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Thermodynamic predictions for the formation of ceramic–metal composite by self-propagating high-temperature synthesis

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The development of ceramic materials to the point where they can be used with confidence in a wide range of thermomechanical applications such as heat engines, energy generation or chemical process plant, has been the subject of major international research programmes. The advantages of ceramics are clear with respect to hardness, strength, wear, corrosion and creep resistance. Major disadvantages lie in the unreliable mechanical performance (brittle fracture and distribution of strength values) and in the cost associated with chemically prepared powders, high-temperature processing and machining to size.

The low reliability of ceramic components arises from the brittle fracture behaviour. Two methods can be followed to overcome the problem; first by the preparation of components free from flaws of size greater than about 10 μm in dimension and secondly by the preparation of components with toughened microstructures via whisker or fibre addition, metal inclusions or transformation toughening. Although great improvements in flaw control have been achieved with refined powders, clean-room fabrication or fluid shaping methods, the costs are correspondingly high and the materials continue to be damage-sensitive during installation or use. Therefore, investigations of potentially more-economic routes and systems that could well provide superior toughness have received further attention.

The objective of this letter is to present a thermodynamic forecast for the case where a ceramic matrix composite containing Al_2O_3, ZrO_2 and metallic Nb might be obtained by self-propagating high-temperature synthesis (SHS) using thermite reactions. The three reactions analysed (Equations 1–3, below) are highly exothermic, and hence present various advantages regarding energy saving, simplicity of the process and higher purity of the products, owing to the high temperatures that can be reached. The toughness in this class of material can be improved by virtue of the metallic inclusions (Nb), the incorporation of fibres (Al_2O_3) as diluent, and by microcrack and transformation toughening (ZrO_2):

$$\mathrm{Nb_2O_5} + \mathrm{Al_2Zr} + v\mathrm{Al_2O_3} \rightarrow 2\mathrm{Nb} + \mathrm{ZrO_2} + \mathrm{Al_2O_3} + v\mathrm{Al_2O_3} \qquad (1)$$

$$\mathrm{Nb_2O_5} + 2\mathrm{Al} + \mathrm{Zr} + v\mathrm{Al_2O_3} \rightarrow 2\mathrm{Nb} + \mathrm{ZrO_2} + \mathrm{Al_2O_3} + v\mathrm{Al_2O_3} \qquad (2)$$

$$\mathrm{Nb_2O_5} + \tfrac{10}{3}\mathrm{Al} + v\mathrm{Al_2O_3} + \phi\mathrm{ZrO_2} \rightarrow 2\mathrm{Nb} + \tfrac{5}{3}\mathrm{Al_2O_3} + v\mathrm{Al_2O_3} + \phi\mathrm{ZrO_2} \qquad (3)$$

where v and ϕ are the extent of dilution.

Considering the reaction time to be very short, the exothermicity of the reaction is expressed by the adiabatic temperature (T_{ad}), which can be evaluated by the general criteria

$$\mathrm{R}_1 + \mathrm{R}_2 + \ldots + \mathrm{R}_i \rightarrow \mathrm{P}_1 + \mathrm{P}_2 + \ldots + P_j + \Delta H^{\circ}_{\mathrm{reaction}}(T_0) \qquad (4)$$

$$\Delta H^{\circ}_{\mathrm{reaction}}(T_0) = \sum_{j=1}^{N}\left\{\int_{T_0}^{T_j^1} C_p,P_j(T)\,\mathrm{d}T + \Delta H_{\mathrm{t}}^{1}(T_j^1) + \sum_{l=2}^{M}\left[\int_{T_j^{l-1}}^{T_j^l} C_p,P_j(T)\,\mathrm{d}T + \Delta H_{\mathrm{t}}^{l}(T_j^l)\right] + \int_{T_j^M}^{T_{\mathrm{ad}}} C_p,P_j(T)\,\mathrm{d}T\right\} \qquad (5)$$

where R_i are the reactants or diluents, P_j are the products or diluents, $\Delta H^{\circ}_{\mathrm{reaction}}(T_0)$ is the change of reaction enthalpy at temperature T_0, $\Delta H_{\mathrm{t}}^{l}(T_j^l)$ is the enthalpy of the transformation l (change of phases of aggregation state) to the product P_j at the transition temperature T_{t}, l is the transformation index, T_0 the reaction temperature, T_j^l the temperature of the transformation l to the product P_j, N the total number of products, M the total number of transformations, T_{ad} the adiabatic temperature and $C_p,P_j(T)$ is the molar heat capacity of the product P_j, valid in the temperature range between the integration limits.

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Although the adiabatic temperature represents the maximum temperature to which the reaction product can be raised as a result of the exothermic reaction, in actual experiments this theoretical temperature is seldom, if ever, achieved due to heat losses.

In the general equation (Equation 5) the diluent is only found as a product, since its function is to extract part of the enthalpy of the reaction. However, due to the stoichiometric balance in the chemical reactions (Equations 1–3) the diluent is placed on both sides of the equation, having no participation in the reaction itself, although it will influence the final phases and microstructure.

As far as the data available have allowed, the Gibbs free energy of Equation 1, not presented here, has corroborated its thermodynamic prediction feasibility with the temperature. Applying values of the thermodynamic properties listed in Table I and II to Equation 5, the variation of the enthapies ($H_{(T)}$) of reactants and products with respect to temperature were obtained. The energy balance is given by the enthalpy curves (Figs 1–3), from which the maximum temperature of the products for an adiabatic process may be estimated. Practical measurements of Figs 1–3 might be expected to demonstrate errors due to the sources of the thermodynamic data and the assumptions considered in Tables I and II.

TABLE I Molar heat capacities used to generate the $H(T)$ versus T curves

Compound or element	$C_p(T) = a + (b \times 10^{-3}T) + (c \times 10^5 T^{-2})$			Temperature range of validity (K)	Ref.
	a	b	c		
$\langle Al_2O_3 \rangle$	25.48	4.25	−6.82	298–1800	[1]
$\{Al_2O_3\}$	33.05	–	–	2320–2500	[2]
$\langle Nb_2O_5 \rangle$	38.76	3.54	−7.32	298–1700	[1]
$\{Nb_2O_5\}$	57.90	–	–	m.p.–1810	[1]
$\langle ZrO_2 \rangle$ monoclinic	16.64	1.80	−3.36	298–1478	[1]
$\langle ZrO_2 \rangle$ tetragonal	17.80	–	–	1478–1850	[1]
$\langle ZrO_2 \rangle$ cubic^c	17.80	–	–	–	–
$\{ZrO_2\}$	24.04	–	–	2963–6000	[2]
$\langle Al_2Zr \rangle^b$	17.86	2.08	−3.0	–	–
$\{Al_2Zr\}^c$	24.36	–	–	–	–
$\langle Nb \rangle^d$	5.57	1.048	–	298–2740	[3]
$\{Nb\}$	8.00	–	–	2740–5500	[3]
$\langle Al \rangle$	4.94	2.96	–	298–m.p.	[1]
$\{Al\}$	7.6	–	–	m.p.–2400	[1]
$\langle Zr \rangle$-α	5.25	2.78	–	298–1135	[1]
$\langle Zr \rangle$-β	5.55	1.11	–	1135–m.p.	[1]
$\{Zr\}$	8.00	–	–	2125–5000	[3]

$C_p(T)$ are the molar heat capacities, $\langle\ \rangle$ indicates solid phase and $\{\ \}$ liquid phase; m.p., melting point.

[a] Assumed to be the same value as the tetragonal structure.

[b] Estimated by the Ünall and Kellog method [1].

[c] Estimated by the average ratio C_p,solid$^{(m.p.)}$/C_p,liquid$^{(m.p.)}$ for compounds A_2B listed in [1].

[d] Estimated from data given in [3] assuming a linear behaviour.

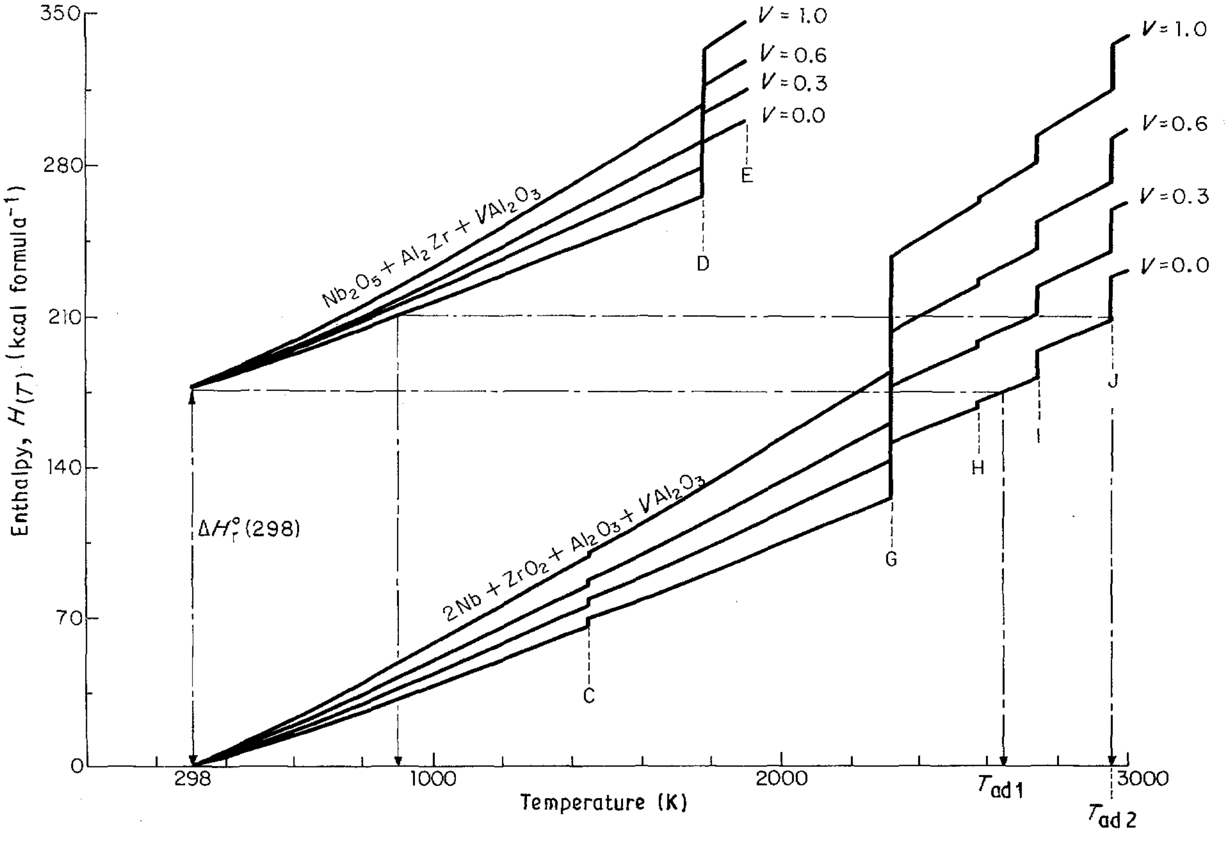

Figure 1 Dependence of enthalpy ($H_{(T)}$) on the temperature of reactants and products for the reaction in Equation 1. Transformations C to J are indicated in Table II. T_{ad1}, adiabatic temperature for ignition at 298 K; T_{ad2}, adiabatic temperature for ignition at 900 K ($v = 0.0$); v, extent of Al_2O_3 dilution; and $\Delta H_f^\circ(298)$, change of reaction enthalpy at 298 K. 1 kcal ≈ 4.2 kJ.

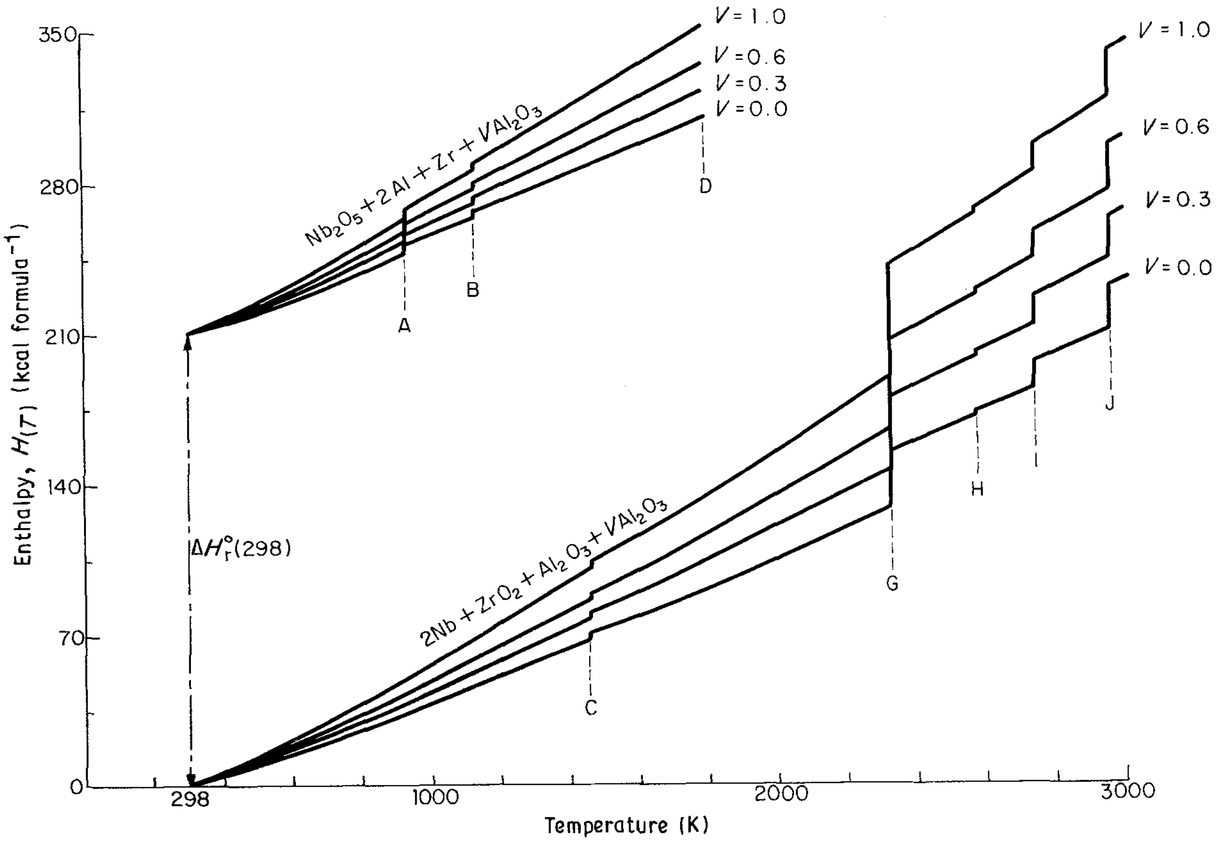

Figure 2 Dependence of enthalpy ($H_{(T)}$) on the temperature of reactants and products for the reaction in Equation 2. Transformations A to J are indicated in Table II. v, extent of Al_2O_3 dilution and $\Delta H^\circ_r(298)$, change of reaction enthalpy at 298 K. 1 kcal ≈ 4.2 kJ.

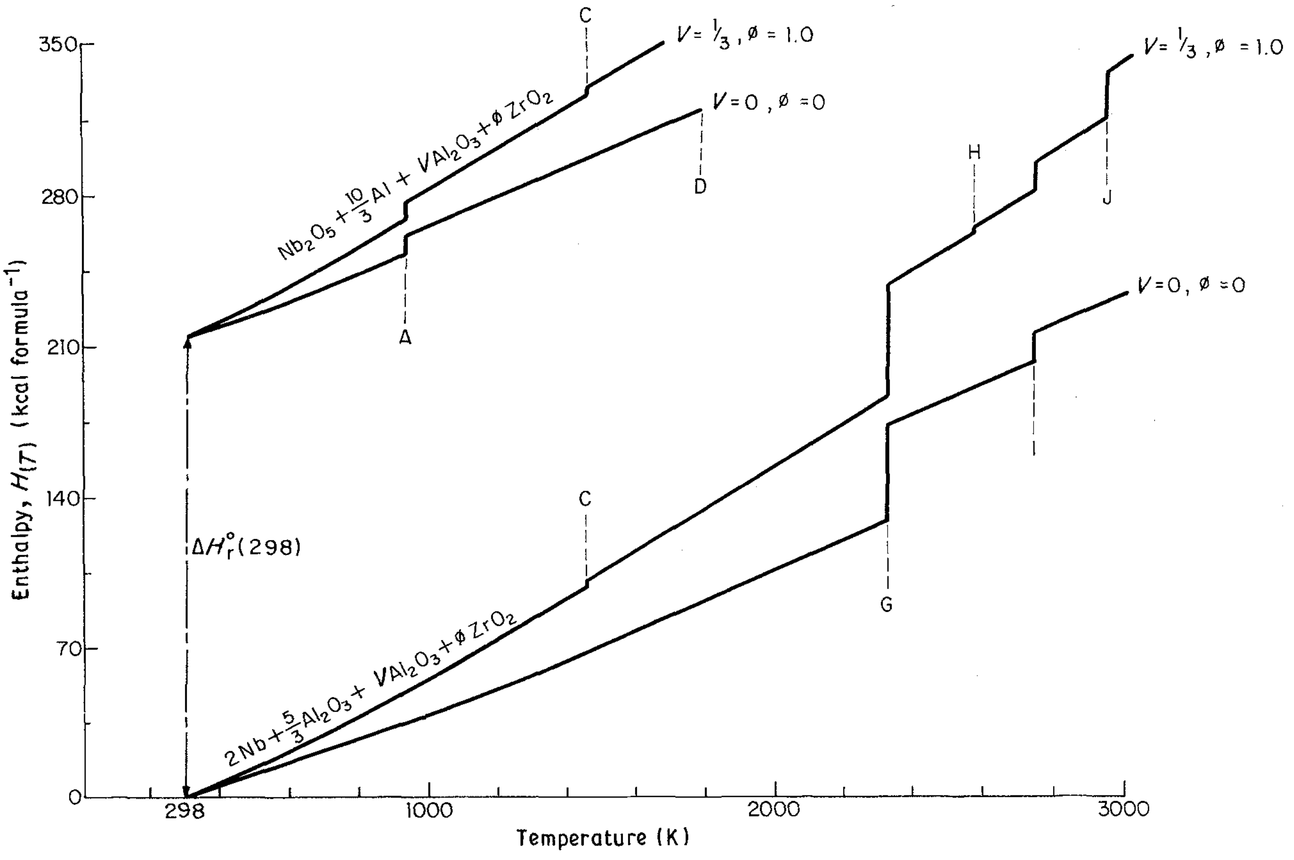

Figure 3 Dependence of enthalpy ($H_{(T)}$) on the temperature of reactants and products for the reaction in Equation 3. Transformations A to J are indicated in Table II. v and ϕ, extent of Al_2O_3 and ZrO_2 dilution, respectively, and $\Delta H^\circ_r(298)$, change of reaction enthalpy at 298 K. 1 kcal ≈ 4.2 kJ.

TABLE II Thermodynamic properties used to generate the $H(T)$ versus T curves

Compound or element	$\Delta H^0_{f(298)}$ (kJ mol^{-1})	T_t(K); phase transformation; ΔH_t (J mol^{-1})	Melting point (K)	ΔH_m (kJ mol^{-1})	Symbols used in Figs 1–3	Ref.
Al_2O_3	−1678		2324	108	G	[1]
Nb_2O_5	−1901		1785	103	D	[1]
ZrO_2	−1102	1448; monoclinic → tetragonal; 5946			C	[1]
		2568; tetragonal → cubic; 5946			H	[1]
			2953	87	J	[1]
Al_2Zr	−138		1910		E	[4,5]
Nb	0		2740	26.4	I	[3]
Al	0		932	10.5	A	[1]
Zr	0	1125; $\alpha \rightarrow \beta$; 3768			B	[1]
			2130	19.3	F	[1]

$\Delta H^0_{f(298)}$, Enthalpy of formation at 298 K; T_t, transformation temperature; ΔH_t, transformation enthalpy; and ΔH_m, enthalpy of fusion.

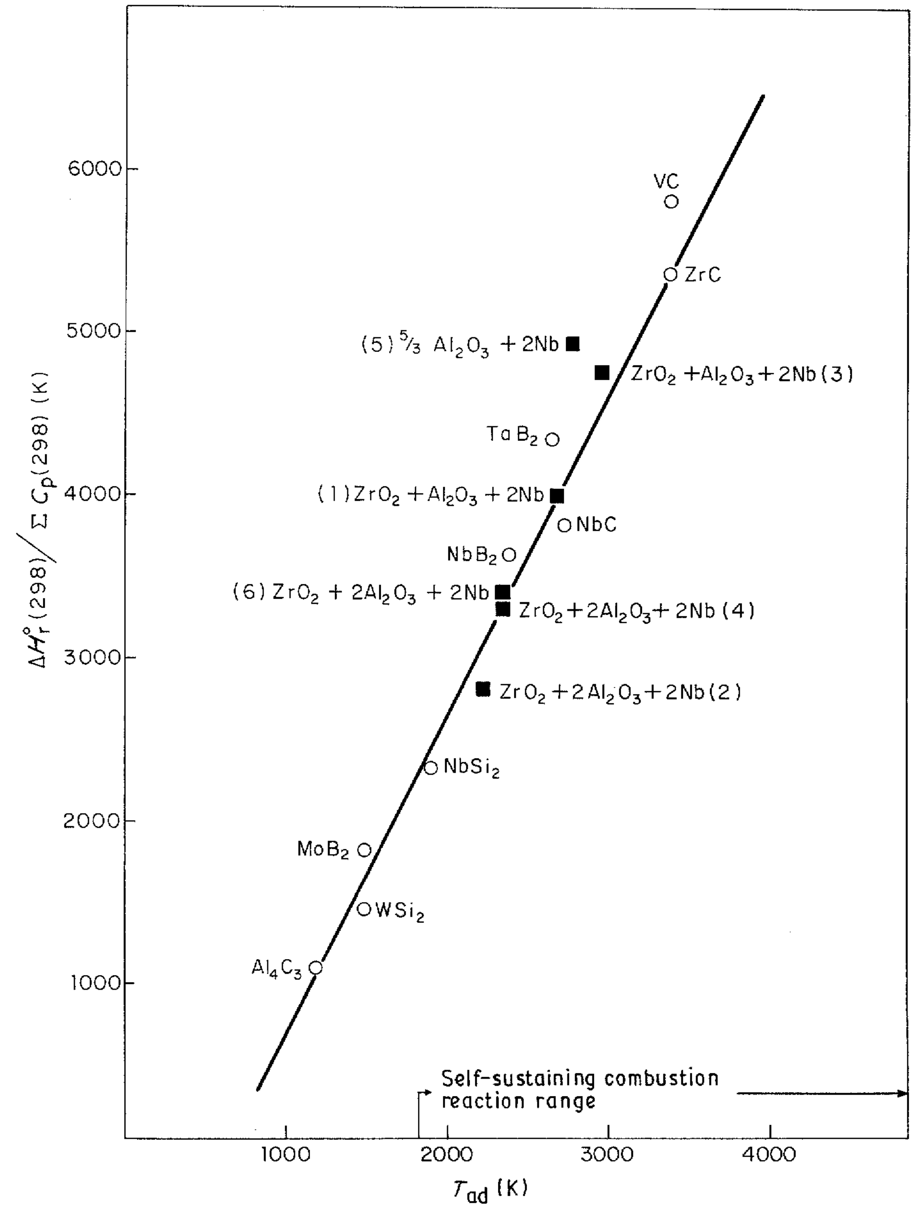

Figure 4 Relationship between $\Delta H^0_f(298)/\Sigma C_p(298)$ and the adiabatic temperatures for selected compounds (○) [6] and the reactions suggested in this work (■). (1) and (2), the reaction in Equation 1 for $v = 0$ and 1, respectively; (3) and (4), the reaction in Equation 2 for $v = 0$ and 1, respectively; and (5) and (6), the reaction in Equation 3 for $v = 0$, $\phi = 0$ and $v = 1/3$, $\phi = 1$, respectively.

The extent of reaction product formed with various amounts of diluent was also considered in the energy balance (Figs 1–3) in order that evaluation for better control of the reaction or to increase the volume fraction of oxide content in the matrix might be made. Due to the high exothermicity of the reactions, the presence of liquid caused by the melting of some of the reaction product can be found even when the reaction is diluted and ignited at room temperature. This observation may provide advantages for the reaction kinetics and densification process in practical tests.

Munir [6] and Munir and Anselmi-Tamburini [7] indicated by experimental observations that the ratio of the enthalpy of formation of the product and its heat capacity at 298 K is a good parameter to evaluate the synthesis of the reaction nature of high-temperature materials. A self-sustaining combustion reaction is achieved for materials with a ratio $\Delta H_r^0(298)/C_p(298) \geqslant 2.0 \times 10^3$ or $T_{ad} \geqslant 1800$ K. In Fig. 4 the $\Delta H_r^0(298)/C_p(298)$ ratio is plotted versus adiabatic temperature for some synthesized compounds [6, 7] and for the proposed reactions in this work. The figure shows tht the heat absorbed by the diluents in the range of dilution considered does not affect the self-sustaining combustion nature of the reactions outlined. All of the evaluations consider the reactants as being at room temperature; however, preheating the reactant mixture (bulk or thermal explosion reaction) will result in an even higher combustion temperature as shown in Fig. 1 (T_{adz}). In the case of dilution (values of v and $\phi > 0$) the $H_{(T)}$ curves for reactants and products must be taken to the correct T_{ad} estimation.

Recent efforts have been directed towards the practical evaluation of the forecast reactions in order to characterize the microstructure of the products and to obtain dense bodies to carry out mechanical tests. Results obtained in preliminary experiments show that the heating rate is critical in order to avoid oxidation of the reducing metal (Al and Zr) before combustion, otherwise the reaction might be inhibited or the formation of complex oxides with Nb_2O_5 [8, 9] might be promoted.

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