Phase evolution in the Ti-Al-B and Ti-Al-C systems during combustion synthesis: Time resolved study by synchrotron radiation diffraction analysis

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Self-propagating high-temperature synthesis (SHS), also known as combustion synthesis, is a modern technique for producing refractory compounds and materials [1]. This method is based on the use of internal chemical reaction heat rather than external (furnace) heating for material synthesis and processing. Initial mixture consists of two or more powders, which are able to react exothermically with each other. Being locally initiated, the reaction becomes self-sustaining, heat produced in the reaction front igniting the nearest part of the mixture.

Ceramic-intermetallic composites, composed of ceramic grains (TiC, TiB_2, etc.) and TiAl intermetallic binder, possess attractive properties for potential applications as cutting tools, aerospace materials, hard and refractory structural materials. As the enthalpies of reaction between Ti and C, B or Al are large, these materials can be produced through combustion synthesis (SHS) by means of heterogeneous reactions in the ternary mixtures of elemental powders. Formation mechanisms of the materials have been studied in the present work. Since the characteristic features of SHS are fast temperature variations and short duration of the product formation (usually from a few seconds to a few minutes), Time-Resolved Synchrotron Radiation Diffraction (TRSRD) is used for monitoring phase transformations. This method, firstly developed for investigation of SHS in the Ni–Al system [2], have been further improved in order to reach extremely short temporal resolution of 5 ms per diffraction pattern [3], or to combine it with thermal vision system [4].

Powders of Ti ($\sim 40\ \mu$m average size, 99.8% purity), C (carbon black, $\sim 0.1\ \mu$m, 99% purity) and B (amorphous black, $\sim 0.1\ \mu$m, 99% purity) were dry-mixed and pressed into rectangular ($20 \times 10 \times 5$ mm) samples with a remainig porosity of roughly 40%. Two initial compositions were studied: 2Ti+Al+2B and 2Ti+Al+C. The samples were put in a specially designed chamber with an X-ray transparent window [4], under He atmosphere at normal pressure. Radiation, produced by one of L.U.R.E. (Orsay, France) synchrotron source, was monochromized and focused on the lateral surface of the sample. Radiation wavelenght was chosen equal to 2.53 Å, intensity of the incident beam was $\sim 10^{10}$ photon per second. The sample surface exposed to synchrotron radiation (region of analysis), was a rectangle of 0.1 mm $\times$ 1.5 mm, with its long side parallel to the reaction front. Reaction was initiated locally by an electrically heated W wire. A gasless combustion front propagated along the sample with a velocity of 3 cm/s (Ti–Al–B) or 0.4 cm/s (Ti–Al–C), maximum averaged temperatures in the reaction zone were 2200 and 1960 K, respectively. Synchrotron ray diffraction patterns were recorded continuously (before, during and after reaction) by a curved linear detector which covered the range (theta) from 28 to 73 °, divided into 512 or 1024 channels. Sequence of 1024 SRD patterns was stored without time interval on a PC during 40.96 s. Hence, every pattern represents information about sample current phase composition during an interval of 40 ms. The stored data files were further converted into bitmap images, where larger intensity of radiation correspond to darker areas. These images give general information about phase evolution during combustion synthesis of the materials.

TRSRD pattern of phase transformations in the Ti–Al–B system is shown in the Fig. 1. Lines of Ti and Al can be observed before reaction, amorphous boron does

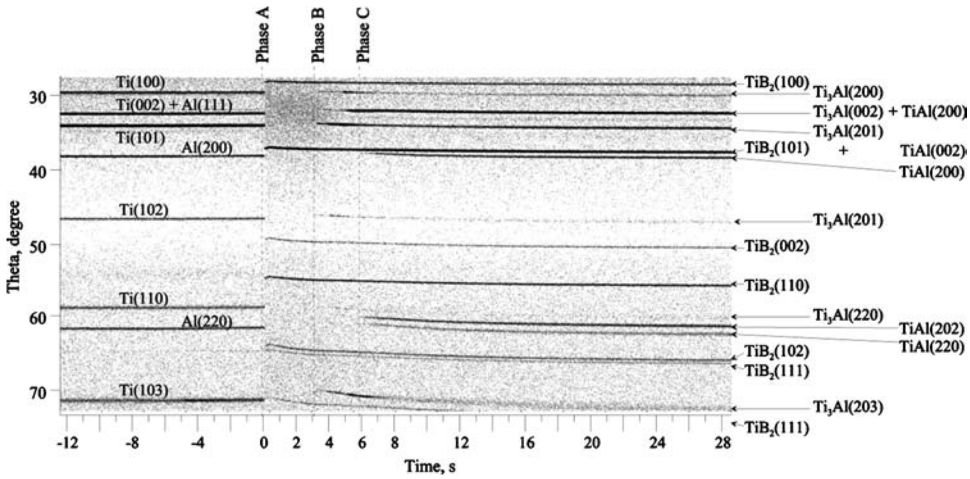

Figure 1 TRSRD pattern of phase transformations in the Ti–Al–B system.

not yield any diffraction peak. The diffraction pattern changes sharply when the combustion front crosses the region of analysis. This point of time is marked as 0 s on the SRD patterns. The only phase appearing immediately in the reaction front, is TiB_2, identified by six major peaks (Phase A in Fig. 1). Evidently, when TiB_2 crystallizes, Al and the rest of Ti remain in the melt. When the temperature of the products goes down behind the combustion front, due to radiation, conduction and convection heat losses, two more crystal phases appear after TiB_2. Phase C, which crystallizes 6 s behind the combustion front, can be clearly recognized as γ-TiAl. Phase B, after cooling down, corresponds to α_2-Ti_3Al intermetallic compound. However, Ti_3Al maximum temperature (1473 K) is lower than γ-TiAl crystallization temperature from the Ti-Al melt ($\sim$1723 K). Therefore, Ti_3Al cannot precipitate before TiAl. Careful consideration of the Ti–Al phase diagram and TRSRD pattern (Fig. 1) allows us to conclude that B, which appears at 3.2 s behind the front, is α-Ti solid solution. We may further assume that this phase chemical composition is close to that of Al saturated Ti_3Al. When temperature decreases, the high-temperature α-Ti solid solution transforms into low-temperature α_2-Ti_3Al. Relatively intense lines at $\sim 35^\circ$ and $\sim 71^\circ$ belong to solid solution; broadening and diminution of these lines at $\sim$7 s correspond to phase transformation from solid solution into ordered intermetallic Ti_3Al. Following this transformation, the mentioned two lines pass into the lines Ti_3Al(201) and Ti_3Al(203), respectively.

Phase evolution in the Ti–Al–C system is shown in Fig. 2. Initial SRD patterns are similar to those shown in Fig. 1, since amorphous carbon does not produce any peak. The first phase appearing is TiC, probably non-stoichiometric (e.g., TiC_x with $x \sim 0.5$–0.7). After 2.9 s behind TiC appearance, a second phase crystallizes (Phase B, Fig. 2). Phase B was recognized as Ti_3AlC_2 [5] ($a = 0.3076$ nm, $c = 1.8543$ nm, isotypic with Ti_3SiC_2). One minor line, which might belong to Ti_2AlC, is also observed. It is known from literature that Ti_3AlC_2 was found at temperatures of 1573 K $\leq T <$ 1633 K. Therefore, this phase can appear in Ti–Al–C, when products cool down below 1633 K from the maximum combustion temperature 1960 K. It should be noted that direct synthesis of the Ti_3SiC_2 in the combustion mode (by SHS) was reported earlier [6, 7], while authors donot know any previous publication about SHS production of the Ti_3AlC_2.

Microstructures of combustion products are presented in Fig. 3. Identification of phases was made using EPMA and EDS analyses. Products of the combustion

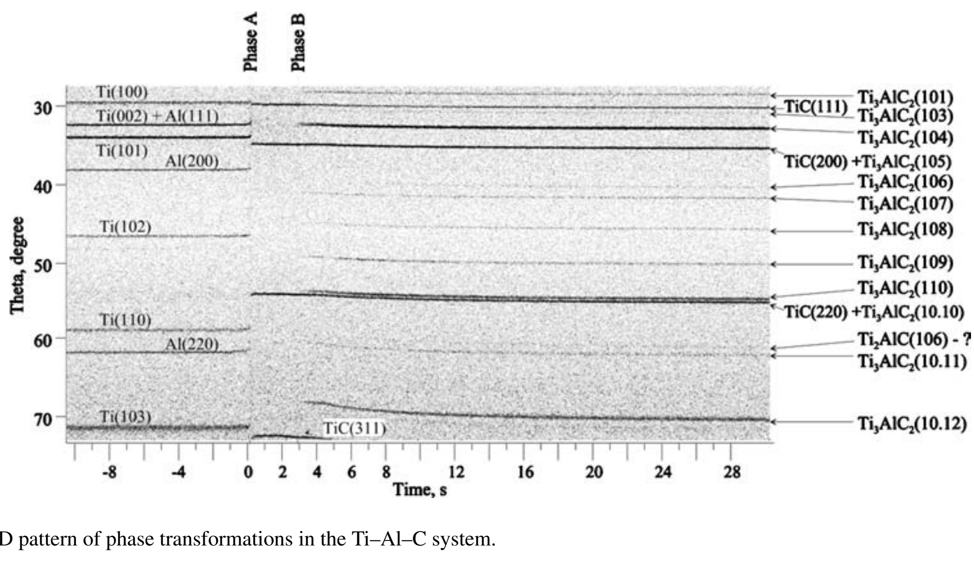

Figure 2 TRSRD pattern of phase transformations in the Ti–Al–C system.

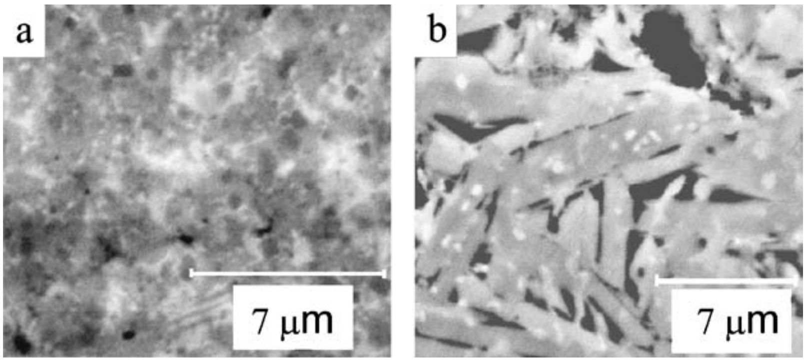

Figure 3 Microstructure of the products in Ti–Al–B (a) and Ti–Al–C (b) systems.

synthesis in the Ti–Al–B system (Fig. 3a) consist of fine rounded TiB_2 grains (gray phase) and intermetallic binder (white phase). Ti–Al–C products contain TiC_x (light gray), Ti_3AlC_2 (dark phase), and small inclusions (white), which are probably Ti_2AlC.

Thus, the results of TRSRD study show the following sequences of phase transformations in the Ti–Al–B and Ti–Al–C systems. Disappearance of initial phases and formation of the first products (TiC or TiB_2) happen during a short time interval, at the most 40 ms (time resolution of the method). At this moment, temperature rises sharply up to its maximum value, which exceeds temperature ranges of existence of the other phases. Therefore, the first products of combustion reactions are refractory titanium carbide or diboride and melt. Then temperature decreases due to heat losses to surrounding medium, and other phases precipiate from the melt, according to phase diagram. This process takes a few seconds more, depending on the cooling rate. It is important to note that in the samples of moderate size, when cooling rate is fast enough, thermodynamic equilibrium between the first carbide/boride phase and other phases precipitated from the melt is not achieved. For example, equilibrium phases in the mixture 2Ti+Al+2B are TiB and Al, however, fast SHS process allows to produce the material composed of TiB_2 grains and intermetallic binder. This feature of the combustion synthesis method can be used for production of new materials with tailored phase constitution, microstructure and properties.

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