JOURNAL OF MATERIALS SCIENCE 29 (1994) 2187–2191

Limits of the self-propagating high-temperature synthesis wave propagation in eutectic composite materials

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Phase formation during the self-propagating high-temperature synthesis in the Ti–C–M (M = Ni, Co, Cr) eutectic-type ternary systems with and without preheating has been studied. It was found that the synthesis proceeds via origination of quasi-binary TiC–M eutectics, the principle reaction being that of TiC formation. The dependence of the combustion temperature on the preheating temperature and the initial charge composition has been evaluated by thermodynamic analysis.

1. Introduction

The combustion synthesis, or the so-called self-propagating high-temperature synthesis (SHS), is a promising cost- and energy-effective method to produce high-purity refractory compounds (carbides, borides, nitrides, intermetallics, etc.) and composite materials [1]. Producing final articles of composite materials by the SHS method has the advantage of relative simplicity and low energy expenditure over traditional methods, such as sintering, hot pressing, etc. A vast diversity of structure formation patterns in the SHS wave has been observed in various systems [1–5]. Among them, those involving the appearance of a transient liquid phase are of particular interest.

Nowadays, the eutectic composite materials of M_1–M_2X type are widely used in industry [6]. The binding metal, M_1, constitutes a matrix, while the refractory compound, M_2X, acts as a reinforcing component. Eutectic composite materials have a lower melting temperature than individual components. This allows injection moulding and/or related methods to be applied to produce final articles of diverse shapes immediately after the SHS wave has passed across a specimen. The composition of the media at the combustion temperature should correspond to the two-phase region (liquid + solid) of the M_1–M_2–X ternary equilibrium diagram, i.e. it should constitute a suspension of refractory particles in a binding metal–base melt.

The structures of composite materials produced by SHS in the Ti–C–Ni system have been examined at relatively low nickel concentrations (below 60 wt %) [4, 5]. Usually the eutectic point corresponds to a rather high concentration of binding metal which exceeds the bounds of a region where the product formation by the gasless combustion is possible with the charge being initially at room temperature. This necessitates preheating the charge before initiating the SHS process. Therefore, it is important to evaluate the dependence of the preheating temperature on the composition of the initial mixture.

In this connection, the present work was aimed at obtaining solid–liquid systems, which contain refractory particles as reinforcing components, by the SHS method. Composite materials should contain a rather small amount of refractory inclusions (i.e. should be as close to the eutectic point as possible) in order to possess a relatively long melt lifetime and a high fluidity and provide the opportunity of applying methods of deforming semisolid (semimolten) materials. Ternary systems of the type Ti–C–M, where M = Ni, Co, Cr, have been chosen as subjects of investigation. Nickel-, cobalt- and chromium-based composite materials possess a good combination of properties, namely, plasticity, high-temperature strength, and wear resistance [6, 7]. For the above systems, reinforcement by dispersed particles of titanium carbide may be obtained.

Quasi-binary TiC–Ni and TiC–Co systems have eutectic-type phase diagrams, their respective melting temperatures being 1553 and 1633 K [10, 11]. The TiC solubility is 9.3 mol % (9.44 wt %) in liquid nickel [10] and about 6 mol % (6.1 wt %) in liquid cobalt [11] at the melting temperature.

In the Cr–Ti–C ternary system, the $Cr_{0.969}$-$Ti_{0.031}$–$TiC_{0.8}$ cross-section with the eutectic temperature of 1943 K is strictly a quasi-binary one, with the eutectic point composition of 76Cr + 14.09Ti + 9.91C (mol %) [12] that corresponds to 24.1 wt % $TiC_{0.8}$, while the solidus temperature in the Cr–$TiC_{1.0}$ cross-section is 1803 K [13].

2. Experimental procedure

The following commercial powders were used to prepare the charge compositions: titanium (particle diameter ~ 0.18 mm; major impurities, (wt %): 0.08 Fe, 0.06 Cl, 0.03 N, 0.03 C, 0.04 Si), nickel (particle diameter ~ 70 μm; major impurities (wt %): 0.1 Fe, 0.2

Co, 0.02 C, 0.03 Si, 0.06 Cu, 0.008 S), cobalt (particle diameter ~ 70 μm; major impurities (wt %): 0.2 Fe, 0.4 Ni, 0.02 C, 0.025 Si, 0.04 Cu), chromium (98 wt % Cr); major impurities (wt %): 0.5 Fe, 0.04 C, 0.5 Si, 0.04 Cu, 0.7 Al, 0.03 S, 0.03 P), and carbon black. Powders with a total mass of about 200 g were mixed in a laboratory ball mill for 3 h. Then mixtures were compacted into cylindric samples (14.5 or 25 mm diameter and 10–12 mm high), their density being 3.2–4.1 $\mathrm{g\,cm^{-3}}$.

The binding metal content of the mixture was varied over a wide range, while the titanium-to-carbon molar ratio retained a stoichiometric value corresponding to $TiC_{1.0}$.

Samples were ignited either at room temperature or after preheating. The preheating temperature was varied from 300–1523 K. A diagram of the experimental apparatus is shown in Fig. 1. The effect of preheating was examined in chamber 1 of an electric furnace; the total power of heating elements 2 was 2.4 kW. Samples 5 with W–Re 0.1 mm diameter thermocouple 4 pressed into it was placed into specimen holder 3. Specimens of fixed composition and specimens with variable concentrations of a binding metal, M, were used, the latter were made of two or three tablets having different M content. The SHS wave in a preheated specimen was initiated by supplying an electric current ($U = 22$ V, $I = 20$–40 A) via electrodes 7 and 8 to the incendiary tablet 6 (a compacted mixture of titanium and boron powders to give the exothermic $Ti + 2B \rightarrow TiB_2$ reaction). Tablet 6 thickness was 1–2 mm, its diameter was equal to that of the specimen.

For every composition, a minimum temperature of the charge preheating was selected under which the SHS process could proceed. The samples were air-cooled after combustion.

The phase constitution and chemical composition of the combustion product were identified by X-ray diffraction (XRD) analysis and electron-probe microanalysis (EPMA).

3. Results and discussion

Both XRD and EPMA revealed that the titanium carbide is the prevailing reinforcing refractory component in the composite material formed by the gasless combustion of the given systems. Thus, the titanium carbide formation was the principle reaction in the charge at high temperatures

$$x(Ti + C) + (1 - x)\,M \rightarrow xTiC + (1 - x)M \quad (1)$$

where x is the (Ti + C) molar fraction in the charge mixture.

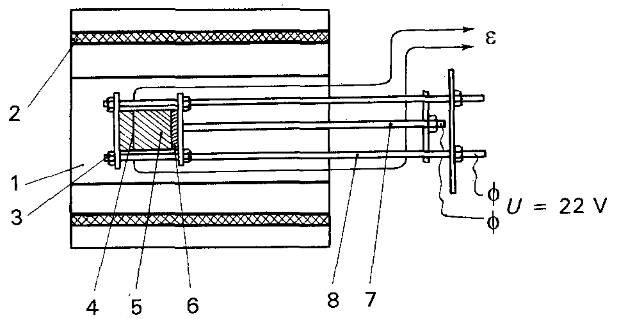

Figure 1 Schematic illustration of the experimental apparatus for details, see text.

In addition to this reaction, titanium forms a certain amount of intermetallic compounds with a binding metal. Thus, the TiNi phase was observed in the Ti–C–Ni mixtures while the intermetallics TiCo, $TiCo_3$ and Ti_2Co were found to be formed in the Ti–C–Co system. As well as the carbides TiC and $Cr_{23}C_6$, the intermetallic compound $TiCr_2$ was observed to appear in the Ti–C–Cr mixtures.

It is known that the phase constitution and morphology of an SHS product are dependent both on the combustion regime and the cooling rate after the SHS wave has passed along the sample. Microstructures of combustion products formed in the Ti–C–Co mixtures with different cobalt contents are shown in Fig. 2. A porous final product of a granular structure has been formed. The size of the pores (dark regions in Fig. 2) is 10–100 μm. The titanium carbide grain size increased as the binding metal content of the initial mixture rose; it constituted about 1 μm at 60 wt % Co, 1–3 μm at 70 wt % Co, and 10–20 μm at 80 wt % Co. Because the diffusivities of dissolved carbon and titanium in the melt are rather high, $D \simeq 10^{-5}\ \mathrm{cm\,s^{-1}}$, the observed results may be connected with a decrease in the number of the TiC nucleation sites due to an increase in the concentration of the binding metal. The SHS wave velocities for the systems examined are shown in Fig. 3.

Previously, the macrokinetics of the phase and structure formation in the SHS wave in Ti–C and Ti–C–Ni systems has been examined at a nickel content below 60 wt % [2–5] when combustion is possible without preheating, i.e. the sample to be ignited is at room temperature. It has been shown that the primary process is the titanium-based melt formation. Carbon particles are gradually dissolved in the melt, while particles of the refractory titanium carbide are crystallized from the melt at the same time. Data on physical and chemical properties of the above systems allow us to suggest that a similar structure-forming mechanism in the SHS wave should operate in all of the eutectic-type systems examined in the present work.

The polythermic cross-sections of the ternary diagrams of the systems under investigation [10–12] are shown in Fig. 4. The measured combustion temperature, T_c^{ex}, is plotted which is obtained at the minimum preheating temperature, T_0, necessary for SHS wave propagation in the system. The eutectic temperatures of the TiC–M quasi-binary systems [10–12] and Ti–M binary systems [14–16] are shown for comparison in the relevant concentration ranges. The Ti–TiC eutectic temperature is 1918 K [12, 14–16].

It is readily seen from the above data that the T_c^{ex} value correlates with the temperature of the TiC–M quasi-binary eutectic. This result is easy to interpret. Owing to the high value of the thermal diffusivity of the charge, $a \simeq 10^{-2}$–$10^{-1}\ \mathrm{cm^2\,s^{-1}}$, the

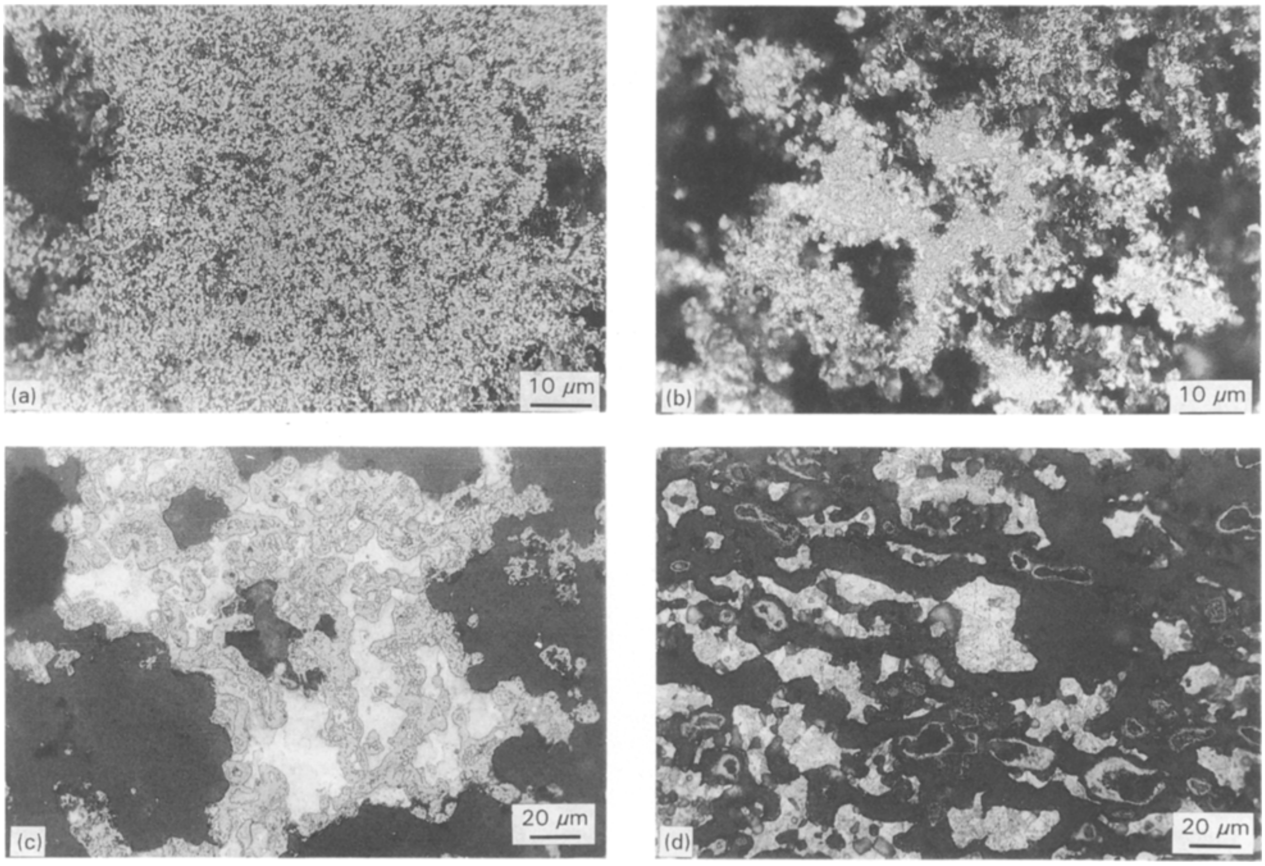

Figure 2 Optical micrographs of the microsections of composite materials produced by the SHS in the Co–Ti–C system: (a) 60 wt % Co; (b) 70 wt % Co; (c) 80 wt % Co, (d) 90 wt % Co.

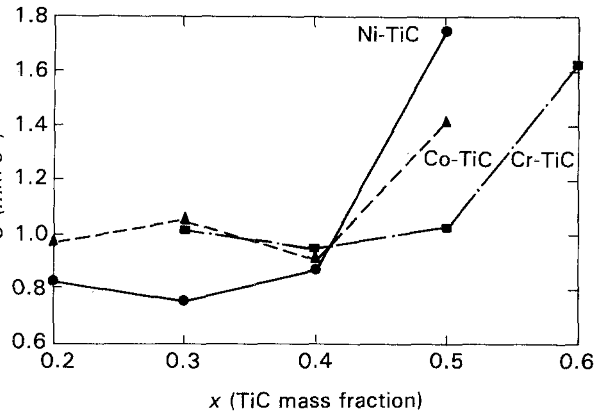

Figure 3 The SHS wave velocity versus the (Ti + C) content in the charge.

characteristic time of phase and structural transformations in the SHS wave, $t_c \simeq 10^{-3}$–10^{-1} s, is enough to level the temperature in a macroscopic region having a size of $\delta \simeq (at_c)^{1/2} \simeq 10^2$–$10^3$ μm [3]. This size exceeds considerably the diameter of initial particles $d \simeq 10$ μm (for metals) to $d \simeq 1$ μm (for carbon black). In the charge, all possible interparticle contacts, namely the Ti/C, Ti/M, and M/C, are present, and the contact-melting phenomenon primarily occurs in a couple with the minimum eutectic temperature. However, the appearance of a melt in a macroscopic region containing a great number of particles is possible only at the temperature close to that of the quasi-binary eutectics, because melting is accompanied by the formation of refractory titanium carbide particles.

The combustion synthesis of intermetallic compounds is possible in M_1–M_2 systems, such as Ti–Ni, Ti–Co, etc. [17]. However, the Gibbs energy of the titanium carbide formation (i.e. for the reaction $Ti + C \rightarrow TiC$) $\Delta G^0_{298} = \Delta H^0_{298} - T\Delta S^0_{298} \approx -180$ kJ mol^{-1}, is greater than that for intermetallic compounds by a factor of about 3. For example, these values for TiNi and TiCo are about -64 and -73 kJ mol^{-1}, respectively [18–20]. Therefore, the heat released due to the formation of the titanium carbide predominates and the SHS wave characteristics correlate with the parameters of the TiC–M quasi-binary phase diagrams.

4. Estimation of thermal characteristics of the SHS wave

The experimental results obtained in this study enable us to evaluate the dependence of the preheating temperature on the composition of the initial mixture.

After the appearance of the melt, the compositions of the liquid and solid phases move, respectively, over the liquidus and the solidus surfaces of the equilibrium ternary diagram, until the combustion temperature is attained. Nevertheless, the final compositions of solid and liquid phases to be obtained in the SHS wave at the combustion temperature are defined by the quasi-binary TiC–M phase diagram. Thus, the parameters of this diagram can be used for estimating the

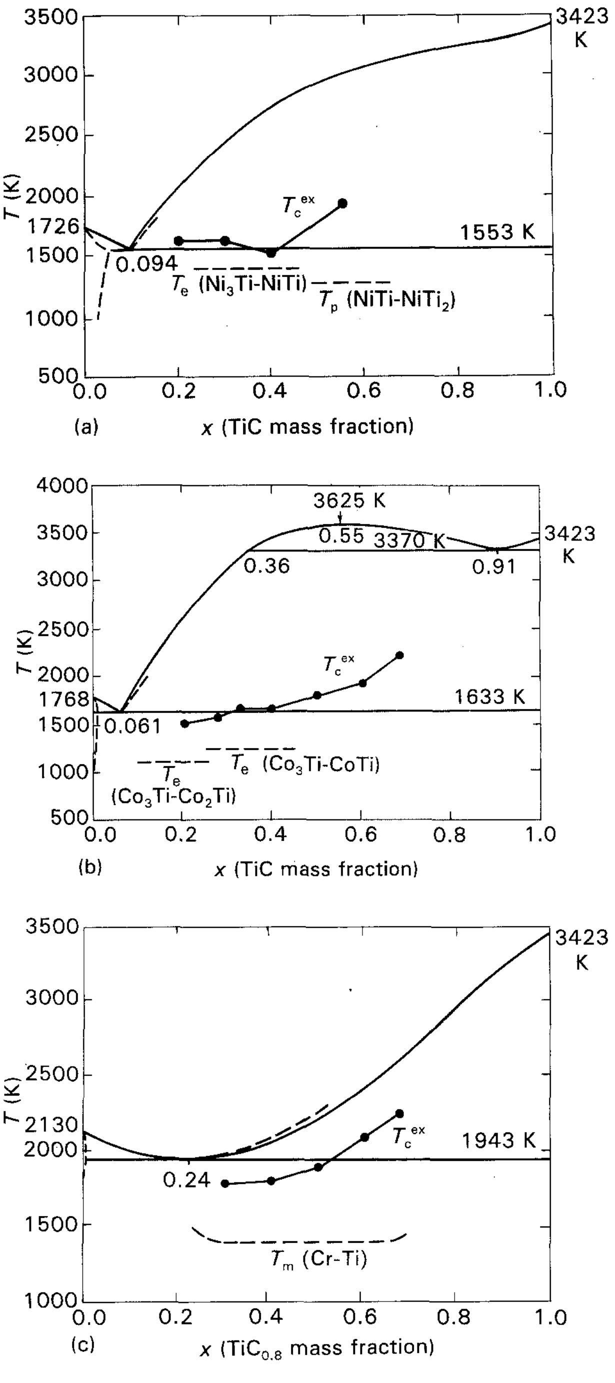

Figure 4 The M–TiC quasi-binary equilibrium diagram ((– – –) experimental [10–13], (——) calculated) and the measured combustion temperature, T_c^{ex}: (a) Ni–TIC; (b) Co–TiC; (c) Cr–TiC; (T_e is the eutectic temperature of the M–Ti binary system, T_p is the peritectic temperature, T_m is the melting temperature of the Cr–Ti system [14–16]).

adiabatic temperature, T_{ad}, and the preheating temperature T_0 that is necessary for the SHS wave propagation. Under adiabatic conditions, the heat-balance equation for Reaction 1 is written as

$$H_r^0(T_0) = H_p^0(T_{ad}) \tag{2}$$

where T_0 is the initial temperature of the reagents and T_{ad} the final temperature of products. The enthalpy of reagents, H_r^0, and that of products, H_p^0, are defined as

$$H_r^0(T_0) = x\{\Delta_f H_{298}^0(\mathrm{TiC}) + \int_{298}^{T_0} [c_p(\mathrm{TiC}) - c_p(\mathrm{Ti}) - c_p(\mathrm{C})]\mathrm{d}T\} \tag{3a}$$

$$H_p^0[T_{ad}] = (1-\nu)\int_{T_0}^{T_{ad}} c_p(\mathrm{TiC})\mathrm{d}T + \nu\Delta H_m^0(T_{ad}) \qquad \nu = \frac{1-x}{1-x_L(T_{ad})} \tag{3b}$$

where $\Delta_f H_{298}^0$(TiC) is the standard enthalpy of the TiC formation [18]; $c_p(i)$ is the specific heat per mole of the ith substance; ν is the liquid phase portion in a two-phase region of a quasi-binary diagram; x_L is the titanium carbide content of the melt, according to the liquidus line. The standard enthalpy of the melt, ΔH_m^0, is given by

$$\Delta H_m^0 = x_L \Delta h_{\mathrm{TiC,m}}^0 + (1 - x_L)\Delta h_{\mathrm{M,m}}^0 + \Delta h_m^{ex} \tag{4}$$

where $\Delta h_{\mathrm{TiC,m}}^0$ and $\Delta h_{\mathrm{M,m}}^0$ are the standard enthalpies of TiC and the metal M in the molten state; Δh_m^{ex} is the excess enthalpy of mixing. To define the excess enthalpy of the melt, the regular solution model [21] has been used

$$\Delta h_m^{ex} = (1 - x_L)x_L[A_2(1 - x_L) + A_1 x_L] \tag{5}$$

where subscripts 1 and 2 indicate metal, M, and titanium carbide, respectively. Within this model, the activity coefficient, γ, of metal M and TiC in the quasi-binary melt are defined as [19]

$$\begin{aligned} RT\ln\gamma_M &= x_L^2[2(1 - x_L)A_{21} + (2x_L - 1)A_{12}] \\ RT\ln\gamma_{\mathrm{TiC}} &= x_L^2[2x_L A_{12} + (1 - 2x_L)A_{21}] \end{aligned} \tag{6}$$

The liquidus line of the quasi-binary system is described by the following expressions

$$\begin{aligned} RT\ln[1 - x_L)\gamma_M] &= -\Delta h_{\mathrm{M,m}}^0(1 - T/T_{\mathrm{M,m}}) \\ RT\ln[x_L\gamma_{\mathrm{TiC}}] &= -\Delta h_{\mathrm{TiC,m}}^0(1 - T/T_{\mathrm{TiC,m}}) \end{aligned} \tag{7}$$

where $T_{\mathrm{M,m}}$ and $T_{\mathrm{TiC,m}}$ are the melting temperatures of pure metal, M, and TiC, respectively. The model parameters, A_{12} and A_{21}, have been calculated from Equations 6 and 7 using available experimental data on eutectic points of the quasi-binary systems [10–13] and thermochemical data [18–20]. The A_{12} and A_{21} values are given in Table I.

The adiabatic combustion temperature, T_{ad}, for various (Ti + C) molar fractions in the charge, x, and preheating temperatures, T_0, have been calculated numerically from Equations 2–5. The temperature dependence of the specific heat of the component substances [18, 19] has been taken into account. Because the liquidus line in the quasi-binary M–TiC phase diagrams has been examined only in the immediate vicinity of the eutectic point [10–13], the equilibrium liquid-phase composition, x_L, involved in Equations 2 and 3 is calculated by the use of Equations 6 and

TABLE I Subregular solution parameters for the liquid phase of M–TiC quasi-binary systems

System	A_{12} (kJ mol^{-1})	A_{21} (kJ mol^{-1})
Ni–TiC	28.12	– 18.63
Co–TiC	98.94	– 12.18
Cr–TiC	– 45.60	17.28

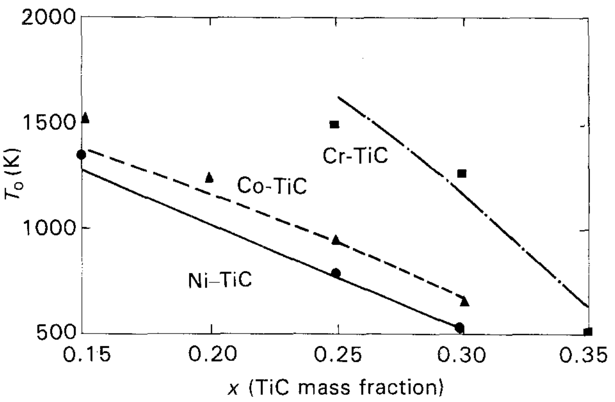

Figure 5 The calculated preheating temperature, T_0, necessary for SHS wave propagation in diluted M–(Ti + C) systems versus the (Ti + C) content in the charge. Experimental data (●) Ni–Ti–C, (▲) Co–Ti–C, (■) Cr–Ti–C.

TABLE II Adiabatic combustion temperature, T_{ad}, in the Ni–TiC system wihout preheating

Ni content (wt %)	Calculated T_{ad} (K)	Experimental T_{ad} (K) [5]
20	2900	2600–2700
30	2630	≈ 2500
40	2350	2300–2400
50	2055	≈ 2000
60	1760	1730

7 over a wide temperature range. The calculated liquidus line for quasi-binary systems (Ni–TiC, Co–TiC, and Cr–TiC), as well as the experimental data [10–13], are plotted in Fig. 4.

The approach developed gives us the opportunity of estimating the minimum value of the preheating temperature, T_0, that is necessary for the SHS process to proceed in dilute M–TiC systems. The dependence of this value on the content of a binding metal in the initial charge has been calculated from Equations 2 and 3 assuming that the adiabatic temperature, T_{ad}, is close to the quasi-binary eutectic temperature in the system. The estimated value of the preheating temperature is consistent with that found experimentally (Fig. 5).

For the Ni–TiC system having a nickel content from 20–60 wt %, the SHS wave can propagate without preheating of the charge [4, 5]. The adiabatic temperature, T_{ad}, calculated from Equations 2–5 at $T_0 = 298$ K correlates with experimental data [5] (Table II).

5. Conclusion

The results obtained have demonstrated the possibility of producing eutectic composite materials by the SHS method. The thermodynamic approach developed can be used to estimate the preheating temperature that is necessary to provide the SHS wave propagation in dilute M–(Ti + C) systems.

Acknowledgements

The authors thank Dr A. S. Rogachev and Dr A. S. Mukasian for performing the EPMA of the samples. This work was supported by the Byelorussian Fundamental Research Foundation (Grant T16-221).

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Received 25 March
and accepted 21 September 1993