

# Phase formation mechanism of the Ni + Zr + polytetrafluoroethylene reactive mixture

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**Abstract** The combustion process in the Ni + Zr + Polytetrafluoroethylene (PTFE) system is investigated. Effect of PTFE addition on the process parameters and characteristics of products are studied. The reacting mixtures and product obtained are studied by differential thermal analysis (DTA) and thermogravimetric (TG) techniques, mass-spectroscopy, ion-chromatography, and XRD analysis. Results are discussed in terms of literature data. The mechanism of combustion process is proposed according to which at initial stages monomer formed at PTFE decomposition reacts with metals to form ZrC, ZrF<sub>2</sub>, and NiF<sub>2</sub>. At elevated temperatures, ZrF<sub>2</sub> disproportionate to form gaseous ZrF<sub>4</sub>. Heat generated at early stages of the process stimulates the formation of Ni–Zr intermetallic phases.

**Keywords** Combustion · Differential thermal analysis · NiZr alloy · Reaction mechanism

## Introduction

Bones and joints are of various shapes and structure depending on their function [1, 2]. Bones having “spongy” inner structure called cancellous [2]. Implants to replace damaged and worn cancellous bone should mimic its

structure and contain interconnected pores with dimension 100–500 μm [2, 3]. These scaffolds can support new bone formation and bone cells, blood vessel, and soft tissues ingrowth to merge the implant with the host bone [1–3]. Porous metals (alloys) have so far considering as potential scaffold material for cancellous bone replacements [4]. Commonly accepted fabrication methods for porous alloys are furnace sintering of metallic powders [5, 6], space holder and replication methods [4, 7, 8], and rapid prototyping [4, 9], etc.

A novel and effective method for producing highly porous alloys is known as combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) [10–14]. For instance, porous NiTi has been created from elemental Ni and Ti powders through CS technique [11–13]. The most widely used porous NiTi in biological studies is Actipore™, a commercially available product made by Biorthex (Canada) through the CS process, which offers porosity of 65% and average pore size of 215 μm [13].

Recently, combustion synthesis conditions in the Ni + Zr + polytetrafluoroethylene (PTFE) mixture were studied to obtain porous (≈65%) NiZr-based materials with 50–600 μm pore sizes [14–16]. The obtained materials were found to be cytotoxic for human cell lines in vitro [14]. Toxic components are thought to be fluorine derivatives, most likely NiF<sub>2</sub> and ZrF<sub>4</sub>. Fourfold washing with water enabled to dissolve and elute these compounds. In that way their levels in the materials were possible to lower to concentrations that were nontoxic for cells in vitro. The materials themselves, after extraction of toxic components, were nongenotoxic and have no effect on the cell proliferation rate. Therefore, studying the formation of fluorine-containing compounds and their further behavior during the combustion in the Ni + Zr + PTFE system is of special importance.

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The objective of the present work is to investigate the phase formation mechanism in the Ni + Zr + PTFE mixtures with emphasis on the formation of fluorine containing compounds.

## Experimental

### Materials used and sample preparation

Powdered zirconium (PZrK-1; Tech. Condition of manufacturing 48-4-234-76, Russia), nickel (PNE-1; High grade, Norilsk Nickel, Russia) and PTFE (FT-4; High grade, Ur-alChimPlast, Nizhni Tagil, Russia) were used as raw materials. Particle size of all reagents was less than 10  $\mu\text{m}$ .

Table 1 displays the composition and designations of reacting mixtures used. [17%Ni + 83%Zr] + 4% PTFE mixture was selected as it provides formation of material with desired properties for biomedical applications [14–16]. During experiments, mixture of metals with 17 wt%Ni + 83 wt%Zr composition were prepared in a ceramic mortar for 0.5 h. PTFE powder (4 wt% from overall metallic mixture) was added and continued to mix for 0.5 h. Cylindrical samples with 2.0–2.3 g cm<sup>-3</sup> density, 2 cm in diameter, and 3.5–4.0 cm of height were prepared from the green mixtures.

### Combustion synthesis

Combustion experiments were conducted in a 3 litre volume reacting vessel (CPR-31). The samples were placed into the reactor and then it was sealed, evacuated, and purged with argon with three cycles. Argon (purity 99.95%, oxygen content not more than 0.02%) was used as an inert atmosphere. During the experiment, the pressure of inert atmosphere was automatically kept at 0.5 MPa by using an electronic valve (ASCO SCE272A046MS) and a pressure gauge (OMEGA PX4100-0.4KGV).

The combustion reaction was initiated by short-term (1 s) annealing a tungsten coil placed on the top of the sample. Time–temperature distributions in the reacting samples were recorded by BN-coated tungsten–rhenium thermocouples (W/Re-5 and W/Re-20, thermocouples 100  $\mu\text{m}$  in diameter).

The output signals of thermocouples were transformed by a data acquisition system at the rate of 2 kHz, and were recorded by a computer. The average values of combustion velocity were calculated from the data of distance between thermocouples and temporal distance between the signals of thermocouples. Detailed procedure of measurement of combustion parameters was described elsewhere [14, 17].

### Characterization of initial mixtures and products

Thermal analyses for Ni + Zr + PTFE mixtures were conducted using a PC-linked Q-1500 Derivatograph (MOM, Hungary). Differential thermal analysis (DTA) and thermogravimetric (TG) curves were recorded at argon flow (rate 7 ml/s). Heating rate of material was adjusted at 20 °C min<sup>-1</sup>.  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference material for the thermal measurements.

XRD method (DRON-3.0, Burevestnik, Russia) with monochromatic CuK $\alpha$  radiation was used to analyze the phase composition of reaction products. Microstructures of reacted materials were studied by BS-300 (Tesla, Czech Republic) scanning electron microscope.

The reacted products were crashed to fine powder and washed by deionized water for 5 days at 40 °C. ELAN-9000 ICP-mass-spectrometer and Dionex ICS-1000 chromatograph were applied to determine ZrF<sub>4</sub> and NiF<sub>2</sub> concentrations in the water extracts.

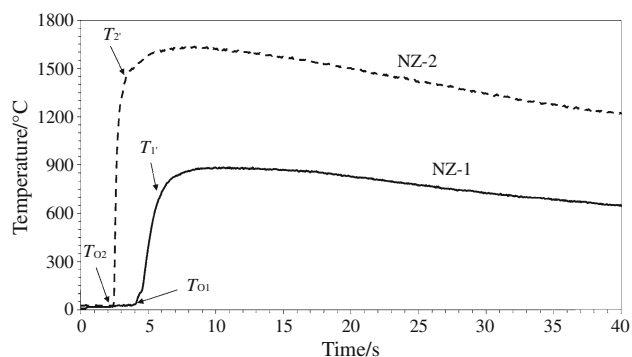
## Results

### Reaction in the Ni–Zr–PTFE mixtures

To demonstrate the influence of PTFE on the self-sustaining reaction additive-free NZ-1 mixture was firstly investigated. The maximum temperature of reaction determined from the time–temperature distribution (Fig. 1) for that mixture is about 920 °C (Table 1). PTFE addition rises the maximum combustion temperature for the NZ-2 mixture up to 1,600 °C (Fig. 1, Table 1). Other parameters for combustion process, e.g. velocity and heating rate, are also significantly affected by the PTFE addition (Table 1). The combustion front propagating velocity increases ten

**Table 1** Compositions, designations of the investigated initial mixtures, their combustion parameters, and phase composition of products

Composition/wt%	Designation	$T_c/^\circ\text{C}$	$U_c/\text{cm s}^{-1}$	Heating rate in combustion front/ $^\circ\text{C s}^{-1}$	Phase composition
17%Ni + 83%Zr	NZ-1	920	0.15	300	Zr, Ni, and Ni <sub>10</sub> Zr <sub>7</sub>
[17%Ni + 83%Zr] + 4%PTFE	NZ-2	1,600	1.5	1,400	Ni <sub>10</sub> Zr <sub>7</sub> , NiZr, Zr, and ZrC
Zr + 4%PTFE	NZ-3	1,550	1.35	1,250	Zr and ZrC
Ni + 4%PTFE	NZ-4	–	–	–	–



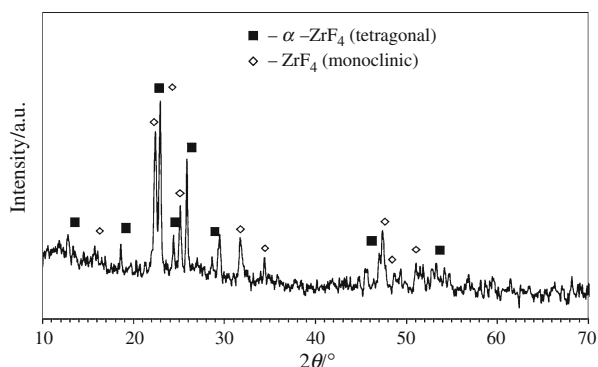
**Fig. 1** Time-temperature distributions for NZ-1 (a) and NZ-2 (b) mixtures

times (0.15 to 1.5 cm s<sup>-1</sup>). Heating rate of reactants determined from the temperature profile grows approximately five times (from 300 to 1,400 °C s<sup>-1</sup>). Note, that heating rate was calculated from data of  $T_o$  and  $T'$  taken from temperature profiles presented in Fig. 1.

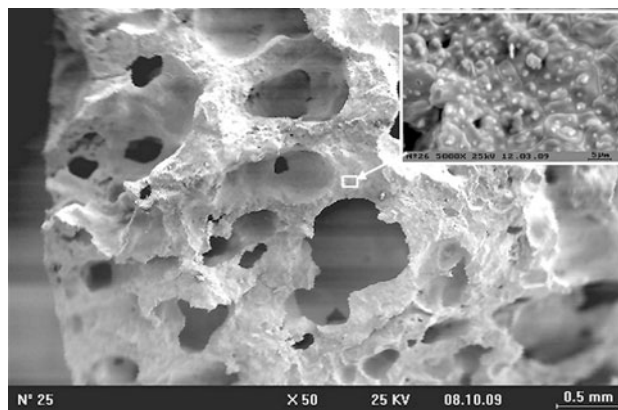
PTFE addition drastically influences on the phase composition of products too. Results of XRD analysis (not shown) testify that combustion product of NZ-1 sample among the initial metals contains some amount of Ni<sub>10</sub>Zr<sub>7</sub> intermetallic phase (Table 1). The reacted sample made from NZ-2 mixture contains NiZr and Ni<sub>10</sub>Zr<sub>7</sub> intermetallic phases, zirconium and zirconium carbide (Table 1).

It is worthy to note that the combustion of the PTFE containing NZ-2 mixture accompanied with the emission of gaseous compound, which then precipitates on the reactor walls as a white solid compound. XRD pattern of that compound shows diffraction lines of two crystalline modifications (monoclinic and tetragonal) of ZrF<sub>4</sub> (Fig. 2). Mass-spectroscopic investigation shows that major metal in white precipitate is zirconium and its concentration about 1,000 times is higher than that of other metals.

The weight-loss for the NZ-2 samples after the reaction makes approximately 6.2%. Calculated weight-loss associated with ZrF<sub>4</sub> formation when whole fluorine in the PTFE reacts with Zr makes 6.4%. Mass-spectrometric and



**Fig. 2** XRD pattern of precipitate



**Fig. 3** SEM micrographs of the product formed at combustion of the NZ-2 mixture

chromatographic study of water extracts of crashed solid products show that they contain 0.185 wt% NiF<sub>2</sub> and 0.02 wt% ZrF<sub>4</sub>.

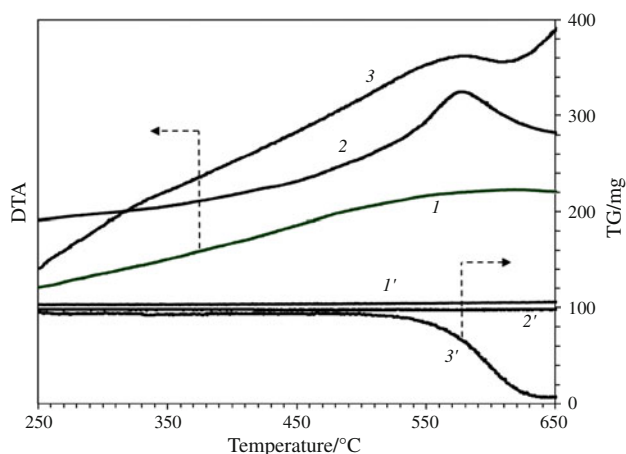
Main combustion parameters for the NZ-3 mixture are close to those for the NZ-2 (Table 1) and the major phases in the product are metallic zirconium and ZrC. In the case of sample made from NZ-4 mixture (Ni + 4%PTFE) the interaction may not be organized in the self-sustaining manner.

Comparison the results obtained one may suggest that at combustion of [17%Ni + 83%Zr] + 4%PTFE mixture polymer (or the products of its decomposition) mainly reacts with zirconium to form ZrF<sub>4</sub>. This compound is volatile (temperature of sublimation is about 900 °C) at reaction temperature and it mainly removed from the product. As the combustion wave propagates throughout the sample, liquid intermetallic compounds (melting points of NiZr-intermetallics are about 1,200 °C) are formed at the reaction front. The convective flow of ZrF<sub>4</sub> gas through the molten product results in forming open-cell non-homogeneous pores (Fig. 3). High magnification SEM images in Fig. 3 show that the product is fully melted.

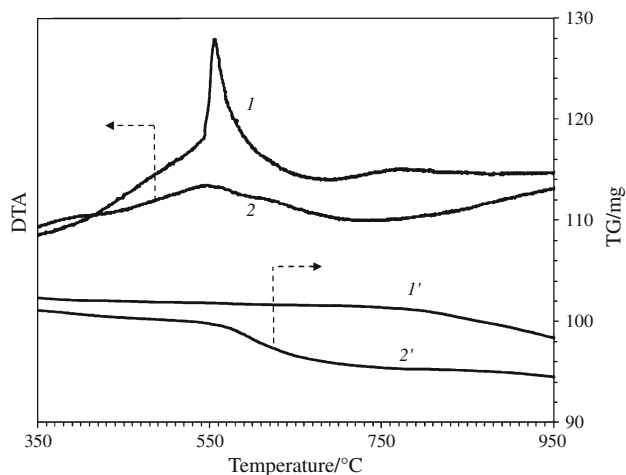
#### Thermal analysis of the Ni-Zr-PTFE mixtures

DTA track of PTFE-free NZ-1 mixture does not contain any expressed peaks (Fig. 4, curve 1) in temperature range from 250 to 650 °C. Unlike this finding, intensive exothermic peak appears at 500–600 °C for NZ-2 mixture (Fig. 4, curve 2). The onset of exothermic reaction (500 °C) coincides with the PTFE decomposition temperature (Fig. 4, curves 3, 3'). According to the TG curve, PTFE decomposition completes at 630 °C (Fig. 4, curve 3'). Thermogravimetric curves for NZ-1 and NZ-2 mixtures are recorded as straight lines without any weight-losses (Fig. 4, curves 1' and 2').

DTA curve for the NZ-3 mixture contains intensive exothermic peak at the 500–650 °C (Fig. 5, curve 1).



**Fig. 4** DTA/TG curves for NZ-1 (1/1'), NZ-2 (2/2') mixtures and PTFE (3/3')



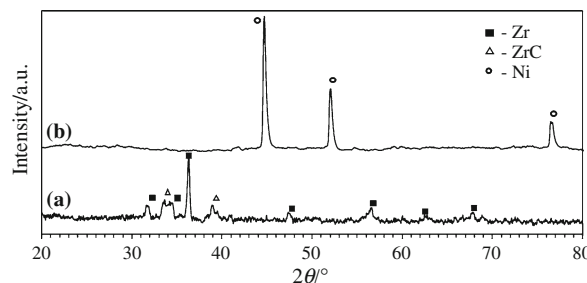
**Fig. 5** DTA/TG curves for NZ-3 (1/1') and NZ-4 (2/2') mixtures

However, 4–5% fall in the TG curve is appeared only at 800–950 °C (Fig. 5, curve 1'). In the case of NZ-4 mixture, about 5% weight-loss corresponding to the endothermic decomposition of polymer recorded at 550–630 °C (Fig. 5, curves 2 and 2').

XRD pattern for the NZ-3 mixture taken after DTA analysis (heated up to 950 °C) shows diffraction lines of Zr and ZrC (Fig. 6a). XRD pattern (not shown) for the same mixture heated up to 650 °C contains lines for Zr, ZrC, ZrF<sub>2</sub>, and Ni. Product for the NZ-4 mixture (heated up to 950 °C) contains only metallic nickel (Fig. 6b).

## Discussion

Minor addition of PTFE into the Ni + Zr mixture drastically changes combustion parameters, e.g. temperature, and phase composition of product. At high reaction

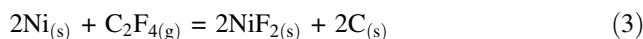
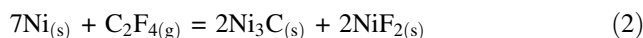
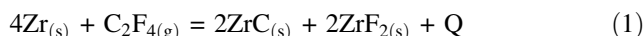


**Fig. 6** XRD patterns for NZ-3 (a) and NZ-4 (b) mixtures heated up to 950 °C

temperature molten NiZr and Ni<sub>10</sub>Zr<sub>7</sub> intermetallics are formed. The convective flow of formed ZrF<sub>4</sub> through the molten product contributes to the pore formation. A small amount of NiF<sub>2</sub> is also formed during the reaction, which mainly remains in the sample.

DTA/TG analysis in current research shows that interaction onset in the Ni + Zr + PTFE mixture coincides with PTFE decomposition (about 500 °C). Note, that thermal decomposition onset of PTFE was reported to be at 500–600 °C [18, 19]. According to the literature data [19–21] at inert atmosphere, the principal product of PTFE thermal decomposition is monomer (C<sub>2</sub>F<sub>4</sub>). Small amount of other compounds, e.g. CF<sub>4</sub>, may also be formed at polymer decomposition [19, 20].

Therefore, at temperatures above 500 °C following reactions may occur in the combustion of Ni + Zr + PTFE mixture:

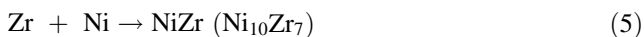


The probability of occurring of reaction (2) is very low because of the metastable nature of Ni<sub>3</sub>C. Decomposition of this carbide starts at ~465 °C [22, 23]. Most likely, NiF<sub>2</sub> presented in the reaction product is formed by the reaction (3). However, the role of the reaction (3) at combustion process is small because the fact that reacted sample contains small amount of NiF<sub>2</sub>. DTA/TG investigation also shows that nickel practically dose not react with PTFE. During heating, the polymer endothermically decomposes and removes from the Ni + PTFE mixture. On the other hand zirconium alone exothermically reacts with PTFE. Close combustion features for NZ-2 and NZ-3 (Table 1) allow to assume that leading-stage of combustion process is the reaction (1). Reaction (1) is also responsible for heat generation at self-sustaining process.

It is well documented in the literature [24, 25] that under 800 °C ZrF<sub>2</sub> is most stable fluoride of zirconium. However, at 800–900 °C ZrF<sub>2</sub> is disproportionate by the following reaction [24, 25]:



It is highly possible that the weight-loss for the Zr + 4%PTFE mixture at >800 °C (Fig. 5) is caused by ZrF<sub>4</sub> sublimation formed by the reaction (4). Eventually, at the final stage of combustion process heat generated from the reaction (1) stimulates the interaction between zirconium and nickel by following scheme:



Recently, it was reported that in Ni–Zr multilayer nanolaminated system formation of intermetallic phases may start even at 600 °C [26].

## Conclusions

Results of this study show that minor addition (4 wt%) of polytetrafluoroethylene in the Ni + Zr mixture increases main combustion parameters. In particular, combustion temperature rises from 900 to 1,600 °C, front propagation velocity from 0.15 to 1.5 cm s<sup>-1</sup>. Additive affects also on the products phase composition. Investigations indicate that at early stages of process (500 °C) PTFE decomposition takes place. Monomer formed at polymer decomposition mainly reacts with zirconium to form ZrC and ZrF<sub>2</sub>. This exothermic reaction is shown to be leading-stage of the process. Heat generated from that reaction stimulates the formation of molten NiZr and Ni<sub>10</sub>Zr<sub>7</sub> intermetallic compounds (melting points of those phases are about 1,200 °C). At the elevated temperatures (800–900 °C) gaseous ZrF<sub>4</sub> forms by disproportionation of ZrF<sub>2</sub>. Convective flow of gaseous ZrF<sub>4</sub> through the melted products creates nonuniformly distributed pores with sizes of 100–500 μm.

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