

New frontiers in characterising ZrB₂-MoSi₂ ultra-high temperature ceramics

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Abstract

The structure-property(S-P) correlation, especially in the context of high-temperature oxidation, in ZrB₂-MoSi₂ based Ultra High-Temperature Ceramic Matrix Composites (UHTCMCs) have been extensively investigated for quite some time since the last 25 years and a countless amount of published data is presently available in this field. On the other hand, emergence of correlative microscopy [1-10] has completely revolutionised the world of materials research, in a number of ways. However, owing to the challenges of sample preparation, there has hardly been a literature aimed at understanding the aforesaid phenomenon of understanding S-P correlation, based on oxidation in ZrB₂-MoSi₂ UHTCMCs, which, in future, may open up new frontiers of research in UHTCMCs. The present review intends to discuss some of the most interesting data published existing in this field and intends to provide a brief overview of the challenges associated along with some of the currently unexplored avenues in this field, especially in terms of fundamental research. However, in view of the enormous amount of research already done in understanding oxidation-based S-P correlation in these materials, the author does not claim to address all the issues which may be associated with understanding the same.

Keywords: Ultra High-Temperature Ceramic Matrix Composite (UHTCMC), Microscopy, Microstructure, Oxidation.

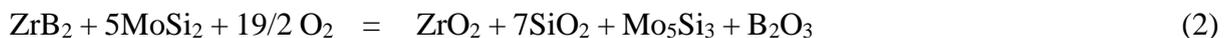
1. Introduction

Since the early 2000s, the search for materials which may withstand extreme conditions of temperature, chemical reactivity, mechanical stress, radiation, and ablation, especially in the context of hypersonic and space aviation (Re-entry vehicles, most presently) [2,3], has been a driving force for an enormous volume of research based on the borides and carbides of a number of transition metals (such as, Zr, Hf etc.). ZrB₂ can be considered a leading material in this field of research owing to a unique combination of properties such as melting point above 3000°C, relatively low density (than the other diborides), high thermal conductivity coupled with good mechanical strength and remarkable refractoriness at elevated temperatures [11-16], ZrB₂ has been the centre of attraction in this field. On the contrary, Sinterability of ZrB₂ is

extremely low, owing to the presence of strong covalent bonds and low self-diffusivity [16], and therefore it requires pressure-assisted sintering techniques at extremely high temperatures (nearly~ 1900°C) in order to eliminate porosity [17]. Furthermore, the ZrB₂ exhibits poor oxidation resistance [16] and mechanical properties [17, 18] owing to the fact that powder surface is always associated with a number of oxides, mainly: B₂O₃ and ZrO₂, leading to an evaporation-condensation mechanism, which subsequently causes mass transfer without effective densification at low temperature and abnormal grain growth at high temperatures, both resulting in poor mechanical properties^{17, 18}. This is due to the reason that formation of glassy B₂O₃ and crystalline ZrO₂ upon exposure in air at temperatures above 800°C [16, 17, 19], due to reaction (1):



With increase in temperature above 1100°C, the evaporation of protective glassy B₂O₃ layer on ZrO₂ occurs, thereby leaving behind a porous ZrO₂ scale. With further increase in temperature, the porous ZrO₂ scale shows a change in grain morphology: from equiaxed to columnar grains, thus aiding the oxidation process [20, 21]. Effective approaches for simultaneous improvement in sinterability, mechanical properties [16, 18-20] and oxidation resistance of these borides, based on the incorporation of additives have been developed [17-19, 21-25] among which MoSi₂ has been reported to be one of the most beneficial, to enhance the densification of ZrB₂ at ~1750°C, owing to the formation of transient liquid phases [26-28]. The formation of glassy SiO₂ layer [23, 29] as an effective oxygen diffusion barrier, coupled with the formation of phases such as MoB and Mo₅Si₃, and the suppression of volatile species [23], may be attributed to be responsible for the beneficial effect of MoSi₂ during oxidation. These aforementioned factors have been reported to be additionally responsible for hindering the formation of columnar ZrO₂ grains in the subsurface. This hinders the inward oxygen diffusion into the ceramic matrix [20, 25]. The oxidation reactions of ZrB₂ - MoSi₂ UHTCMCs have been shown [16, 23, 29-32]:



However, unfortunately, the influence of different interfaces, for instance, Grain boundaries (GBs), Interphase Boundaries (IBs) etc. on the grain growth kinetics and during change in grain morphology at elevated temperatures in ZrB₂, still needs a lot of experimental understanding, in order to be able to come up with a novel methodology of interface-controlled engineering of

microstructures in these UHTCs and UHTCMCs during oxidation at elevated temperatures (> 1900°C). The novel concept of “Correlative Microscopy”, developed a few years back, may be a tool for future investigation of ‘structure-property (S-P)’ correlation in these materials and coupled with the 1st principle calculations, may be extensively used to address a number of presently unexplored fundamental issues, associated with high-temperature oxidation of these materials. This will be discussed in greater details in the upcoming section.

2. Oxidation behaviour of pressureless sintered ZrB₂-MoSi₂ ceramics based on Sciti et al. [33]

2.1 Between 800 and 1000°C

Based on the report of Sciti et al. [33], the rate of formation of protective silica (from reaction (4)), between 800 and 1000 °C, is not high enough to prevent rapid oxidation. Therefore, the oxidation of ZrB₂ to zirconia (reactions (5) and (6)), along with the formation of volatile MoO₃ by reaction (4), has been reported to be the main phenomenon in this temperature regime [34, 35].



At these temperatures, ZrO₂ and liquid B₂O₃ are semi-protective and protective, respectively, as confirmed by the kinetic curves, which resemble those for the oxidation of pure ZrB₂ [34] in this temperature regime. The consequent volume expansion due to the two aforesaid phenomenon, combined with the escape of gases, leads to formation of voids and cracks in the oxide layer. The presence of crystalline MoB during oxidation at 1000°C, indicates the occurrence of reaction (5) besides reactions (3) and (4) [35].



Reaction (7) has been reported to be thermodynamically favoured at all temperatures between 700 and 1400°C, with highly negative values of ΔG at 700 and 1400 °C [35]. However, owing to the slow formation of SiO₂, especially at 1000 °C, molybdenum oxide [36–40] and liquid B₂O₃ may be expected to undergo some amount of vaporisation.

2.2 Between 1000 and 1200°C

Based on Sciti et al. [33], the production of SiO₂ due to oxidation of MoSi₂ has been reported to occur at a rate, high enough to prevent inward oxygen transport from the atmosphere. At ~ 1200 °C, formation of cracks in ZrB₂, evaporation of liquid B₂O₃ has been reported to occur. However, this phenomenon is highly time-dependent viz. after ~ 100 min, a drop in the weight gain, caused due to formation of a continuous silica-rich layer, exhibiting protective action, has been reported [33] wherein, formation of ZrO₂ and oxides of Mo, favouring the penetration of oxygen and, consequently, its contact with ZrB₂ along MoSi₂ particles also in the bulk, have been reported to be responsible for the formation of crack in ZrB₂ at ~1200°C. At the interface between the oxide and the unreacted bulk, owing to low partial pressure of oxygen, selective oxidation of Si occurs; resulting in MoSi₂ getting depleted of Si and reaction of Mo with B from ZrB₂ to form MoB. A very little amount of borosilicate glass, however, has been reported to be observed in the oxide layer, unlike that in ZrB₂-SiC composites [35] and besides, formation of MoB through reaction (5) has also been reported to be thermodynamically and kinetically more favourable than the formation of borosilicate glass. According to previous studies [36] when ZrO₂ grains are embedded in an SiO₂ layer, diffusion and dissolution of interstitial silicon into crystalline zirconia occurs until the solubility limit is attained; after which zircon precipitates out, thereby leading to the formation of zirconia grains, surrounded by a ZrSiO₂ shell, further, embedded in the amorphous silica, as shown in reaction (8) [34]:



The nearly parabolic kinetics of oxidation at 1200 and 1300 °C and the pure parabolic kinetics found at 1400 °C have been reported to be the prime indication for diffusion of oxygen through the silica-rich oxide layer, similar to ZrB₂ -SiC UHTCMCs.

2.3. Other notable reports on oxidation of ZrB₂-MoSi₂ ceramics

2.3.1 Between 700 and 1200°C

ZrB₂ is well-known to oxidize according to the reaction [41, 42]:



The low melting point (450 °C) and high vapor pressure reported for B₂O₃ make it undergo vaporisation at low temperatures:



At temperature below 1100 °C, the presence of B₂O₃ in the form of a liquid has been reported to hinder oxygen transport [41], thereby following parabolic kinetics [20], while at temperatures higher than 1100°C, the protective action of B₂O₃ fades owing to the significant vaporisation of B₂O₃, thereby following paralinear kinetics [20]. Formation of MoO₃ from MoSi₂ has already been shown in Reaction (4). Figs. 1, 2 and 3 show the Scanning Electron Microscopy (SEM) images of ZrB₂-20 vol.% MoSi₂ oxidised at 700, 1000 and 1200°C, respectively.

MoO₃ with high vapor pressure is volatile between 500 and 800 °C and melts at ~ 801 °C [42]. At temperatures higher than 1200 °C, SiO₂ tends to act as a barrier against oxidation, whereas, at lower temperatures, formation of MoO₃, at a much higher rate than that of SiO₂, [43, 44] tends to dominate the oxidation of monolithic MoSi₂, as a result of which there is a volume expansion leading to the build-up of a huge amount of internal stresses at grain boundaries (GBs).

The production of silica between 700 and 1000 °C has been reported to be slow enough for protecting the surface [30, 41]. With an increase in oxidation temperature above 1000 °C, the formation of MoB and ZrC secondary phases, mainly concentrated near the sample surface, has been reported during sintering [41]. Oxidation of MoB has been reported to occur, according to Reaction (11) [30, 41, 45]:



The oxide growth leads to ZrC undergoing catastrophic oxidation at relatively low temperatures, resulting in high stress levels along GBs [46]. Oxidation of ZrC has been reported to occur based on Reaction (12)

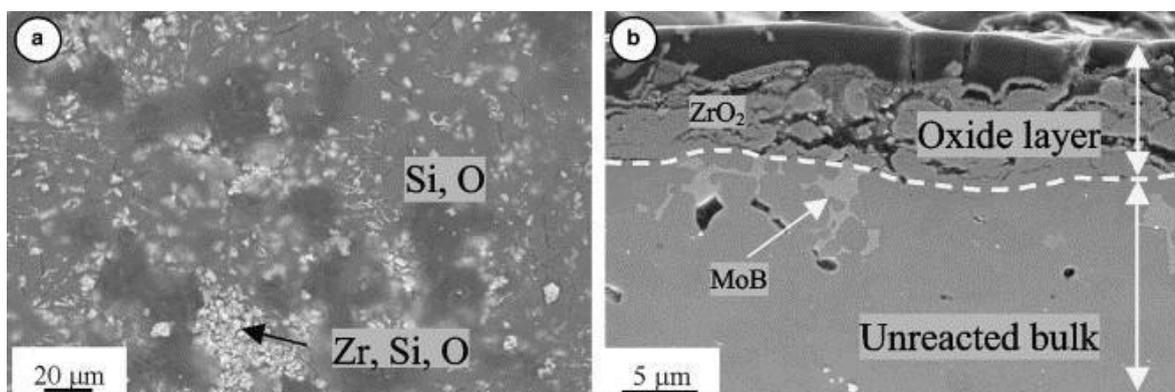


Fig. 1 SEM images showing (a, b) Surface and (c) Cross-section of $ZrB_2-20 \text{ vol.}\% MoSi_2$ oxidised at $700^\circ C$ [41].

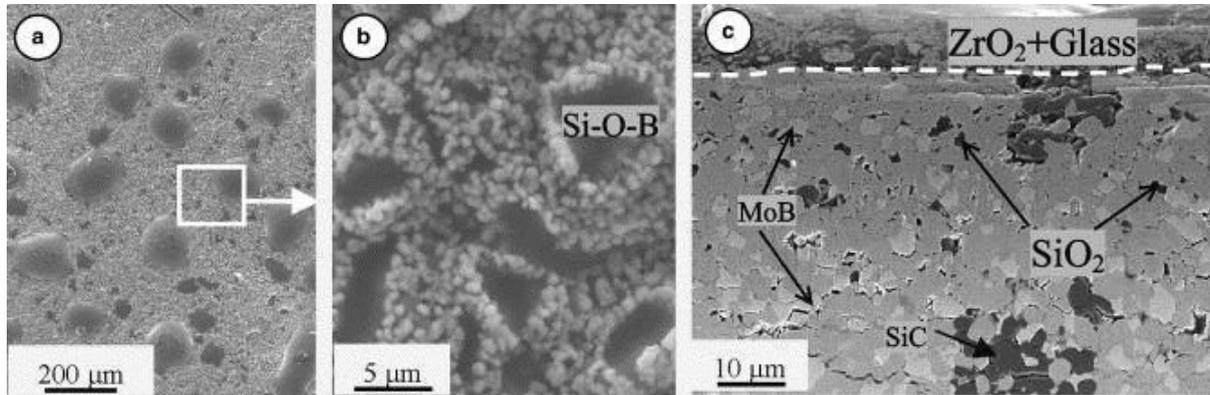


Fig. 2 SEM images showing (a, b) Surface and (c) Cross-section of $ZrB_2-20 \text{ vol.}\% MoSi_2$ oxidised at $1000^\circ C$ [41].

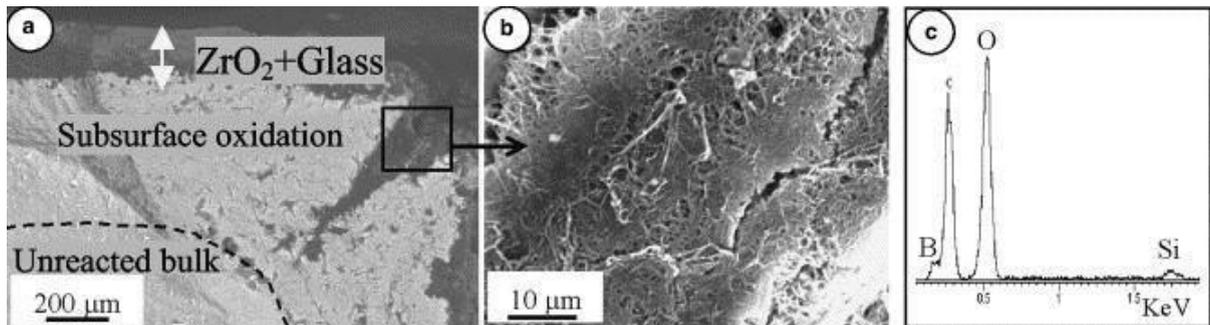


Fig. 3 SEM images showing (a, b) Surface and (c) Cross-section of $ZrB_2-20 \text{ vol.}\% MoSi_2$ oxidised at $1200^\circ C$ [41].

2.3.2 Between 1200 and $1400^\circ C$

Based on Silvestroni et al. [30] and Sciti et al. [41], the formation of SiO_2 , as shown in reaction (4), may be expected to be rapid enough to protect the ZrB_2-MoSi_2 UHTCMC. It was hypothesized in the reports [30, 41] that at the early stage of oxidation of the UHTCMC, SiO_2 may not have been completely formed and that the Reactions (4) and (9)–(12) led to an extremely rapid rate of degradation and this process is also aided by the presence of fast-oxidizing species such as MoB and ZrC. The formation of cracks, in a way, is detrimental, not only from the mechanical point of view but also because cracking leads to rapid transport of oxygen to the internal regions in the sample and this subsequently, leads to an increase in the area exposed to oxidation. Liquid B_2O_3 has been reported to react with SiO_2 , thereby forming a borosilicate glass, similar to that observed for ZrB_2-SiC composites [47-49] and which,

owing to low viscosity, may get easily penetrated into the bulk of $\text{ZrB}_2\text{-MoSi}_2$ sample, through voids left behind by the oxidation of ZrB_2 .

Based on the work of Sciti et al. [41], formation of cracks and the presence of fast oxidizing species such as ZrC and MoB in the sub-surface of the sintered samples leading to rapid sub-surface oxidation have been reported to be the main factors for controlling the degradation of $\text{ZrB}_2\text{-MoSi}_2$ UHTCMC between 1200 and 1400 °C.

On the other hand, based on the work of Silvestroni et al. [30], consumption of B_2O_3 content in the subsurface liquid through reaction with MoSi_2 to form solid MoB [50], may be attributed to the retardation in formation of ZrO_2 , on adding MoSi_2 . In addition, the dissolution of a small amount of Mo into the SiO_2 scale, which has actually been reported to act as a reticulating agent in glass structures [51, 52], may increase the viscosity of the liquid phase, thereby acting as an effective barrier against inward diffusion of oxygen from the atmosphere to the sample surface. Besides, the pronounced bubbling activity on the surface of the oxidized sample at 1800 °C, reported by Silvestroni et al. [30], indicates that various gaseous species are formed in the subsurface layers. Interestingly, during the oxidation of $\text{ZrB}_2\text{-MoSi}_2$ UHTCMC, MoB has been reported to occur in 2 morphologies, [27, 30, 41] depending on the oxidation temperature. At ~1650 °C MoB is homogeneously spread and presently mostly in nano-inclusions within zirconia grains, whereas, at 1800 °C, a thick cordillera ~5mm is observed.

From the mechanical point of view, degradation caused due to oxidation of ZrB_2 has been reported to be responsible for the massive drop in flexural strength in the material at 1300 and 1400°C [41]. Till date, there is limited data available for $\text{ZrB}_2\text{-MoSi}_2$ UHTCMCs, for oxidation at temperatures exceeding 1400 °C, although considerable amount of work has been done in investigating phase evolution during oxidation at 1650 and 1800 °C by Silvestroni et al. [30].

The major conclusion from the work of Silvestroni et al. [30, 53] is that a homogeneous distribution of Mo-rich phases, i.e., a continuous $(\text{Zr, Mo})\text{B}_2$ solid solution without large Mo-phases, is desirable for enhancing the oxidation resistance of $\text{ZrB}_2\text{-MoSi}_2$ UHTCMCs.

3. Criterion for design of UHTCMCs with improved oxidation resistance

The choice of cation to be dissolved into the boride matrix is of extreme importance. As long as the nano-inclusions within ZrO_2 grains are located at oxygen partial pressure values of below 10^4 - 10^6 MPa between 1650-1850°C (Fig. 4), they may be considered to be stable compounds [30]. Hence, the main criterion, to be focussed on for the design of UHTCMCs should be based on using suitable additives (Me) with ZrB_2 , in order to form a homogeneous $(Zr, Me)B_2$ solid solution with an extremely high phase stability in the region of the highest partial pressure of oxygen, without any amount of GB segregation, whatsoever. Based on the Predominance diagrams at different temperatures, Mo, Cr and W have been reported to possess the highest stability field at the highest oxygen partial pressures, [30, 53] in-line with the experimental findings of Kazmedashi et al. [54] and Talmy et al. [55].

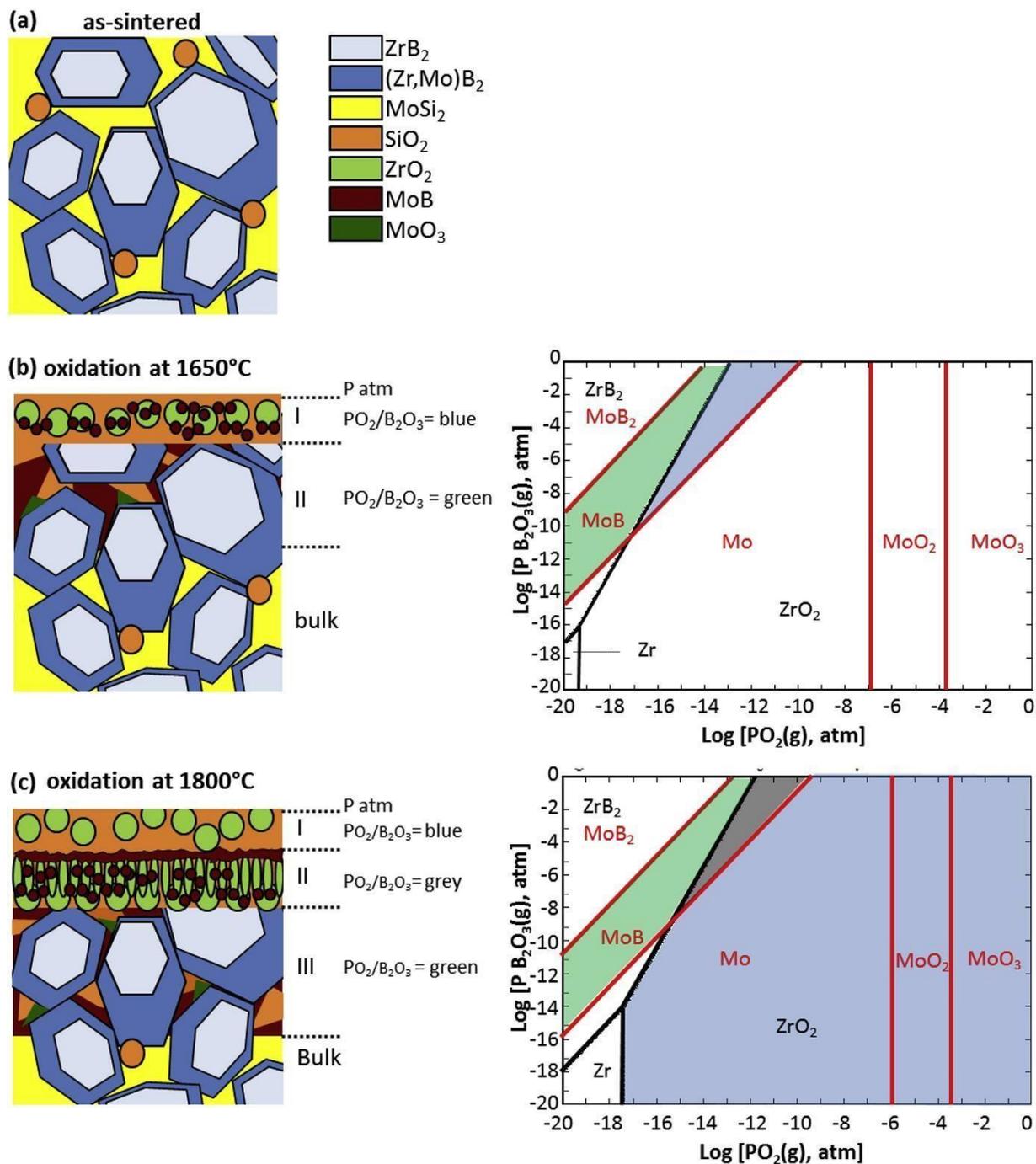


Fig. 4 Left-hand side: Schematic of microstructural evolution starting from (a) as-sintered state up to oxidation at (b) 1650 and (c) 1800 °C. Right-hand side: phase stability diagrams for the Zr-B-O (black) and Mo-B-O (red) system as a function of partial pressures of oxygen and boron oxide at (b) 1650 °C and (c) 1850 °C [30].

4. Anisotropy in oxidation of hot-forged (textured) $\text{ZrB}_2\text{-MoSi}_2$ UHTCMCs

Liu et al. [56] investigated the anisotropic oxidation behaviour of textured $\text{ZrB}_2\text{-MoSi}_2$ UHTCMCs, prepared by reactive hot pressing and subsequent hot forging, for different

exposure times (ranging from 0.5 h to 12 h) at 1500°C and reported that on exposure in air for a relatively short period of time (0.5 h and four h), the ceramics, textured as a result of the aforesaid deformation process, exhibit a good amount of anisotropy in oxidation i.e., the V-direction surface has a much better oxidation resistance than the P-direction surface (Fig. 5). The V-direction surface of the texture ceramics also shows a better oxidation resistance, in contrast to the V-direction surface in non-textured ceramics, which may be certainly attributed to the higher atomic density of ZrB_2 grains and a much higher diffusion path length in the V- than in the P- direction. However, with passage of time, the formation of thick SiO_2 layer, preventing the inward diffusion of oxygen from the outer atmosphere, has been reported to weaken the anisotropy in oxidation. Liu et al. [56] have finally concluded that the combination of good oxidation resistance and flexural strength in the V-direction surface for textured ZrB_2 - $MoSi_2$ UHTCMCs may enable these materials to act as promising candidates for future applications, especially for improving the performance of nosecones of the most trending hypersonic re-entry vehicles.

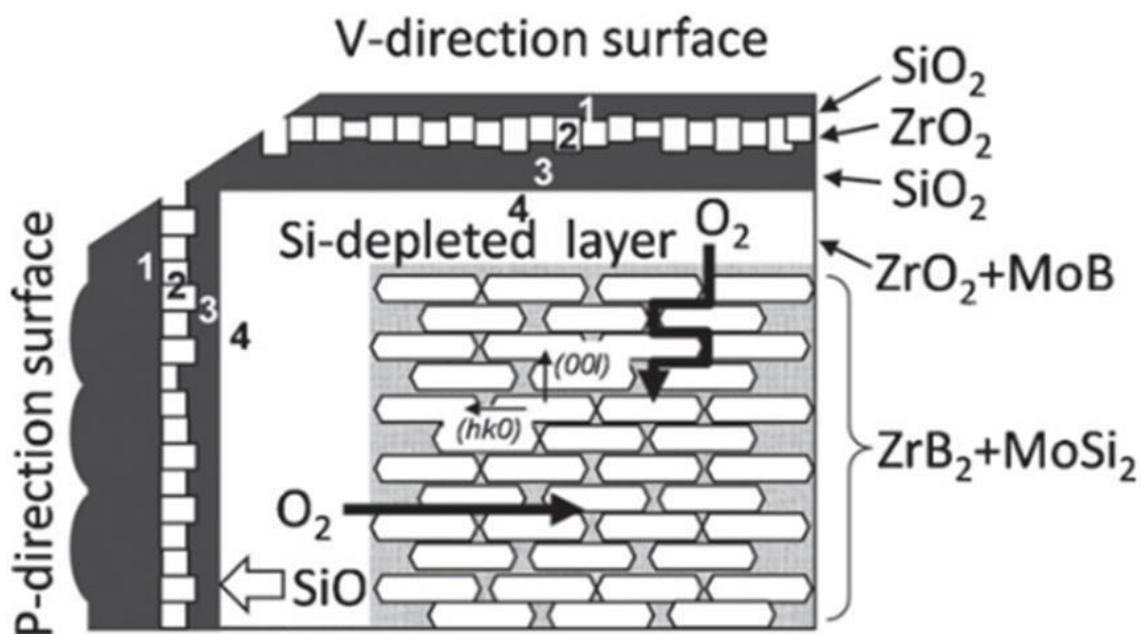


Fig. 5. Schematic representation of both V- and P-direction cross sections in textured ZrB_2 - $MoSi_2$ ceramics oxidized for four h at 1500°C, illustrating anisotropy in oxidation behaviour [56].

5. Mechanical properties of ZrB_2 - $MoSi_2$ ceramics due to oxidation

Grohsmeyer et al. [57] have reported that the Elastic properties (Fig. 6(a)) and Vickers microhardness (Fig. 6(b)) of ZrB_2 - $MoSi_2$ ceramics follows rule of mixture trends based on the constituent phases and that the Young's modulus also decreases with decreasing ZrB_2 average particle size due to the presence of higher amounts of low modulus tertiary oxide phases such as SiO_2 in compositions prepared from finer ZrB_2 powders and is highly coherent with the previous experimental investigations [58-68]. Besides, the Flexural strength at 1500 °C for $MoSi_2$ contents above 25 vol.% has been reported to vary slightly between 420 and 460 MPa for all compositions, whilst for lower contents, two trends were reported [57]. For fine and medium ZrB_2 grades, flexural strength was reported to increase with $MoSi_2$ content due to a probable transition from unprotective to protective mechanism of oxidation. Besides, for these compositions, a continuous borosilicate glassy scale was observed and this attributed as the main factor for limiting the depth of oxidation damage. For coarse ZrB_2 particles, flexural strength was reported to decrease with increasing $MoSi_2$ content owing to the ductilization of the disilicide, thereby leading to the partial masking of the beneficial effect of absorbing fracture energy possessed by the solid solution shell [57].

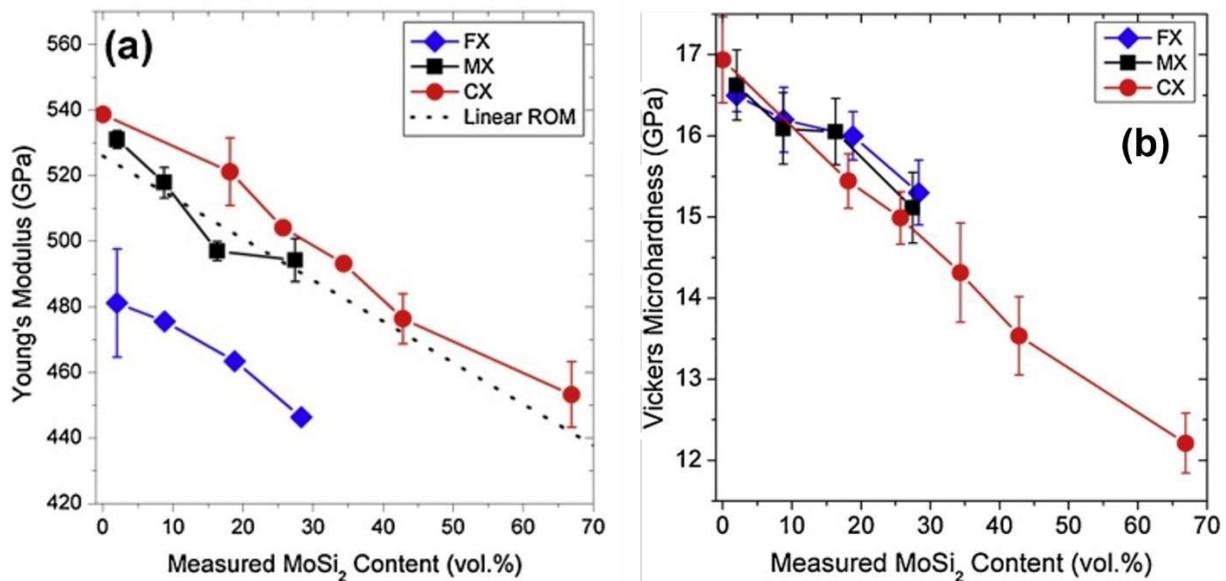


Fig. 6 (a) Young's modulus and (b) Vickers microhardness as a function of $MoSi_2$ content in ZrB_2 - $MoSi_2$ ceramics. N, M and C indicate coarse, medium and fine powder grades of ZrB_2 , respectively. X indicates vol.% of $MoSi_2$. In part (a), ROM refers to volumetric rule of mixtures [57].

6. A few presently unexplored avenues in this field and outlooks for the future

The onset of correlative microscopy [1] has completely revolutionised the field of research in structural materials. Ranging from the study of segregated atoms [4, 5, 10] to characterising nanoscale precipitates at different interfaces [5], the novel technique has enabled material scientists to correlate the properties of a material with its bulk and interfacial structure, simultaneously. From the fundamental viewpoint, there still remain a lot of unexplored avenues, in the context of oxidation studies in the UHTCMCs, which may be potentially addressed by this novel technique. For instance, in the context of oxidation of MoSi₂ in ZrB₂-MoSi₂ based UHTCMCs at temperatures lower than 1200 °C, formation of MoO₃, has been reported by Silvestroni et al. [30], to occur at a rate which is much lower than that of SiO₂, thereby leading to a volume expansion and a consequent piling up of a huge amount of internal stresses at grain boundaries (GBs). Unfortunately, at present, there is limited understanding of the effect of volume expansion associated with the formation of MoO₃ at temperatures lower than 1200 °C on the stress pile-up at GBs. Hence, its the GB cohesion [10] and GB energy [5] which needs to be addressed, for a detailed understanding of the influence of the same on the stress pile-up associated with volume expansion, due to formation of MoO₃, in the present context. Besides, adhesion between the oxide layer and the surface of the base material (ZrB₂-MoSi₂, in the present context) is also something which needs to be addressed as a function of the local chemistry at the substrate-oxide interface before subjecting these materials to service at elevated temperatures.

Although a number of theoretical studies based on the kinetics of oxidation as a function of the diffusivity of oxygen, have illustrated the properties of the oxides, formed during oxidation of ZrB₂-MoSi₂ at different temperatures [26-30], but however, there exists a huge possibility of understanding the same experimentally, through detailed study of oxygen-defect interaction, using extensive defect and orientation based microscopy techniques such as Electron Backscatter Diffraction (EBSD) [10], Electron Channeling Contrast Imaging (ECCI) [69, 70] e.t.c. and correlating the structural information, obtained henceforth with the atomic-level chemistry using Atom Probe Tomography (APT) [7] technique, using Focussed Ion Beaming (FIB) [7] as a lift-out technique to prepare samples for APT. This, in a way, may also be used as a means to understand the change in GB character [5] of different crystalline oxides formed during oxidation at different temperatures and determining there is a localised phase formation at GBs, due to the same, as recently reported by Meiners et al. [71]. Addressing a couple of fundamental issues, as these may, henceforth be used as a pre-requisite to design ZrB₂-MoSi₂ based

UHTCMCs, in future, with even better mechanical properties during oxidation at elevated temperatures.

7. Conclusions

There is no doubt that ZrB₂-MoSi₂ UHTCMCs will find numerous applications in future, owing to the excellent combination of physical, mechanical, and electrical properties of these materials, and that the research associated with these materials, would be aimed at further improvement in different properties of these materials, however, exploring the currently unaddressed avenues, would be the pre-requisite for aiming at property enhancement based on understanding structure-property correlation at different oxidation conditions in these materials.

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Conflict of Interest

The author hereby declares no conflict of interest.

References

[1]. Saha M. New frontiers in characterising ZrB₂-MoSi₂ ultra-high temperature ceramics. arXiv preprint arXiv:2202.11162. 2022 Feb 5.

[2]. Saha M, Pramanik S, Banik R, Maurya P, Singh S, Raj SV, Madhur DP, Paul TR, Mitra R, Mondal MK, Mallik M. An Insight Into Cyclic Oxidation behavior of ZrB₂-20 Vol.% MoSi₂ Based Ultrahigh Temperature Ceramic Matrix Composite. In Modern Manufacturing Systems (pp. 149-163). Apple Academic Press.

[3]. Saha M. Densification and Characterization of Pressureless Sintered ZrB₂-20 Vol% MoSi₂ Ultra High Temperature Ceramic Composites. M. Mallik et al. Densification and characterization of pressureless sintered ZrB₂-20 vol% MoSi₂ ultra high temperature ceramic composites. 2022 Jun 8;47:77-82.

[4]. Saha M. Grain boundary segregation in steels: Towards engineering the design of internal interfaces. arXiv preprint arXiv:2202.12971. 2022 Feb 5.

[5]. Saha M. New frontiers in characterising ZrB₂-MoSi₂ ultra-high temperature ceramics. arXiv preprint arXiv:2202.11162. 2022 Feb 5.

- [6]. Saha M. Fly ash composites: A review. arXiv preprint arXiv:2202.11167. 2022 Feb 5.
- [7]. Saha M, Mallik M. Additive manufacturing and characterisation of biomedical materials. In *Advanced Materials for Biomechanical Applications 2022* May 30 (pp. 29-57). CRC Press.
- [8]. Saha M, Mallik M. Surface engineering of nanomaterials: Processing and applications. In *Surface Engineering 2022* Sep 14 (pp. 95-119). CRC Press.
- [9]. Saha M. 3D printing of nanoceramics: Present status and future perspectives. arXiv preprint arXiv:2210.06948. 2022 Sep 1.
- [10]. Saha M. On the advanced microstructural characterisation of additively manufactured alumina-zirconia based eutectic ceramics: Overview and outlook.
- [11]. E. Wuchina, E. Opila, M. Opeka, W.G. Fahrenholtz, I. Talmy, UHTCs: ultra-high temperature ceramic materials for extreme environment applications, *Electrochem. Soc. Interf* 16 (2007) 30-36.
- [12]. D.M. Van Wie, J.R. Drewery, D.E. King, C.M. Hudson, The hypersonic environment: required operating conditions and design challenges, *J. Mater. Sci.* 39 (2004) 5915-5924.
- [13]. F. Monteverde, A. Bellosi, S. Guicciardi, Processing and properties of zirconium diboride-based composites, *J. Eur. Ceram. Soc.* 22 (2002) 279-288.
- [14]. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, D.T. Ellerby, High strength ZrB₂-based ceramics, *J. Am. Ceram. Soc.* 87 (2004) 1170-1172.
- [15]. J.K. Sonber, A.K. Suri, Synthesis and consolidation of zirconium diboride: Review, *Adv. Apl. Ceram.* 10 (2011) 321-334.

- [16]. W.G. Fahrenholtz, G.E. Hilmas, I. Talmy, J.A. Zaykoski, Refractory diborides of zirconium and hafnium, *J. Am. Ceram. Soc.* 90 (2007) 1347-1364.
- [17]. S.Q. Guo, Densification of ZrB₂-based composites and their mechanical and physical properties: a review, *J. Eur. Ceram. Soc.* 29 (2009) 995-1011.
- [18]. F. Monteverde, A. Bellosi, Oxidation of ZrB₂-based ceramics in dry air, *J. Electrochem. Soc.* 150 (2003) B552-B559.
- [19] T.A. Parthasarathy, R.A. Rapp, M. Opeka, R.J. Kerans, A model for the oxidation of ZrB₂, HfB₂ and TiB₂, *Acta Mater.* 55 (2007) 5999-6010.
- [20] W.C. Tripp, H.C. Graham, Thermogravimetric study of the oxidation of ZrB₂ in the temperature range of 800°C to 1500°C, *J. Electrochem. Soc.* 118 (1971) 1195-1999.
- [21] I.G. Talmy, M.M. Opeka, S. Dallek, Oxidation of ZrB₂ ceramics modified with SiC and group IV-VI transition metal diborides, *Electrochem. Soc. Proc.* 12 (2001) 144-158.
- [22] L. Silvestroni, G. Meriggi, D. Sciti, Oxidation behavior of ZrB₂ composites doped with various transition metal silicides, *Corrosion Sci.* 83 (2014) 281e291.
- [23] A.D. Panasyk, O.N. Grigoriev, A.V. Koroteev, Interaction between ZrB₂-MoSi₂ cermets and oxide melts, *Powder Metall. Met. Ceram* 53 (2014) 330-334.
- [24] P. Hu, X.-H. Zhang, J.C. Han, X.G. Luo, S.Y. Du, Effect of various additives on the oxidation behavior of ZrB₂-based ultra-high temperature ceramics at 1800°C, *J. Am. Soc.* 93 (2010) 345-349.
- [25] D. Sciti, F. Monteverde, S. Guicciardi, G. Pezzotti, A. Bellosi, Microstructure and mechanical properties of ZrB₂-MoSi₂ ceramic composites produced by different sintering techniques, *Mater. Sci. Eng.* 434 (2006) 3003-3009.
- [26] L. Silvestroni, H.-J. Kleebe, S. Lauterbach, M. Müller, D. Sciti, Transmission electron microscopy on Zr- and Hf-borides with MoSi₂ addition: densification mechanisms, *J. Mater. Res.* 25 (2010) 828-834.

- [27] L. Silvestroni, D. Sciti, Effects of MoSi₂ additions on the properties of Hf- and ZrB₂ composites produced by pressureless sintering, *Scripta Mater.* 57 (2007) 165-168.
- [28] D. Sciti, M. Brach, A. Bellosi, Long-term oxidation behavior and mechanical strength degradation of pressurelessly sintered ZrB₂-MoSi₂ ceramic, *Scripta Mater.* 53 (2005) 1297-1302.
- [29]. M.M. Opeka, I.G. Talmy, J.A. Zaykoski, Oxidation-based materials selection for 2000°C hypersonic aerosurfaces: theoretical considerations and historical experience, *J. Mater. Sci.* 39 (2004) 5887-5904.
- [30]. L. Silvestroni, K. Stricker, D. Sciti, H-J Kleebe, The oxidation behaviour of a ZrB₂-MoSi₂ composite at ultra-high temperatures, *Acta Mat.* 151 (2018) 216-228.
- [31]. J.K. Sonber, A.K. Suri, Synthesis and consolidation of zirconium diboride: Review, *Adv. Appl. Ceram.* 10 (2011) 321-334.
- [32]. W.G. Fahrenholtz, G.E. Hilmas, I. Talmy, J.A. Zaykoski, Refractory diborides of zirconium and hafnium, *J. Am. Ceram. Soc.* 90 (2007) 1347-1364.
- [33]. D. Sciti, M. Brach, and A. Bellosi, Oxidation behavior of a pressureless sintered ZrB₂-MoSi₂ ceramic composite, *J. Mat Res* 20(4) (2005) 922-930.
- [34]. W.C. Tripp, H.H. Davis, and H.C. Graham: Effect of an SiC addition on the oxidation of ZrB₂. *Ceram. Bull.* 52, 612 (1973).
- [35]. A.E. McHale: Phase Diagram for Ceramists (Am. Ceram. Soc., 10, Westerville, OH, 1994), p. 174.
- [36]. C.G. McKamey, P.F. Tortorelli, J.H. Devan, and C.A. Carmichael: A study of pest oxidation in polycrystalline Mo Si₂. *J. Mater. Res.* 7, 2747 (1992).
- [37]. P.J. Meschter: Low-temperature oxidation of molybdenum disilicide. *Metall. Trans.* 23, 1763 (1992).
- [38]. T.C. Chou and T.G. Nieh: Mechanism of MoSi₂ pest during low temperature oxidation. *J. Mater. Res.* 8, 214 (1993).

- [39]. K. Natesan and S.C. Deevi: Oxidation behaviour of molybdenum silicides and their composites. *Intermetallics* 8, 1147 (2000).
- [40]. Y.T. Zhu, L. Shu, and D.P. Butt: Kinetics and products of molybdenum disilicide powder oxidation. *J. Am. Ceram. Soc.* 85, 507 (2002)
- [41]. D. Sciti, M. Brach, A. Bellosi, “Long-term oxidation behaviour and mechanical strength degradation of a pressurelessly sintered ZrB_2 - $MoSi_2$ ceramic”, *Scripta Materialia* 53 (2005) 1297–1302
- [42]. YT Zhu, M. Stan, SD Conzone, DP Butt. Thermal Oxidation Kinetics of $MoSi_2$ -Based Powders, *J Am Ceram Soc* 1999; 82: 2785.
- [43]. YT Zhu, L. Shu, DP Butt. Kinetics and products of molybdenum disilicide powder oxidation, *J Am Ceram Soc* 2002; 85: 507.
- [44]. K Natesan, SC Deevi. Oxidation behaviour of molybdenum silicides and their composites, *Intermetallics* 2000; 8: 1147.
- [45]. HSC Chemistry for Windows 5, Outokumpu Research Oy, Pori, Finland.
- [46]. JB Berkovich-Mattuck. *J Electrochem Soc* 1967; 114: 1030.
- [47]. YL Jang, EJ Lavernia. Processing of molybdenum disilicide, *J Mater Sci* 1994;29:2557
- [48] F Monteverde, S Guicciardi, A Bellosi. Advances in microstructure and mechanical properties of zirconium diboride based ceramics, *Mater Sci Eng A.* 2003; 346: 310.
- [49] F Monteverde, A Bellosi. Beneficial Effects of AlN as Sintering Aid on Microstructure and Mechanical Properties of Hot-pressed ZrB_2 , *Adv Eng Mater* 2003; 7: 508.
- [50]. E.A. Gulbransen, K.F. Andrew, F.A. Brassart, Oxidation of molybdenum 550° to 1700°C, *J. Electrochem. Soc.* 110 (1963) 952-959.
- [51]. A.D. Panasyk, O.N. Grigoriev, A.V. Koroteev, Interaction between ZrB_2 - $MoSi_2$ cermets and oxide melts, *Powder Metall. Met. Ceram* 53 (2014) 330-334.

- [52]. L. Silvestroni, H.-J. Kleebe, Critical oxidation behavior of Ta-containing ZrB₂ composites in the 1500-1650°C temperature range, *J. Eur. Ceram. Soc.* 37 (2017) 1899-1908.
- [53]. L. Silvestroni, S. Failla, I. Nehpor, O. Grigoriev, Method to improve the oxidation resistance of ZrB₂-based ceramics for reusable space systems, *J. Eur. Ceram. Soc.* 38 (2018) 2467-2476.
- [54]. M. Kazemzadeh Dehdashti, W.G. Fahrenholtz, G.E. Hilmas, Effects of transition metals on the oxidation behavior of ZrB₂ ceramics, *Corrosion Sci.* 91 (2015) 224-231.
- [55]. I.G. Talmy, J.A. Zaykoski, M.M. Opeka, High-temperature chemistry and oxidation of ZrB₂ ceramics containing SiC, Si₃N₄, Ta₅Si₃, and TaSi₂, *J. Am. Ceram. Soc.* 91 (2008) 2250-2257.
- [56]. HT Liu, J Zou, DW. Ni, JX Liu, GJ Zhang, Anisotropy oxidation of textured ZrB₂-MoSi₂ ceramics, *J Eur Cer Soc.* 32(12) (2012) 3469-3476.
- [57]. R. J. Grohsmeyer, L Silvestroni, G. E. Hilmas, F. Monteverde, W. G. Fahrenholtz, A.D. Angio, D. Sciti, ZrB₂-MoSi₂ ceramics: A comprehensive overview of microstructure and properties relationships. Part II: Mechanical properties, 39(6) (2012) 1948-1954.
- [58]. V.O. Lavrenko, V.A. Shvets, V.M. Talash, V.A. Kotenko, T.V. Khomko, Electrochemical oxidation of ZrB₂-MoSi₂ ceramics in a 3% NaCl solution, *Powder Metall. Met. Ceram.* 50 (11–12) (2012) 749–753.
- [59]. D. Sciti, L. Silvestroni, L. Mercatelli, J.-L. Sans, E. Sani, Suitability of ultra-refractory diboride ceramics as absorbers for solar energy applications, *Sol. Energy Mater. Sol. Cells* 109 (2013) 8–16.
- [60]. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, Characterization of zirconium diboride-molybdenum disilicide ceramics, *Ceram. Trans.* 153 (2003) 299–308.
- [61]. E.W. Neuman, G.E. Hilmas, W.G. Fahrenholtz, A. Dominguez-Rodriguez, Strength of zirconium diboride to 2300°C, *J. Am. Ceram. Soc.* 96 (1) (2013) 47–50.

- [62]. W.G. Fahrenholtz, Thermodynamic analysis of ZrB₂-SiC oxidation: formation of a SiC-Depleted region, *J. Am. Ceram. Soc.* 90 (1) (2007) 143–148.
- [63]. S. Guo, T. Mizuguchi, M. Ikegami, Y. Kagawa, Oxidation behavior of ZrB₂-MoSi₂-SiC composites in air at 1500°C, *Ceram. Int.* 37 (2) (2011) 585–591.
- [64]. L. Silvestroni, H.-J. Kleebe, S. Lauterbach, M. Muller, Transmission electron microscopy on Zr- and Hf-borides with MoSi₂ addition: densification mechanisms, *J. Mater. Res.* 25 (5) (2010) 6.
- [65]. S.R. Srinivasan, R.B. Schwarz, J.D. Embury, Ductile-to-brittle transition in MoSi₂, in: I. Baker, R. Darolia, J.D. Whittenberger, M.H. Yoo (Eds.), *High-Temperature Ordered Intermetallic Alloys V*, vol. 288, 1992, pp. 1099–1104.
- [66]. D.J. Evans, S.A. Court, P.M. Hazzledine, H.L. Fraser, Deformation mechanisms in the intermetallic compound MoSi₂, in: I. Baker, R. Darolia, J.D. Whittenberger, M.H. Yoo (Eds.), *High-Temperature Ordered Intermetallic Alloys V*, vol. 288, 1992, pp. 567–572.
- [67]. O. Unal, J.J. Petrovic, D.H. Carter, T.E. Mitchell, Dislocations and plastic deformation in molybdenum disilicide, *J. Am. Ceram. Soc.* 73 (6) (1990) 1752–1757.
- [68]. S.Q. Guo, T. Mizuguchi, T. Aoyagi, T. Kimura, Y. Kagawa, Quantitative Electron microprobe characterizations of oxidized ZrB₂ containing MoSi₂ additives, *Oxid. Met.* 72 (5–6) (2009) 335–345
- [69]. D. Raabe, H. Springer, I. Gutierrez-Urrutia, F. Roters, M. Bausch, J.B. Seol, et al. “Alloy design, combinatorial synthesis, and microstructure-property relations for low-density Fe-Mn-Al-C austenitic steels”; *JOM*, 66 (2014), pp. 1845-1855.
- [70]. Saha M, Mallik M. Additive manufacturing of ceramics and cermets: present status and future perspectives. *Sādhanā*. 2021 Sep;46(3):162.
- [71]. T. Meiners, T. Frolov, R.E. Rudd, G. Dehm and C.H. Liebscher; “Observations of grain-boundary phase transformations in an elemental metal”; *Nature*, 2020; 579, pages375–378(2020)

