KME 705

$MoSi_2$ matrix composites for components exposed to HT oxidation and hot corrosion

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Aim of KME 705

- $MoSi_2$-based composites without pressure-assisted sintering having improved fracture toughness and mechanical properties over 1200˚C.
- Hot-corrosion resistance at T = 1200 – 1300˚C.

Background of KME X05; x = 1, 3, 4, 5, 7

- $MoSi_2$-based composites reinforced with 30 vol.% ZrO_2 had 2.5 times higher toughness than pure $MoSi_2$ in 1990.
- Toughness measurements were based on crack length measurements around Vickers indents (1981 paper).

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Partially stabilized ZrO_2 particle–$MoSi_2$ matrix composites

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A 30 vol % partially stabilized ZrO_2 particle–$MoSi_2$ matrix composite was synthesized by hot pressing to 96% theoretical density at 1700° C. No chemical reactions between the PSZ and $MoSi_2$ were observed after hot pressing, indicating thermodynamic stability of these species. The composite formed an adherent and coherent glassy-appearing oxidation layer after oxidation at 1500° C. The room temperature indentation fracture toughness of the composite was 2.5 times that of pure $MoSi_2$. These results demonstrate the feasibility of PSZ particle–$MoSi_2$ matrix composites.

TABLE I Indentation fracture toughness results

Material	Hardness (GPa)	Fracture toughness (MPa $m^{1/2}$)
Pure $MoSi_2$	10.00	2.58
30 vol % PSZ–$MoSi_2$	8.49	6.56

4455

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ZrO_2 and ZrO_2–SiC particle reinforced $MoSi_2$ matrix composites

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Abstract

ZrO_2–$MoSi_2$ and (ZrO_2–SiC)–$MoSi_2$ composites were fabricated by hot pressing and hot pressing–hot isostatic pressing at 1700 °C. No reactions between ZrO_2, SiC and $MoSi_2$ were observed. An amorphous silica glassy phase was present in all composites. Composites with unstabilized ZrO_2 particles exhibited the highest room temperature fracture toughness, reaching a level three times that of pure $MoSi_2$. Both the room temperature toughness and 1200 °C strength of (ZrO_2–SiC)–$MoSi_2$ composites were higher than those of ZrO_2–$MoSi_2$ composites, indicating beneficial effects of combined reinforcement phases. Low strength levels were observed at 1400 °C as a result of the presence of the silica glassy phase. Elimination of glassy phases and refinements in microstructural homogeneity are processing routes important to the optimization of the mechanical properties of these types of composites.

A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Crack Measurements

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The application of indentation t… fracture toughness is examined… first part, attention is focused o… direct measurement of Vickers… function of indentation load. A t… is first established, in terms of e… ture mechanics. It is thereby ass… crack response lies in the resid… field. This residual term has imp… the crack evolution, including th… slow growth under environme… tographic observations of cracks… ials are used to determine the m… investigate other potential comp… partures from ideal indentation… from these observations provide … indentation toughness equation… other well-behaved ceramics. … simple in procedure and econom…

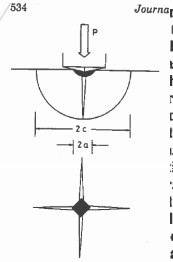

Fig. 1. Schematic of Vickers-produced indentation-fracture system, peak load P, showing characteristic dimensions c and a of penny-like radial/median crack and hardness impression, respectively.

…this …lves …is a …hod …rac- …dial …tact …ing …ion …ac- …ler- …l to …de- …ata …the …to …ely

considerable potential … terizing mechanical … conventional testing t… a unique simplicity an… reliability. A recent su… currently under investi… is useful for placing … this regard.

This study concerns … techniques in the dete… parameter for ceram… proaches, presented in … determination is made … on the indented surface … straightforward basis f… tained indirectly from … pieces, in conjunction … failure formulation. T… the advantages and li…

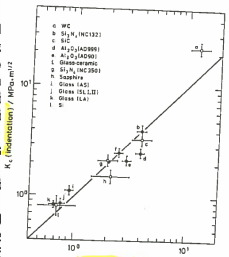

Fig. 5. Plot demonstrating correlation between toughness values determined by indentation and by conventional means. Filled symbols denote reference materials used to evaluate constant $\beta\xi$ in Eq. (4). Vertical error bars represent uncertainty (standard deviation) in parameter $P/c^{3/2}$ calculated from Fig. 4; horizontal error bars nominal accuracy of K_c values taken from Table I.

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HISTORY OF $MoSi_2$

1907 HOENIGSCHMID (Germany) Protective coating for Ductile metal

1907 WEDEKIND & PINTSCH (Germany) Suggested high melting silicides for use in heat conductor material

1907 HOENIGSCHMID (Germany) Suggested high melting silicides for use in heat conductor material

1913 HAEGGLUND & REHNQUIST (Sweden) Suggested 50Mo/50Si Alloys for furnace heating elements

1914 BEIDLER & CAMPBELL (USA) Patent on $MoSi_2$ composition

1947 KIEFFER et al (Austria) Patent on $MoSi_2$ heat conductor by P/M methods

1949 NOWOTNY (Germany) Mo-Si-C Phase diagram

1950 KANTHAL (Sweden) Patent on $MoSi_2$ for Commercial heating element

1951 MAXWELL (USA) First suggested the use of $MoSi_2$ as a structural material

1954 FITZER (Germany) High temperature study of $MoSi_2$

1956 ERDOS (USA) Silicide coatings for gas turbine applications

1971 KEY PAPERS ON $MoSi_2$: FITZER & REMMELE (Germany) GAC & PETROVIC (USA)

1973 Los Alamos Labs./DOE-ECUT $MoSi_2$ developmental Studies(Petrovic)

1984 UMAKOSHI & HIRANO (Japan) Single Crystal $MoSi_2$, WSi_2 Studies

1985 CARTER (LANL-MIT) Thesis on vapor solid whiskers in $MoSi_2$

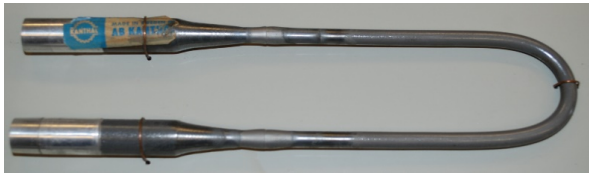
1988 Los Alamos Labs / ONR $MoSi_2$ Composites developmental studies DARPA-PRATT & WHITNEY Intermetallics Review Meeting

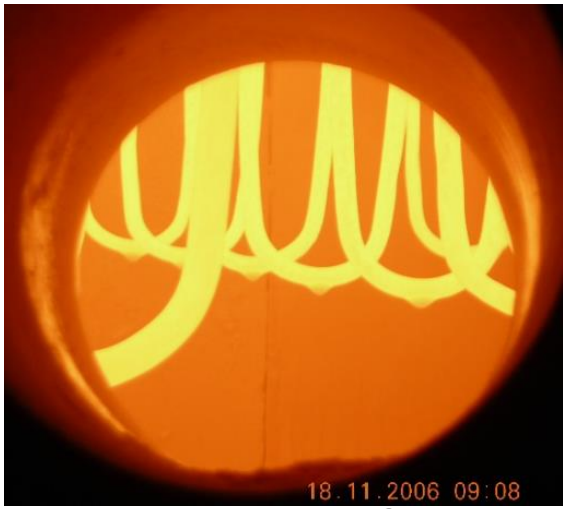
1989 Los Alamos Labs. US - PATENTS (Petrovic) Los Alamos Labs. IR-100 Award

1990 ONR First High Temperature Structural Silicide Conference

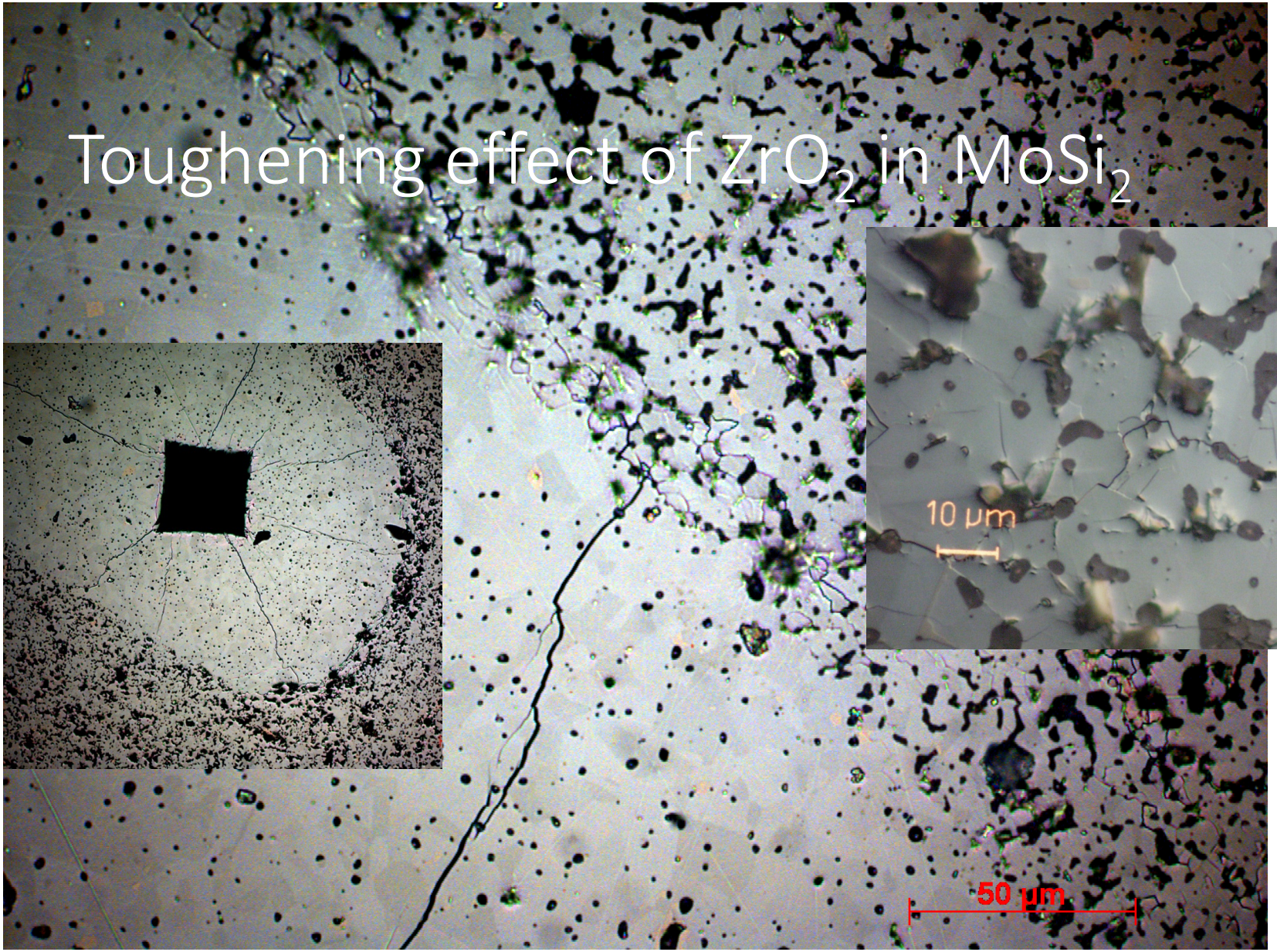
1991

Vasudévan AK, Petrovic JJ. Mater Sci Eng A155 (1992) 1-17.





Toughening effect of ZrO_2 in $MoSi_2$



Summary of results from previous projects

- Project 105
  - + Developed and patented a $MoSi_2$-20 vol.% ZrO_2-10 vol.% MoB-5 vol.% SiC composite
    HV10=9-10 GPa, Kc=7-8 MPa·$m^{1/2}$, RT-bending strength > 450 MPa, creep rate reduced >1 order of magnitude at 1100°C/10 MPa compared to Kanthal Super.
  - – Required very high sintering temperature → unfavourable surface modification
  - – Poor oxidation resistance → lower amount of second phase (from 30 vol.% to 15 and 20 vol.%)
  - + Prototype guide vane for gas turbine by water-jet machining!
  - – Cyclic oxidation test at 1100°C; 3-5 mg/cm^2 after 500 cycles (still quite poor)

- Project 305
  - + Alloying process → reduced oxide content on feed-stock powders $(Mo_{0.9}Cr_{0.1})Si_2$-15 vol.% ZrO_2, improved sinterability
    Kc= 6 MPa·$m^{1/2}$ (KIC = 4.2 MPa·$m^{1/2}$) , improved As Sintered oxidation resistance at 1400°C for 100h compared with that of the AS unalloyed composites.
  - Feasibility study of prototype heat shield of reduced dimensions by conventional machining of green body!
  - Reduced hardness

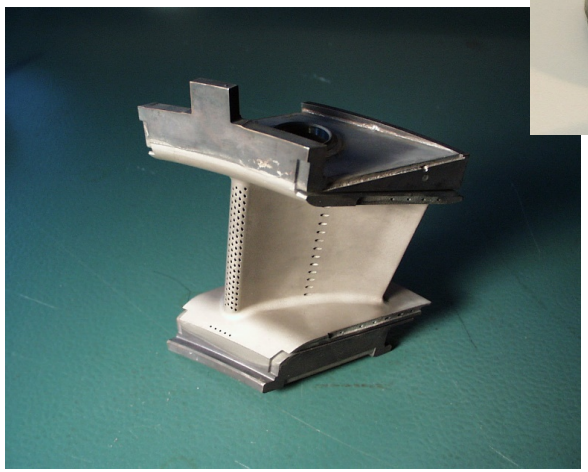
- Project 405
  - + Optimisation of experimental set-up for oxidation testing
  - + Optimisation of material processing
  - + Full-scale prototype heat shield made by machining of pre-sintered material!

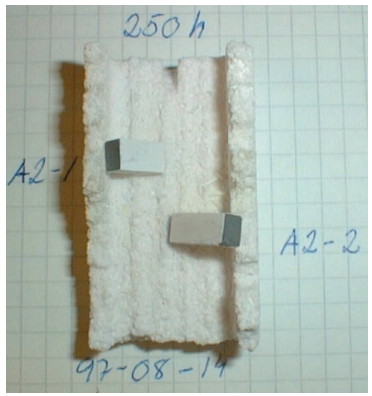
Summary of results from previous projects

- Project 505
  - Mechanical testing at RT and 1200C; Si3N4 reference
  - Fracture toughness from SEVNB and 4-point bending – discrepancy between indentation method and SEVNB
  - Improved dispersion of second phase → better mechanical properties
  - Physical properties measured (CTE, thermal conductivity)
  - Prototype guide vane for gas turbine by water-jet machining!
  - Cyclic oxidation testing at 1200 and 1300°C disqualifies Cr!!! (1200°C: **15** mg/cm^2 (0.10 Cr) vs **<2** (0 Cr) after 500 cycles; 1300°C: **7** (0.10 Cr) vs **3** (0.06 Cr) vs **2** (0 Cr))
  - Cr weakens matrix. Surface condition key to properties!

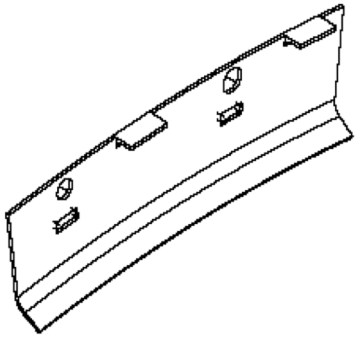
- Project 705
  - Extrusion successful → easier to obtain longer samples; additional heat treatment (e.g. Final Sintering) made easier
  - Mechanical testing at RT and 1200°C on extruded samples of AS and FS $MoSi_2$-15 vol.% ZrO_2
  - SEVNB method for cylindrical samples developed → easier to obtain true fracture toughness
  - Creep properties by simple test method
  - Feasibility of SiC instead of ZrO_2 for reduced oxide growth rate; elimination of Mo_5Si_3 surface layer

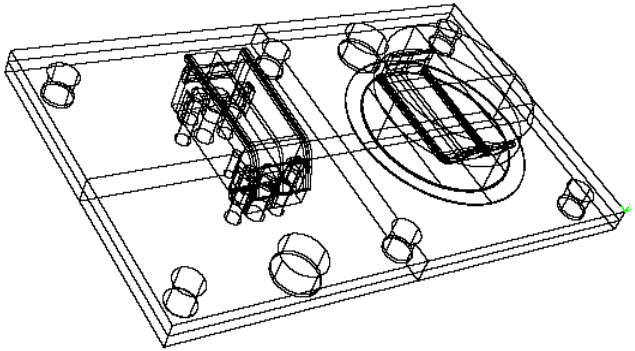
2004: Prototype guide vane for 30 MW gas turbine by water-jet machining starting from 18 kg silicide piece

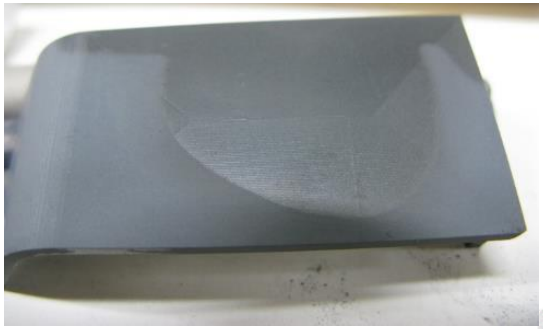


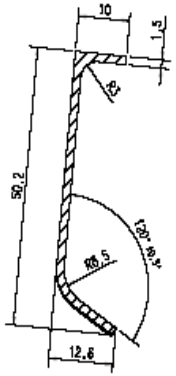


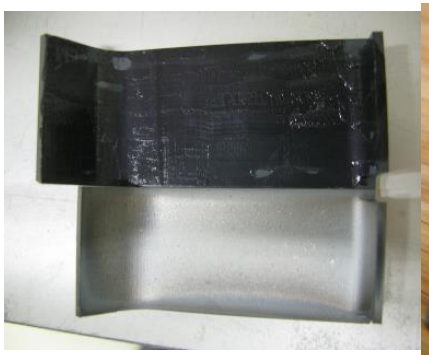
2008: Green machining of shield profiles









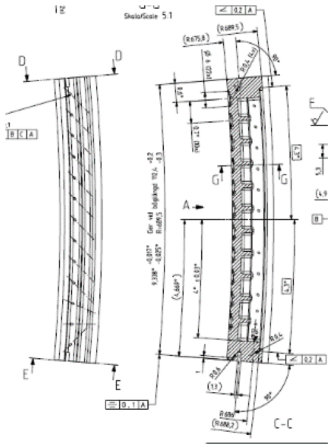


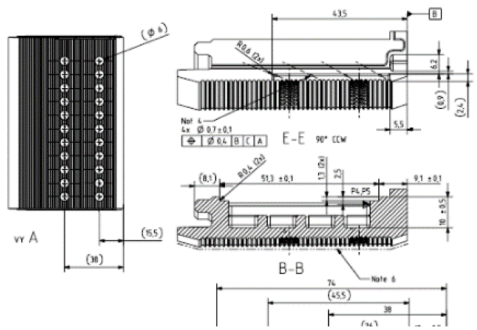
Modig 7200

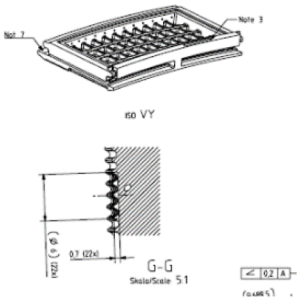
- blank is ”glued” with wax and cut to remove excess material
- machining from above to scoop out the hollow shape
- glue hollow profile with wax on the aluminium core to machine back side
- Shape distortion during sintering!

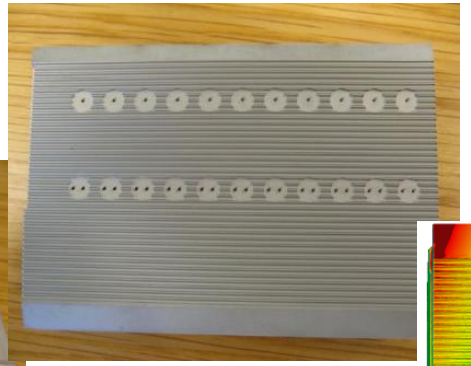
2010: Full-scale prototype heat shield for industrial gas turbine

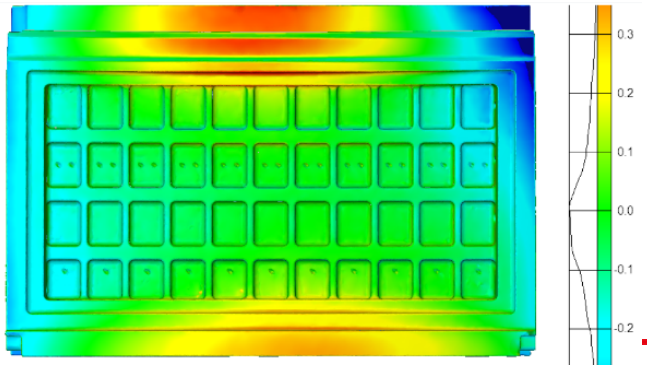
- Granulation of $MoSi_2$+ZrO_2+additives → CIP → pre-sintering → machining → sintering

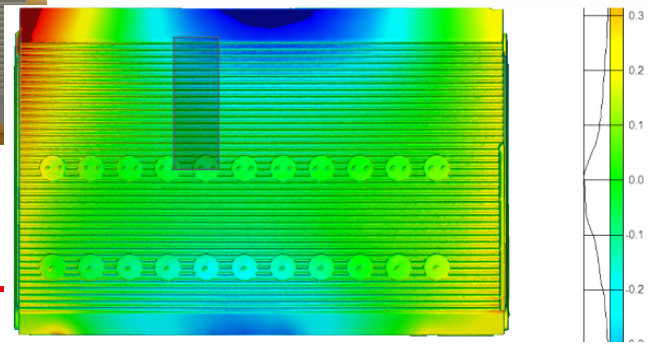




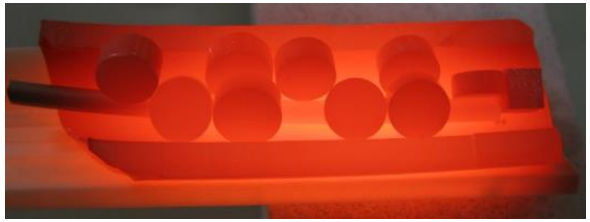


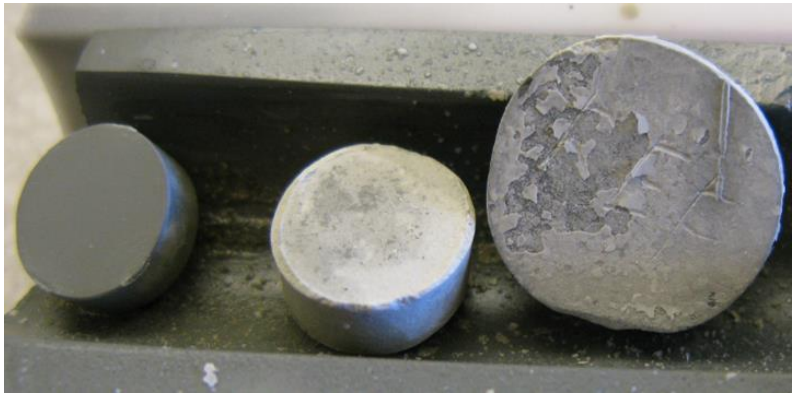






Influence of Cr on isothermal oxidation at 1400°C in air
As sintered material benefits from Cr additions.





$MoSi_2$-ZrO_2 ground

$MoSi_2$-ZrO_2 H_2

$MoSi_2$-ZrO_2 Ar

Cr08-DK1, Ar

$MoSi_2$ ground

Cr08-DK1, H_2

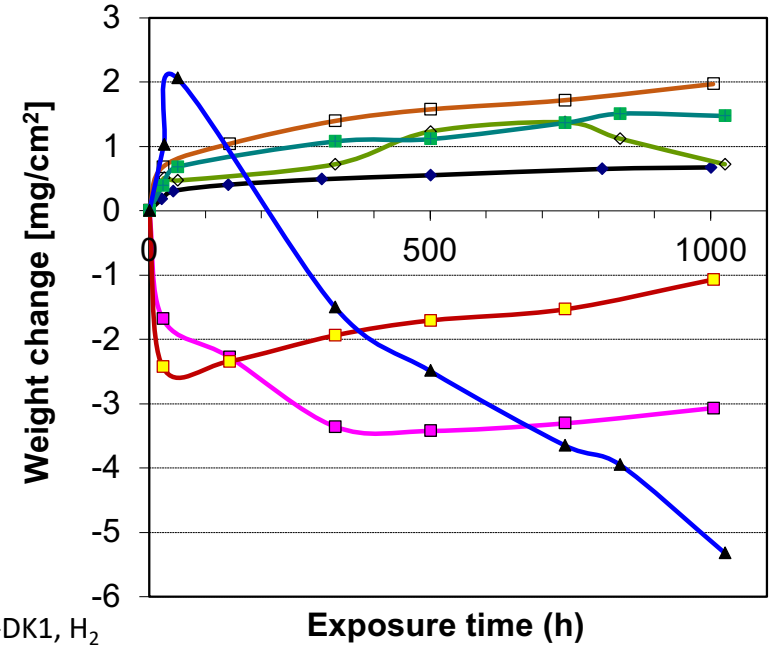
Cr12-DK1, H_2

Si_3N_4

$MoSi_2$-ZrO_2 ground

Cr10-DK1, Ar

Cr10-DK1, H_2



KS1700

MoSi2-ZrO2 Ar-sintered

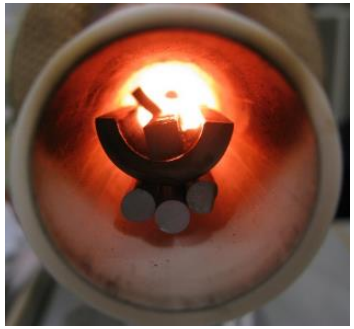
MoSi2-ZrO2 H2-sintered

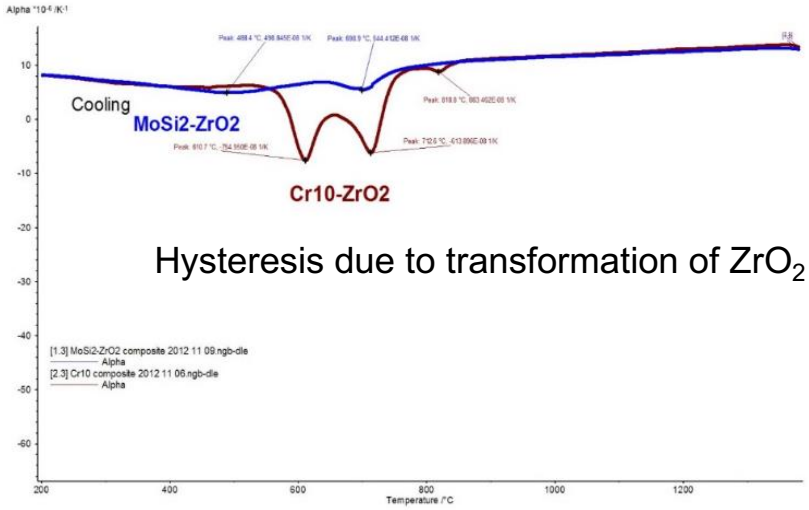
MoSi2-ZrO2 ground

Mo0.9Cr0.1Si2-ZrO2 Ar-sintered

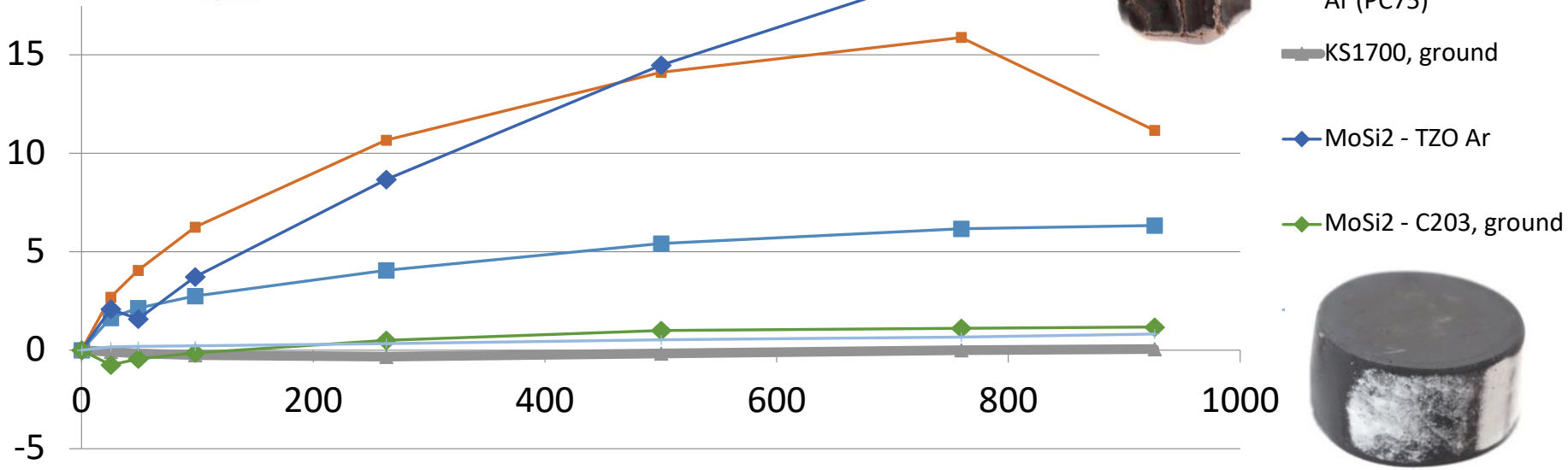
Mo0.92Cr0.08Si2-ZrO2 Ar-sintered

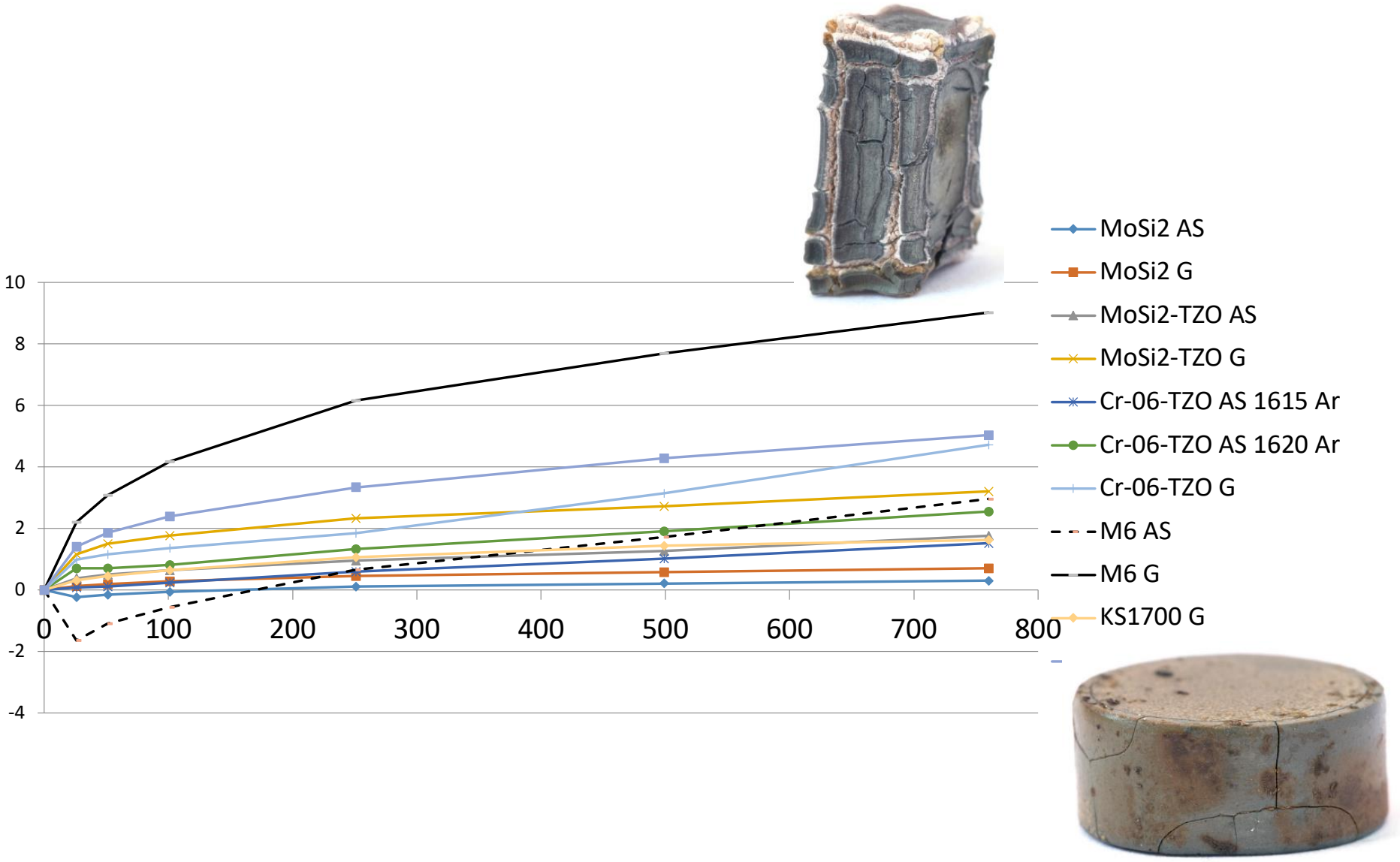
Hot pressed Si3N4

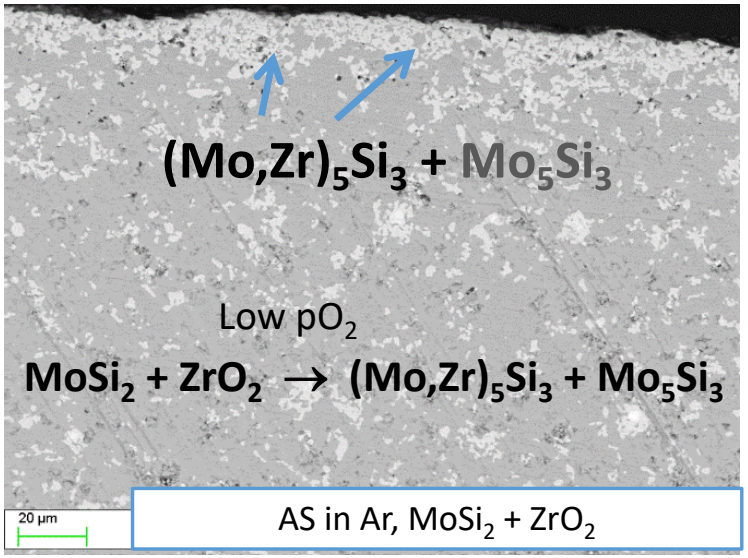




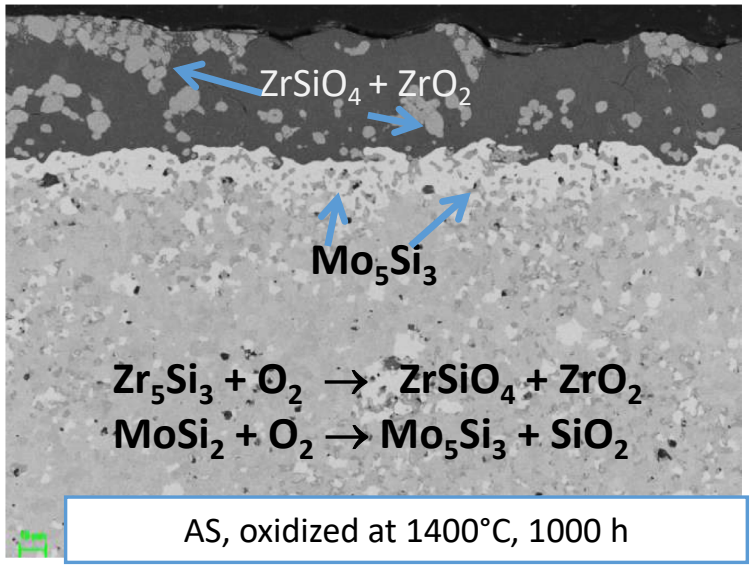
Hysteresis due to transformation of ZrO_2



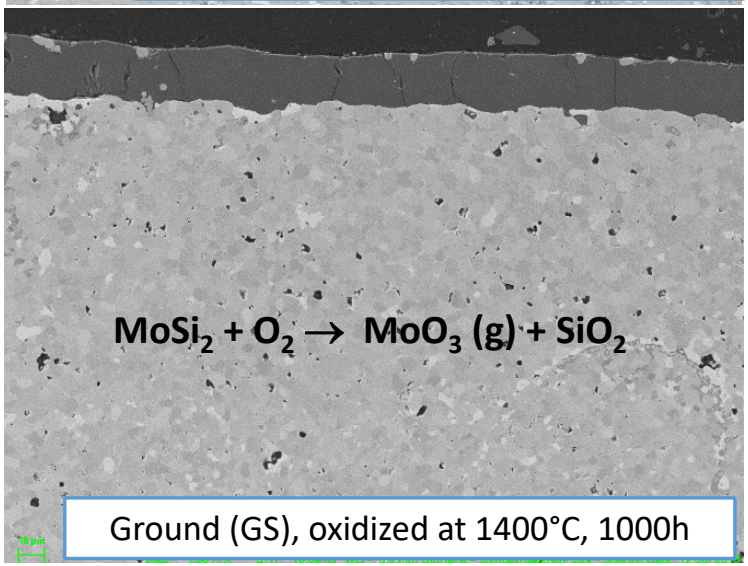

10
8
6
4
2
0
-2
-4
0
100
200
300
400
500
600
700
800
MoSi2 AS
MoSi2 G
MoSi2-TZO AS
MoSi2-TZO G
Cr-06-TZO AS 1615 Ar
Cr-06-TZO AS 1620 Ar
Cr-06-TZO G
M6 AS
M6 G
KS1700 G



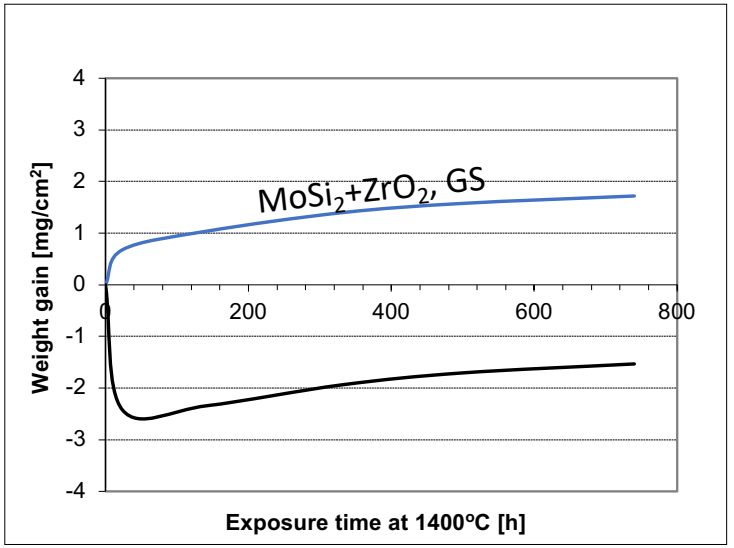
AS in Ar, $MoSi_2 + ZrO_2$



AS, oxidized at 1400°C, 1000 h

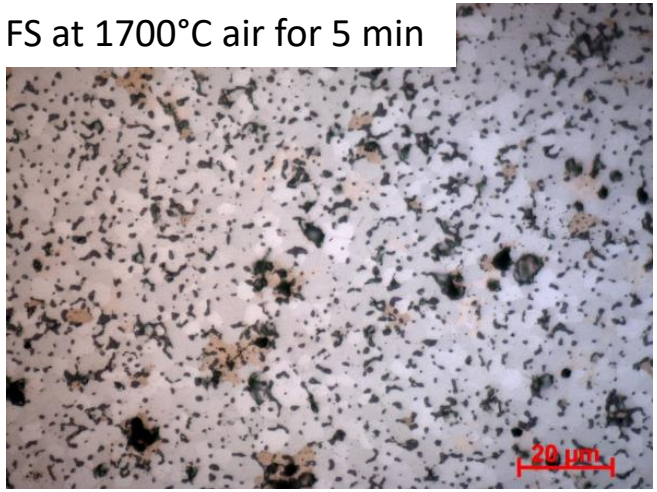


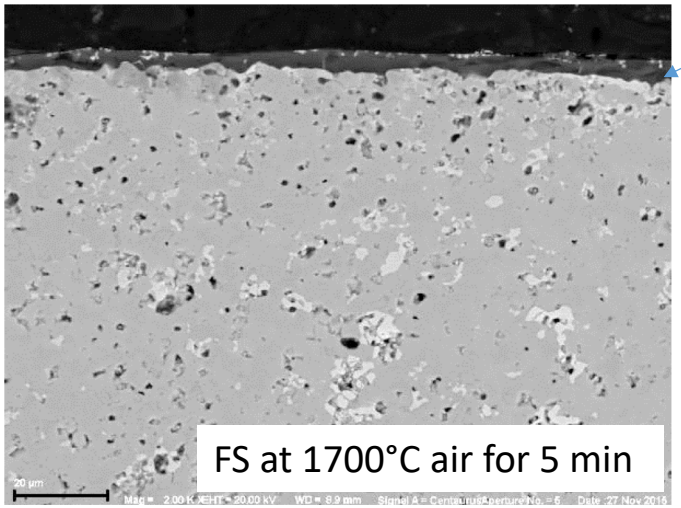
Ground (GS), oxidized at 1400°C, 1000h



Final Sintering at different temperatures

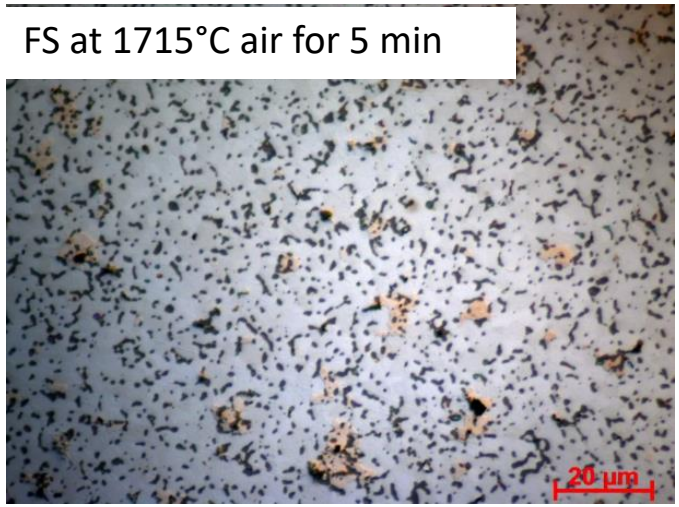
FS at 1700°C air for 5 min



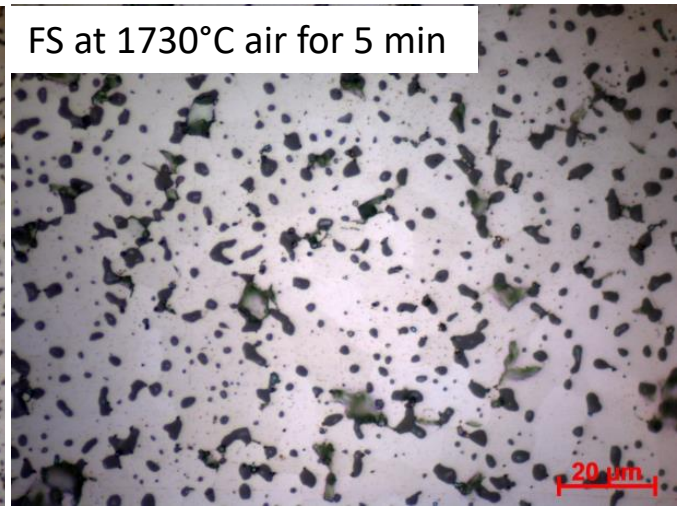


Protective SiO_2

FS at 1715°C air for 5 min



FS at 1730°C air for 5 min



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On the Vickers Indentation Fracture Toughness Test

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The Vickers indentation fracture toughness test, or VIF, is addressed by considering its origins and the numerous equations that have been applied along with the technique to estimate the fracture resistance, or the K_{Ic} of ceramics. Initiation and propagation of cracks during the VIF test are described and contrasted with the pre-cracking and crack growth for internationally standardized fracture toughness tests. It is concluded that the VIF test technique is fundamentally different than standard fracture toughness tests. The VIF test has a complex three-dimensional crack system with substantial deformation residual stresses and damage around the cracks. The VIF test relates to an ill-defined crack arrest condition as opposed to the rapid crack propagation of the standardized fracture toughness tests.

Previously published fracture toughness results employing the VIF technique are reviewed. These reveal serious discrepancies in reported VIF fracture toughness values. Finally, recent fracture resistance measurements by the VIF technique for the Standard Reference Material SRM 2100 are presented. These are compared with standardized test results for the same material. It is concluded that the VIF technique is not reliable as a fracture toughness test for ceramics or for other brittle materials. What the VIF actually measures in terms of fracture resistance cannot be readily defined. It is recommended that the VIF technique no longer be acceptable for the fracture toughness testing of ceramic materials.

Evans and Charles[2] in the mid-1970s. Evans and Charles applied the VIF to materials from single crystal oxides to cemented carbides, all of which seemed amenable to the test. The technique rapidly achieved popularity because of its expediency. It seemed to be a convenient way to determine K_{Ic}. It requires only a small volume of material and the actual measurements can be quickly completed with only a short sample preparation time and at a minimum financial cost. In nearly all respects the VIF method seemed to be practically ideal, although it is admittedly a rather non-conventional approach for determining the fracture toughness.

The VIF technique has been thoroughly described in two independent, comprehensive reviews of the fracture toughness testing of brittle materials.[3,4] Recently, a third review, that by Morrell[5] categorizes the VIF as "not meeting fracture mechanics criteria," a stunning indictment. The present authors believe a fair assessment of the VIF is that most currently active researchers do not consider the VIF to be an accurate, nor a reliable method for determining K_{Ic} or any other fracture resistance parameter. These concerns were amplified when the VIF test experienced difficulties in three international round robin exercises.[6,7] Unfortunately, the VIF method is being considered in some quarters as a possible method for evaluating fracture toughness for materials specifications. These combined issues have prompted this re-examination of the validity of the VIF

resistance testing of ceramics.
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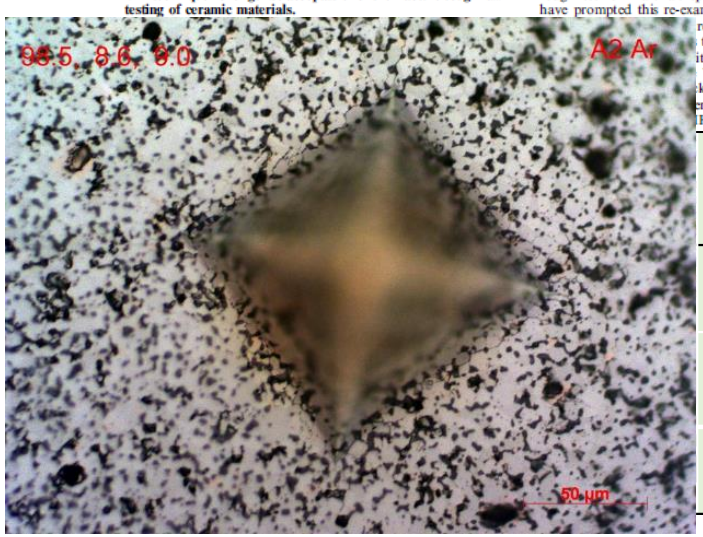

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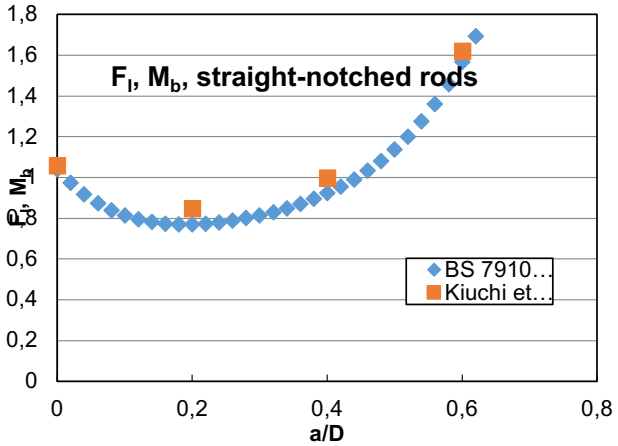
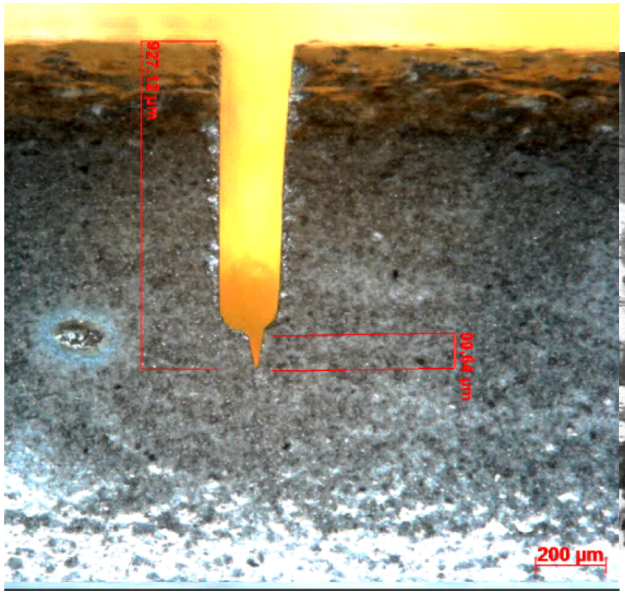
	Prep.	RT-σ_f (MPa)	HT-σ_f (MPa)	E-modulus (GPa)	K_{IC} (MPa·m$^{1/2}$)	Hv (GPa)	K_C (VIF) (MPa·m$^{1/2}$)
(Mo,Cr)Si_2+ZrO_2	PLS	293±25	200±27 (at 1200°C, 0.2 mm/min)	310	4.7 ± 0.25	8-9	8 - 9
KS1800	PLS	456±40	>330 (at 1100°C, 1.0 mm/min)	312	~3	9-10	2 - 3
Si_3N_4	HP	629±24	294±29 (at 1200°C, 0.2 mm/min)	294	5.2±0.07	13	5

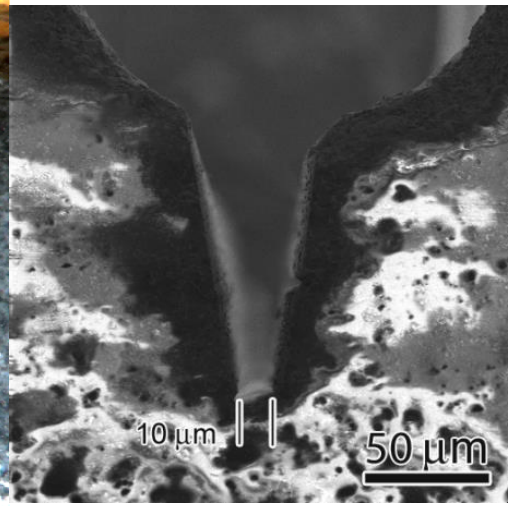
Fracture toughness (SEVNB) for cylindrical sample



	Relative density (T.D.)	HV10 (GPa)	KIc (SEVNB) (MPa·m$^{1/2}$)	σ_f, RT (MPa)	σ_f, 1200°C (MPa)
$MoSi_2$-ZrO_2 (AS)	98%	9.5	4.4	320	334 ± 13
$MoSi_2$-ZrO_2 (FS)	98%	9.0	4.4	357	427 ± 24
Si_3N_4 (HP)	100%	13.5	5.2	629	294 ± 29

Mean, MP	Std dev, MPa					
			Using BS7910 App.M10.1			
356.5	**31.5**			Using equation in supplied calibration		
Force N	d/D	M, FI	KIc, MPa r	Mean	Std dev	Check
109.8	0.2475	0.7844	4.181			3
120.3	0.2286	0.7772	4.425			3
113.2	0.2612	0.7910	4.434			3
115.9	0.2546	0.7877	4.458			3
114.9	0.2358	0.7797	4.289	**4.36**	**0.12**	3





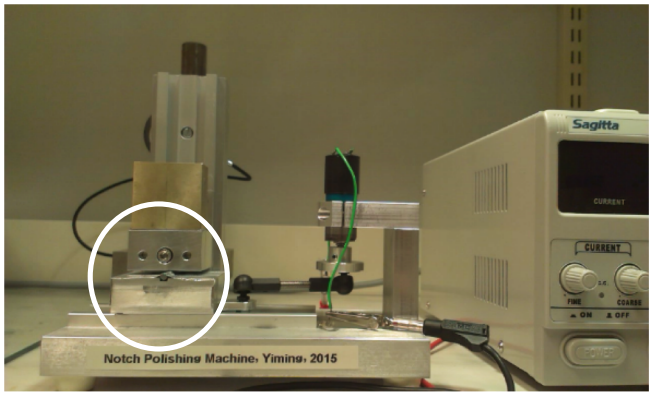
SEVNB and IF measurements on $MoSi_2$ - ZrO_2 composite

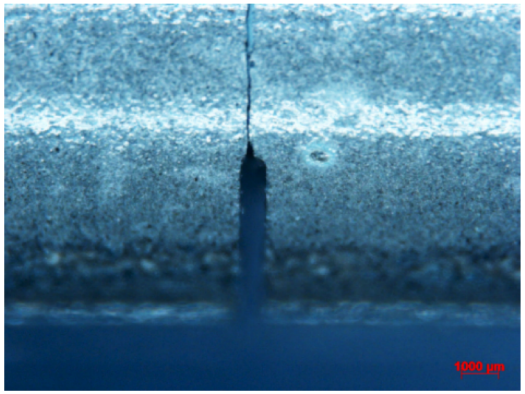
$MoSi_2$ – 15 vol.% ZrO_2 :

PM and extruded, sintered at 1620°C for 30 – 60 min in Ar, final sintered at 1715°C for 5 min in air, ρ = 6.03 g/cm^3, silica glassy layer thickness of 5 μm.

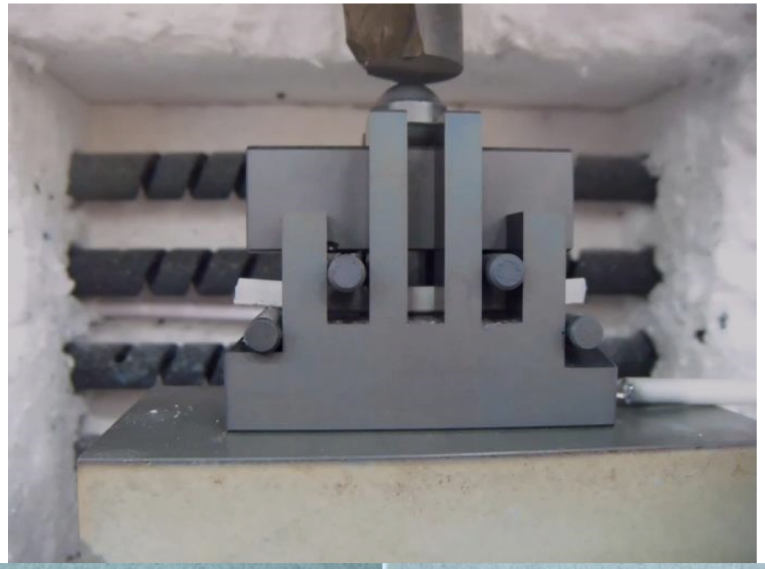
Measurements averaged from 4 pieces of specimens with dimension of ϕ4 x 40 mm.

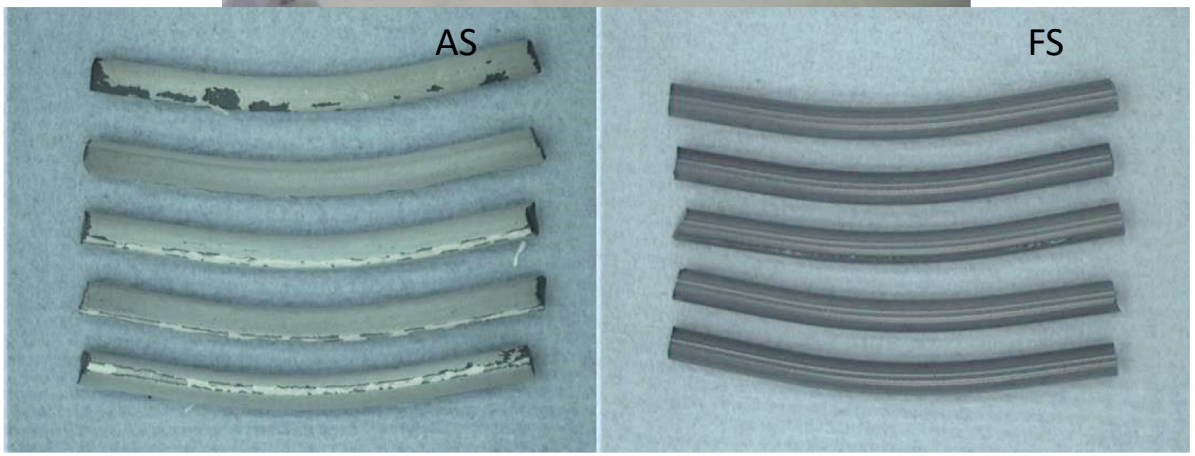
	HV10 (GPa)	K_C (MPa·m$^{1/2}$) (Anstis' formula)	K_{IC} (MPa.m$^{1/2}$) (3 – point)	K_{IC} (MPa.m$^{1/2}$) (4 – point)
NPL UK	9.47 ± 1.11 (on radial direction) 9.03 ± 0.09 (on longitudinal)	3.04 ± 0.47 (on radial direction) 4.41 ± 0.53 (on longitudinal)	-	4.36 ± 0.12
MoT Chalmers	9.55 ± 0.52 (on radial direction) 9.11 ± 0.08 (on longitudinal)	3.14 ± 0.24 (on radial direction) 4.51 ± 0.32 (on longitudinal)	5.05 ± 0.55	4.39 ± 0.52

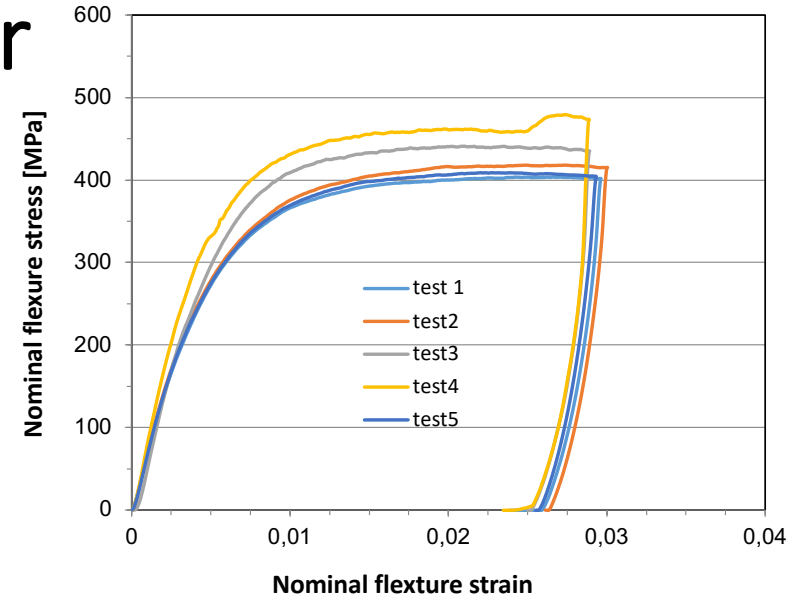


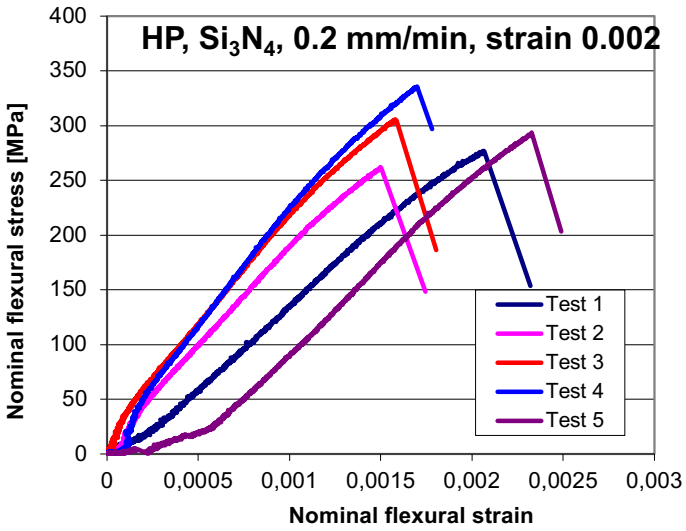


4-p bending test at 1200°C in air









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