Features of high-temperature synthesis in mechanoactivated gamma-irradiated mixtures of triple systems Ti-Al-C and Ti-Al-Nb

A V Sobachkin¹, A Yu Myasnikov¹, A A Sitnikov¹, M V Loginova¹, V I Yakovlev¹ and A V Gradoboev²

¹ Polzunov Altai State Technical University, 46, Lenin ave., Barnaul, 656038, Russia
² National Research Tomsk Polytechnic University, 30, Lenin ave., Tomsk, 634050, Russia

E-mail: anicpt@rambler.ru

Abstract. Effects of gamma-irradiation on the process of SHS of mechanoactivated mixtures Ti-Al-C and Ti-Al-Nb were studied. Mechanical activation was performed for 7 minutes in planetary ball mill at energy intensity 40 g. SHS was initiated by induction heating with varying time of annealing. Gamma-irradiation was performed on ⁶⁰Co isotope to absorbed dose 3·10⁵ Gy. Structural parameters of cells of components were calculated. Gamma-irradiation affects components of triple systems in different ways, leading to unsystematic changes in elementary cells. After SHS in powder mixture 80% Ti + 12% Al + 8% C without gamma-irradiation, it was found that product contains Ti₂AlC, Ti₃AlC₂, TiC and unreacted C. Irradiated mixture react fully – diffractogram identifies Ti₂AlC, Ti₃AlC₂ and TiC. Annealing for 2 minutes produces a product with dominant Ti₂AlC. SHS in mixture 45% Ti + 12% Al + 43% Nb revealed that product consists of Ti₃AlNb, B2-phase, α₂-phase and residual Nb and Ti. During synthesis in irradiated mixture without annealing, diffractograms show decrease in level of diffuse background and increase in values of reflection intensities, structural state of products is stabilized. Effect of gamma-irradiation contributes to growth of phases and stabilization of structure synthesized product.

1. Introduction

The development of titanium-based powder materials is an urgent task for space, aviation, automotive and energy industries. Titanium aluminides are heat-resistant, have a high elastic modulus and have a low density [1, 2]. To improve the properties of titanium aluminides, they are doped with Hf, Mo, Nb, Ta, V, W, C and some other elements. For example, addition of niobium to Ti-Al system makes it possible to obtain hydride-forming material Ti₂AlNb, which can be used in alternative energy as a hydrogen storage material [3, 4]. If carbon is used as an additive, MAX-phases Ti₂AlC and Ti₃AlC₂ can be synthesized, which combine advantages of intermetallic and ceramic [5, 6].

One of the ways to obtain new materials using combustion processes is the method of self-propagating high-temperature synthesis (SHS) in thermal explosion mode [7-10]. The main advantages of SHS technologies include: simplicity of equipment, low energy consumption and short duration of synthesis process. SHS is based on exothermic chemical reaction of initial reagents in the form of combustion, where the target product of combustion is solid chemical compounds (carbides, nitrides, borides, oxides, etc.) and materials based on them.

There are known publications that studied effect of gamma-irradiation on mechanocomposites Ti-Al binary system [11-13], but the question of the effect of gamma-quanta on powder composite mixtures of triple systems is practically unexplored.

2. Materials and methods

The object of study was titanium, aluminum, niobium and carbon powders. Mixtures of the following compositions were prepared from them in the ratio by weight %:
1) 80% Ti + 12% Al + 8% C;
2) 45% Ti + 12% Al + 43% Nb.

For mechanical activation processing a planetary ball mill AGO-2 was used. The ratio of mass of initial powder mixture to the mass of grinding media was 1: 20. The grinding modes are selected as follows: centrifugal acceleration – 40 g, mechanical activation time – 7 minutes.

To protect against oxidation, air was pumped out of the cylinders, then they were filled with argon at a pressure of 0.3 MPa. After mechanical activation, powders were extracted from cylinders in a special box in argon atmosphere.

To implement high-temperature synthesis, the installation shown in figure 1 was used.

Powder mixture 1 was poured into cylindrical graphite crucible 2. Temperature control was carried out using chromel-aluminum thermocouples 4. Microwave heating of crucible was carried out by induction coil 3. Signal from thermocouples was fed to computer via analog-to-digital converter. The system was located under a vacuum cap 5. To prevent interaction with oxygen, the volume under the hood was continuously purged with argon. The advantages of this method include: first, possibility of rapid heating of mixture to high temperatures; second, possibility of prolonged exposure of system at high temperatures immediately after synthesis (high-temperature annealing); and third, possibility of rapid cooling of mixture to room temperatures. Thus, there is a possibility of a continuous transition from rapid reaction process to high-temperature annealing process, followed by rapid cooling, which provides a controlled thermal effect on powder mixture.

Structural-phase analysis of the samples was performed on diffractometer DRON-6 with CuKα-radiation (λ = 15.418 nm). Diffractograms of all samples were recorded under identical conditions, which made it possible to compare obtained values more correctly. Scan step h = 0.05°, exposure time t = 3 seconds, shooting angle range 2Theta = 20°…80°. The analysis of diffraction peak shapes, as well as calculation of second moments and intervals for their determination, were performed using preprocessing program PDWin. The intensities were adjusted for Lorentz factor and polarization factor. The unit cell parameters were refined using standard least squares method using PDWin software package. The broadening of diffraction lines of all samples was calculated with an adjustment for instrumental broadening, using experimental data from reference material, as well as the broadening calculated for main instrumental aberrations (goniometer parameters and linear absorption coefficient of sample were set).

Experimental studies on irradiation of mechanoactivated mixtures were carried out on a certified stationary installation «Explorer» (isotope 60Co) (Tomsk) under normal climatic conditions. The dose rate of gamma radiation in this case was 1 Gy/s. The level of exposure to gamma-quanta was characterized by absorbed doses, which were 3·10⁴ Gy.

3. Results and discussion

Figure 2 shows radiographs of the composite mixture after mechanical activation (bottom) and after mechanical activation with additional exposure to gamma-quanta with accumulated dose of 3·10⁴ Gy (top).
Analyzing the appearance of diffractograms, we can say that after gamma irradiation, intensity values of diffraction maxima for both systems remain at the same level. Broadened diffraction reflections indirectly indicate the preservation of nanostructural state of crystallites and presence of residual micro-deformations that occurred during mechanical activation.

The structural parameters of cells of components of both systems were calculated from obtained radiographs. The calculated values are summarized in tables 1-4.

**Table 1. Structural parameters of titanium**

| cell parameters (nm) | after MA | after MA and gamma irradiation | Ti Reference |
|----------------------|---------|-------------------------------|--------------|
| system Ti-Al-C       |         |                               |              |
| a                    | 29.56   | 29.55                         | 29.5         |
| c                    | 46.84   | 46.91                         | 46.83        |
| system Ti-Al-Nb      |         |                               |              |
| a                    | 29.3    | 29.4                          | 29.5         |
| c                    | 47.2    | 46.8                          | 46.83        |

**Table 2. Structural parameters of aluminum**

| cell parameters (nm) | after MA | after MA and gamma irradiation | Al Reference |
|----------------------|---------|-------------------------------|--------------|
| system Ti-Al-C       |         |                               |              |
| a                    | 40.47   | 40.49                         | 40.41        |
| system Ti-Al-Nb      |         |                               |              |
| a                    | 40.3    | 40.4                          | 40.41        |

**Table 3. Structural parameters of niobium**

| cell parameters (nm) | after MA | after MA and gamma irradiation | Nb Reference |
|----------------------|---------|-------------------------------|--------------|
| a                    | 33.1    | 33.0                          | 33.0         |

**Table 4. Structural parameters of carbon**

| cell parameters (nm) | after MA | after MA and gamma irradiation | C Reference |
|----------------------|---------|-------------------------------|--------------|
| a                    | 24.5    | 24.54                         | 24.56        |
| c                    | 67.55   | 67.18                         | 66.96        |

At the next stage, it was carried out high-temperature synthesis in mechanoactivated and mechanoactivated irradiated mixtures of specified compositions of Ti-Al-C and Ti-Al-Nb systems. During experiment, synthesis modes were varied. Synthesis was performed with the source switched off when the system reached maximum temperature and with isothermal annealing ($\tau = 2$ min.)

Figure 3 shows the results of determining phase composition of SHS materials in Ti-Al-C system.
Figure 3. Diffractograms of synthesis products after thermal explosion in mechanoactivated mixture of 80% Ti + 12% Al + 8% C: (a) mixture without irradiation, (b) mixture with accumulated dose of $3 \cdot 10^4$ Gy.

X-ray phase analysis of sample, synthesized from mechanically activated non-irradiated mixture of Ti-Al-C system without additional annealing ($\tau = 0$ min), showed that reaction products contain several phases: MAX-phases Ti$_2$AlC and Ti$_3$AlC$_2$, titanium carbide TiC and unreacted carbon C. If the system is held for $\tau = 2$ min annealing immediately after reaction is completed, phase composition of SHS sample is preserved. However, the system is in non-equilibrium state – amplitude and intensity of diffraction reflections change, and diffusion background increases.

When SHS is implemented in mechanoactivated and irradiated Ti-Al-C mixture (figure 3, b), MAX-phases Ti$_2$AlC and Ti$_3$AlC$_2$, and titanium carbide TiC are observed on diffractograms. There are no unreacted components. However, the system is still in non-equilibrium state – diffraction maxima are broadened, and their intensity is at the same level as in experiment on synthesis of a mixture without irradiation. However, when the system is kept for additional annealing for $\tau = 2$ min, intensity values increase, and phase composition of the product is characterized by dominant Ti$_2$AlC phase.

Figure 4 shows the results of study of phase compositions of products obtained by high-temperature synthesis of Ti-Al-Nb powder mixtures.

According to results of X-ray phase analysis after synthesis of mechanically activated non-irradiated mixtures Ti-Al-Nb without additional annealing ($\tau = 0$ min) the reaction products contain several phases: O-phase (Ti$_2$AlNb), $\beta_0$(B2)-phase and small content of $\alpha_2$-phase (Ti$_3$Al). Reflections of residual niobium and titanium are also recorded. When exothermic annealing is performed for $\tau = 2$ min. after chemical reaction is completed, phase composition is preserved, but new additional reflections corresponding to the O-phase appear. However, there is a decrease in intensity of diffraction maxima, their broadening and an increase in level of diffuse background. This may indirectly indicate that holding system for 2 minutes leads to thermal vibrations of atoms, which reduces amplitude and intensity of peaks with transition of the system to non-equilibrium state.

Figure 4. Diffractograms of synthesis products after thermal explosion in mechanoactivated mixture
of 45% Ti + 12% Al + 43% Nb: (a) mixture without irradiation, (b) mixture with accumulated dose of $3 \cdot 10^4$ Gy.

After SHS without subsequent annealing in mechanoactivated and gamma-irradiated powder mixture Ti-Al-Nb system, final product is multiphase (figure 4, b): O-phase (Ti$_2$AlNb), $\beta_0$(B2)-phase and small content of $\alpha_2$-phase (Ti$_3$Al). Reflections of residual niobium and titanium are also recorded, which is identical to experiment without gamma-irradiation. However, diffraction patterns show decrease in level of diffuse background and increase in values of reflection intensities (compared to synthesis without gamma-irradiation) by almost two times. Thus, preliminary effect of gamma-irradiation on powder mixture contributes to growth of phases and stabilization of structure of synthesized product [14, 15]. Further exposure of system for additional annealing ($\tau = 2$ min.) leads to transition of system to non-equilibrium state.

4. Conclusion

1. After SHS in powder mixture 80% Ti + 12% Al + 8% C without gamma irradiation, it was found that reaction product contains MAX-phases Ti$_2$AlC and Ti$_3$AlC$_2$, titanium carbide TiC and unreacted C. When system is annealed for 2 minutes, system transitions to non-equilibrium state. In case of synthesis of irradiated mixture, components react fully – diffractogram identifies reflections of Ti$_2$AlC, Ti$_3$AlC$_2$ and TiC. Annealing for 2 minutes allows obtaining a product with dominant Ti$_2$AlC phase.

2. After high-temperature synthesis in powder mixture 45% Ti + 12% Al + 43% Nb without gamma-irradiation, it was found that O-phase (Ti$_2$AlNb), $\beta_0$(B2)-phase, $\alpha_2$-phase (Ti$_3$Al) and reflections of residual niobium and titanium are fixed in final product. When annealing time is increased to $\tau = 2$ min. the number of O-phase reflections increases, and system goes into non-equilibrium state. When synthesized in an irradiated mixture without annealing, structural state of products is stabilized. Diffraction patterns of final product show low level of diffuse background and increase in intensity of main diffraction reflections, compared to synthesis product of non-irradiated mixture. Exposure for additional annealing ($\tau = 2$ min.) leads to transition of system to non-equilibrium state.

3. Gamma-irradiation affects the components of powder mixture of triple systems in different ways, leading to unsystematic changes in elementary cells. This is due to both different quantitative content of components in initial mixture and structure of activated mixture, which depends on degree of plasticity of components. Also, preliminary effect of gamma irradiation on powder mixture contributes to growth of phases and stabilization of structure of synthesized product.

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