

## WETTING and JOINING of HfB<sub>2</sub> and Ta with Ni ZWILŻANIE i ŁĄCZENIE HfB<sub>2</sub> i Ta z Ni

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### Abstract

The wetting behavior of Ni on a HfB<sub>2</sub>/Ta assembly was examined in vacuum using dense HfB<sub>2</sub> (99.5% purity) produced, without sintering aids, by HP-HT at 7 GPa. The real-time imaging by a high resolution digital camera and precise temperature control demonstrated solid-state Ni/HfB<sub>2</sub> interaction resulting in metal contact melting at ~1300°C. Ongoing heating, the in situ formed Ni-B alloy wets, spreads over HfB<sub>2</sub> and penetrates the HfB<sub>2</sub>/Ta capillary interface to form a joint of complex graded structure and good bonding.

Keywords: wetting, joining, hafnium boride, tantalum, nickel

### Streszczenie

Przeprowadzono badania procesu zwilżania w próżni układu HfB<sub>2</sub>/Ta przez Ni. Zwarte próbki HfB<sub>2</sub> (czystość 99.5%) otrzymano sposobem spiekania w wysokiej temperaturze bez dodatków aktywujących spiekanie, stosując wysokie ciśnienie 7 GPa. Rejestracja procesu zwilżania w czasie rzeczywistym za pomocą kamery cyfrowej o wysokiej rozdzielczości w połączeniu z zastosowanym precyzyjnym pomiarem temperatury wykazały, że intensywne oddziaływanie w parze Ni/HfB<sub>2</sub> zachodzi podczas wspólnego nagrzewania w temperaturze kiedy Ni jest jeszcze w stanie stałym a nadtopianie metalu w obszarze kontaktu dwóch materiałów występuje już w temperaturze ~1300°C. Następnie stop Ni-B, powstający in situ podczas nagrzewania, zwilża i rozplływa się po całej powierzchni HfB<sub>2</sub>, wypełniając szczelinę pomiędzy dwoma materiałami w parze HfB<sub>2</sub>/Ta, tworząc połączenie o złożonej strukturze gradientowej i dobrej wytrzymałości.

Słowa kluczowe: zwilżanie, połączenie, borek hafnu, tantal, nikiel

## Introduction

Both HfB<sub>2</sub> and Ta belong to a family of ultra high temperature materials whose joining presents an important technological challenge. Therefore, information on the wetting behavior of different possible brazing alloys in contact with these materials is a key factor in the production of the Ta-HfB<sub>2</sub> joints by liquid phase routes. From the standpoint of requirements for joining dissimilar materials to be employed at extreme temperature conditions, it is essential that both materials have comparable thermo-physical properties [1–8], particularly thermal conductivity and coefficient of thermal expansion (CTE), responsible for thermo-mechanical compatibility of this couple of materials. Moreover, HfB<sub>2</sub> and Ta conduct heat better than high-temperature steels and Ni alloys while Ta, due to its good durability, surpasses most of the refractory alloys in workability. It can be easily rolled, drawn, swaged and cold formed thus making possible the design of different and more complex shapes of joints with other materials.

Experimental data on wettability of HfB<sub>2</sub> are limited to pure metals and binary Ni alloys [9–17]. Ge [10] and In [14] were found not to wet hafnium boride (contact angle  $\theta > 90^\circ$ ). Wetting with Al was recorded at a temperature  $T > 1100^\circ\text{C}$  [10, 11]. For HfB<sub>2</sub> substrates produced by SPS method, relatively good wetting ( $\theta = 47^\circ$ ) was reported for Cu, contrary to Ag ( $130^\circ$ ) and Au ( $98^\circ$ ) [15]. Among high-temperature metals, Fe was found not to wet HfB<sub>2</sub> at  $T = 1538\text{--}1650^\circ\text{C}$  [10, 11], contrarily to Co, which can form contact angles of  $54\text{--}10^\circ$  at  $1500\text{--}1600^\circ\text{C}$  [13].

Contact angle data for pure Ni are very scattered, showing values of  $\theta = 18\text{--}102^\circ$  [9–12, 14, 16, 17], depending on production process, chemical composition of boride and testing conditions (atmosphere, procedures for sample preparation and testing). At a temperature of  $1520^\circ\text{C}$  and for the same HfB<sub>2</sub> substrates containing either 7 vol% B<sub>4</sub>C or 5 vol% HfSi<sub>2</sub>, alloying Ni with 3 at% Ti does not affect the contact angle value ( $\theta^{\text{Ni}} = 18^\circ$ ;  $\theta^{\text{NiTi3}} = 20^\circ$ ) while the introduction of 5 at% or 50 at% Ti results in its strong decrease ( $\theta < 10^\circ$ ) [16]. Significant effects of alloying on the wetting behavior and interface structure with the same substrates has been recently reported for boron [16, 17]. At high temperature ( $1520^\circ\text{C}$ ), the alloys containing 17 and 50 at% B form the same contact angle  $\theta \sim 10^\circ$ . Decreasing the temperature to  $1200^\circ\text{C}$  results in wetting worsening ( $\theta = 37 \pm 2^\circ$ ). On the contrary, at the lower temperature of  $1130^\circ\text{C}$ , the NiB17/HfB<sub>2</sub> couple demonstrates near perfect wetting ( $\theta < 5^\circ$ ) caused by the formation of ternary boride Hf<sub>2</sub>Ni<sub>21</sub>B<sub>6</sub> at the solid-liquid interface [17].

Several papers emphasize that the contact angles on TiB<sub>2</sub> and ZrB<sub>2</sub> are strongly affected by the gaseous environment [12, 13, 19–21] (e.g., for Ni in vacuum -  $20^\circ$  and  $65^\circ$ , in argon -  $72^\circ$  and  $78^\circ$ , respectively [12]). In the first study [12], this effect was explained by the influence of oxide films on the metal surface since they are not eliminated in neutral gas atmosphere. However, the later studies on Ni/ZrB<sub>2</sub> [14], Au-Ni/ZrB<sub>2</sub> [19], Cu/ZrB<sub>2</sub> [20] and Fe/TiB<sub>2</sub> [21] clearly evidenced that the presence of oxides on the boride surface (residual oxides from as-received powder [8] or oxidized substrate surface either primarily [14] or during wettability tests in the high-P<sub>O<sub>2</sub></sub> environment [19, 20]) is the key factor responsible for significant worsening of their wetting properties. The only boride, whose oxidation was found not to influence wetting by liquid Ni is CrB<sub>2</sub> [18]. In another work [20], the positive effect of alloying Cu with 3% B on wettability of ZrB<sub>2</sub> was postulated to be related with deoxidation of Cu and reaction of B with ZrO<sub>2</sub>.

High-temperature borides are known to have poor sinterability due to their high melting point and low self-diffusion coefficients, thus their densification needs either high-

temperature pressure-assisted sintering procedures or application of sintering aids. In case of  $\text{HfB}_2$ , usually  $\text{SiC}$ ,  $\text{AlN}$ ,  $\text{B}_4\text{C}$ ,  $\text{HfSi}_2$  and  $\text{MoSi}_2$  are used for sintering [3, 4, 6–8]. All literature data on wetting properties of hafnium boride were obtained using sintering aids whose type and amount are often overlooked. Following reported effects of such additions on boride properties, one may conclude that they might also affect the wetting behavior of molten metals, as reported for  $\text{TiB}_2$  [22] and  $\text{ZrB}_2$  [23].

In this study, an attempt has been done to produce dense pure  $\text{HfB}_2$  substrates free of sintering aids to be used for examination of wetting behavior of pure Ni on the  $\text{HfB}_2/\text{Ta}$  assembly and the formation of  $\text{HfB}_2$  to Ta joint using the in situ formed Ni-B alloy.

## Experimental setup

Several  $\text{HfB}_2$  substrates of  $\text{Ø}15.5 \times 4$  mm dimensions were obtained by high-temperature pressing ( $p = 70$  MPa,  $T = 2032\text{--}2236^\circ\text{C}$ ,  $I = 4.5\text{--}5.5$  kW) in Nb-caps (99.5%) of 0.05 mm thickness using two kinds of commercially available  $\text{HfB}_2$  powders of the same grade (325 mesh) of different source and purity given by producers as follows: 1) 99.9% (Atlantic Equipment Engineers, USA); 2) 99.5% (Hf + Zr) but Zr can be as high as 2% (ABSCO Materials, UK). All substrates produced from the  $\text{HfB}_2$  powder of 99.9% purity had numerous cracks and porosity and thus they were excluded from further examination. For the second  $\text{HfB}_2$  powder of 99.5% purity that may contain residual Zr, the following processing conditions were found to be the most suitable in order to produce high quality dense substrates:  $p = 70$  MPa and  $T = 2236^\circ\text{C}$  using  $I = 5.5$  kW for 5 s heating to and 60 s heating at processing temperature, followed by 5 s cooling. Moreover, a Nb layer some tens of microns thick all around the sample to be sintered, to act as a diffusion barrier for C. Structural characterization of these substrates evidenced the second phase inclusions of 5–10  $\mu\text{m}$  size, having irregular shape of sharp edges. They were identified as residual  $\text{B}_4\text{C}$  phase introduced from the raw powder although not declared by the producer.

## Methodology of measurements

The examination of the wetting behavior of Ni on the  $\text{HfB}_2/\text{Ta}$  assembly was carried out in an experimental complex that, in particular, allows sample loading and transportation without opening the vacuum chamber, as described in detail in [24]. The tests were done under a vacuum of  $\sim 10^{-6}$  mbar during contact heating to  $1500^\circ\text{C}$  using continuous real-time recording of temperature (by four thermocouples, three located in different positions around the sample as shown in Fig. 1 and the third one near the heater), vacuum level and residual gases by quadruple gas spectrometer (SRS RGA 200, Standard Research Systems). Note that the thermocouples, except that located inside Ta specimen, were movable thus allowing the control of temperature field inside the heater and showing the only  $\sim 100^\circ\text{C}$  difference in about 30 mm distance above the sample. The sample imaging was obtained with a rate of 12 frames/min by a digital camera (Canon 350D) with CMOS matrix of 8.1 Mpix resolution and equipped with mirror filter. The collected images were used for image analysis by the ASTRAVIEW® software [25, 26] for automatic calculation of contact angles and determination of kinetics of metal spreading.

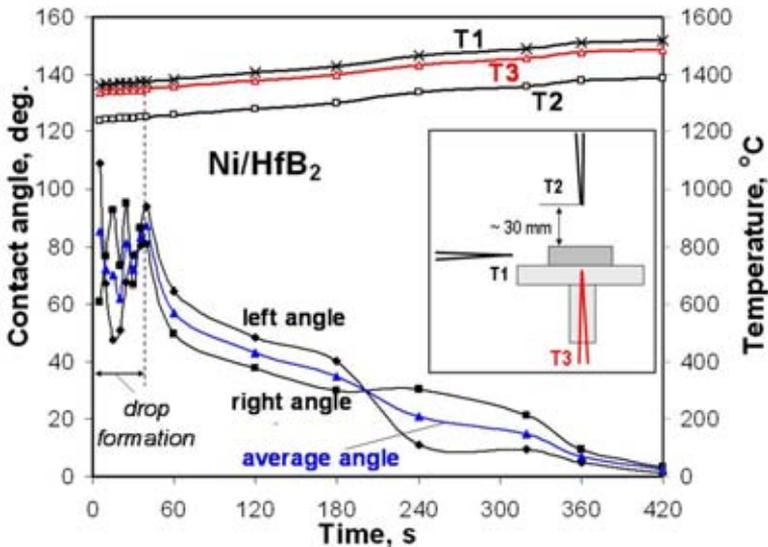


Fig. 1. Wetting behavior of the Ni/HfB<sub>2</sub> couple during contact heating to 1450°C with the corresponding temperature profile recorded by three thermocouples (T1, T2 and T3)

Rys. 1. Zwilżanie połączenia Ni/HfB<sub>2</sub> podczas wspólnego nagrzewania do 1450°C z jednoczesną rejestracją przy pomocy trzech termopar (T1, T2 i T3) przebiegu zmian temperatury

Just before placing the specimen in the vacuum chamber, the top surface of the HfB<sub>2</sub> substrate was grinded using SiC discs of different grades, polished using diamond pastes up to 0.25 µm and ultrasonically cleaned in acetone. Next, the HfB<sub>2</sub> substrate was placed on the polished side of the Ta-support (Ø30 × 5 mm), already heat treated in vacuum at 1500°C for several hours and kept under vacuum. Prior to wettability test, the HfB<sub>2</sub>/Ta assembly was heat treated in a vacuum after reaching  $p = 1.20 \times 10^{-6}$  mbar by heating with the Ta-heater up to 1470°C with a rate of 12°C/min, 15 min holding and subsequent cooling with a rate of 10°C/min. Next, without opening chamber, the mechanically and chemically cleaned Ni (99.999%) sample was loaded and placed on the polished HfB<sub>2</sub> surface. After that, the Ni/HfB<sub>2</sub>/Ta assembly was contact heated in a vacuum to 1200°C with the same rate of 12°C/min and to 1200–1450°C with a rate of ~21°C/min.

After testing, the solidified sample was carefully cross-sectioned by spark erosion cutting tool in order to produce the samples for structural characterization and mechanical properties. The surface and interface structure was examined by means of optical (OM) and scanning electron microscopy (SEM) coupled with energy dispersion surface analysis (EDS). For identification and characterization of the heterogeneous structure of HfB<sub>2</sub> to Ta joint, microhardness measurements were done using a Vickers indenter at a load of 50 g applied for 12 s. Additionally, the joint mechanical strength was evaluated by shear measurements using an INSTRON 8501 machine in displacement control (crosshead speed 0.1 mm/min). Prior to the shear tests of the joints, a blank test was done for machine calibration in order to avoid misinterpretation of data due to plastic deformation of the metal part of the sample holder.

During the heat treatment under vacuum of the  $\text{HfB}_2$  substrate itself a sudden vacuum worsening was recorded at 400–450, 950–1000 and 1400–1450°C due to the release of gaseous products from the substrate (mainly  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_8$ ). At high temperature, this phenomenon is accompanied with the substrate surface roughening, most probably due to the formation of small  $\text{B}_2\text{O}_3$  droplets on its surface [8].

## Results and discussion

During wettability tests (Fig. 1), the real-time imaging by a high resolution digital camera coupled with precise temperature control has demonstrated a strong solid-state Ni/ $\text{HfB}_2$  interaction during heating. Thus, under the conditions of this study (especially heating rate), it was recorded that the Ni sample starts melting in contact with the  $\text{HfB}_2$  substrate at  $\sim 1300^\circ\text{C}$  ( $\sim 150^\circ\text{C}$  lower than melting point of Ni). Ongoing heating, it becomes wholly molten at  $\sim 1350^\circ\text{C}$ , forming after  $\sim 40$  s a spherical droplet of the in situ formed a low-temperature Ni-B alloy with a contact angle of about  $85^\circ$ . These observations are in a good agreement with recent thermodynamic calculations [17], confirming that the interaction in Ni/ $\text{HfB}_2$  system, accompanied by alloying Ni with B and Hf, results in the decrease of the metal melting temperature: the first amount of liquid can be formed at  $\sim 1100^\circ\text{C}$  (Fig. 2).

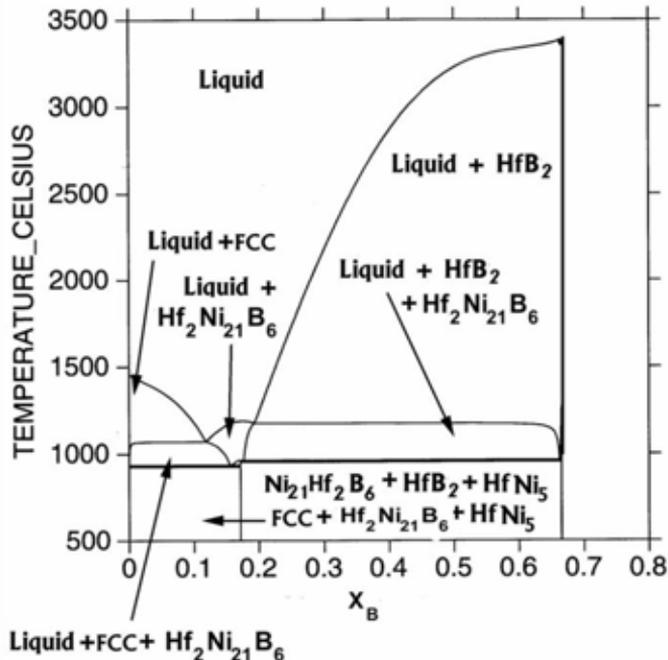


Fig. 2. Calculated isopleth along the Ni- $\text{HfB}_2$  join [17], given by the equation:  $X_B - 2 \cdot X_{\text{Hf}} = 0$ , where  $0 < X_{\text{Hf}} < 0.333$  and the sum of the mole fractions of  $(X_B + X_{\text{Hf}} + X_{\text{Ni}}) = 1$

Rys. 2. Izopleta obliczona wzdłuż połączenia Ni- $\text{HfB}_2$  [17], wyrażona równaniem  $X_B - 2 \cdot X_{\text{Hf}} = 0$ , gdzie  $0 < X_{\text{Hf}} < 0.333$ , a suma udziałów molowych  $(X_B + X_{\text{Hf}} + X_{\text{Ni}}) = 1$

During the subsequent ~5 min heating to the test temperature of 1450°C, the liquid alloy wets and spreads over the whole surface of HfB<sub>2</sub>, with simultaneous penetration into the HfB<sub>2</sub>/Ta capillary interface and the formation of HfB<sub>2</sub> to Ta joint. Note that a similar effect of contact melting of Ni sample was reported also for the Ni/TiC couple in [27].

The structural analysis of sample cross-sections reveals several features (Fig. 3):

1. The presence of a small number of microcracks was recorded in the HfB<sub>2</sub> substrate.
2. At the top surface of HfB<sub>2</sub>, the interface of the solidified drop has a sigmoidal shape, similar to that recorded for pure Ni on HfB<sub>2</sub> substrates containing sintering aids (7 vol% B<sub>4</sub>C or 5 vol% HfSi<sub>2</sub>), as described in [16]. Hence these results evidence no effect of B<sub>4</sub>C and HfSi<sub>2</sub> additions on the interface shape in the pure Ni/HfB<sub>2</sub> couple.
3. The melt, after spreading on the HfB<sub>2</sub> substrate, drained out forming a meniscus at the corner between Ta and HfB<sub>2</sub> and penetrated the capillary space between the two materials, forming an intermediate region.
4. In the intermediate region, there are two main layers: the HfB<sub>2</sub>-side layer is rich in niobium, while the Ta-side layer is rich in nickel and tantalum.

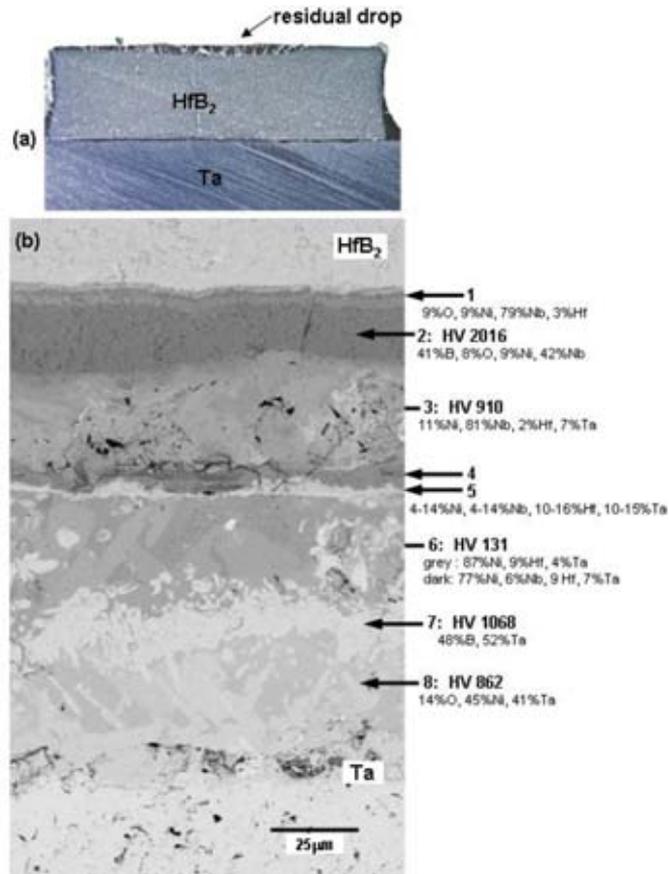


Fig. 3. OM image of cross-sectioned Ta/Ni-B/HfB<sub>2</sub> joint structure (a) and its SEM/EDS/microhardness analysis (b)

Rys. 3. Mikrostruktura połączenia Ta/Ni-B/HfB<sub>2</sub> (a) mikroskopia optyczna; (b) SEM wraz z analizą zawartości pierwiastka metodą EDS i pomiary mikrotwardości poszczególnych stref połączenia

The structural characterization coupled with microhardness measurements shows clear evidence of high reactivity of Ta with the in situ formed Ni-B alloy, resulting in a very complex structure of  $\text{HfB}_2$  to Ta joint formed by a pattern of 8 layers of different microhardness (Fig. 3). Local chemical analysis on the solidified samples shows that the interaction between liquid Ni-B alloy and Ta is accompanied by the formation of a  $\text{TaB}_2$  layer resulting in the consumption of B from the Ni-B interlayer. Moreover, the presence of Nb used as a diffusion barrier in the sintering process and still present on the lateral and bottom surfaces of the  $\text{HfB}_2$  specimens, was found to play an important role in reactive spreading and development of the joint graded structure.

The joint produced had a shear strength of  $\sim 44$  MPa typical of brittle materials, as it can be seen from the load-displacement curve in Fig. 4a. After these tests, the samples were observed again in order to identify failure location. No cracks were noted at the periphery of the  $\text{HfB}_2$  part as it usually takes place in case of significant mismatch in CTE of materials, thus confirming the thermo-mechanical compatibility of Ta/ $\text{HfB}_2$  couple. Although the joint fails mainly in the intermediate layer, the detailed examination evidenced that cracking starts in the  $\text{HfB}_2$  (Fig. 4b) with peeling cracks also at the interface between the Nb layer and the intermediate region, resulting in a mixed character of the joint failure. From the engineering point of view, it means that the measured value of shear strength does not reflect the bonding of the joint itself and the joint shear strength is higher than that of the  $\text{HfB}_2$  material used in this study. For verification, additional shear tests were done on different portions cut from a single substrate. This had a lower strength of  $\sim 34$  MPa and a brittle failure caused from the presence of preexisting microcracks and weakly-bonded  $\text{HfB}_2$  grains, as evidenced by OM and SEM examinations.

These observations suggest that the processing parameters used to produce dense  $\text{HfB}_2$  without sintering aids, as it was aimed to for wettability tests, are not sufficient to obtain a sufficiently tough material. Thus structural defects preexisting in  $\text{HfB}_2$  substrates are responsible for the joint weakening.

Furthermore, Ni-rich layers remained perfectly adhered to the tantalum substrate while rupture in the intermediate region occurred mainly in the layers identified before as number 4 & 5 (transition zone between the Ni-rich and Nb-rich layers). It should be highlighted that these joints were obtained as a result a total spreading of Ni on the ceramic substrate and further infiltration between metal and ceramic. Moreover, a layer of Nb, evidenced at the bottom and at the side face of  $\text{HfB}_2$  sample as a consequence of the sintering process, was found to affect significantly the interactions in the Ta/Ni/ $\text{HfB}_2$  contacting system, suggesting the possible positive role of Nb in optimizing the wettability of the solid substrate, decreasing also the interdiffusion process of Ni, and creating Ta- $\text{HfB}_2$  joints of favorable graded structure with corresponding improved properties as required under extreme operation conditions. Above all, it might play a double role as a protective layer preventing a strong reactivity in the Ni/ $\text{HfB}_2$  as well as one of the interlayer materials in transition liquid phase (TLP) bonding since it consumes B from the Ni-B alloy, resulting in the increase of the alloy melting temperature. Note that TLP is the preferred joining process because it produces joints with better properties at high operating temperatures than brazing. The results obtained imply also that the joint toughness could be improved by adding elements to the brazing alloy and, in particular, taking more into account the processing conditions, especially the cooling process.

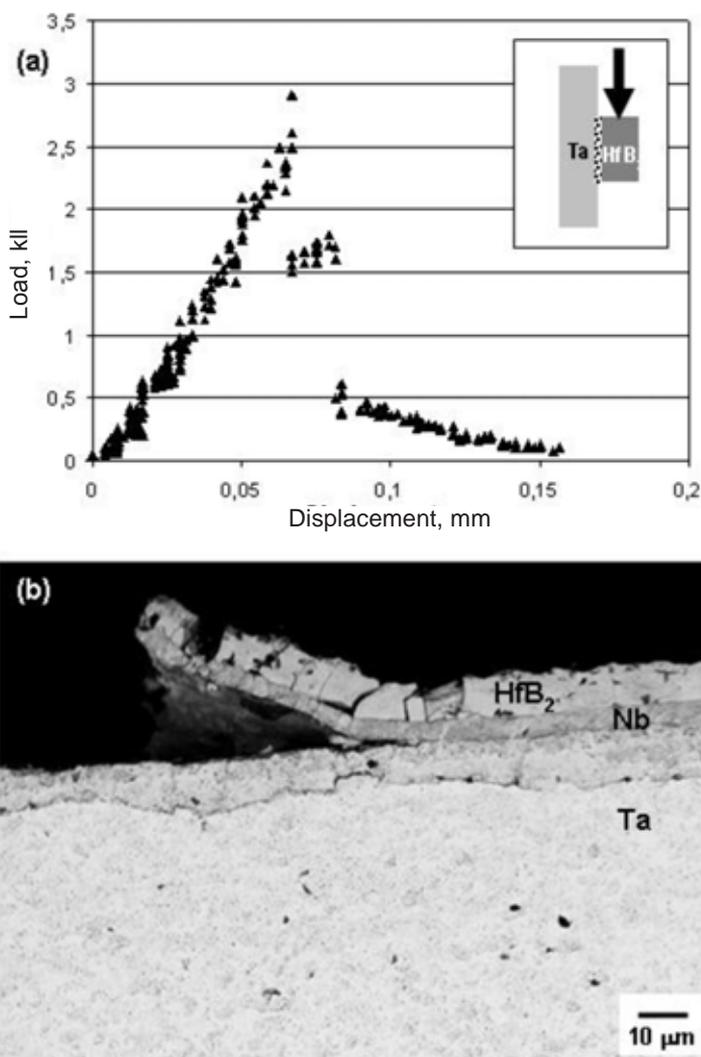


Fig. 4. Shear behavior of Ta/Ni-B/HfB<sub>2</sub> joint (a) and cross-section of the joint after shear test (b) showing failure in the HfB<sub>2</sub> substrate and cracking at the interface between Nb layer and the newly formed transition multilayer region

Rys. 4. Wytrzymałość na ścinanie połączenia Ta/Ni-B/HfB<sub>2</sub> (a) oraz przekrój poprzeczny połączenia po próbie ścinania (b) pokazujący uszkodzenie w podłożu HfB<sub>2</sub> i pęknięcie na granicy rozdzielu faz pomiędzy warstwą Nb i nowoutworzonym przejściowym obszarem wielowarstwowym

## Conclusions

During wettability test, the melting of Ni specimen was observed at about  $150^\circ\text{C}$  below the melting temperature of pure Ni. This observation indicates a strong solid state reaction between Ni and  $\text{HfB}_2$ , producing in situ Ni-B-Hf alloy in a good agreement with the Ni-Hf-B phase diagram calculated by Passerone et al [17]. Moreover wettability tests showed a perfect wetting between molten Ni and  $\text{HfB}_2$  substrate ( $\theta < 5^\circ$ ). Structural examination additionally showed a perfect wetting between Ni and Ta. The produced Ta to  $\text{HfB}_2$  joints using in situ formed Ni-B alloy have a graded structure and good bonding. Niobium interlayers can be used for optimizing the wettability, decreasing interdiffusion and creating Ta- $\text{HfB}_2$  joints of favorable graded structure.

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