

Synchrotron *in situ* studies of mechanical activation treatment and γ -radiation impact on structural-phase transitions and high-temperature synthesis parameters during the formation of γ -(TiAl) compound

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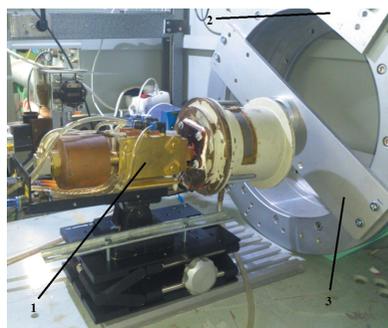
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In situ synchrotron studies of structure and phase formation dynamics in mechanically activated ($t = 7$ min, power density 40 g) and mechanically activated with subsequent irradiation by γ -quanta ^{60}Co powder mixture (Ti 64 wt% + Al) during high-temperature synthesis by the method of thermal explosion using induction heating are described. *In situ* high-temperature synthesis was carried out on the created experimental complex adapted for synchrotron X-ray diffraction methods. The sequence of formation and time-temperature interval of the metastable and main phases were determined. The impact of preliminary mechanical activation and of γ -irradiation on the macrokinetic parameters of the synthesis were studied experimentally *in situ*. It has been established that the impact of γ -irradiation on the mechanically activated powder mixture of the composition Ti 64 wt% + Al leads to a change in the thermal parameters of combustion: the maximum synthesis temperature and the burning rate decrease. The heating rate for the non-irradiated mixture is 204.8 K s^{-1} and that for the irradiated mixture is 81.6 K s^{-1} . The dependences of mass fractions of the synthesized compounds on time and temperature were calculated from the stage of preheating until completion of the thermal explosion. A single-phase equilibrium product of the composition γ -(TiAl) is formed in γ -irradiated mechanically activated mixture when the system reaches maximum temperature. The synthesized product of the mechanically activated mixture without γ -irradiation contains 72% γ -(TiAl); TiAl_3 (26%) and residual Ti (2%) are also observed.

1. Introduction

One of the most promising areas in the development of new metallic materials with a high level of heat resistance and thermal stability is the creation of intermetallic alloys of the Ti–Al system (Weimer & Kelly, 2008; Clemens & Kestler, 2000). These alloys can seriously compete with nickel-based superalloys, since titanium aluminides are lighter, have high corrosion resistance, resistance to high-temperature oxidation, high modulus of elasticity and strength, and do not require expensive and scarce elements for alloying. Obtaining single-phase compositions of titanium aluminides of various stoichiometry, including the method of high-temperature synth-



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esis (SHS), has been the subject of many research works (Lagos *et al.*, 2010; Novák *et al.*, 2009; Illeková *et al.*, 2008). However, the traditional SHS method allows only a strictly single-phase TiAl₃ compound to be obtained (Wang & Zhang, 2006). The strictly single-phase compound Ti₃Al (α_2 -phase) was synthesized using the microwave ultrafast heating method (Vaucher *et al.*, 2011) or the method of mechanically activated SHS (Filimonov *et al.*, 2014). An attempt to obtain a single-phase compound TiAl (γ -phase) using the mentioned methods was unsuccessful (Shi *et al.*, 2015). At the same time, out of all stable compounds this compound is the most practically significant both as refractory and heat-resistant (Appel & Oehring, 2003). Therefore, additional *in situ* experimental studies should be made to identify the peculiarities of the phase transformations in obtaining the γ -phase of TiAl, by the method of high-temperature synthesis.

Mechanical activation is one way of carrying out a targeted impact on a powder mixture, which allows an ideal contact between the reagents to be made and the reactivity of the mixture to be increased. However, such processes in solid phase materials have a number of important differences with processes in liquids or gases. These differences occur primarily due to the low diffusion rate in solids which prevents rapid levelling of the components' concentration in the system and obtaining of single-phase compounds. Thus, spatial localization of the processes occurs. A fast one-step dissolution and crystallization chemical reaction, as a rule, is observed in the composite precursors formed during the mechanical activation process (MA), where bulk mixing of reagents is achieved at the nanolevel with the formation of juvenile contact surfaces. Intermediate products formation occurs during many solid-phase reactions. These products then react with the starting components or with each other and give a final product of the reaction. Such solid-phase reactions are divided into several stages, each of them having a particular mechanism and kinetics. These reactions can be significantly affected by the size and shape of the reacting particles, the degree of their mixture homogeneity, the gas phase composition and temperature. The hierarchy of structural inhomogeneities has multiple phase boundaries and consequently chemical heterogeneity which leads to chemical transformations staging and multiphase product. It should be noted that mechanical activation is a method of hard impact on the powder mixture due to the high-energy effect of the planetary mill on the powder mixture. Indeed, the duration of mechanical treatment is measured in minutes, and the possibilities of structure management are very limited (Gras *et al.*, 2006). To implement a more accurate (sensitive) structure management method, γ -irradiation can be used. It has been found that in many cases γ -irradiation can serve as an effective technological tool that allows high-quality materials to be obtained, significantly improving and cheapening the production of many powder materials, improving their quality, and also changing the properties (Naundorf, 1992; Neklyudov & Voyevodin, 1994). It is important that radiation defects are formed on an even basis over the sample volume while being irradiated with fast electrons or ⁶⁰Co γ -quanta. The primary acts of radiation

damageability of the irradiated materials are connected to their electronic and atomic subsystems excitation, nuclear reactions and the displacement of the crystal lattice atoms from the initial equilibrium positions.

It is known that a substance turns into an amorphous state while reaching a certain critical concentration of defects, which can vary from ~5 to 20% of displaced atoms or vacancies in the total number of atoms. As the irradiation dose increases, the increase in the number of defects should occur gradually and uniformly in the whole volume of the sample. It can be assumed that the processes of radiation-stimulated diffusion contribute to the processes of dissolution and homogenization, and alter the areas of the phases homogeneity and solid solutions in the volume of the mechano-composite, creating favourable conditions for heterogeneous reaction at the interphase boundaries. Thus, the effect of γ -irradiation can be considered to be a subtle tool for changing the structural state of activated mixtures. It should be noted that γ -irradiation impact on the matrix structure of activated mixtures has not been studied well enough. It can be suggested that the preliminary impact on the powder materials of the Ti–Al system with the use of mechanical activation treatment followed by γ -irradiation will influence the processes of phase formation and the macrokinetic parameters of high-temperature synthesis (Sobachkin *et al.*, 2018a; Merzhanov & Abramov, 1981).

In order to obtain products with specified properties in the synthesis of mechanically activated and γ -irradiated systems, one should understand the fundamental formation processes of structural and phase transitions in dynamic conditions. This requires achieving reliable information about the phase composition of intermediate products and the sequence of stages through which final product formation takes place. It is possible to solve these problems with the help of a 'diffraction movie' – an *in situ* diffractometry synchrotron radiation method: diffraction field analysis (sequential shooting of a series of diffractograms) allows structural transformations in matter to be observed during the processes of deformation, melting, crystallization, synthesis, *etc.* (Mukasyan *et al.*, 2010; Liss *et al.*, 2009; Loginova *et al.*, 2019).

Based on the above, the purpose of this work is to study the impact of mechanical activation and γ -irradiation in the Ti + Al powder mixture on *in situ* structure formation, phase formation and macrokinetic parameters during high-temperature synthesis in the thermal explosion mode.

2. Experimental technique

Mechanical mixtures of aluminium and titanium powders in the ratio Ti (64 wt%) + Al were used as the objects of the study. Mechanoactivation treatment of the initial powder mixtures was carried out for 7 min, with the energy intensity of the mill being 40 g (Loginova *et al.*, 2015; Filimonov *et al.*, 2008). Then, mechanically activated powder mixtures were irradiated with γ -quanta in the certified stationary setup 'Researcher' (isotope ⁶⁰Co) under normal climatic conditions (Sobachkin *et al.*, 2018b; Loginova *et al.*, 2018a,b). The level of

γ -quanta exposure was characterized by the absorbed dose $D\gamma = 5 \times 10^4$ Gy.

The next stage included *in situ* studies of the phase formation dynamics of the mixtures obtained during the process of high-temperature synthesis which were carried out using the method of dynamic diffractometry in synchrotron radiation (SR) beams. Radiation from the electron storage ring VEPP-3 of the ‘Diffraction movie’ 5b station at the Budker Institute of Nuclear Physics of Siberian Branch Russian Academy of Sciences (Novosibirsk, Russia) was used. Continuous shooting of diffraction patterns was performed using monochromatic radiation at a wavelength of $\lambda = 1.505$ Å, in the scanning angle range 36–68°. The shot rate for the non-irradiated powder mixture was 1 s per shot, and for the γ -irradiated mixture (for a more detailed study) was 0.3 s per shot. High-temperature synthesis was carried out under identical conditions for each object of the study.

Registration of phase formation dynamics during the synthesis was carried out using an experimental complex on the basis of a microwave inductor (heating source), which was developed and adapted to the SR method. The powder mixture was poured into a graphite crucible which was quickly heated up by the inductor electromagnetic field. Temperature was controlled using a chromel–alumel thermocouple placed in the volume of the powder mixture. During the experiment, the inductor was disconnected when the maximum synthesis temperature was reached (Popova *et al.*, 2013; Sobachkin *et al.*, 2019). The inductor and crucible were placed in an evacuated vacuum chamber and then filled with argon. The complex was mounted in the installation unit of the SR 5b station of the VEPP-3 drive (Fig. 1) (Loginova *et al.*, 2019).

Heating was carried out using an inductor coil. The induction coil heated the graphite crucible, which in turn heated the powder mixture. Registration of the ‘diffraction film’ was activated at the moment of self-ignition.

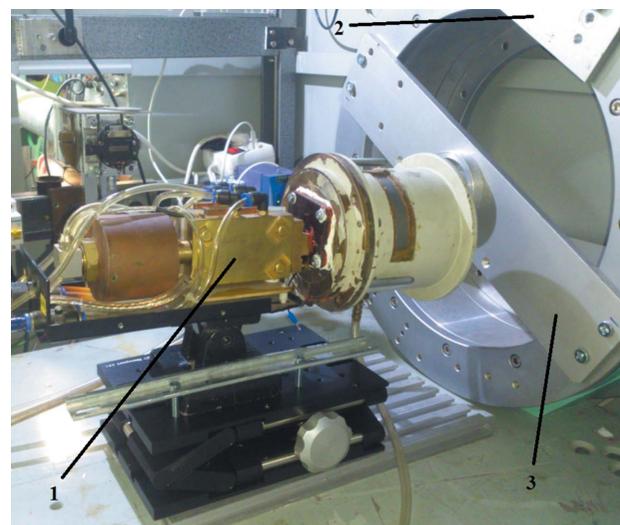
The stream of synchrotron radiation through the beryllium window falls on the surface of the reacting charge, and the diffracted radiation enters the detector. The experimental complex is equipped with a cooling system.

Phase and structural analysis of the *in situ* data were carried out using the *dqv2* program developed at Institute of Nuclear Physics of Siberian Branch Russian Academy of Sciences (Novosibirsk, Russia) especially for processing the ‘diffraction movie’ obtained by the SR method.

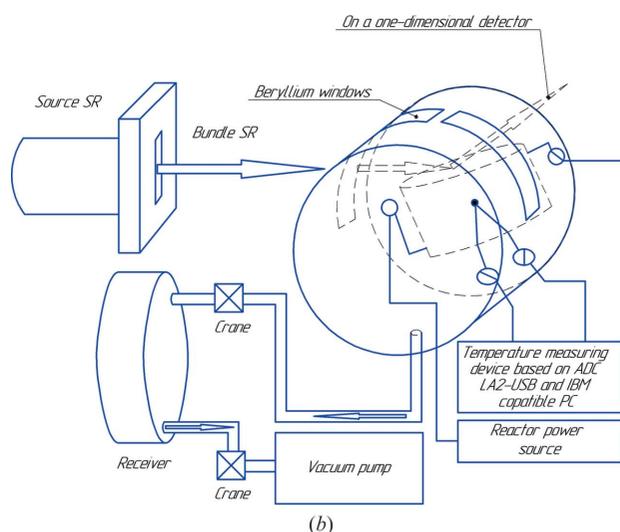
The percentage of the recorded phases was calculated by a semi-quantitative method using the ratio of the maximum peaks values in the diffractograms without taking into account the mass absorption coefficients of the phases (determination error is 1–3%).

3. Results of the experiment and discussion

Fig. 2 shows *in situ* thermograms of the high-temperature synthesis process for Ti + Al powder mixtures (mechanically activated unirradiated and mechanically activated following γ -irradiation).



(a)



(b)

Figure 1 Experimental complex for registration of the dynamics of phase formation during high-temperature synthesis in thermal explosion mode: (a) mounted installation (1: experimental complex; 2: detector; 3: goniometer); (b) schematic of the experimental setup.

Analysis of the thermograms shows that the thermal explosion temperature for the unirradiated powder mixture [the corresponding inflection point; Fig. 2(a)] is $T = 616^\circ\text{C}$; the maximum burning temperature is $T_{\text{max}} = 1287^\circ\text{C}$. The thermal explosion temperature for the γ -irradiated powder mixture is $T = 620^\circ\text{C}$; the maximum burning temperature is $T_{\text{max}} = 1173^\circ\text{C}$ [Fig. 2(b)]. Herewith, the interaction rate of the reactants for the γ -irradiated mixture decreases. The average rate of temperature increase for the non-irradiated mixture is 204.8 K s^{-1} and for the irradiated mixture is 81.6 K s^{-1} .

On the shown *in situ* thermograms of the high-temperature synthesis process (Fig. 2), two sections can be distinguished: section 1–2 is the heating stage of the powder mixture and section 2–3 is the thermal explosion stage (fast heating mode). Each section will be considered separately.

Figs. 3 and 4 show the ‘diffraction movie’ projections taken from section 1–2, heating the powder mixture.

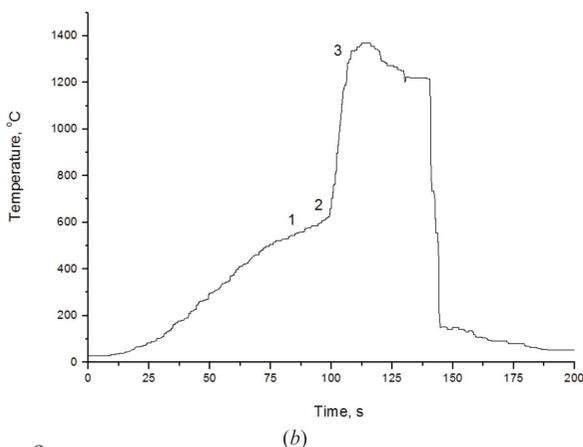
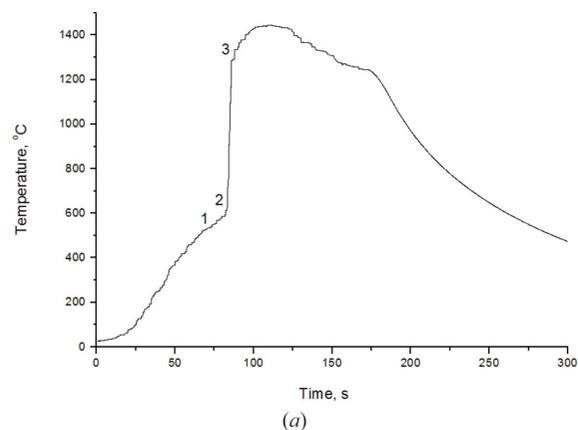


Figure 2
In situ thermograms of the high-temperature synthesis process of a Ti + Al powder mixture: (a) without γ -irradiation; (b) with γ -irradiation.

The first shot of the ‘diffraction movie’ for the mechanically activated powder mixture without irradiation (Fig. 3) was recorded at the heating temperature of the system, $T = 554.8^\circ\text{C}$, and the time from the beginning of heating the mixture was $t = 76$ s. The time from the beginning of heating the mixture to thermal explosion was $t = 82$ s. Seven shots of the ‘diffraction movie’ with a frequency of 1 s per shot were recorded in this section.

The first shot of the ‘diffraction movie’ for the mechanically activated and then γ -irradiated mixture (Fig. 4) was recorded at the system heating temperature of $T = 558.5^\circ\text{C}$, and the time from the beginning of heating the mixture was $t = 86.9$ s. The time from the beginning of heating the mixture to thermal explosion was $t = 98.6$ s. In section 1–2 of the powder mixture heating, 40 shots of the ‘diffraction movie’ were recorded *in situ* with a frequency of 0.3 s per frame.

The transition from the initial components to the synthesis products in both cases already occurred at the first stage (1–2) of heating the powder mixture. The main phases TiAl and TiAl₃, in both cases, had been formed before the systems reached maximum temperatures. However, there are some differences in the phase formation processes.

Besides the presence of the initial components and the formation of stable compounds TiAl, TiAl₃, Ti₃Al and TiAl₂, metastable short-lived compounds Ti₃Al₅, Ti₅Al₁₁ and Ti₉Al₂₃ were formed in the mechanically activated and γ -irradiated

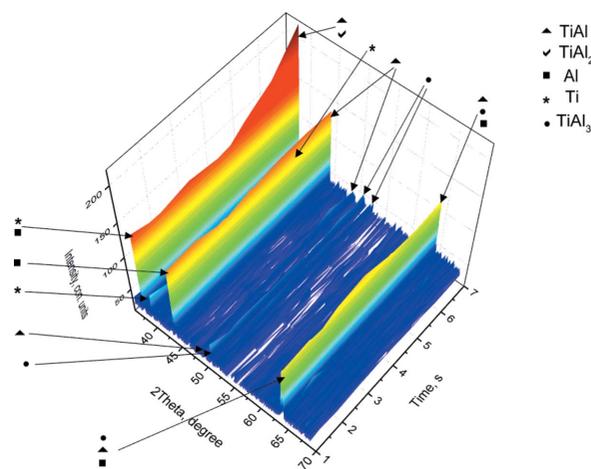


Figure 3
 ‘Diffraction movie’ projections in the section of heating 1–2 of the mechanically activated non-irradiated powder mixture Ti + Al [Fig. 2(a)].

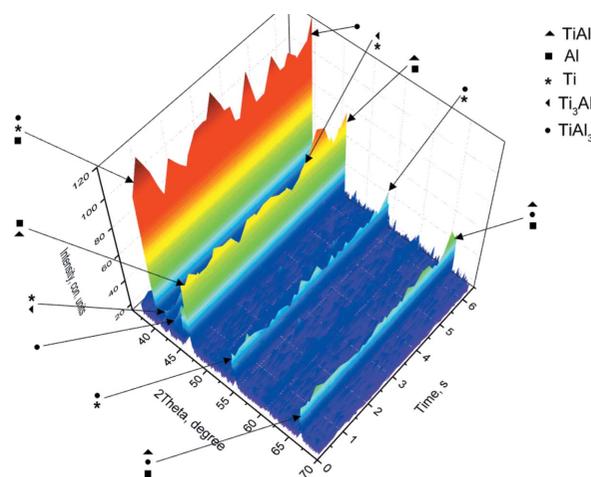


Figure 4
 ‘Diffraction movie’ projections in the section of heating 1–2 of the mechanically activated and γ -irradiated powder mixture Ti + Al [Fig. 2(b)].

powder mixture, in the heating stage (Fig. 4) (recorded from $T = 558^\circ\text{C}$). TiAl₃ became the main phase in the whole section starting from the temperature $T = 558^\circ\text{C}$.

A higher content of the initial components Ti and Al was observed in the mechanically activated powder mixture without γ -irradiation, in the heating section (Fig. 3) at $T = 555^\circ\text{C}$, compared with the previous experiment. TiAl, TiAl₃ and TiAl₂ were formed along with these compounds. The formation of the metastable phase Ti₅Al₁₁ also occurred. In both cases the formation of the reaction products had already occurred at the initial stage of heating to $T = 555$ – 558°C .

Fig. 5 shows the ‘diffraction movie’ projection of a mechanically activated powder mixture, taken from section 2–3 of the thermal explosion.

The thermal explosion stage for the MA mixture begins with a particular breakpoint at $T = 616^\circ\text{C}$ ($t = 83$ s) [Fig. 2(a)]. A sudden increase in temperature was registered from shot 8. The temperature at the end of the high-temperature synthesis reaction [point 3 in the thermogram, Fig. 2(a)] is $T = 1334^\circ\text{C}$

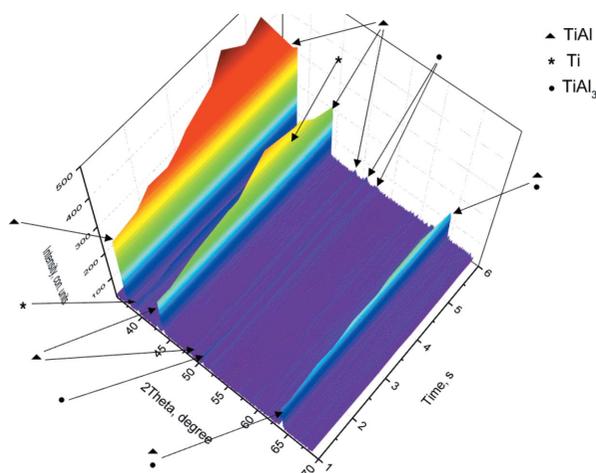


Figure 5
'Diffraction movie' projections in the thermal explosion section 2–3 of the mechanically activated non-irradiated powder mixture of Ti + Al [Fig. 2(a)].

($t = 88$ s); the reaction duration is 6 s. The end of the reaction corresponds to the 13th shot of the 'diffraction movie'. Six shots of the 'diffraction movie' were recorded *in situ* with a frequency of 1 s per shot in section 2–3.

Single peaks of TiAl (111) and TiAl₃ (202), recorded at section 2–3 starting from $T = 586.9^\circ\text{C}$, $t = 81$ s (Fig. 6), were used for analysis of the dependence of the interplanar spacing on temperature for the MA mixture at the stage of thermal explosion.

A decrease in interplanar spacing for TiAl (111) has been observed with an increase in temperature. At $T = 756.5^\circ\text{C}$, $t = 84$ s, the interplanar spacing $d = 2.3266$ Å; at $T = 1334^\circ\text{C}$, $t = 88$ s, and $d = 2.3160$ Å [standard TiAl (111), $d = 2.31$ Å, Card 5-678, J. Met., Duwez, Taylor, 4, 70, 1952; International database of powder diffractometry PDWin 3.0]. The interplanar spacing for TiAl₃ (202) increases during the reaction with $d = 1.7556$ Å at $T = 756.5^\circ\text{C}$, $t = 84$ s, up to $d = 1.7596$ Å

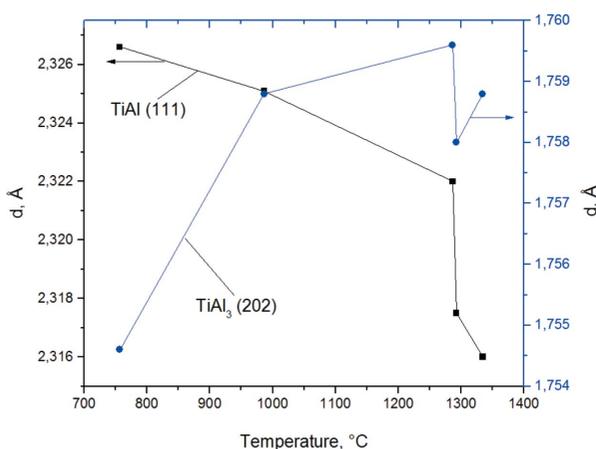


Figure 6
In situ variation of the interplanar spacing in the TiAl (111) and TiAl₃ (202) planes with an increase in temperature during the high-temperature synthesis at the stage of chemical transformations (thermogram section 2–3) according to the SR 'diffraction movie' [for the unirradiated mixture, Fig. 2(a), Fig. 5].

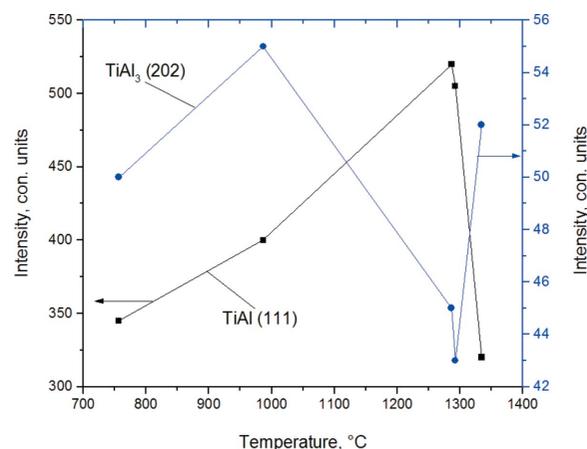


Figure 7
In situ intensity variation of the main reflections of TiAl (111) and TiAl₃ (202) with an increase of temperature during high-temperature synthesis at the stage of chemical transformations (thermogram section 2–3) according to the SR 'diffraction movie' [for the unirradiated mixture, Fig. 2(a), Fig. 5].

at $T = 1286.5^\circ\text{C}$, $t = 86$ s [standard TiAl₃ (202), $d = 1.75$ Å, Card 2-1121, Z. Anorg. Chem., Brauer, 242, 4, 1939; International database of powder diffractometry PDWin 3.0]. Then a non-monotonic decrease in the interplanar spacing for TiAl₃ (202) occurs.

Fig. 7 shows the *in situ* dependences in the intensity variation of the diffraction maxima of the main phases TiAl and TiAl₃ in section 2–3 with temperature. Reflections corresponding to TiAl (111) and TiAl₃ (202) were taken as information reflections.

In the area of the thermal explosion (section 2–3), an increase in the intensity of TiAl (111) occurs, which, at $T = 1286$ – 1292°C and $t = 86$ – 87 s, reaches $I_{\text{max}} = 520$ conventional (conv.) units, which indicates an increase in the volume fraction of the intermetallic compound TiAl. The intensity of TiAl₃ (202) has a small value ($I_{\text{med}} = 50$ conv. units) and remains constant throughout the entire section 2–3. The dependences presented in Fig. 8 show that the half-width

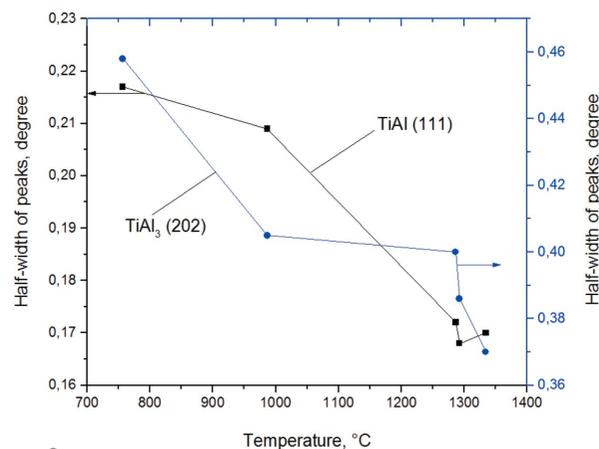


Figure 8
In situ variation of the half-width main reflections of TiAl (111) and TiAl₃ (202) with temperature during high-temperature synthesis at the stage of chemical transformations (section 2–3 of the thermogram) according to the SR 'diffraction movie' [for unirradiated mixture, Fig. 2(a), Fig. 5].

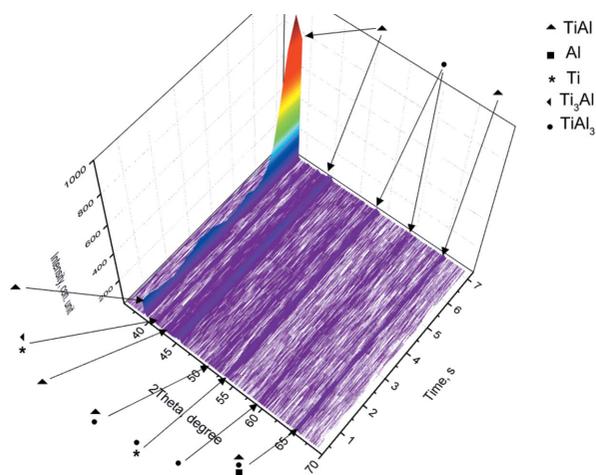


Figure 9
‘Diffraction movie’ projections at section 2–3 of the thermal explosion for a γ -irradiated powder mixture of Ti + Al during high-temperature synthesis [Fig. 2(b)].

of the peak TiAl (111) decreases with time during the thermal explosion.

With regard to compound TiAl₃ (202), the peak half-width is twice as large as that of TiAl (111) (from 0.46°, at the moment of thermal explosion, up to 0.37°, towards its completion).

Fig. 9 shows the ‘diffraction movie’ projection of a mechanically activated and γ -irradiated powder mixture, recorded in the thermal explosion section 2–3.

For the mechanically activated and then γ -irradiated mixture, the thermal explosion stage begins with a particular break point at $T = 620^\circ\text{C}$ ($t = 98.6$ s) [Fig. 2(b)]. The implementation of the high-temperature synthesis process takes place in this section. A sharp increase in temperature begins from shot 41 (when the system heating starts at $t = 98.9$ s). The temperature at the end of the reaction [corresponding to point 3 in the thermogram, Fig. 2(b)] is 1190°C ($t = 106.1$ s), and the reaction time is 7.5 ± 0.3 s. The end of the reaction is shot 65 of the ‘diffraction movie’. Twenty-five frames of the ‘diffraction movie’ were recorded *in situ* with a frequency of 0.3 s per frame in section 2–3.

In the thermal explosion section, the main phase composition for the mechanically activated and then γ -irradiated mixture starting at $T = 620^\circ\text{C}$ [Fig. 2(b)] is TiAl, TiAl₃, Ti and Ti₃Al. Then, due to a sharp increase in temperature, the content of TiAl increases and its structure stabilizes. A small amount of phase TiAl₃ is detected when the temperature reaches 1172.5°C (Fig. 9).

It should be noted that the main phase composition for the mechanically activated mixture without γ -irradiation powder in this section is TiAl, TiAl₃ and residual Ti. The phase composition remains stable at the maximum temperature. The content of TiAl increases, but becomes less in contrast to the previous experiment. The quantitative phase analysis is shown later in Figs. 13 and 14.

In situ, one can trace the interplanar spacing variation of the main phases with temperature in the thermal explosion section

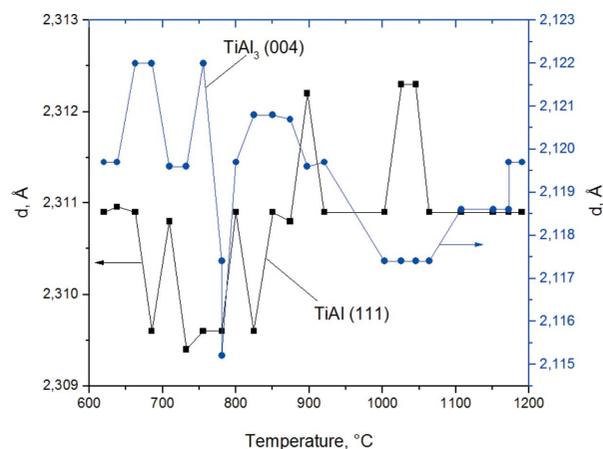


Figure 10
In situ interplanar spacing variation of the TiAl (111) and TiAl₃ (004) cells with temperature during high-temperature synthesis at the thermal explosion stage (section 2–3 of the thermogram) according to the SR ‘diffraction movie’ [for γ -irradiated mixture, Fig. 2(b), Fig. 9].

for reflections TiAl (111) and TiAl₃ (004) (Fig. 10). For analysis, we selected the strongest reflections of these phases recorded in this area. The nonmonotonic change in the interplanar spacing for TiAl (111) and TiAl₃ (004) occurs with an increase in temperature. Thus, for TiAl₃ (004) at temperature $T = 790^\circ\text{C}$ there is a minimum interplanar spacing $d = 2.115$ Å in this section; maximum $d = 2.122$ Å corresponds to $T = 690\text{--}720^\circ\text{C}$ [standard TiAl₃ (004), $d = 2.14$ Å, Card 2-1121, Z. Anorg Chem., Brauer, 242, 4, 1939; International database of powder diffractometry PDWin 3.0]. At the temperature $T = 1063.8^\circ\text{C}$ for TiAl (111) the interplanar spacing stabilizes and remains stable until the end of the explosion: $d = 2.3109$ Å [standard TiAl (111), $d = 2.31$ Å, Card 5-678, J. Met., Duwez, Taylor, 4, 70, 1952; International database of powder diffractometry PDWin 3.0].

Fig. 11 shows the *in situ* variation dependences in the diffraction maxima intensity of the main phases of TiAl and TiAl₃ in section 2–3 with temperature. The most intense

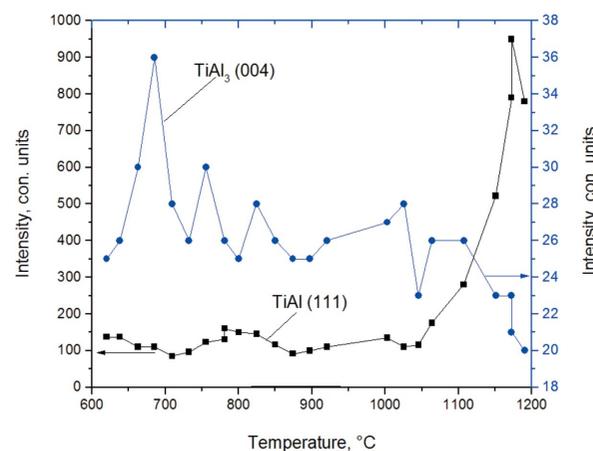


Figure 11
In situ variation in the main reflections intensity of TiAl (111) and TiAl₃ (004) with temperature during the high-temperature synthesis at the thermal explosion stage (section 2–3 in the thermograms) according to the SR ‘diffraction movie’ [for γ -irradiated mixture, Fig. 2(b), Fig. 9].

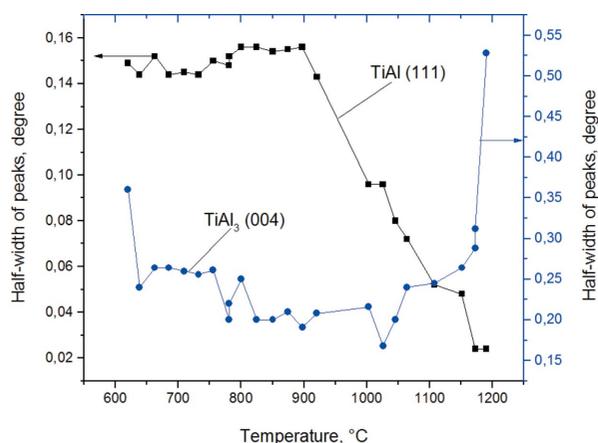


Figure 12

In situ variation of the main reflections half-width of TiAl (111) and TiAl₃ (004) with temperature during high-temperature synthesis at the stage of chemical transformations (section 2–3 of the thermograms) according to the SR ‘diffraction movie’ [for γ -irradiated mixture, Fig. 2(b), Fig. 9].

reflections in the diffractograms corresponding to TiAl (111) and TiAl₃ (004) were taken as information reflections.

The analysis of the dependences shows that the intensity of second phase TiAl₃ (004) has a small value ($I_{\max} = 22\text{--}28$ conv. units) and remains constant throughout the entire section 2–3. For TiAl (111) with an increase in the heating rate and an output to a thermal explosion, the intensity value increases rapidly from $I_{\max} = 100$ conv. units at $T = 1025^\circ\text{C}$ and $t = 103.4$ s to $I_{\max} = 950$ conv. units at $T = 1172^\circ\text{C}$ and $t = 105.2$ s.

Fig. 12 shows *in situ* dependences on temperature of the half-widths of peaks of diffraction maxima of the main phases TiAl (111) and TiAl₃ (004) in section 2–3. By the end of the thermal explosion the TiAl (111) half-width decreases sharply (from 0.15° to 0.024°). The structure of the phase TiAl₃ (004) is disordered, and the half-width increases (from 0.36° to 0.53°).

Figs. 13 and 14 show a quantitative picture of the *in situ* recorded phases percentage. The mass fractions of the observed phases have been calculated from the moment of the beginning of shooting up to the end of the thermal explosion. The formation of products, in both cases, begins already at the stage of heating the mixture; the initial components of Ti and Al are also present. At the warm-up stage TiAl₃ (32–40%) dominates in terms of percentage in the mechanically activated and then γ -irradiated powder mixture (Fig. 13); the content of TiAl increases from 14% to 25% with the temperature rise. The percentage of other phases is less than 20%. The original components of Ti and Al disappear when a thermal explosion starts in the system. The Al content at the beginning of shooting was about 21%, and for Ti about 25%. The content of metastable phases is less than 5%.

In the thermal explosion section, the TiAl content increases rapidly with a sharp increase in temperature; the amount of TiAl reaches 92% at the system maximum temperature. The rest is occupied by TiAl₃. In contrast to the previous experiment (Fig. 13), the content of the initial components in the mechanically activated mixture (Fig. 14) in the initial part of the heating exceeded the content of the formed compounds, e.g. Ti was about 27–28% and Al was about 26%. The content

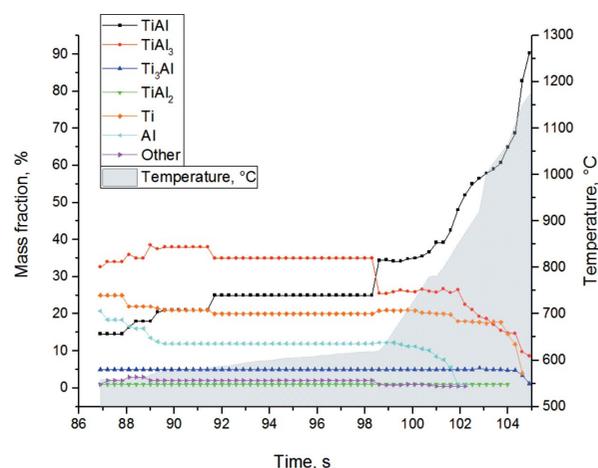


Figure 13

Mass fractions dependences of the *in situ* recorded phases on time and temperature at the stage of heating the γ -irradiated powder mixture (1–2) up to the end of the thermal explosion (2–3).

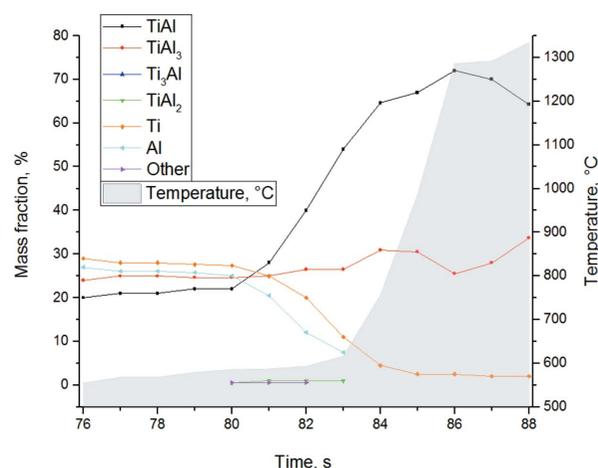


Figure 14

Mass fractions dependences of the *in situ* recorded phases on time and temperature at the stage of heating the mechanically activated non-irradiated powder mixture (1–2) up to the end of the thermal explosion (2–3).

of TiAl at the stage of heating is about 20%, and for TiAl₃ is 25%. When the system reaches thermal explosion, the TiAl content increases dramatically; at the time of the end of the thermal explosion, the TiAl content reaches 72%. At the same time, TiAl₃ remain at 26% and Ti at 2%.

The experimental data analysis shows that the rearrangements of the obtained *in situ* diffraction patterns of the unirradiated and γ -irradiated mechanically activated powder mixtures reflect a complex process of structural phase transformations at all stages of high-temperature synthesis. It should be noted that the results of previous experiments (Loginova *et al.*, 2018a,c) showed that preliminary γ -irradiation leads to partial annealing of defects, while the nanoscale scale of crystallites is preserved. Presumably, radiation-stimulated diffusion leads to the intensification of diffusion processes, the formation of transition zones at the contact boundary of reactants, and thus the creation of favourable

conditions for accelerating mutual solid-phase diffusion at the interphase boundaries.

It is likely that, due to these effects, the rate of heating and maximum temperature of the irradiated sample decrease. The main difference in phase formation is the fact that the γ -irradiated sample is characterized by the presence of α_2 -phase (Ti_3Al), which possibly determines a different direction in the development of synthesis processes. It can be assumed that the presence of the Ti_3Al compound in the irradiated sample is associated with the formation of an extended diffusion zone in the contact area of the reactants upon irradiation. The latter may contribute to the formation of the wider range of compounds in the synthesis process (in accordance with the equilibrium diagram). With the disappearance of the α_2 -phase, the reaction product contains two phases, with the dominant content of the TiAl compound. The narrow diffraction peaks of γ -(TiAl) at the diffractograms of the irradiated mixture indicate that the composition has become homogenized despite the complexity of the reaction.

4. Conclusion

The following conclusions have been made on the basis of *in situ* experimental studies and processed results:

(1) An additional preliminary impact of γ -irradiation on mechanically activated $\text{Ti} + \text{Al}$ powder mixture leads to a change in the thermal parameters of combustion: the maximum synthesis temperature and the burning rate decrease. For an unirradiated mixture $T_{\text{max}} = 1287^\circ\text{C}$; for an irradiated mixture $T_{\text{max}} = 1173^\circ\text{C}$. The characteristic heating rate for an unirradiated mixture is 204.8 K s^{-1} , and for an irradiated mixture is 81.6 K s^{-1} .

(2) The ‘diffraction movie’ projections show that in both cases the formation of products occurs at the initial stage of heating the system before the start of thermal explosion. During high-temperature synthesis of both powder mixtures, the formation of both stable TiAl , TiAl_3 , TiAl_2 and metastable Ti_3Al_5 , $\text{Ti}_5\text{Al}_{11}$, $\text{Ti}_9\text{Al}_{23}$ phases is observed by the start of shooting at the temperature $T = 555\text{--}558^\circ\text{C}$. A specific feature of the phase formation process in a γ -irradiated sample is the existence of the α_2 -phase (Ti_3Al), which is not seen in the unirradiated sample.

(3) A nearly single phase equilibrium product γ -(TiAl) containing TiAl (92%) and TiAl_3 (8%) is synthesized after γ -irradiation of the mechanically activated mixture. In the unirradiated mechanically activated mixture the content of TiAl in the synthesized product is 72%; the existence of TiAl_3 (26%) and residual Ti (2%) is recorded.

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