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Allotropic strengthening and *in situ* phase transformations during ultra-high-temperature flexure of bulk tantalum nitride

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Abstract

TaN samples were prepared using the spark plasma sintering at 1800°C. Samples consisted of cubic tantalum nitride with the lattice parameter of a = 4.338 Å. The formation of ~~multiple~~ hexagonal and cubic (a = 4.44 Å) TaN ~~TaN~~ phases *in situ* during the flexural tests ~~increases the high-temperature strength as values exceeding 500 MPa were observed at 1600 °C~~was analyzed using X-ray diffraction. ~~Cubic TaN phases with lattice parameters of a = 4.338 Å and a = 4.44 Å were observed below 1600 °C and above 1600 °C, respectively.~~

Keywords: binary phase diagram; flexural strength; toughness; high-temperature materials.

1. Introduction

The demand for ultra-high temperature, high modulus, high-strength structural ceramics with particular emphasis on high-temperature stability has led to the investigation of tantalum nitride, with a reported high-temperature cubic phase and a melting point of 3090 °C [1–3]. This compound has a number of structural

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variations that can be formed when exposing TaN to a high temperature or varying nitrogen pressure [1, 4]. The use of TaN as a potential ultra-high temperature ceramic was discussed in [2, 3]. These reports focused on the structural stability or ablation resistance of tantalum nitride at elevated temperatures. The conditions for the synthesis of the bulk TaN are widely reported with the emphasis of this ceramic to be used as thin-film resistor of low temperature coefficient of resistivity or diffusion barrier between silicon and metal overlayers ~~an electrode or diffusion barrier in the form of thin films~~ [5]. However, almost no information is available about the consolidation behavior of this compound or its high-temperature properties. Therefore, the present study was concerned with spark-plasma sintering, strength, and phase transformations of the TaN bulks consolidated using commercially-available tantalum nitride powder.

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2 Materials and Methods

The as-received TaN powder (Alfa Aesar Lot #T08C032) was placed in a graphite die (30-mm in diameter) and was subjected to spark plasma sintering (SPS) consolidation using flowing nitrogen. The specimens were heated in 4 minutes to 800 °C. At this temperature, the SPS system was outgassed and maintained under vacuum for 5 minutes. After this, a constant pressure of 32 kN was applied, and nitrogen was introduced. Nitrogen gas at the flow rate of 2 L/min was used throughout the consolidation procedure. From 800 °C, the temperature was increased to the 1800 °C at the rate of 200 °C/min. Dwell was not used at 1800 °C. Cooling was performed in 15 minutes to 600 °C. After reaching this temperature, the pressure was released, and the specimen was slowly cooled in the die. Ta foil has been used to restrict diffusion of carbon to the powder specimen during the SPS [6] in order to prevent formation of the TaC or TaCN phases.

The polished SPSed specimens and bars after flexural tests examined by X-ray diffraction using a D8 Advance diffractometer with Cu-Kα radiation. The bulk density of the polished specimens was determined by the ~~water-immersion~~ Archimedes method.

Hardness was determined by an MMT-7 Vickers hardness using a load of 9.8 N with a dwell time of 15 s following the standard procedure (ASTM C 1327–15). Toughness was evaluated by indentation using the approach proposed by Anstis [7]. The three-point flexural strength was determined using rectangular blocks (1.5×2×25 mm, ASTM C1211−13, configuration A) and strength testing equipment that was previously described in detail [8]. Details of the heating/cooling schedule are presented in [8], (also see *supplementary data*). The 10-min dwell to equalize temperature and prevent shock-related behavior was used. Measurements were performed with a loading speed of 0.5 mm/min. The flexural strength data were averaged based on 4–6 tests. The modulus of elasticity was analyzed from linear ~~portions~~ part of the strain-stress curves with an accuracy of ±20 GPa. The results for the various temperatures are summarized in **Table 1**.

3 Results and Discussion

The bulk density of the fully dense tantalum nitride ceramic was 14.35 g/cm^3. XRD results suggested that after the SPS the ceramic was 100% cubic TaN with the lattice parameter a = 4.338 Å. Specimens free of macroscopic cracks and with the mean grain size of 6–10 µm were prepared for the flexural strength tests.

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The fractographic analysis revealed that the grain size and the grain shape changed ~~following~~ during the high-temperature strength tests, suggesting the *in situ* phase transformation during flexure (**Figure 1**). The X-ray diffraction results (**Figure 2**) confirmed this assumption. ~~as at~~At least four different phases were observed after flexure.

The phase diagrams (**Figure 3**) [4,9] suggest that the low-temperature phase should have a #191 hexagonal structure, whereas the result obtained by this study suggested that TaN has the cubic structure #225 a = 4.338 Å, which is considered as a high-temperature phase in [1,2,4,9]. TaN cubic phases with these lattice parameters were the main phase up to 1600 °C. TaN with the lattice parameter of 4.42 Å has been reported in the case of thin film experiments [5], but not in the case of the bulk samples [1,2].

Peculiar changes in the microstructure were observed by SEM (**Figure 1**). First, exposure to ~~*in situ* heating to~~ 1000 °C resulted in ~~a binary grain size distribution as the~~ the appearance of ~~growth of~~ large-sized grains ~~was observed~~. Second, further increase in temperature would result in the gradual increase in grain size, after the test ~~while the~~at 1600 °C or 1800 °C the formation of quasi-layered grains was seldomly observed. Third, voids would seldom be observed after tests at 1000 °C or 1600 °C. These can be connected to the change in the volume of the crystal cell of the cubic phase (~7~~8~~%), but also with partial transformation of the cubic phase into a hexagonal one (16~~–~~20 % ~~of volume change~~, see *supplementary data*). Finally, fracture at 1600 °C or 1800 °C resulted in a high contribution of quasi-transgranular fracture as activation of homogeneous fine slips was frequently observed [2]. The presence of cracks was common at 1800 °C, this feature can be explained by the *in situ* change in the crystal cell volume and grain morphology.

Furthermore, after tests at 2000 °C, we did not observe any spherical pores with a size of ~1μm that were present in the SPS~~ed~~ ceramic and usually accommodated grain-growth process [6]. Tests in argon at 2000 °C produced similar results. This suggested that the allotropic changes and growth of TaN were not greatly influenced by the N_2 gas, but are controlled by temperature.

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carbides [11] would show at most 250 MPa at 2000 °C which is consistent with data in **Table 1**.

We observed a ~~peak~~ maximum in strength at 1600 °C where the strength up to 560 MPa was observed. This strength level is typical for the bulk TaC at room temperature [12,13], but at 1600 °C, the strength of 200 MPa was reported in [13]. Considering the limited amount of reported data for nitrides, we anticipated that the high-strength in this case can be attributed to a specific ratio between ~~*in situ*~~ transformed TaN grains. A roughly 75~~3~~:25 vol.%~~1~~ ratio between the cubic and hexagonal phases was estimated based on the XRD refinement data.

Some hexagonal–cubic ceramic composites, e.g., TiN–TiB_2 [14], are known to possess a high strength at ~~ambient~~ room temperature. High strength in such cases can be ~~connected~~ regarded to the presence of coherent interfaces between the cubic and hexagonal phases [15]. A common example of a fully coherent interface was obtained when a crystal with a closed packed crystal structure (e.g., TaN with #189 or #191 structure) is placed in contact with a crystal having a face-centered cubic lattice, i.e., TaN with the #225 structure, ~~with one atom on each lattice point,~~ such that the (0001) plane of the hexagonal crystal is in contact with the {111} plane of the cubic crystal. As it is possible that quasi-coherent interfaces that are formed *in situ* during the flexural tests due to allotropic transformation ~~would explain~~ is responsible the abnormal strength at 1600 °~~C were observed in this study~~C.

Conclusions

During the flexural tests of tantalum nitride bulks at 1000–2000 °C we observed an *in situ* phase transformation and grain morphology evolution. Hexagonal and cubic tantalum nitrides were observed. ~~Two~~ The cubic tantalum nitride phases ~~with~~ had the lattice parameters ~~of~~ a = 4.338 Å ~~and~~ or a = 4.44 Å ~~were observed~~. The presence of the ~~latter~~ cubic phase with lattice parameter a = 4.44 Å has not been previously

reported for the binary Ta–N phase diagrams. The ability to manipulate the allotropic form of hexagonal TaN and the possible formation of multiple TaN phases with different crystal structures during the flexural tests indicated the possibility to explore a new strengthening mechanisms and thus promote the generation of a new class of high-temperature ceramics.

Acknowledgements

Authors express their sincere appreciation to Dr. Toshiyuki Nishimura (NIMS) for providing access to the evaluation of high-temperature strength.

Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

Data Availability Statement

The raw/processed data required to reproduce these findings are availble upon request by contact with the corresponding author(s).

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Table 1. Summary of physical and mechanical properties ~~for~~ of TaN after the high-temperature flexural tests.

Temperature, °C	Bulk density, g/cm^3	Mean grain size, μm	Phase analysis, vol.%		Lattice parameter of cubic phase, Å	Hardness, GPa^Y	$K_{IC}{}^Y$, MPa m$^{1/2}$	Strength, MPa	Elastic modulus, GPa
			Cubic	Hex.					
25	14.355	6.5±3.2	100	-	4.339	23.2±1.1	4.1±0.2	406±12	490
1000	14.415	4.3±1.1 / 22±6	92	8*	4.337	17.2±1.5	3.5±0.3	318±30	420
1600	14.415	5.2±1.2 / 17±8	76	24**	4.445	17.5±1.4	3.7±0.2	560±10	396
1800	14.526	25±6	92	8***	4.444	20.8±1.2	3.9±0.3	420±30	344
1900	14.585	34±12	100	-	4.449	22.3±2.4	3.6±0.1	298±16	332
2000	14.608	80±40	100	-	4.454	24.5±0.4	3.3±0.2	192±16	320

*#189 space group, lattice parameters a = 5.192 Å , c = 2.908 Å
**#191 space group, lattice parameters a = 5.190 Å , c = 2.910 Å
***#191 space group, lattice parameters a = 5.191 Å , c = 2.911 Å
^{Y} for specimens at elevated temperatures, performed on the top polished surface of the bar after flexure. Load of 9.8 N was used.

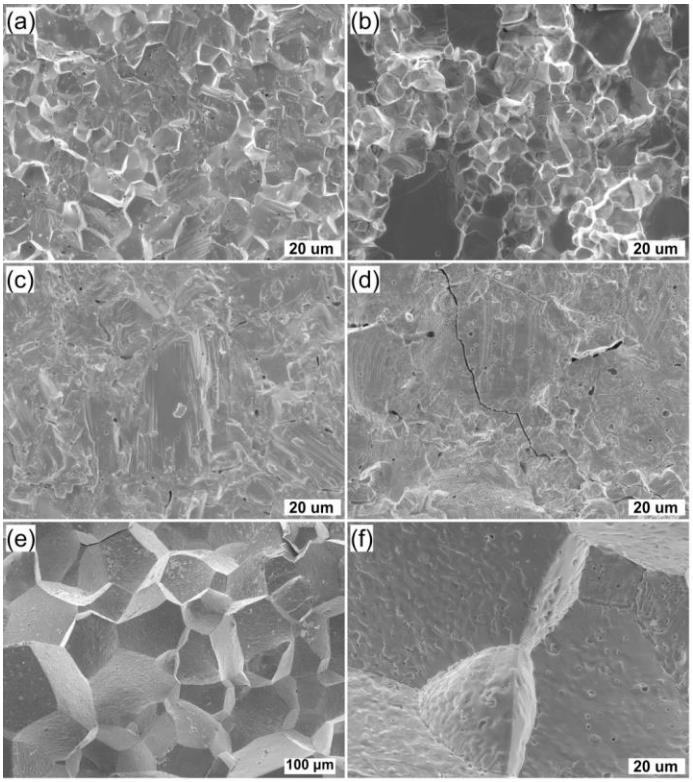

Figure 1. Effect of temperature on microstructure of tantalum nitride ~~following~~ after the three-point flexural strength tests: (a) room temperature, (b) 1000 °C; (c) 1600 °C, (d) 1800 °C, and (e,f) at 2000 °C. All specimens were subjected to a 10-min dwell at the testing temperature before the flexural test.

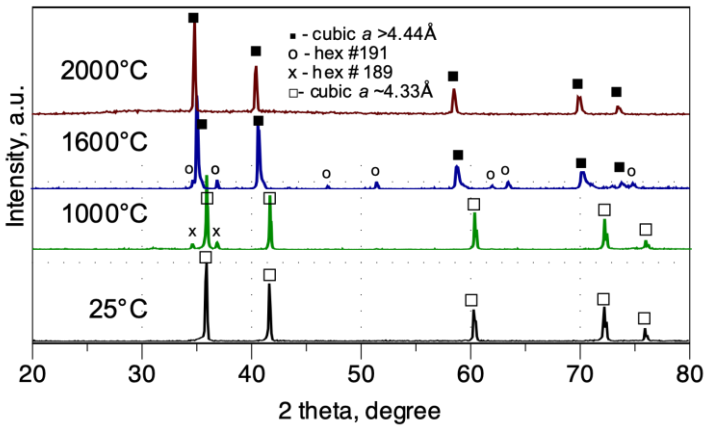

Figure 2. X-Ray diffraction details of bulk tantalum nitride after flexural tests at ~~elevated~~ high temperatures. ~~Details~~ Results on the refinement ~~(blue difference during refinement, black refinement curve and red open cycles – observed data)~~ are listed in **Table 1**. For details see *supplementary data*.

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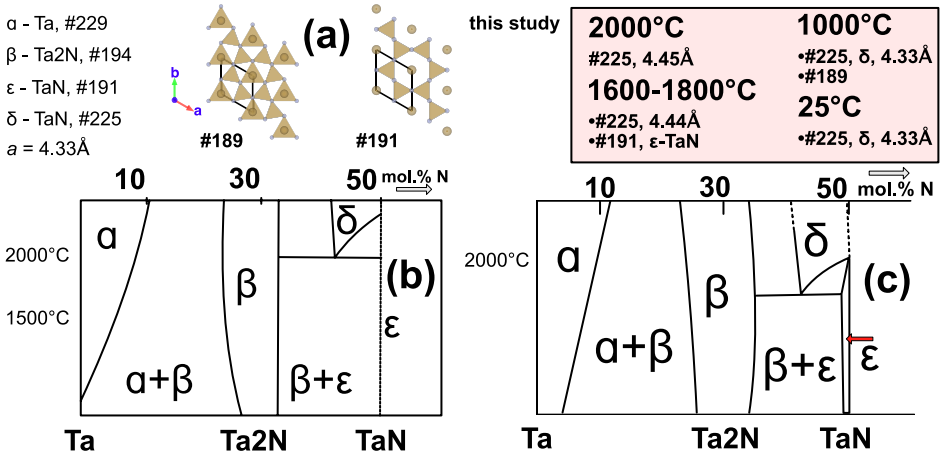

Figure 3. Phase relations in the Ta–N binary system. (a) summarizes results of this study and shows the *z* projection of the hexagonal lattice changes from #189 to #191

as observed above 1000 °C. (b) and (c) are phase diagrams based on data at ambient pressure [9] and nitrogen overpressure [4], respectively.

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TaN samples were prepared using the spark plasma sintering at 1800°C. Samples consisted of cubic tantalum nitride with the lattice parameter of $a = 4.338$ Å. The formation of hexagonal and cubic ($a = 4.44$ Å) TaN phases *in situ* during the flexural tests was analyzed using X-ray diffraction.

Keywords: binary phase diagram; flexural strength; toughness; high-temperature materials.

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Conclusions

During the flexural tests of tantalum nitride bulks at 1000–2000 °C we observed an *in situ* phase transformation and grain morphology evolution. Hexagonal and cubic tantalum nitrides were observed. The cubic tantalum nitride phases had the lattice parameters $a = 4.338$ Å or $a = 4.44$ Å. The presence of the cubic phase with lattice parameter $a = 4.44$ Å has not been previously reported for the binary Ta–N phase diagrams. The ability to manipulate the allotropic form of hexagonal TaN and the possible formation of multiple TaN phases with different crystal structures during the flexural tests indicated the possibility to explore a new strengthening mechanisms and thus promote the generation of a new class of high-temperature ceramics.

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Table 1. Summary of physical and mechanical properties of TaN after the high-temperature flexural tests.

Temperature, °C	Bulk density, g/cm^3	Mean grain size, μm	Phase analysis, vol.%		Lattice parameter of cubic phase, Å	Hardness, GPa^Y	$K_{IC}{}^Y$, MPa m$^{1/2}$	Strength, MPa	Elastic modulus, GPa
			Cubic	Hex.					
25	14.355	6.5±3.2	100	-	4.339	23.2±1.1	4.1±0.2	406±12	490
1000	14.415	4.3±1.1 / 22±6	92	8*	4.337	17.2±1.5	3.5±0.3	318±30	420
1600	14.415	5.2±1.2 / 17±8	76	24**	4.445	17.5±1.4	3.7±0.2	560±10	396
1800	14.526	25±6	92	8***	4.444	20.8±1.2	3.9±0.3	420±30	344
1900	14.585	34±12	100	-	4.449	22.3±2.4	3.6±0.1	298±16	332
2000	14.608	80±40	100	-	4.454	24.5±0.4	3.3±0.2	192±16	320

*#189 space group, lattice parameters a = 5.192 Å, c = 2.908 Å
**#191 space group, lattice parameters a = 5.190 Å, c = 2.910 Å
***#191 space group, lattice parameters a = 5.191 Å, c = 2.911 Å
^{Y} for specimens at elevated temperatures, performed on the top polished surface of the bar after flexure. Load of 9.8 N was used.

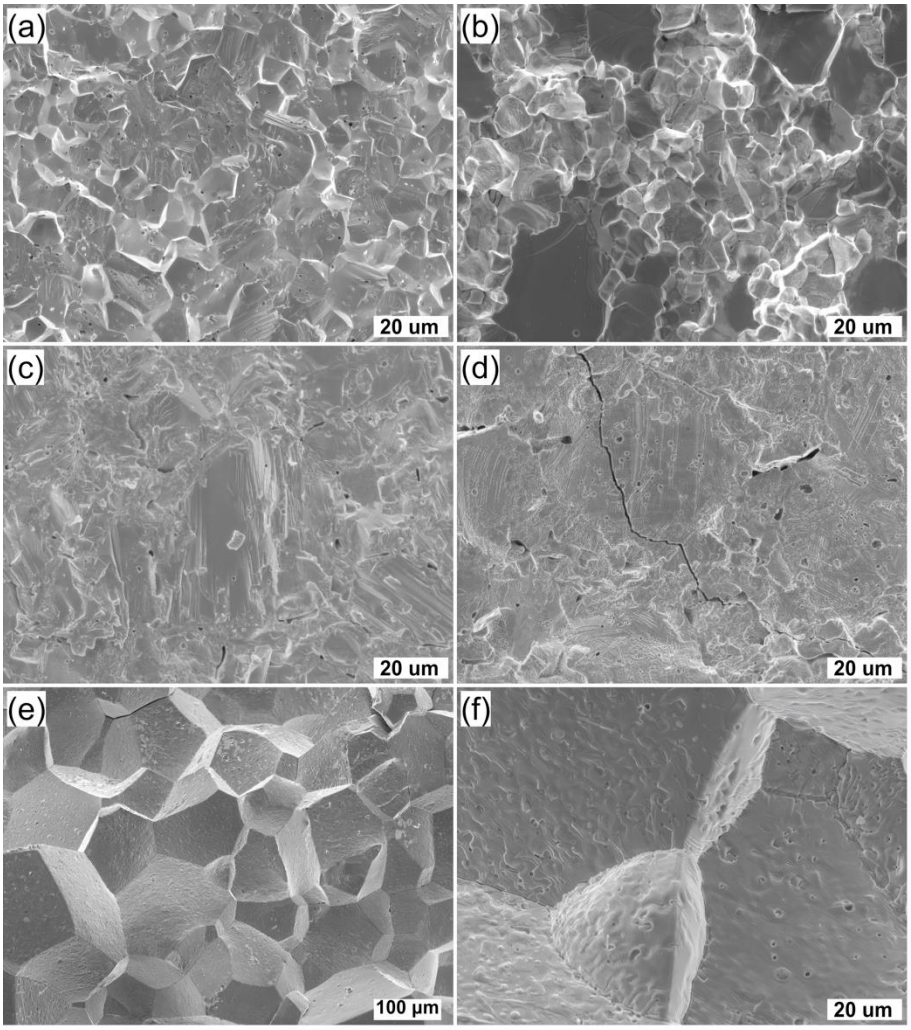

Figure 1. Effect of temperature on microstructure of tantalum nitride after the three-point flexural strength tests: (a) room temperature, (b) 1000 °C; (c) 1600 °C, (d) 1800 °C, and (e,f) at 2000 °C. All specimens were subjected to a 10-min dwell at the testing temperature before the flexural test.

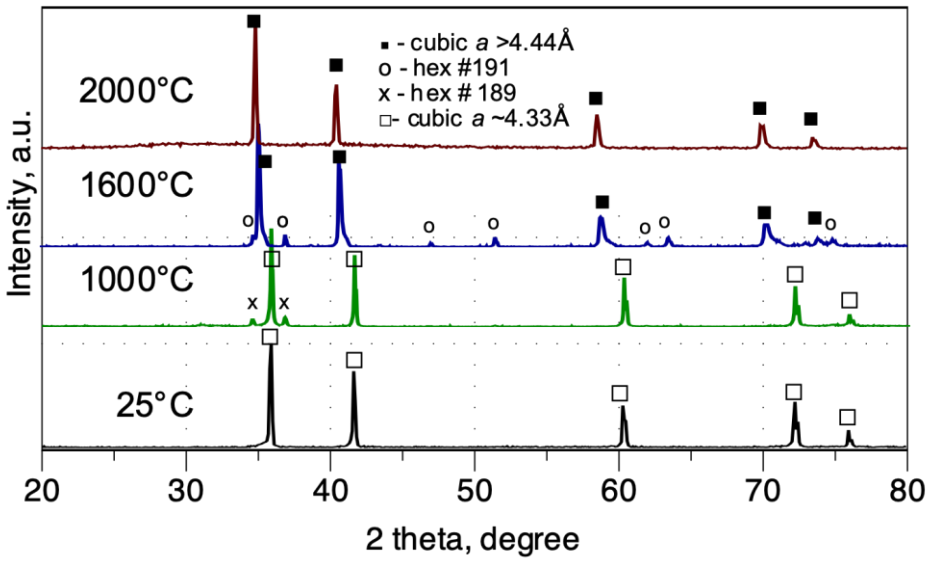

Figure 2. X-Ray diffraction details of bulk tantalum nitride after flexural tests at high temperatures. Results on the refinement are listed in **Table 1**. For details see *supplementary data*.

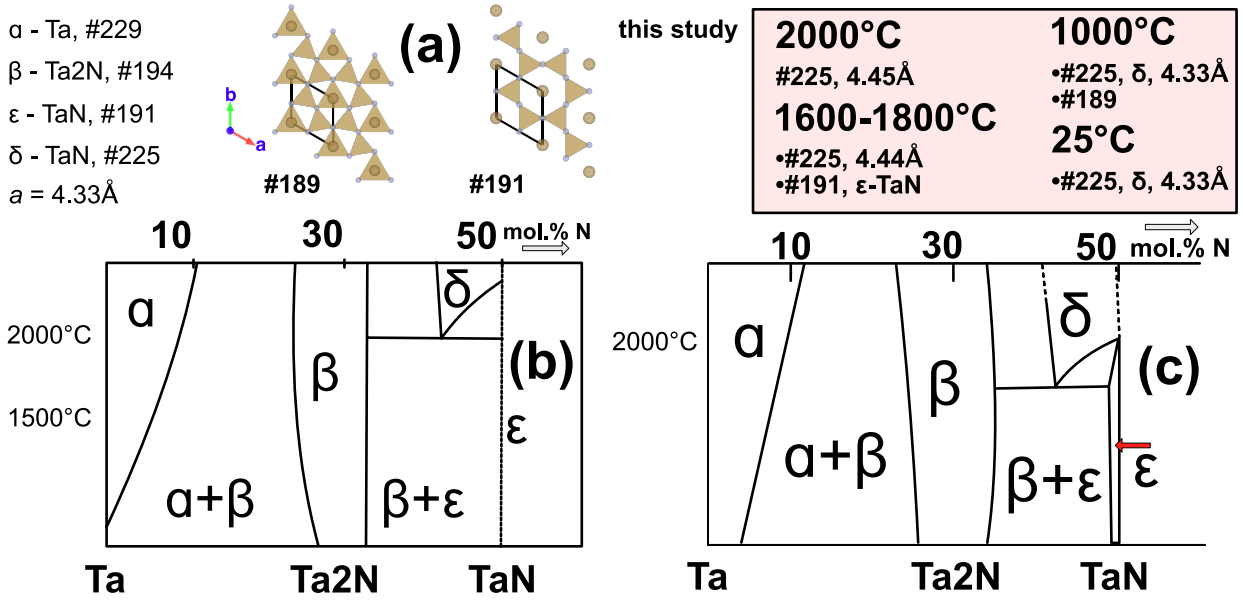

Figure 3. Phase relations in the Ta–N binary system. (a) summarizes results of this study and shows the *z* projection of the hexagonal lattice changes from #189 to #191 as observed above 1000 °C. (b) and (c) are phase diagrams based on data at ambient pressure [9] and nitrogen overpressure [4], respectively.

Supplementary Interactive Plot Data (CSV)
Click here to access/download;Table(s);appendix_msea_r1_revision_clean.do

Allotropic strengthening and *in situ* phase transformations during ultra-high-temperature flexure of bulk tantalum nitride

D. Demirskyi (a,b,c), O. Vasylkiv (b), and K. Yoshimi (c).

Supporting Data

Change in crystal cell volume during phase transformation in TaN. **Table S1** summarizes the data on crystal cell volume of different modifications of tantalum nitride. Using these volume one can evaluated the relative change in the volume cell during the phase transformation. Here the negative values indicate the decrease in the volume of the crystal cell.

Table S1. Summary of the crystal cell volume change in TaN.

TaN structure	Lattice parameter, Å	Crystal cell volume, Å^3	(vol i – vol ref)/ vol ref, %		(vol i / vol ref), %	
			4.33 Å	4.44 Å	4.33 Å	4.44 Å
#225, cubic	a = 4.33	81.7013	-	-6.65	-	93.34
#225, cubic	a = 4.44	87.5283	6.65	-	107.13	-
#189, hex	a = 5.192 c = 2.908	67.9081	-20.31	-22.41	83.11	77.58
#191, hex	a = 5.191 c = 2.911	67.9320	-16.82	-20.10	85.59	79.89

Heating profile during flexural test. **Figure S1** illustrates the heating schedule for the low-temperature flexure (left, below 1600 °C) and the high-temperature flexure (i.e., 1800 °C, 2000 °C). Noticeably, all the specimens before the flexural tests were placed in the hot-zone where they were subjected to a 10-min dwell in order to equilibrate temperature within the specimen and to minimize the influence of the thermal shock on the flexural strength.

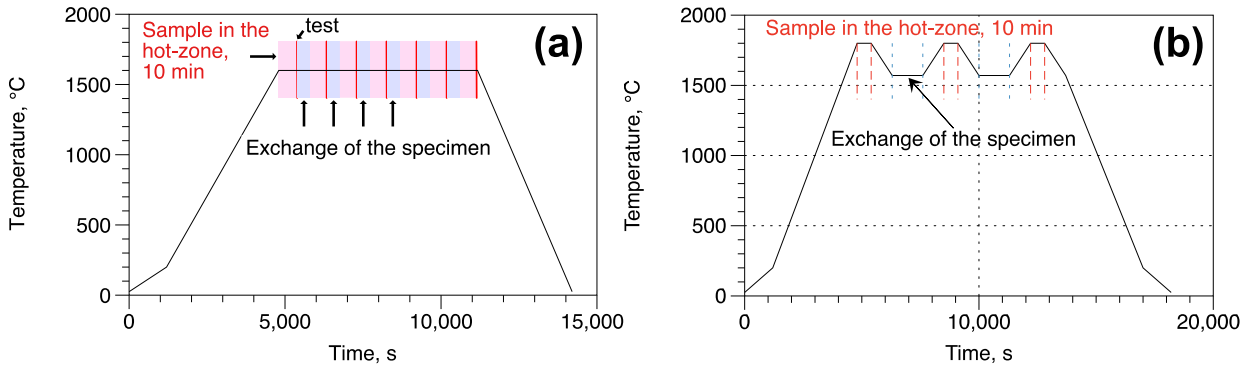

Figure S1. Representative heating profiles used for the high-temperature flexural tests at (a) 1600 °C and (b) 1800 °C .

Details on the X-ray diffraction and the Rietveld refinement. The XRD results revealed that the raw powder was a mixture of six different tantalum nitride phases (**Figure S2**). The main phase was found to be a hexagonal #189 (*P-62m*) tantalum nitride. The minor amount of cubic tantalum nitride was evaluated (4 wt.%) with the lattice parameter of a = 4.33(7) Å . **Figures S3–S7** show results of the refinement procedure performed on the bulk TaN after the SPS (**Fig. S3**) and after the ultra-high-temperature flexural tests (**Figs. S4–S7**)

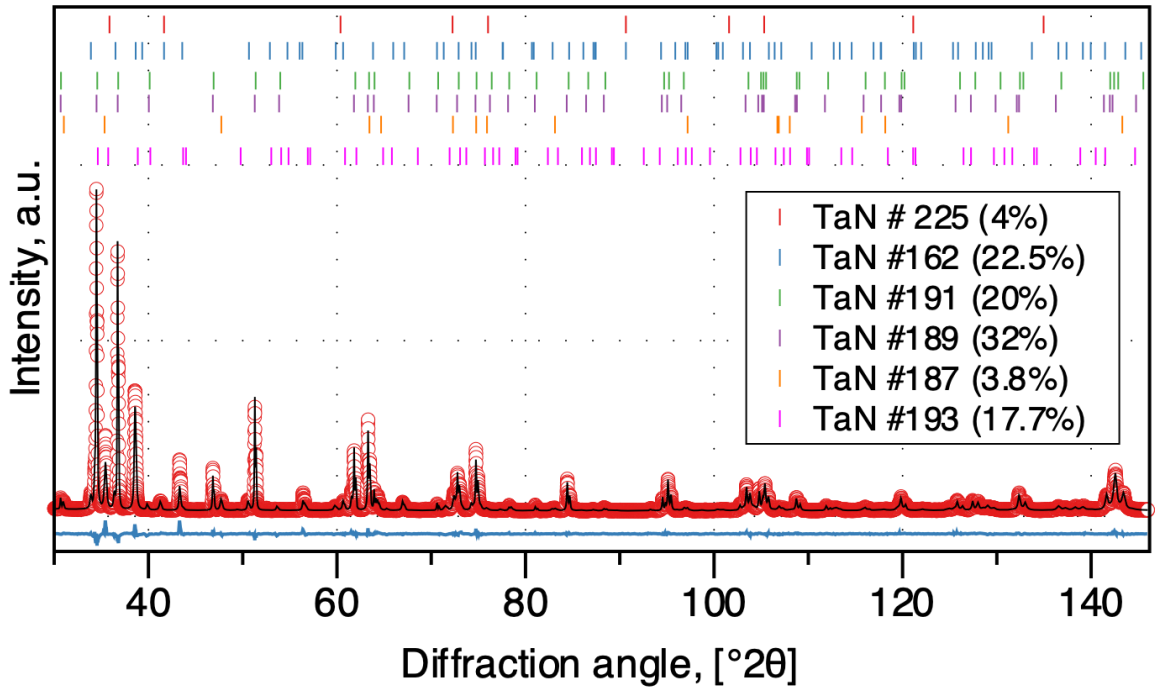

Figure S2. X-Ray diffraction details of tantalum nitride powder used for the SPS consolidation. The short vertical bar indicates the Bragg peak position of tantalum nitride phase. Blue curve is the difference during refinement, black refinement curve and red open cycles–observed data.

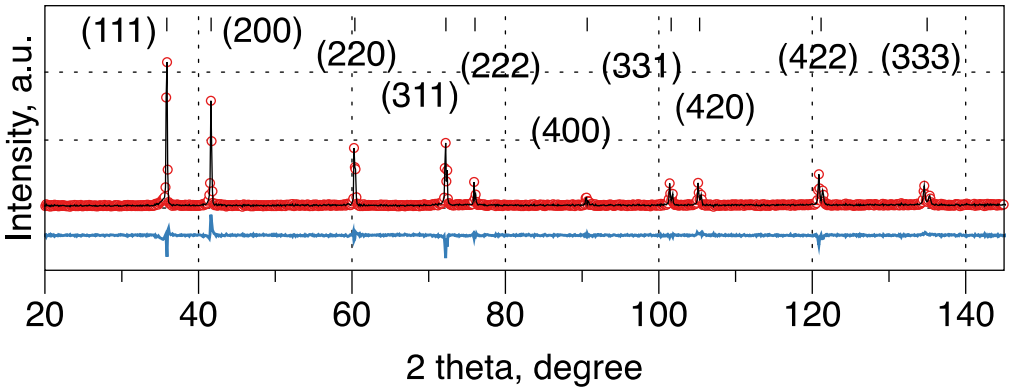

Figure S3. X-Ray diffraction details of tantalum nitride after the SPS. The short vertical bar indicates the Bragg peak position of cubic tantalum nitride phase (4.33Å). Blue curve is the difference during refinement, black refinement curve and red open cycles–observed data.

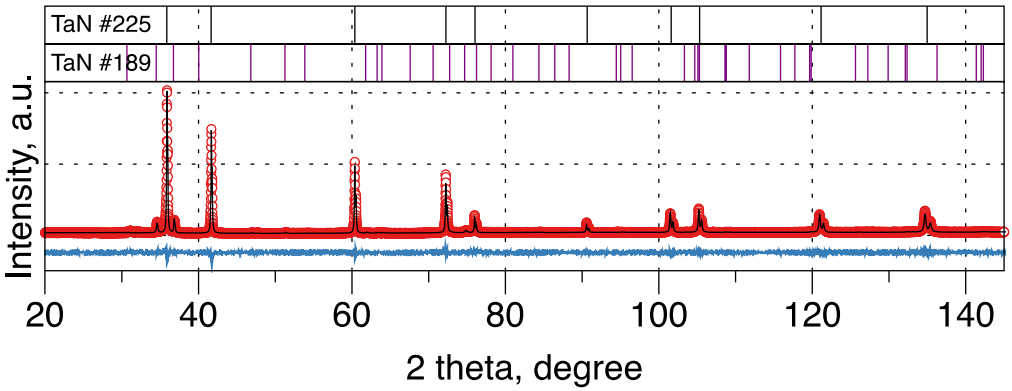

Figure S4. X-Ray diffraction details of tantalum nitride after flexural test at 1000 °C. The short vertical bar indicates the Bragg peak position of cubic and hexagonal tantalum nitride phases. Blue curve is the difference during refinement, black refinement curve and red open cycles–observed data.

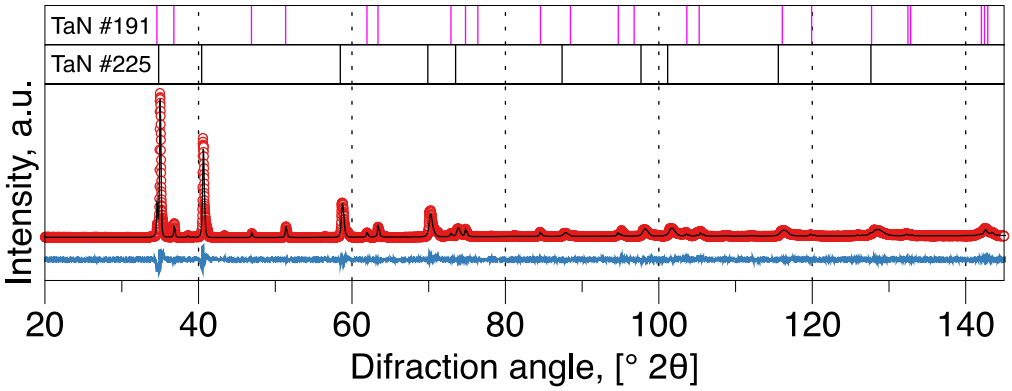

Figure S5. X-Ray diffraction details of tantalum nitride after flexural test at 1600 °C. The short vertical bar indicates the Bragg peak position of cubic and hexagonal tantalum nitride phases. Blue curve is the difference during refinement, black refinement curve and red open cycles–observed data.

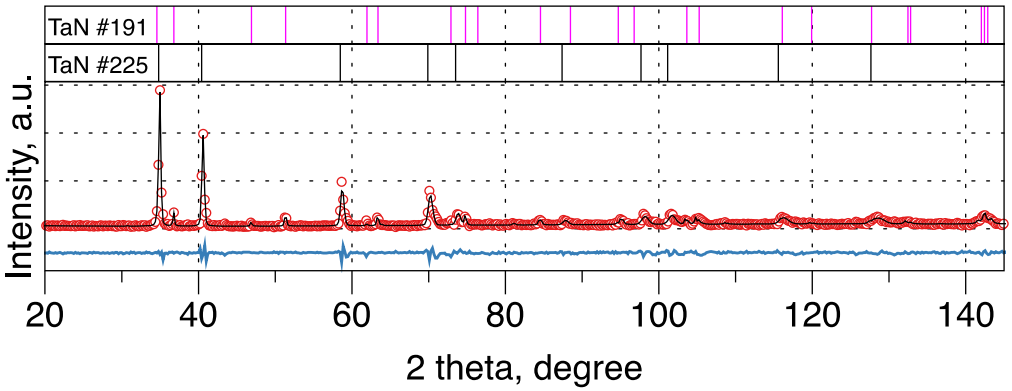

Figure S6. X-Ray diffraction details of tantalum nitride after flexural test at 1800 °C. The short vertical bar indicates the Bragg peak position of cubic and hexagonal tantalum nitride phases. Blue curve is the difference during refinement, black refinement curve and red open cycles–observed data.

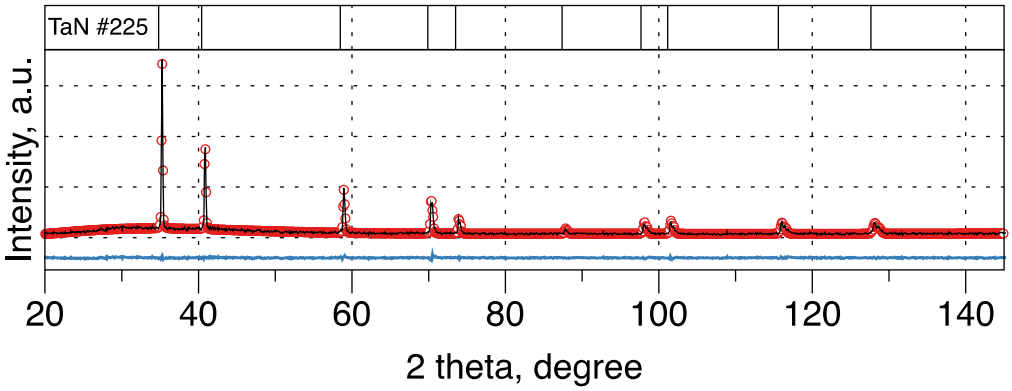

Figure S7. X-Ray diffraction details of tantalum nitride after flexural test at 2000 °C. The short vertical bar indicates the Bragg peak position of cubic tantalum nitride phase. Blue curve is the difference during refinement, black refinement curve and red open cycles–observed data.

Effect of annealing on structure of bulk specimens. **Table S1** summarizes data on the Rietveld refinement of specimens after *in situ* phase transformation during the flexural test and the reference specimens annealed in the tube furnace in the nitrogen flow. For the latter experiments the heating and cooling rates were 20 °C/min. A

dwell of 10 min was used at the annealing temperature. Reference samples for the annealing tests were cut the areas not used for the flexural tests (**Figure S8**). Data in **Table S2** indicate that there is a good agreement between two data sets. However, one may expect a different structural changes when the unpressed powder is being annealed.

Table S2. Summary of the Rietveld refinement results for TaN bulks after the annealing and after the ultra-high-temperature flexural tests.

Temperature, °C	In situ flexure, vol.%				Reference specimen, vol.%			
	Cubic #225 4.33 Å	Hex #189	Hex #191	Cubic #225 4.44 Å	Cubic #225 4.33 Å	Hex #189	Hex #191	Cubic #225 4.44 Å
1000	92	8	-	-	90	10	-	-
1600	-	-	24	76	-	-	30	70
1800	-	-	8	98	-	-	20	80
2000	-	-	-	100	-	-	5	95

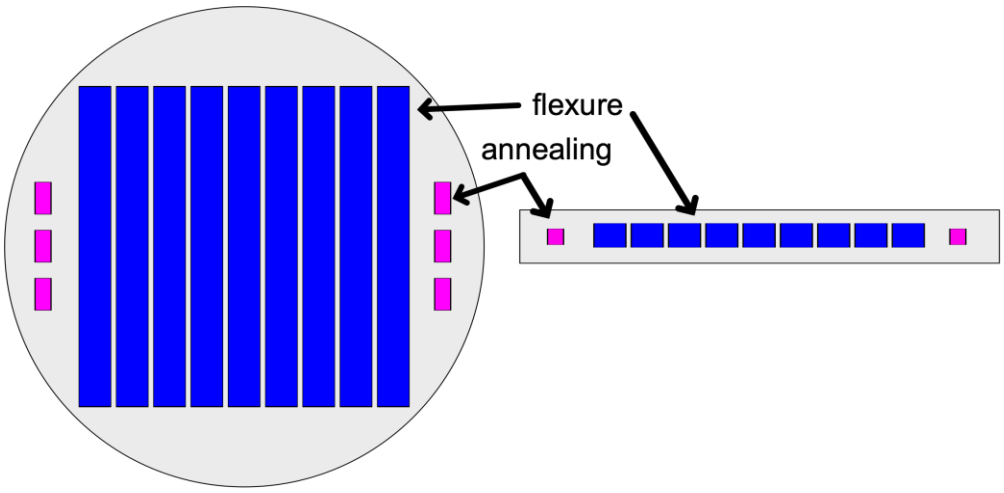

Figure S8. Specimen preparation for the flexural tests and for the reference annealing.

Effect of thermal cycling on the structure and flexural strength of TaN. In order to refine or control the grain size at elevated temperature, we attempted to apply thermal cycling. The schedule RT – 2000 – 1600– 2000 – 1600 – 2000 °C, based on preliminary values for the 1600 °C tests, remains the most effective in decreasing the grain size, and perhaps, responsible for the extremely high strength of up to 422 MPa at 2000 °C (see microstructure in **Figure S9**). **Table S3** summarizes the Rietveld refinement details and flexural strength of tantalum nitride specimens after the thermal cycling procedure. The minor presence of the secondary hexagonal phases was observed only after cycles with the maximum temperature during the cycle of 1600 °C. When the thermal cycle included the dwell at 2000 °C, only cubic phase was observed. **Figure S10** illustrates the effect of thermal cycling on the flexural strength; the data on TaC [1] shows a typical strength behavior of bulk carbide UHTC ceramic. The higher strength during the ultra-high-temperature flexural strength tests can be due to the decrease in the grain size (**Fig. S9**).

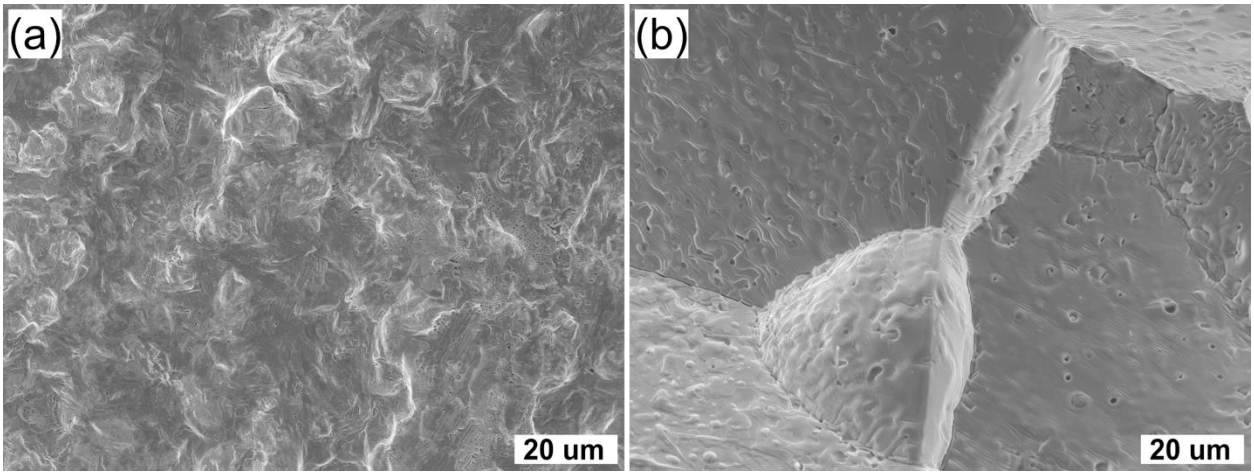

Figure S9. Effect of temperature on microstructure of tantalum nitride following the three-point flexural strength tests at 2000 °C. (a) specimens were subjected to a thermal cycling of RT – 2000 – 1600 – 2000 – 1600 – 2000 °C, and a dwell of 10 min was used at every step in the cycle. (b) after regular flexural testing at 2000 °C.

Table S3. Summary of mechanical properties for TaN after the thermal cycling before the ultra-high-temperature flexural tests.

Cycle, °C[X1]	Mean grain size, μm	Phase analysis, vol.%		Lattice parameter of cubic phase, Å	Strength, MPa[X2]	
		Cubic	Hex.		min	Max
RT–1000–1600	10.1±3.3	98	2[X3]	4.444	288	421
RT–1600–1000–1600	14.3±2.3	99	1[X3]	4.445	312	440
RT–1600–RT–1600	14.3±3.7	100	-	4.445	340	360
RT–1600–RT–2000	13.5±1.5	100	-	4.451	315	355
RT–2000–1600–2000–1800	14.6±4.2	100	-	4.452	290	425
RT–2000–1600–2000–1600	12.0±4.5	100	-	4.452	416	462
RT–2000–1600–2000–1600–2000	15.2±3.4	100	-	4.454	366	422

Notes:

X1 – 10 min dwell at each temperature, test at the final temperature of the cycle

X2 – Data based on four measurements.

X3 – #191 space group, lattice parameters a = 5.19 Å, c = 2.91 Å

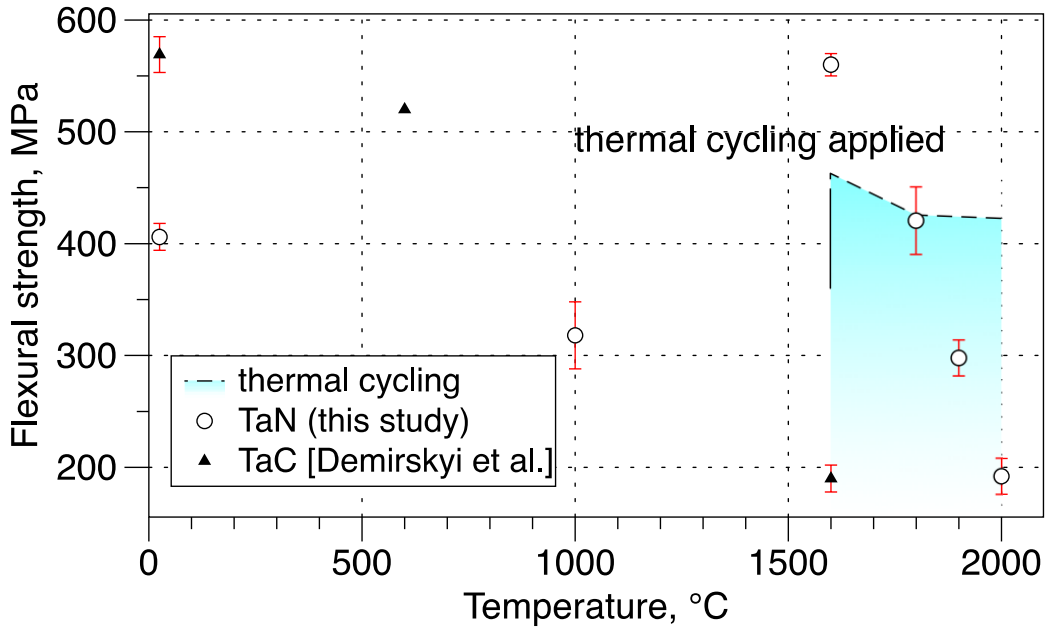

Figure S10. Effect of temperature on flexural strength of TaN and TaC [1].

References

[1] D. Demirskyi, T. Nishimura, Y. Sakka, O. Vasylkiv, High-strength TiB2-TaC ceramic composites prepared using reactive spark plasma consolidation. Ceram. Int. 42[1] (2016) 1298–1306. doi: https://doi.org/10.1016/j.ceramint.2015.09.065.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Allotropic strengthening and *in situ* phase transformations during ultra-high-temperature flexure of bulk tantalum nitride" by Dmytro Demirskyi, Oleg Vasylkiv and Kyosuke Yoshimi for publication in Materials Science and Engineering: A.

Dmytro Demirskyi: Conceptualization, Methodology, Investigation, Visualization, Writing- Original draft preparation.
Oleg Vasylkiv: Validation, Investigation, Writing- Reviewing and Editing.
Kyosuke Yoshimi: Validation, Writing- Reviewing and Editing.