



Combustion Synthesis of Titanium Carbonitrides

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Abstract: Titanium carbonitride ($\text{TiC}_{0.5}\text{N}_{0.5}$) micron powders were synthesized in reactions of titanium with zinc dicyanide: $\text{Zn}(\text{CN})_2 + 4\text{Ti} \rightarrow 4\text{TiC}_{0.5}\text{N}_{0.5} + \text{Zn}$. The reactions are sufficiently exothermic to propagate in the reactant mixture to form a self-sustaining, high-temperature synthesis (SHS). The final product was separated and the only byproduct (zinc) was removed by dissolution in dilute hydrochloric acid. The use of zinc dicyanide as the source of carbon and nitrogen causes the titanium carbonitride to contain only these elements in an atomic ratio of one. The reaction temperature can be easily reduced by the addition of zinc powder to the green mixture. Synthesis in the presence of zinc yields $\text{TiC}_{0.5}\text{N}_{0.5}$ powders consisting of round-shaped and unagglomerated particles.

Keywords: combustion synthesis, titanium carbonitride, ceramics, refractory materials

1 Introduction

Carbides and nitrides of transition metals, that is compounds of carbon and nitrogen with the elements of blocks (*d*) and (*f*) of the Periodic Table, have been known for over 100 years [1]. The structural similarity of carbides and nitrides makes it possible to partially replace the carbon atoms with nitrogen atoms. In this way a solution of both carbon and nitrogen in the metal is formed and the resulting compounds are named carbonitrides [2]. Depending on the atomic ratio of carbon and nitrogen, carbonitrides of different stoichiometry are produced. Their formulae can be written as $\text{MeC}_{1-x}\text{N}_x$, or more generally as $\text{Me}(\text{C},\text{N})$. The physicochemical and mechanical properties of most carbonitrides change

smoothly with changes in the nitrogen and carbon content of the metal – from the characteristics of pure carbides MeC ($x = 0$) to those typical of pure nitrides MeN, when $x = 1$ [3].

Titanium carbonitrides share several unique properties, such as elevated hardness, chemical inertness (even at high temperatures) and high thermal conductivity [4-6]. Therefore they are used for the production of cutting tools, abrasives and abrasion- and corrosion-resistant parts of machines [7]. For the same reasons, titanium carbonitrides can be applied in dental alloys [8, 9], and thanks to their good electrical conductivity, also in electrodes for work in aggressive media [10]. The growing interest in these materials generates the need to search for cheap and efficient methods for their synthesis.

Titanium carbonitrides are produced in the form of thin layers and powders [11-14]. Layers of Ti(C,N) can be formed on the surface of almost any base using the Chemical Vapour Deposition (CVD) method [15]. Ti(C,N) powders are prepared by hot pressing of TiC and TiN powder mixtures – for 5 hours at 1800 °C and 27.6 MPa [5], or for 1 hour at 1600 °C and 300 MPa [4]. High-temperature nitriding (1700 °C) of mixtures of titanium carbide and titanium also yields Ti(C,N) powders [16]. The powders can be synthesized by reducing titanium dioxide with carbon in a nitrogen atmosphere: $2\text{TiO}_2 + 2(3-x)\text{C} + x\text{N}_2 = 4\text{CO} + 2\text{TiC}_{1-x}\text{N}_x$ [17]. Low-temperature and pressure, but still quite complex methods for Ti(C,N) synthesis have also been developed. These include thermal decomposition of titanium tetrachloride complexes with organic amines [18], reduction of titanium tetrachloride and carbon tetrachloride solutions with sodium azide, and high-energy milling of carbon and titanium powders in a nitrogen atmosphere [13].

The known methods of Ti(C,N) synthesis are energy-intensive and require complicated apparatus, involving the creation and long-term maintenance of appropriate reaction conditions (high temperatures and pressures). Even though Ti(C,N) can be prepared from TiO_2 , the last traces of dissolved oxygen are difficult to remove from the product. Solid phase reactions between titanium nitride and carbide do not guarantee the uniformity of the product. Furthermore, owing to the high temperature and pressure during synthesis, the product is in the form of a hard sinter (agglomerate) that must be ground to obtain a fine powder. This increases the synthesis time and adds to the product's cost.

The method proposed in this paper is devoid of the above-mentioned drawbacks. After local initiation, the reaction between Ti and Zn(CN)_2 propagates in the green mixture in the form of a reaction (combustion) wave, because the energy needed to sustain the process comes from the reaction itself. The use of zinc dicyanide as the only source of carbon and nitrogen causes the titanium

carbonitride to contain these elements in an atomic ratio of one. The main product can be easily isolated from the post-reaction mixture by dissolving unreacted substrates and by-products in dilute hydrochloric acid. The reactions are sufficiently exothermic to sustain stable propagation of the reaction wave in the Ti/Zn(CN)₂ mixtures diluted with zinc. Ti(C,N) powders prepared under these conditions are not agglomerated: the particles are round-shaped and have micron sizes.

2 Experimental

Because the temperature in the combustion synthesis is very high, it leads to considerable coarsening of the ceramic particles during the reaction. To prevent particle agglomeration in the combustion synthesis, inert, inorganic compounds such as sodium chloride [19, 20] or metals [21, 22] can be added. In our experimental setup, we added zinc metal powder. Zinc is characterized as have one of the lowest melting and boiling points (m.p. ~ 419 °C and b.p. ~ 907 °C) of metals and chlorides, so it is highly effective in decreasing the reaction temperature. Moreover, during the Ti(C,N) synthesis reaction, zinc is one of the by-products of the synthesis, so the introduction of an additional amount of metal does not make the product mixture more complicated. Molten zinc creates an effective and protective shell around the Ti(C,N) crystals and prevents the ceramic particles from further growth until the reaction is complete.

The starting mixtures contained reactants in molar ratios of: Zn(CN)₂ + 4Ti + *k*Zn, where *k* was 0, 2 or 3. According to supplier declarations, the reagents had the following properties: Zn(CN)₂ (MERCK, Cat. No. 8823, purity 99%), Ti (ABCR, Cat. No. AB210733, purity 99.5%, -325 mesh) and Zn powder, (ABCR, Cat. No. AB122300, 99.9%, -325 mesh). The tested compositions were prepared by mixing the substrates in the stated proportions. The mixtures were manually stirred in a ceramic mortar for 15 minutes.

Approximately 40 g of the mixed powder was hand pressed into a graphite cup of inner diameter 28 mm and length 25 mm. The cup containing the green mixture was placed in an hermetic steel reactor of volume approx. 300 cm³, which was subsequently filled with argon at an initial pressure of 3.0 MPa. The combustion process was initiated with an electrically heated carbon fibre (Quorum Technologies) placed at the top of the sample, which was turned off immediately after the initiation of the reaction.

Tungsten-rhenium thermocouples (type C, W/Re-5 versus W/Re-26, 250 μm in diameter, OMEGA Engineering) were used to monitor the combustion

temperature (T_c), as well as to determine the combustion velocity (u_c). The response time of such thermocouples (with an unsheathed, butt-welded measuring junction) appeared to be no greater than a few milliseconds [23]. Two thermocouples were placed in the sample, perpendicular to the cylinder axis, at a spacing of approx. 10 mm. The upper thermocouple was located approx. 10 mm from the top of the specimen. A computer-assisted data logger (NI 9219, National Instruments) recorded the thermoelectric power continuously with a sampling frequency of 100 Hz. The combustion velocity was calculated from the recorded temperature profiles and the known distance between the thermocouples.

The collected raw products were sequentially purified with dilute hydrochloric acid and water to remove by-products, unreacted reactants and other residual soluble impurities. The purification procedure included: 2 h boiling in a solution of hydrochloric acid (250 cm³, concentration 10 wt.%), then washing with distilled water and ethanol. As-prepared Ti(C,N) powders were dried in air at 50 °C. The reaction yield in all cases was in the 85-90% range.

The purified combustion products were analyzed to identify their composition and morphology. XRD spectra were measured using a D500 Diffractometer (Siemens) in conjunction with CuK α radiation in the range of 2θ from 10° to 70°. The morphology and elemental composition were studied by means of SEM (Carl Zeiss Ultra Plus, operating at 3 kV), equipped with an EDX analysis unit (Bruker, Quantax 400). Two EDX analyses were performed for each sample of the combustion products, and the signal was collected from a surface of 100 μm^2 .

3 Results and Discussion

The XRD patterns of the purified reaction products from mixtures of $\text{Zn(CN)}_2 + 4\text{Ti}$ (solid line) and $\text{Zn(CN)}_2 + 4\text{Ti} + 3\text{Zn}$ (dashed line) are presented in Figure 1. In both patterns, there are only three intense peaks that can be indexed to the solid solution phase of carbon and nitrogen in titanium, *i.e.* Ti_2CN lattice structure (PDF 01-071-6059).

The Rietveld method of refinement of structural parameters was applied to determine the unit cell parameters. The DBWS-9807 program [24] was used for all calculations. The unit cell dimensions were calculated to be: $a = 4.2809 \text{ \AA}$ in the case of the $\text{Zn(CN)}_2 + 4\text{Ti}$ sample and $a = 4.2847 \text{ \AA}$ for the sample synthesized with the presence of zinc in the starting mixture. Knowing that the unit cell parameters of pure titanium carbide and titanium nitride are $a_{\text{TiC}} = 4.3274 \text{ \AA}$ (PDF 00-32-1383) and $a_{\text{TiN}} = 4.2417 \text{ \AA}$ (PDF 00-38-1420), and assuming that the lattice constant changes linearly with the carbon and nitrogen

contents in titanium carbonitride, the molecular formulae of the reaction products were found to be: $\text{TiC}_{0.46}\text{N}_{0.54}(\text{Zn}(\text{CN})_2 + 4\text{Ti}$ sample) and $\text{TiC}_{0.50}\text{N}_{0.50}(\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$ sample). The average results of the chemical composition analyses of the purified reaction products by EDX spectroscopy are shown in Table 1 and Figure 2.

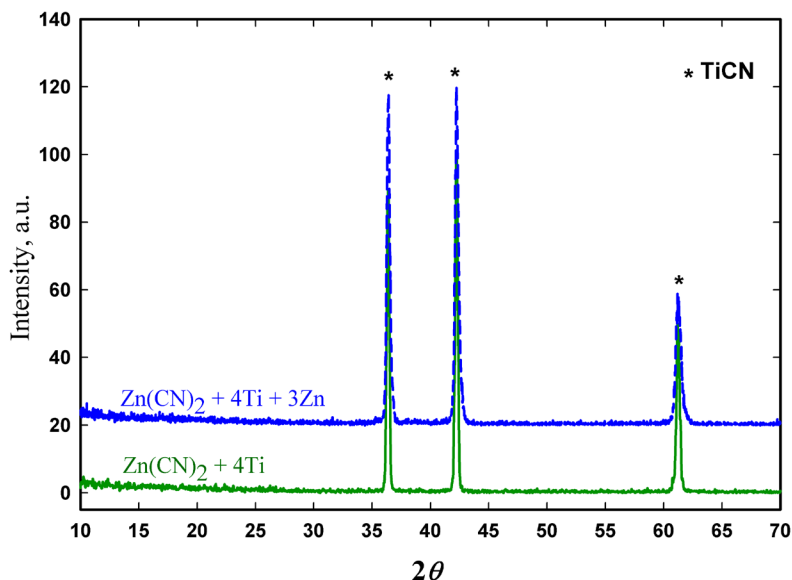


Figure 1. XRD patterns of the purified reaction products from mixtures of $\text{Zn}(\text{CN})_2 + 4\text{Ti}$ (solid line) and $\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$ (dashed line).

The molecular formulae of the products obtained from the green mixtures, with and without zinc, determined using the data from Table 1, were $\text{Ti}_{1.02}\text{C}_{0.49}\text{N}_{0.48}\text{Zn}_{0.01}$ and $\text{Ti}_{0.99}\text{C}_{0.50}\text{N}_{0.51}$. Thus the results of the EDX studies agree with the phase identification using XRD patterns. The atomic ratio of titanium atoms to carbon and nitrogen atoms in the samples was approximately 1:0.5:0.5.

Table 1. Elemental composition (EDX) of the tested samples

Sample	Elemental composition [at. %]			
	Ti	C	N	Zn
$\text{Zn}(\text{CN})_2 + 4\text{Ti}$	49.40	24.93	25.67	0.00
$\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$	50.71	24.42	24.01	0.86

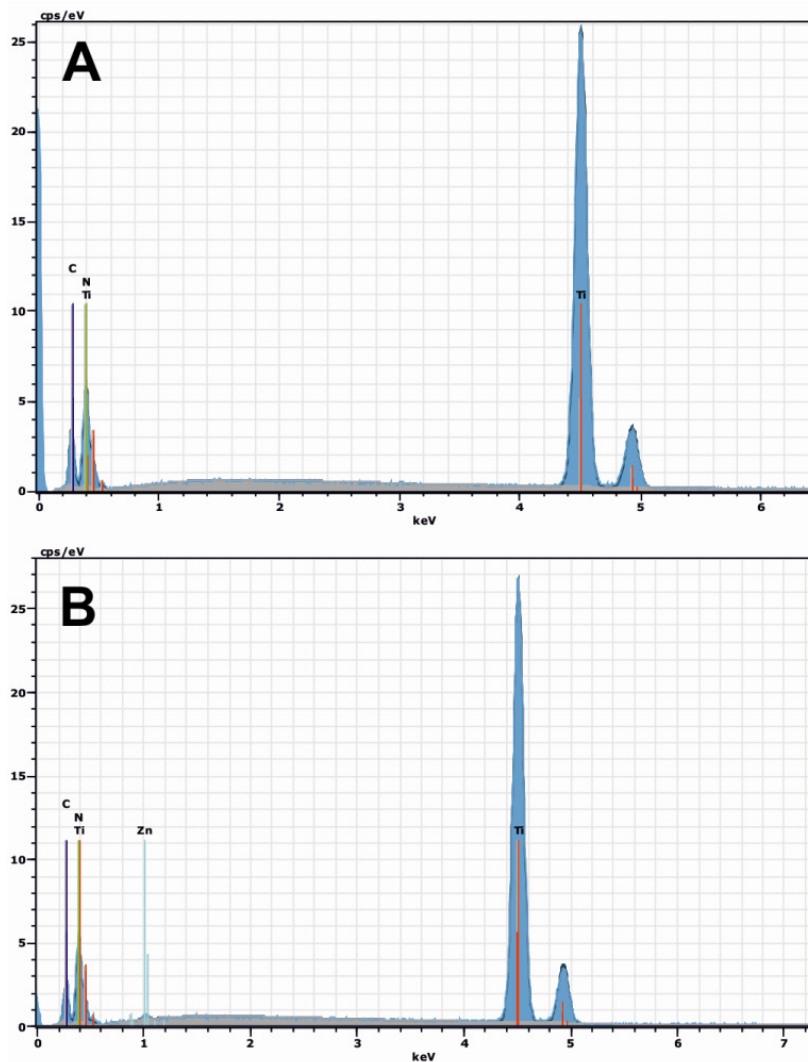


Figure 2. EDX analysis data of Ti(C,N) powders obtained without zinc ($k=0$) Figure 2A, and with 3 mol of Zn ($k=3$) Figure 2B.

The averaged and smoothed (spline method) temperature profiles in the combustion wave of the mixtures: $\text{Zn}(\text{CN})_2 + 4\text{Ti} + k\text{Zn}$, where $k = 0, 2$ or 3 , are shown in Figure 3. The observed multi-stage temperature distributions result from melting and boiling of the reactants. The combustion reaction in the systems investigated starts after the melting and decomposition of $\text{Zn}(\text{CN})_2$,

i.e. at approx. 800 °C. The plane at which the reaction temperature reaches $T^* = 800$ °C separates the combustion wave into two zones – the pre-flame zone (left side) and the chemical reaction zone (right side). For mixtures with $k = 2$ or 3, in the pre-flame zone, zinc melts at 420 °C and dissolves titanium forming various Ti-Zn phases [25], but these processes are not detected easily because of a blocking effect of the combustion temperature and the comparatively low melting enthalpy of zinc (6.67 kJ/mol).

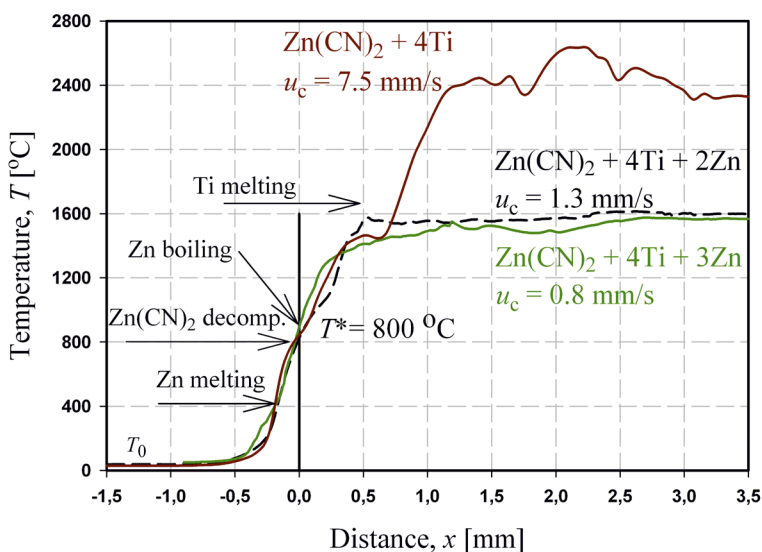


Figure 3. Averaged temperature distributions in the combustion wave of $\text{Zn}(\text{CN})_2 + 4\text{Ti} + k\text{Zn}$ system.

A noticeable decrease in the rate of temperature increase in the combustion wave can be seen in the temperature range 800-1000 °C. This seems to be connected with the heat consumed in the evaporation of zinc (907 °C, 115.3 kJ/mol) and decomposition of zinc dicyanide (800 °C). Next, in the initial part of the reaction zone, the temperature increases rapidly up to approx. 1500 °C, and with $k = 2$ or 3, a long tail of the after-burning zone appears. In the case of the $\text{Zn}(\text{CN})_2 + 4\text{Ti}$ mixture ($k = 0$), the combustion temperature T_c is higher by approx. 1000 °C, *i.e.* it reached approx. 2600 °C. The small isothermal area, at approx. 1500 °C, on the temperature distribution for the $4\text{Ti} + \text{Zn}(\text{CN})_2$ case, can be attributed to titanium melting in the presence of titanium-zinc phases, and to the elevated pressure (the measured peak pressure in the reactor was approx. 11 MPa).

The combustion velocities u_c decreased with increasing Zn concentration. In the mixture without Zn, pressed to a density of approx. 1.67 g/cm^3 , the combustion wave propagated at approx. 7.5 mm/s . For $k=2$ and $k=3$, the combustion velocity was only 1.3 and 0.8 mm/s , at densities of 1.95 and 2.09 g/cm^3 , respectively.

The morphology of the purified combustion products is shown in the SEM images (Figure 4). $\text{TiC}_{0.5}\text{N}_{0.5}$ produced in the reaction of $\text{Zn}(\text{CN})_2 + 4\text{Ti}$ (without zinc in the starting mixture) is in the form of a porous agglomerate (sponge-like sinter) of particles with irregular shape and size (Figure 4A), whereas synthesis in the presence of zinc, $\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$, yields powders containing unagglomerated particles that are quite regular in shape and size (Figure 4B). The SEM images confirm that the $\text{TiC}_{0.5}\text{N}_{0.5}$ particles are round-shaped and not sintered, with diameters of approximately $1 \mu\text{m}$. The change in product morphology was undoubtedly caused by the reduction in the combustion temperature by approx. $1000 \text{ }^\circ\text{C}$. Therefore the SHS process in a $\text{Zn}(\text{CN})_2 + 4\text{Ti} + k\text{Zn}$ system can produce sub-micrometer-sized titanium carbonitride powders by changing the Zn concentration in the green mixture.

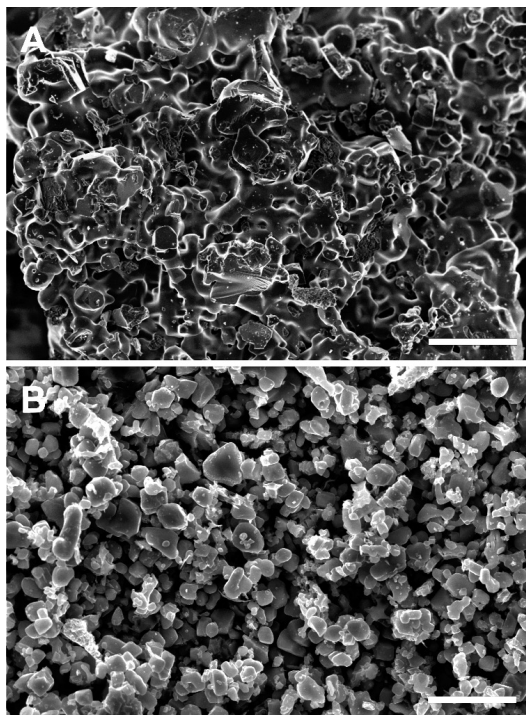


Figure 4. SEM images of $\text{TiC}_{0.5}\text{N}_{0.5}$ powders: A sample, from $\text{Zn}(\text{CN})_2 + 4\text{Ti}$, and B sample, from $\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$; scale bar length is $4 \mu\text{m}$.

Unfortunately the purity of the titanium carbonitride decreases with increasing content of zinc in the reacting mixture. The chemical composition analyses by EDX spectroscopy indicated that the purified reaction product from the mixture of $\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$ contained approx. 0.86 wt.% of zinc (Table 1).

4 Conclusions

In conclusion, we succeeded in synthesizing $\text{TiC}_{0.5}\text{N}_{0.5}$ micron powders via a spontaneous reaction of zinc dicyanide with titanium. Generally the reaction can be written as follows: $\text{Zn}(\text{CN})_2 + 4\text{Ti} \rightarrow 4\text{TiC}_{0.5}\text{N}_{0.5} + \text{Zn}$. The sequence of processes in the combustion wave includes: zinc melting (if present), decomposition of $\text{Zn}(\text{CN})_2$, zinc violent evaporation, spattering of molten Ti-Zn phases, dissolving of carbon and nitrogen in the titanium droplets, nucleation and growth of $\text{TiC}_{0.5}\text{N}_{0.5}$ crystallites. The identical number of carbon and nitrogen atoms in the $\text{Zn}(\text{CN})_2$ molecule, plus the fact that they are released in the atomic form or as CN molecules, favour the formation of chemically homogenous titanium carbonitride containing carbon and nitrogen in an atomic ratio of one.

Excessively high temperatures in the reaction zone, propagating in the stoichiometric mixture of $\text{Zn}(\text{CN})_2 + 4\text{Ti}$ (approx. 2600 °C), cause the growing $\text{TiC}_{0.5}\text{N}_{0.5}$ crystallites to connect to each other forming a porous agglomerate. In order to prevent this agglomeration, the reaction can be carried out in the presence of zinc. Phase transitions of zinc occur at low temperatures (420 and 907 °C) and are highly endothermic processes. Thus zinc effectively reduces the combustion temperature (to approx. 1600 °C). Moreover liquid zinc separates the $\text{TiC}_{0.5}\text{N}_{0.5}$ crystallites, which prevents agglomeration, reduces particle sizes, and improves their morphology. It was experimentally confirmed that a hand-pressed mixture of $\text{Zn}(\text{CN})_2 + 4\text{Ti} + 3\text{Zn}$ is capable of self-sustained combustion under an argon atmosphere at an initial pressure of 3.0 MPa.

The advantages of the proposed method for readily scaling-up the synthesis of $\text{TiC}_{0.5}\text{N}_{0.5}$ powder include the facts that it is a simple, fast, low-temperature, low-pressure, and low-cost process. The yield is high, and the starting reactants are readily available. Furthermore the experiments described here may provide a new self-induced and efficient method for producing novel titanium carbonitride based cermets, and even end-shaped elements made of these materials. This is made possible by using cyanides of metals (Me) that are not removed from the combustion products, but remain as a metallic matrix of the Me-Ti(C,N) composite. For example, silver cyanide AgCN and copper dicyanide $\text{Cu}(\text{CN})_2$

may be used to produce Ag-Ti(C,N) and Cu-Ti(C,N) cermets. Other metallic matrices cannot be excluded, but silver and copper are preferred owing to their low melting points, approx. 962 and 1083 °C respectively.

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5 References

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