Thermal Explosion in a 2Co–Ti–Al System:  
Combustion, Phase Formation, and Properties

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Abstract: Combustion and the formation of structures and phases in a 2Co–Ti–Al system during self-propagating high-temperature synthesis in a thermal explosion are under study. It is determined that a single-phase product (a Co$_2$TiAl Geissler compound) can be obtained in this system. Morphology, microstructure, and physical-magnetic properties of combustion products of the system are investigated.

Keywords: intermetallic compounds, thermal explosion, Co$_2$TiAl Heusler phase.

INTRODUCTION

Aside from Ni–Al and Ti–Al systems practically significant for developing structural materials [1, 2], compounds based on ternary intermetallic systems belonging to so-called semimetallic ferromagnetic materials are currently actively studied [3]. These compounds are interesting because of their unique physical properties, such as extreme magnetoresistance, the Hall effect, ferro-, antiferro-, and ferrimagnetism, as well as semiconductor properties, etc. Investigating the properties of such materials and their functional dependence on the chemical composition and structure of the corresponding compound is a promising task for modern electronics. One of such materials is a Heusler alloy, which is a ternary intermetallic compound with a general formula X$_2$YZ, where X and Y are transition metals and Z denotes the elements of groups III and IV [4]. Heusler alloys exhibit shape memory [5], superelasticity, and magnetooptical [6] and magnetocaloric properties [7], and it is also possible to control these effects using a magnetic field. One of the promising compounds based on a Co–Ti–Al ternary intermetallic system is a Heusler alloy Co$_2$TiAl [8]. The first description of a Al–Co–Ti system is given in [9], in which alloys are prepared by melting titanium iodide, cobalt, and aluminum in a helium medium in an arc furnace with a tungsten electrode using a water-cooled copper mould.

Co–Ti–Al ternary system compounds are obtained by different methods: arc melting [8–12], shock-wave synthesis [13], and spark plasma sintering [14]. In most studies, bulk polycrystalline samples of Co$_2$TiAl are obtained by means of arc melting.

In the practice of developing intermetallic materials by self-propagating high-temperature synthesis (SHS), the question of obtaining intermetallic compounds of both binary and ternary systems has been studied quite profoundly [15–18].

The purpose of this study is to investigate the formation of an intermetallic material based on a Heusler phase in a 2Co–Ti–Al system, synthesized by SHS in a thermal explosion.

EXPERIMENTAL METHOD  
AND PROCESSING OF THE RESULTS

Cobalt powder (a particle size of $\approx 20 \mu m$), PTM titanium powder ($\approx 11 \mu m$), and ASD-4 aluminum powder ($\approx 6 \mu m$) were used. Original powders were mixed...
until a uniform 2Co + Ti + Al mixture was obtained, and (15 × 10 × 3)-mm rectangular samples with a mass of 2 g were pressed from it. The pressed samples were placed in a VUP-5 universal vacuum oven and heated at a rate of ≈100°C/min until an SHS reaction was initiated. The temperature was recorded by a tungsten–rhenium ([W + 5% Re]/[W + 20% Re]) thermocouple placed deep in the bottom surface of the sample (a maximum error of no more than ±10°C). Following the initiation of an SHS reaction, the heating in the oven was turned off. Synthesis occurred both in vacuum at a pressure of $13.3 \times 10^{-2}$ Pa and in argon at $\approx 10^5$ Pa.

Phase transformation dynamics during SHS is investigated using a special device by means of time-resolving dynamic radiography [19]. The monochromatic radiation of Fe $K_\alpha$ is used, with pyrolytic graphite being applied as a monochromator. A (13 × 15 × 5)-mm rectangular sample is placed in a resistance furnace with windows for the passage of X-ray radiation, mounted in the reaction chamber. The primary beam is directed to the sample surface at its center at an angle of $\approx 20^\circ$, and irradiates a (2 × 10)-mm area. The angular recording interval is $2\theta = 35–78^\circ$. Several consecutive series are recorded, each containing 64 X-ray patterns and characterizing the evolution of the material in the course of heating and cooling of the sample. Temperature is measured with help of (W + 5% Re)/(W + 20% Re) thermocouple, whose junction touches the sample surface at its center. The experiments are carried out in a helium medium (a pressure of $\approx 0.2 \cdot 10^5$ Pa). The heating rate is 80–100°C/min. As soon as the sample ignites, the heating from the external source is turned off.

The synthesized samples are subjected to an X-ray phase analysis (XPA) on the DRON-3M diffractometer, with the radiation of Fe $K_\alpha$. Diffraction patterns are recorded using a step-scan technique in a range of angles $2\theta = 30–90^\circ$ with a step size of 0.02° and a counting time of 2 s per step. The refinement of the atomic structure and the quantitative analysis are carried out by the full-profile analysis using the PDWin software package of NPP Burevestnik.

The TOF.SIMS-5 time-of-flight mass-spectrometer is used to record mass-spectra and laminar distributions of secondary ions of synthesized materials.

Thermogravimetric differential thermal analysis (TG/DTA) is carried out on the Pyris Diamond thermal analyzer (TG/DTA6300). Magnetic characteristics are measured on powder samples using the M4500 (EG&G PARC, USA) vibration magnetometer in magnetic fields up to 0.8 MA/m at room temperature. The electric resistance of synthesized samples is determined according to the standard four-contact technique.

**EXPERIMENT**

It is shown by experimental results that the samples in the 2Co–Ti–Al system are synthesized in a thermal explosion. The reaction proceeds simultaneously in the entire volume of the sample, and the maximum rate at which temperature rises is 3500°C/s. The temperature at the beginning of the SHS reaction in vacuum (Fig. 1) is $T_{\text{ign}} = 565^\circ$C, which is 100°C below the melting point of Al aluminum and can indicate that the solid phase of the reaction has already started [20]. The maximum temperature of the sample in a thermal explosion in vacuum is 1470°C.
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| Spectrum | Al   | Ti   | Co   |
|----------|------|------|------|
| 1        | 2.32 | 18.00| 73.88|
| 2        | 1.54 | 24.58| 73.88|
| 3        | 15.86| 22.74| 61.40|
| 4        | 15.23| 23.63| 61.13|

Fig. 3. SEM image of the surface of the thin section of the sample of the combustion products of the $2\text{Co}–\text{Ti}–\text{Al}$ system and ethylene diamine (EDA) (at. %)

Fig. 4. Microstructure (a) and distribution of the concentration of the grain–intergranular layer–grain elements (b) along the scanning line (see Fig. 4a).

In the case of combustion in argon ($\approx 10^5$ Pa), the reaction initiation temperature is higher than in vacuum: 690°C. The cooling rate of the samples in argon is also higher, which is explained by a higher heat removal. The maximum combustion temperature in argon is 1476°C, which is close to the melting point of cobalt (1494°C).

The X-ray phase analysis of the material (Fig. 2) synthesized in vacuum shows the presence of the $\text{Co}_2\text{AlTi}$ phase (card PDF No. 030-65-4682) that is the Heusler phase, whose mass content is 99%. The total content of $\text{Co}_3\text{Ti}$ and $\text{Co}_2\text{Ti}$ impurity phases does not exceed 1%.

The elementary cell of $\text{Co}_2\text{TiAl}$ is $a = 5.8433 \pm 0.0002$ Å. The following values of this parameter are known from the literature: 5.870 [21], 5.850 [22], 5.8378 [8], and 5.847 Å [23]. The composition has a face-centered cubic lattice (Fm3m), and the structural prototype is $\text{AlCu}_2\text{Mn}$. 
A heterogeneous microstructure consisting of round grains of the ternary phase Co$_2$TiAl with an average particle size of 20 $\mu$m is typical for a synthesized material (Fig. 3). The results of an energy-dispersive analysis confirm the chemical composition of the main phase Co$_2$TiAl. However, there are sections in which the grains of the ternary phase Co$_2$AlTi are separated by an intergranular layer based on an intermetallic compound of varying composition TiCo$_x$ and of a thickness up to 10 $\mu$m. The release of secondary intermetallic compounds TiCo$_x$ at the cooling stage is possibly associated with a high burning rate and rapid cooling, which affects the completeness of interaction between original reagents and the formation of the ternary intermetallic compound phase Co$_2$TiAl.

Figure 4b illustrates the concentration profiles of elements in the grain–intergranular layer–grain transition zone. The Co$_2$AlTi grains have constant chemical composition relative to Co, Ti, and Al along the entire scanning line (Fig. 4a). The concentration profile of the elements in the intergranular zone shows that the concentration of Al atoms sharply drops to almost zero and that the content of Co and Ti atoms slight increases.

The image illustrating the bending of the synthesized sample shows the grains of the Co$_2$TiAl phase (Fig. 5). The fracture surface of the sample has a characteristic form of brittle fracture with a river bending. The density of the material is 5.9 g/cm$^3$, which is lower than the theoretical density 6.4 g/cm$^3$ and due to the sample porosity. The pore size reaches 50–100 $\mu$m.

It is shown by the results obtained using time-resolving dynamic X-ray diffraction that phase formation occurs in several consecutive stages. With heating from room temperature to the combustion temperature, the diffraction field only has the lines of the original reagents Ti, Al, and Co of cubic and hexagonal modification (Fig. 6). When it comes to an exothermic reaction initiated at a temperature close to the melting point of Al, the lines of the original reagents vanish for a time not longer than 1 s. As these lines vanish, the 200 and 220 lines of the Co$_2$TiAl phase are formed on the diffraction field. Next, one may observe their offset toward the region of large angles because the sample is cooling after the reaction due to intensive heat removal in helium in the absence of an external heat source. In 9 s after ignition, weak diffraction lines are formed on the diffraction field, identified as the 111 and 114 lines of the Co$_3$Ti and Co$_2$Ti intermetallic compounds, respectively (see Fig. 6).

The kinetics of changes in the intensity of the main diffraction lines of the initial components and the phases formed during heating, thermal explosion, and subsequent cooling of the sample is shown in Fig. 7. The appearance and growth in the intensity of the line corresponding to the Co$_2$TiAl phase at the time of the thermal explosion show that the main heat release during synthesis is due to the formation of the Heusler phase.

The X-ray fluorescence analysis (XFA) of the product synthesized during the time-resolving dynamic X-ray diffraction shows that the main phase is Co$_2$TiAl whose mass content is 72%. The contents of secondary phases (Co$_3$Ti, Co$_2$Ti, and Al$_2$O$_3$ intermetallic compounds) are 2, 10, and 16%, respectively. The high con-
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Fig. 7. Phase transformation kinetics in the synthesis of Co$_2$TiAl in a thermal explosion in helium.

Fig. 8. Differential thermal analysis of the compressed sample and the 2Co + Ti + Al powder charge.

The content of Al$_2$O$_3$ in the synthesis products according to the results of dynamic X-ray diffraction can be explained by the fact that the XFA is carried out from the lateral surface of the sample, which contacts with the environment in which oxygen impurities are present due to insufficiently pure helium and its low pressure (0.02 MPa). The time-resolving dynamic X-ray diffraction does not allow for experiments in a totally oxygen-free medium, and the high cooling rate (especially that of the surface layers) is the reason why the composition concentration is heterogeneous. Thus, at the cooling stage, there are secondary intermetallic compound phases Co$_3$Ti and Co$_2$Ti, located in the intergranular zones of the main phase (see Figs. 3 and 4).

It should be noted that, following the SHS, the combustion products on the VUP device in argon are ground into powder, so the XFA is used to determine the bulk content of the phases. In this case, no oxide phases are observed, and the content of secondary intermetallic compounds does not exceed 1% as noted above.

Sufficiently heterogeneous distribution of secondary ions Al$^+$, Ti$^+$, and Co$^+$ on the sample surface is indicated by the spectral analysis of synthesized samples, but one may note the possible boundaries of grains at which the concentration of Al$^+$ aluminum ions decreases. These data correlate with the results of the energy-dispersive analysis of elements in the grain–intergranular layer–grain zone (Fig. 4).

Etching the sample by oxygen ions for an hour reveals that the concentration of the secondary ions Al$^+$, Ti$^+$, Co$^+$, AlCo$^+$, TiCo$^+$, and TiAl$^+$ is constant in relation to the etching depth. During etching, the number of the Al$^+$ aluminum ions locally decreases, which may be caused either by an ion beam falling on an intergranular boundary or possibly by the scattering of secondary ions at the grain–pore boundary.

Determining possible phase transitions and estimating thermal effects required a differential thermal analysis in a temperature range of 20–900$^\circ$C of the reactive powder mixture and the mixture pressed into a pellet with a diameter of 3 mm and a height of 2 mm (Fig. 8).

The DTA of the reactive powder mixture (dashed line in Fig. 8) shows that no SHS reaction is initiated. The DTA curve has two endothermic effects. The first one in the vicinity of 655$^\circ$C denotes the melting of Al aluminum, and the second one in the vicinity of 780$^\circ$C refers to polymorphic transformation of titanium $\alpha$-Ti $\rightarrow$ $\beta$-Ti. The fact that the transition temperature is lower than that of pure titanium (885$^\circ$C) is apparently due to the formation of a solid cobalt solution in titanium. It is known that the temperature of the transition $\alpha$ $\rightarrow$ $\beta$ of the solid solution Ti[Co] drops as the Co content increases and equals 685$^\circ$C at 14.5 at.% of Co [24].

During the DTA of the compressed pellet (the solid line in Fig. 8), the mixture burns in a thermal explosion. The DTA temperature curve exhibits a pronounced exothermic peak at 665$^\circ$C, which corresponds to the melting point of Al aluminum, accompanied by the formation of melt. The absence of heat absorption in the system is due to the fact that the endothermic effect of melting is overshadowed by much more powerful exothermic effect as a result of the SHS reaction.
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Fig. 9. Magnetization versus the strength of the applied magnetic field for Co$_2$TiAl: $\sigma_s$ is the saturation magnetization, $\sigma_r$ is the residual magnetization, $\mu_0$ is the magnetic constant, and $H(T)$ is the magnetic field strength.

A similar result is obtained in the case of a Ti + Al [25] mixture, in which the exothermic peak of the Ti + Al interaction at low heating rates immediately follows the endothermic melting peak of Al, and they practically overlap each other.

It is shown by magnetic measurements at room temperature that there is weak ferromagnetism in the synthesized material (hysteresis loops). Figure 9 shows the dependence of magnetization $\sigma$ on the strength of the applied magnetic field $H$. The maximum specific saturation magnetization at room temperature is 1.64 A·m$^2$/kg. This result can be explained by the presence of free cobalt in the synthesized product (approximately slightly less than 1%).

It is shown by measuring the electrical resistance at room temperature that there is high reproducibility and correlation with the results of other studies: 1.35 $\mu$Ω·m in this study, 0.98 $\mu$Ω·m in [11], and 1.5 $\mu$Ω·m in [10].

**RESULTS AND DISCUSSION**

It can be concluded from the results obtained that the combustion mechanism in the system under consideration is as follows. The data of the time-resolving X-ray diffraction and the heat patterns of the process indicate that the formation of the Co$_2$AlTi phase in a thermal explosion lasts for 1 s. The maximum temperature is 1476°C, i.e., close to the melting point of Co (1495°C). According to [26], the ternary compound Co$_2$AlTi is formed by melting in the electric arc furnace with a nonconsumable tungsten electrode on a water-cooled copper tray in argon at 1640°C in a range of concentrations of 22–27 at.% of Al. It is also known [19] that the maximum temperature of a thermal explosion in a Ti + Al system is 1450°C. It can be concluded that the leading reaction during interaction in the 2Co–Ti–Al system is Ti + Al.

The most probable mechanism implemented at the first step of interaction is the melting of Al at 650°C and the nucleation of TiAl grains by diffusing Al atoms from the melt into the Ti particle lattice. Considering the fact that the diffusion coefficient of Al is approximately $5 \cdot 10^{-18}$ m$^2$/s in $\alpha$-Ti and $3 \cdot 10^{-14}$ m$^2$/s in $\beta$-Ti [27] and in view of the analysis of diffusion couples [28], a conclusion can be made about the leading mechanism of SHS due to diffusion of Al in $\beta$-Ti. The introduction of cobalt reduces the temperature of the transition $\alpha \rightarrow \beta$ of titanium from 885 to 758–806°C. However, the solubility of Co in L in a eutectic temperature does not exceed 0.009 at.%. The solubility of Al in $\varepsilon$-Co is almost equal to zero. The solubility of Co in the AlTi$_x$ intermetallic compounds is quite high: 2.3–9.6 at.%. The solubility of Al in the TiCo$_x$ intermetallic compounds and of Co in Ti is 6.8–13.7 at.%. The solubility of Co in Ti is 10.3 at.%, and that of Ti in Co is 8.5 at.% [23]. Therefore, it can be assumed that the formation of Co$_2$AlTi is induced because of dissolution of Co atoms in the Ti–Al melt. This correlates with the results of [19] in relation to the formation of intermetallic compounds in Ti–Al, which occurs for 1–2 s during the principal heat release. Moreover, regardless of the stoichiometry of the mixtures, the equimolar composition phase forms first.

**CONCLUSIONS**

The self-propagating high-temperature synthesis in the thermal explosion was used to obtain the Heusler phase Co$_2$TiAl for the first time. It was shown that the mass content of Co$_2$TiAl in the synthesized material was 99%. The main impurity phases located in the intergranular layers were the Co$_3$Ti and Co$_2$Ti intermetallic compounds. The synthesized product at room temperature manifested the presence of ferromagnetic hysteresis loops, the specific saturation magnetization was 1.64 A·m$^2$/kg, and the electrical resistance was 1.35 $\mu$Ω·m.

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