.; Soltanieh, M.; Boutorabi, M.A. Investigation on the reactions sequence between synthesized ilmenite and aluminum. *J. Alloys Compd.* **2015**, *628*, 113–120. <https://doi.org/10.1016/j.jallcom.2014.12.151>.
30. Korosteleva, E.N.; Knyazeva, A.G.; Nikolaev, I.O. Phase Formation in Reactive Sintering with Reduction. *Phys. Mesomech.* **2023**, *26*, 39–47. <https://doi.org/10.1134/S1029959923010058>.
31. Anisimova, M.A.; Knyazeva, A.G.; Korosteleva, E.N.; Nikolaev, I.O. Chemical Stresses at Composite Synthesis from Ti-Al-Fe-Fe₂O₃ Powder Mixture. *Bull. Russ. Acad. Sci. Phys.* **2025**, *89*, 2017–2024. <https://doi.org/10.1134/S1062873825712887>.
32. Rafiei, M.; Enayati, M.H.; Karimzadeh, F. Kinetic analysis of thermite reaction in Al–Ti–Fe₂O₃ system to produce (Fe,Ti)₃Al–Al₂O₃ nanocomposite. *Powder Technol.* **2014**, *253*, 553–560. <https://doi.org/10.1016/j.powtec.2013.12.028>.
33. De Gelder, R.; Wehrens, R.; Hageman, J.A. A generalized expression for the similarity of powder diffraction patterns. *J. Comput. Chem.* **2001**, *22*, 273–289. [https://doi.org/10.1002/1096-987X\(200102\)22:3<273::AID-JCC1001>3.0.CO;2-0](https://doi.org/10.1002/1096-987X(200102)22:3<273::AID-JCC1001>3.0.CO;2-0).
34. Smith, D.K.; Snyder, R.L. FN: A criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing. *J. Appl. Crystallogr.* **1979**, *12*, 60–65. <https://doi.org/10.1107/S002188987901178X>.
35. NIST-JANAF Thermochemical Tables. Available online: <https://janaf.nist.gov/> (accessed on 3 June 2026).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.