Fracture and property relationships in the double diboride ceramic composites via spark plasma sintering of TiB$_2$ and NbB$_2$

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Supplementary data.

In this appendix, the equations used for calculating the residual stress in TiB$_2$ and NbB$_2$ grains, σm and σi, due to the inclusion of secondary diboride phase. According to a model presented by Taya et al. in [37] for a binary composite, stresses accumulated in matrix during cooling can be estimated as:

$$\sigma_m = \frac{2f\beta\varepsilon^*}{(1-f)(\beta+2)(1+\nu_m)+3\beta f(1-\nu_m)} \qquad (1)$$

where Em is Young's modulus of the matrix, f is the volume fraction of inclusions and β is given by:

$$\beta = \frac{1+\nu_m}{1-2\nu_i}\frac{E_i}{E_m} \qquad (2)$$

Ep, ν_i and ν_m are Young's modulus and Poisson ratio of particle inclusions and matrix, respectively, and ε^* is the thermal expansion misfit strain given by:

$$[\alpha_i - \alpha_m]\,\Delta T \qquad (3)$$

where the α_i, α_m are the thermal expansion coefficients of reinforcement and matrix, respectively and ΔT is the temperature at which stresses begin to accumulate, set as 1800 °C and more realistically at 1200–1400 °C [40].

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Change in flexural strength behaviour can be explained by changes in microstructure that occur during testing or stress state of material during the testing. In general, improvement or decrease in toughness in two-phase ceramic composites is known to be a result of mismatch in CTE [37]. Importantly, in the present study two phases TiB_2 and NbB_2 have similar CTE's in the wide temperature range between 25 and 1900 °C, and more crucially bellow 1200 °C (see **Figure S1.1**) [28]. At room temperature widely accepted values of CTE are 5.6 and $6.3x10^{-6}$, for TiB_2 and NbB_2, respectively. Mind that dashed area in **Fig. S1.1** indicates the zone where CTE of two phases are within the error of their estimation [28, 29].
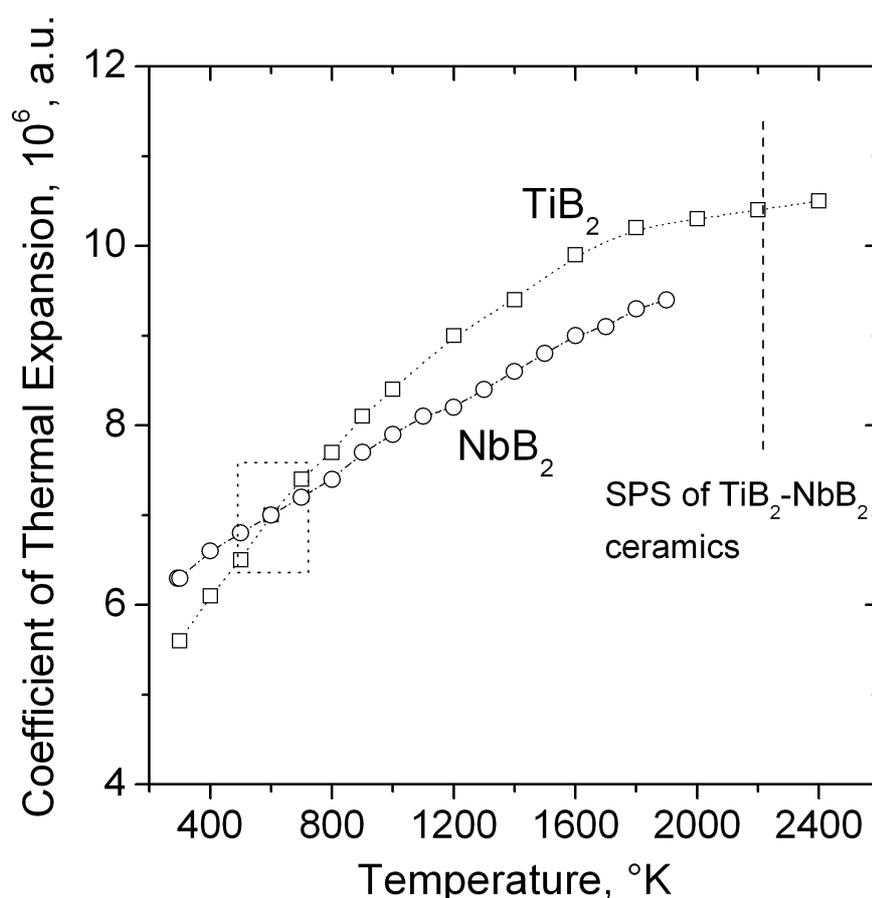

Figure S1.1 – Coefficients of thermal expansion of TiB_2 and NbB_2 the temperature range of 300 K to 2400 K [28].
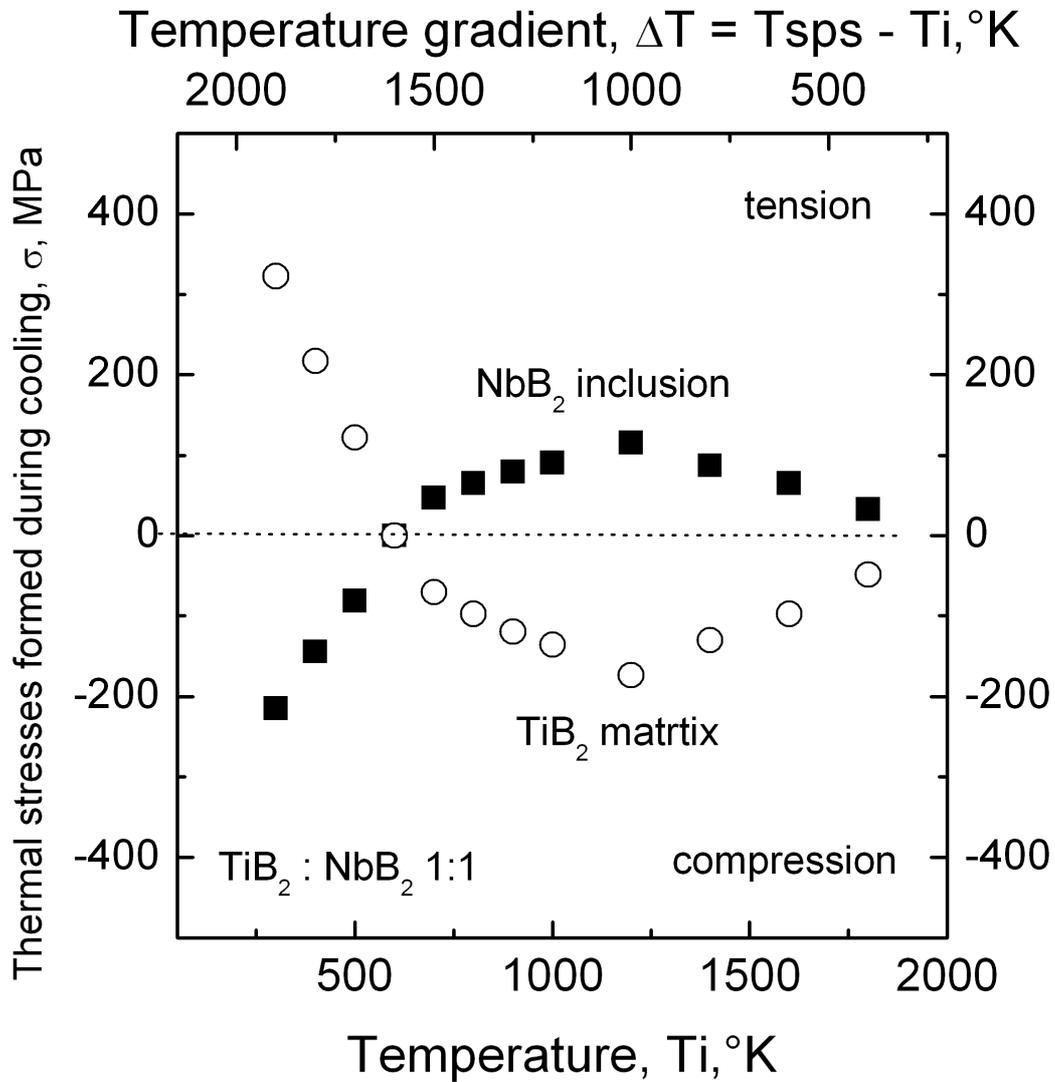
Figure S1.2 – Evaluation of thermal stresses accumulated during cooling of TiB$_2$–NbB$_2$ (1:1) ceramic composite.

Hence, we attempted to estimate the accumulated stresses using Taya's model [37] and available data on mechanical characteristics of TiB$_2$ and NbB$_2$ [28–30,39]. Such analysis using a temperature gradient of 1800 °C, showed that residual stresses on the TiB$_2$ matrix σm (1:1

composite) and NbB$_2$ inclusions σi are -255 MPa and 398 MPa, respectively. A negative value of the residual stress at matrix indicates compression, while a positive value of the residual stress at reinforcement suggests tension. In this case, where the temperature gradient is 1200 °C or 1400 °C [40], values of 115 MPa and -173 MPa can be estimated. Mind, that at higher temperatures the CTE of TiB$_2$ is fairly larger than that of NbB$_2$ (i.e., 9 and 8.2 x10^{-6}, respectively), but they come to equilibrium at the range of 600–800 °K (see **Fig. S1.2**), thus the sign of stresses at matrix and inclusions are reversed. Importantly, the absolute value of stresses induced on the diborides have same magnitude of below 500 MPa. In the case of all compositions used in the present study, the maximum stresses associated with a temperature gradient of 1800 °C are presented in **Table S1**.

Table S1 Evaluation of thermal residual stresses for TiB$_2$–NbB$_2$ ceramic composites.

Composition	Residual stress at matrix, σm, MPa	Residual stress at the secondary phase, σi, MPa
TiB$_2$: NbB$_2$ (1:1)	-255	398
TiB$_2$: NbB$_2$ (2:1)	-156	496
TiB$_2$: NbB$_2$ (1:2)	-378	297