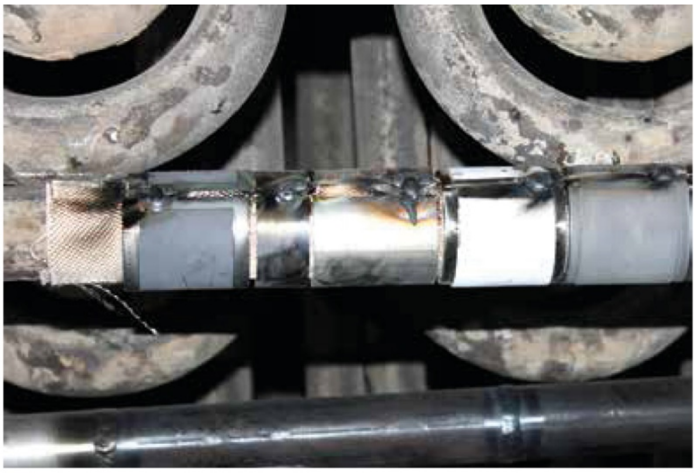
MoSi2 MATRIX COMPOSITES FOR COMBUSTION COMPONENTS EXPOSED TO HIGH TEMPERATURE OXIDATION AND HOT CORROSION

KME-705



CONSORTIUM MATERIALS TECHNOLOGY
for thermal energy processes

KME

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$MoSi_2$ matrix composites for combustion components exposed to high temperature oxidation and hot corrosion

YIMING YAO, ERIK STRÖM

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Energiforsk AB | Phone: 08-677 25 30 | E-mail: kontakt@energiforsk.se | www.energiforsk.se

Preface

The project has been performed within the framework of the materials technology research programme KME, Consortium materials technology for thermal energy processes, period 2014-2018. The consortium is at the forefront of developing material technology to create maximum efficiency for energy conversion of renewable fuels and waste. KME has its sights firmly set on continuing to raise the efficiency of long-term sustainable energy as well as ensuring international industrial competitiveness.

KME was established 1997 and is a multi-cliental group of companies over the entire value chain, including stakeholders from the material producers, manufacturers of systems and components for energy conversion and energy industry (utilities), that are interested in materials technology research. In the current programme stage, eight industrial companies and 14 energy companies participate in the consortium. The consortium is managed by Energiforsk.

The programme shall contribute to increasing knowledge within materials technology and process technology development to forward the development of thermal energy processes for efficient utilisation of renewable fuels and waste in power and heat production. The KME goals are to bring about cost-effective materials solutions for increased availability and power production, improved fuel flexibility and improved operating flexibility, with low environmental impact.

KME's activities are characterised by long term industry and demand driven research and constitutes an important part of the effort to promote the development of new energy technology with the aim to create value and an economic, environmentally friendly and longterm sustainable energy society.

Yiming Yao, Chalmers, has been the project leader. Erik Ström and Qi Lu, Kanthal/ Sandvik Heating Technology AB, and Johan Ahlström, Chalmers, have been project members. Xin-Hai Li, Siemens Industrial Turbomachinery AB, worked as reference group. Kanthal/ Sandvik Heating Technology AB has participated in the project through own investment (60 %) and the Swedish Energy Agency has financed the academic partners (40 %).

Bertil Wahlund, Energiforsk

Abstract

Within KME-705, two types of composites were prepared using a powder metallurgy (PM) and pressure-less sintering (PLS) techniques: (1) pre-oxidized (FS) $MoSi_2$–ZrO_2, and (2) as-sintered $MoSi_2$-SiC and $Mo(Si,Al)_2$–SiC composites. The goal was to develop advanced $MoSi_2$ matrix composites for hot corrosion components in gas turbine engines under operation temperature at 1200˚C. The result from the project revealed that FS $MoSi_2$+15 vol.% ZrO_2 composite has high toughness K_{IC} at room temperature and high strength at 1200°C; Thermal Cycling Fatigue (TCF) resistance at 1200 – 1300˚C was comparable to that of Kanthal Super 1700, and creep resistance at 1600˚C was close to that of KS HT. The oxidation behaviour of as-sintered $MoSi_2$-SiC composite at 1400˚C was comparable to that of KS1700 and FS $MoSi_2$-ZrO_2 composite; creep resistance at 1600 and 1700˚C was comparable to Kanthal HT material and superior to $MoSi_2$+ZrO_2 composite. It was indicated that FS $MoSi_2$+15 vol.% ZrO_2 can be used for structural components at 1200˚C in oxidation environments and for protective components up to 1600˚C. $MoSi_2$-SiC composites can be used as components in oxidising atmosphere and potentially in combustion gas environment up to 1600˚C. Alumina forming $Mo(Si,Al)_2$-SiC composites could be promising in reducing and dry combustion environments experiencing high gas velocities, since alumina provides better protection against flowing gas than silica does.

Single Edge V- Notch Beam (SEVNB) toughness measurement technique was developed for cylindrical samples. High accuracy of K_{IC} data was obtained compared with reference data from National Physics laboratory (NPL) UK. The technique can be directly applied to as-manufactured material without machining. The innovation provides reliable K_{IC} measurements for ceramic and intermetallic materials.

Sammanfattning

Oxidations- och mekaniska testresultat från KME-705 visade att oxidationsmotståndet hos slutsintrad (FS) $MoSi_2$+15 vol.% ZrO_2-komposit var jämförbart med KS1700-material, uppvisat i termisk cyklisk utmattning (TCF) vid 1200-1300˚C och under isoterm exponering vid 1400˚C. Böjhållfastheten hos FS-kompositen var 28 % högre än för enbart gassintrat (AS) material, och brottseghet vid rumstemperatur var 1,5 gånger den för monolitisk silicid. Oxidationsbeteendet hos AS $MoSi_2$-SiC-komposit vid 1400˚C var jämförbart med det för KS1700 och $MoSi_2$-ZrO_2-komposit; krypmotstånd vid 1600 och 1700˚C var jämförbart med Kanthal HT-material och överlägset $MoSi_2$+ZrO_2-komposit. SiC-tillsatser började brytas ner under exponering vid 1700˚C. Mo(Si,Al)$_2$-SiC-material oxiderades kraftigt och uppträdde sprött vid samtliga exponeringar i luft på grund av bildandet av tjocka, icke-skyddande (Al,Si)- och Al-oxidskikt.

Sammanfattningsvis kan PLS-FS $MoSi_2$+15 vol.% ZrO_2 användas för lastbärande komponenter vid 1200˚C i oxidationsmiljöer och som skyddskomponenter upp till 1600˚C. Kompositer baserade på $MoSi_2$-SiC kan användas för oxidation i luft och potentiellt för korrosionskomponenter i förbränningsgas upp till 1600˚C. Mo(Si,Al)$_2$-SiC-kompositer kan ha potential i reducerande och torra förbränningsatmosfärer med höga gashastigheter tack vare att de bildar aluminiumoxid, vilken skyddar bättre än kiseloxid under dessa omständigheter.

Single Edge V-Notch Beam-teknik (SEVNB) är en standardmetod för seghetsmätning av spröda material som kräver bearbetning till ett rektangulärt tvärsnitt. Under KME-705 utvecklades SEVNB för provning av cylindriska tvärsnitt. Utmaningarna innefattade att bilda en förspricka med rotradie <20 µm i en cylindrisk provstav och höga krav på linjering av fixturen. Därför tillverkades en noggrann poleringsmaskin för att göra sprickanvisningen samt speciella fixturer. Den innovativa tekniken kan appliceras direkt på tillverkat material med cirkulärt tvärsnitt. Hög noggrannhet av K_{IC}-resultat erhölls för kompositmaterialet jämfört med referenser från National Physics Laboratory (NPL) UK. Testmetoden gav pålitliga K_{IC}-mätningar för keramiska material.

Nyckelord: $MoSi_2$, ZrO_2, SiC, kompositer, hög-temperatur korrosion, mekaniska egenskaper.

Summary

The oxidation and mechanical testing results from KME-705 showed that oxidation resistance of FS $MoSi_2$+15 vol.% ZrO_2 composite was comparable to Kanthal Super 1700, revealed in TCF tests at 1200 – 1300˚C and isothermal exposure at 1400˚C; creep resistance was close to state of the art heating element material Kanthal Super HT in sag test at 1600˚C. The flexure strength of the FS composite was 427 MPa at 1200°C, which was 28% greater than that of the as-sintered (AS) counterpart, and the room temperature fracture toughness was 1.5 times that of the monolithic silicide. The highest sintered density, 97% of theoretical, was achieved for $MoSi_2$+10 vol.% SiC composite. The oxidation behaviour of AS $MoSi_2$-SiC composite at 1400˚C was comparable to that of KS1700 and FS/base $MoSi_2$-ZrO_2 composite; creep resistance at 1600 and 1700°C was comparable to KS HT material and superior to $MoSi_2$+ZrO_2 composite. It was also revealed that SiC additives in the composite started to decompose in the exposure at 1700˚C. PLSed $Mo(Si,Al)_2$+SiC materials were severely oxidized and behaved brittle in all the oxidation exposures in air due to the formation and spallation of thick, non-protective (Al,Si)- and Al-oxide scales.

In conclusion, PLS-FS $MoSi_2$+15 vol.% ZrO_2 can be used for structural components at 1200˚C in oxidation environments, and protective components up to 1600˚C. PLS-AS $MoSi_2$+10 vol.% SiC composites can be used for air oxidation and potentially for combustion gas CO+H_2 corrosion components ≤ 1600°C. Alumina former $Mo(Si,Al)_2$-SiC composites could be promising in reducing and dry combustion gas atmospheres under high gas velocities.

During KME-705, Single Edge V- Notch Beam (SEVNB) technique of cylindrical testing bars was developed. SEVNB is a standard toughness measurement method for brittle materials. The challenges of the innovation included pre-cracking technique of a V-notch with root radius <20 μm in cylindrical shaped beams, and a high demand for the testing fixture alignment of the notched beam. Therefore, a precise notch polishing machine was built and special fixtures were made. The technique can be directly applied to as-manufactured cylinder specimens. High accuracy of K_{IC} results were obtained for the silicide composite materials compared with the references of National Physics laboratory (NPL) UK. The innovation provided reliable K_{IC} measurements for ceramics materials.

Key words: $MoSi_2$, ZrO_2, SiC, composites, high-temperature corrosion, mechanical properties.

List of content

1 Introduction

1.1 BACKGROUND

In a high power-to-heat ratio biomass power generation system, a gas turbine is integrated with biomass gasification combined cycle systems (IGCC). The biomass gasification process produces a mixture of $CO+H_2$ and other gas product (synthesis gas, syngas, or fuel gas) at a high temperature around 800-1000°C, and then, converted into liquid gas fed into a gas turbine combustor. Therefore, a large amount of hazardous species such as H_2S, K, HCl still remains in the fuel gas and leads to an increased risk of corrosion attack on the high temperature components. In currently existing systems, such as in Värnamo, the fuel gas is cooled down to below the dew-point of alkali compounds to minimize degradation. However, this means that there are heat losses in the currently used systems. Thus, the efficiency of IGCC can be increased if the system would use as-produced gas in terms of high corrosion resistance components. This is a challenge to the component materials with even severe corrosion at high temperatures in biomass gasification systems in future.

$MoSi_2$ matrix composites are potential candidates for HT structural and component material for hot corrosion environments, primarily due to their high melting point (2020˚C) and high service temperature (>1600˚C), excellent oxidation resistance, high thermal conductivity, and higher ductility than conventional structural ceramics [1]. However, low fracture toughness (2-3 $MPa \cdot m^{1/2}$), and reduced strength and creep resistance above 1200˚C have to be improved by reinforcements. Zirconia particle additive has efficient toughening effect owing to a phase transformation toughening effect. So far, the greatest improvement in fracture toughness is to 8 $MPa\sqrt{m}$ reported for $MoSi_2$-ZrO_2-SiC composites [2]. However, hot corrosion resistance in combustion atmosphere has to be validated for this composite.

Regarding non-oxide additives, particle additives of SiC and Si_3N_4 are commonly used for $MoSi_2$ reinforcement. The $MoSi_2$-SiC composites have high maximum service temperature, as the oxide products of $MoSi_2$ and SiC are not influenced by any eutectics. Therefore, $MoSi_2$-SiC composite is an excellent high temperature oxidation-resistant material for aerospace structural applications between 1600 and 1700˚C under oxidizing environment, which has been developed successfully using powder metallurgy techniques using hot pressing to obtain 98.5% of theoretical density [3]. US aerospace manufacturer Pratt & Whitney has been developing advanced $MoSi_2$-SiC and $MoSi_2$-Si_3N_4 for blade outer air seal (BOAS) hot section components used as stationary parts [4]. Gas burner testing has shown that these composites possess significant thermal shock resistance in a simulated jet fuel combustion environment from room temperature to 1500˚C. Recently, TCF and petting resistance behaviour of $MoSi_2$-Si_3N_4 at 500˚C, and improved toughness by a factor of 3 in $MoSi_2$-SiC and $MoSi_2$-SiC-Si_3N_4 have also been reported [5, 6]. Generally, the composites are generally produced using hot pressing due to poor sinterablity of SiC and Si_3N_4. Suitable sintering aids are usually needed, which will risk mechanical property at high temperature. KS ER is an alumina forming $Mo(Si,Al)_2$ based material that is used as a unique heating element material for dry and aggressive gaseous environments [7]. KS ER is also recommended for carburizing atmosphere, endogas and N_2+H_2 as well as inert gases at high temperatures. However, its toughness and HT strength can be improved by reinforcement of non-oxide additives.

KME projects have been continuously engaged in the development of $MoSi_2$ matrix composites for hot corrosion applications since 1997. With collaboration of two industrial companies (Sandvik Heating Technology AB and Siemens Industrial Turbomachinery AB), a series of researches have been carried out aiming at developing silicide composites and manufacturing process for the hot components used in advanced gas turbine. Fracture toughness to 7-8 MPa√m was obtained in $MoSi_2$-ZrO_2-MoB-SiC composite during KME-105 to -305, remaining other properties or improved comparable to KS1800 at 1100˚C. Water jet cutting machining and a practical manufacturing process of CIP – pre-sintering – CAD machining – PLS sintering were developed. A high density heat shield prototype of $(Mo,Cr)Si_2$-ZrO_2 was produced during KME-405. The intrinsic oxidation resistance and TCF property of $MoSi_2$+15vol.%ZrO_2 composite was proved being similar to the KS1700 material up to 1400˚C and at 1200˚C. A detrimental effect of Si depleted Mo-Zr-Si silicide layer on oxidation and TCF properties was found in the as-sintered composite surface. The result in KME-505 showed that the as-sintered surface can be removed and thin protective glassy layer can form by a FS pre-oxidation treatment. KME-705 project is continuation and development of KME-505. For the sake of corrosion resistance for combustion gases, new composites of SiC reinforced $MoSi_2$ and $Mo(Si,Al)_2$ matrix composites by PLS was developed. TCF test, high temperature oxidation, high temperature mechanical test and sagging test were performed on the FS $MoSi_2$-ZrO_2 and AS MoSi-SiC composites, respectively.

1.2 DESCRIPTION OF THE RESEARCH FIELD

The project is a part of KME program, "Materials technology of thermal energy processes", supported by Swedish Energy Agency and participating industrial stakeholders, to investigate the opportunities for the power plants in Sweden to achieve greater electrical efficiency 3-4 % higher than the best technology at present. Accordingly, the KME-705 project is beneficial to the UN goals of sustainable development in the perspectives on industry innovation and infrastructure, sustainable cities and communities, responsible consumption and production, decent work and economic growth, climate action and life on land.

The project aims at developing advanced $MoSi_2$ matrix composites for hot corrosion components under combustion environment over 1200˚C. The composite is produced and manufactured with standard industrial PM techniques, is one of potential candidates to replace expensive Ni-based superalloys with regard to increasing the operation temperature, consequently increasing the efficiency of gas turbine engines.

$MoSi_2$ based material is the soundest heating element material owing to its high melting point, excellent oxidation resistance, high thermal conductivity and thermal stability. Applying $MoSi_2$ matrix composites for hot corrosion components can potentially increase the efficiency of a gas turbine by increasing operation temperature by 100–200˚C. In additional, the cost of component manufacturing would be reduced by using standard powder metallurgy (PM) – PressureLess Sintering (PLS) process. Oxide and non-oxide particles e.g. ZrO_2 and SiC particle additives are efficient additives for improving toughness and creep resistance of silicides. The challenge is that ZrO_2 becomes ion-conductive at elevated temperatures and a Mo_5Si_3 surface layer usually forms on $MoSi_2$-ZrO_2 in PLS, which degrades oxidation and Thermal Cyclic Fatigue (TCF) properties. On the other hand, SiC greatly restricts sintering ability in PLS due to slow diffusion rates. KME-705 was aiming at improving oxidation property of $MoSi_2$+ZrO_2 composite using final sintering (FS) in air treatment; and improving sintered density of SiC reinforced $MoSi_2$ and $Mo(Si,Al)_2$ matrices using PLS process. The improvements were evaluated with high temperature tests.

Regarding evaluation methods, the toughness (Kc or fracture resistance) of ceramic composites is currently measured with Vickers indentation fracture toughness test (VIF). It seems a convenient way because it requires only a small volume of material with simple specimen preparation and minimum testing cost. However, VIF test results in a complex three-dimensional crack system with substantial deformation with residual stresses and complicated damage around the indent. The tests of VIF and SENB on $(Mo,Cr)Si_2$+15 vol.% ZrO_2 has revealed that the toughness can be overestimated by 40% from VIF. Similarly, a report showed 20% measurement discrepancy in Kc from the same composite $MoSi_2$+15 vol.% ZrO_2 [13]. Single edge V-notched beam test (SEVNB) is a conventional standardized testing method, in which bending flexure strength is measured from a pre-cracked beam specimen and the fracture toughness K_{IC} for can be deduced using elastic theory principle. However, the cost of SEVNB test is relatively high for testing bar preparation due to machining rectangular shaped beams, especially for silicide materials. The difficulty can be overcome by employing a cylindrical testing bar that can be readily produced from the manufacturing process. The challenges of the innovation included defining the calibration factor for round bar geometry, a pre-cracking technique of a V-notch having root radius smaller than 20 µm, and a high demand on the testing fixture assembly and alignment of the notched beam. Therefore, a precise notch polishing machine and special fixtures for the bending tests had to be made in the project.

1.3 RESEARCH TASK

Following investigations were implemented:

(1) To investigate the effect of pre-oxidation of MoSi2+15 vol.% ZrO2 composite produced by extrusion – PLS process on TCF resistance, and high temperature mechanical properties through flexure testing at 1200˚C.

(2) To prepare $MoSi_2$-SiC and $Mo(Si,Al)_2$-SiC composites with PLS, and perform isothermal exposure and sagging test at high temperatures.

(3) To finalize the SEVNB testing setup and micron-notch polisher for K_{IC} measurements and to test "true" fracture toughness KIC.

1.4 GOAL

The project aims at developing advanced $MoSi_2$ matrix composites for hot corrosion components in a combustion chamber of gas turbine engines. The goal is to make composite materials having resistance to hot corrosion and thermal cycling in the combustion environment in combination with moderate mechanical properties at 1200˚C. Two types of composites were prepared using powder metallurgy (PM) and pressure-less sintering (PLS) techniques: (1) pre-oxidization treated $MoSi_2$–ZrO_2 composite, and (2) $MoSi_2$-SiC and $Mo(Si,Al)_2$-SiC composites.

1.5 PROJECT ORGANISATION

Yiming Yao, Ph.D, project manager, senior research engineer, Industrial and Materials Science (IMS), Chalmers University of Technology.

Erik Ström, Ph.D, Principal Engineer, High Temperature Ceramic Materials Research, Sandvik Heating Technology AB.

Qi Lu, Ph.D, Senior Engineer, High Temperature Ceramic Materials Research, Sandvik Heating Technology AB.

Johan Ahlström, Docent, Industrial and Materials Science (IMS), Chalmers University of Technology.

Xin-Hai Li, Ph.D, Principal Engineer, Siemens Industrial Turbomachinery AB.

Kanthal/ Sandvik Heating Technology AB has participated in the project through own investment (60 %) and the Swedish Energy Agency has financed the academic partners (40 %).

Present total project budget 100 kSEK/year;

Project has been financed by KME 400 kSEK from 2014-2018.

Sandvik Heating Technology has contributed to the project 600 kSEK as own-investment (in-kind) from 2014-2018, which is a ratio of 60/40 to the total project budget.

Sandvik Heating Technology AB worked with materials design, materials processing, high temperature exposure and sagging testing (working time of 10%).

Chalmers MIS was responsible for project planning and managing, and worked with materials characterization and mechanical testing at room temperature and high temperature (working time of 7 %).

Siemens Industrial Turbomachinery AB, Principal Engineer, working as reference group (no charged cost).

2 Results

2.1 PRE-OXIDATION (FS) TREATED $MOSI_2$+15 VOL.% ZRO_2 COMPOSITE

$MoSi_2$+15 vol.% ZrO_2 composite was produced by extrusion followed by Pressure Less Sintering (PLS) at 1620˚C. Composite with high sintered density over 98% of theoretical density (T.D.) and uniform particle dispersion was produced with the process. Pre-oxidation by final sintering (FS) in air was performed at different temperatures from 1700-1730˚C. Final sintering at ≤ 1715˚C for 5 minutes caused no significant changes in the base microstructure. The FS process removed the as-sintered Mo_5Si_3 surface layer that displays poor oxidation resistance. The Mo_5Si_3 rich surface was replaced with a thin protective silicon oxide scale having 5 – 8 µm thickness after FS treatment (Fig. 1). Isothermal oxidation exposure and Thermal Cyclic Fatigue (TCF) tests were performed. FS composite exhibited excellent protective oxidation behaviour in isothermal exposure test at 1400˚C for 1000 h (Fig. 1). The oxidation kinetics in the FS composite was reduced nearly by a factor of 2.

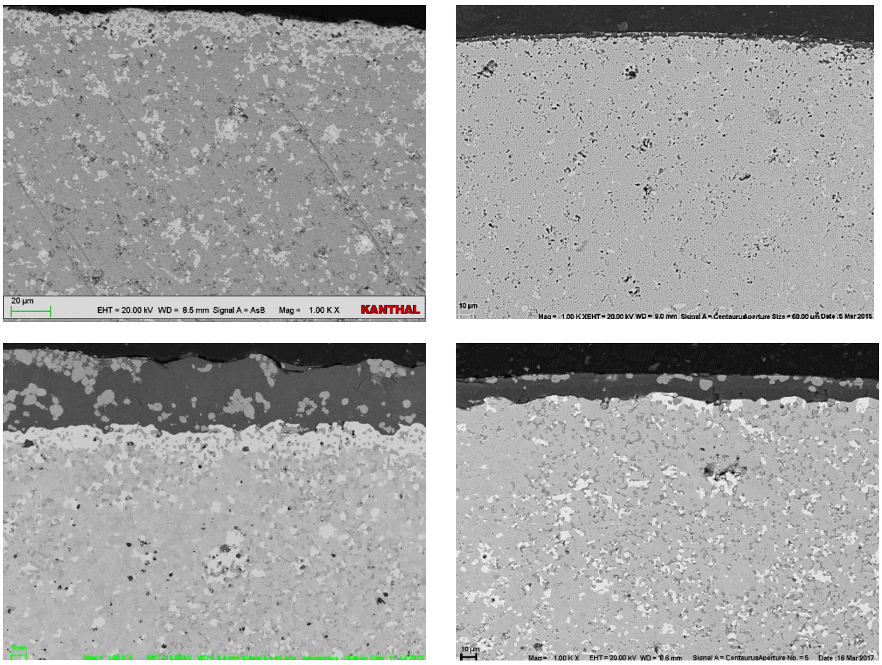
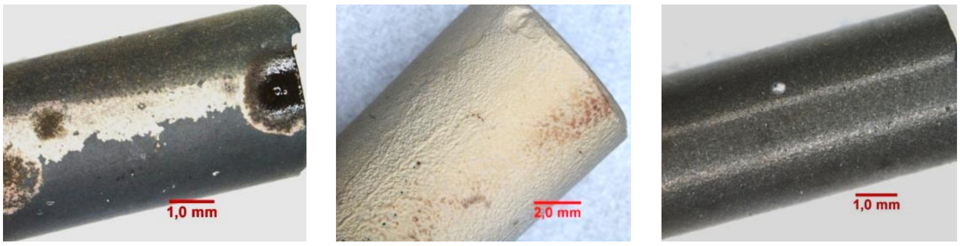
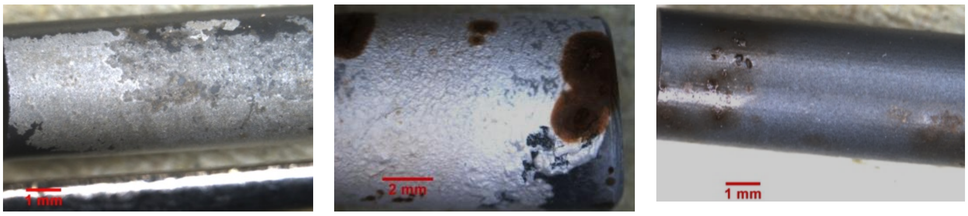


Fig. 1 As-sintered (AS) (upper left) and final sintered (FS) $MoSi_2$+15 vol.% ZrO_2 (upper right); AS (middle left); FS (middle right) $MoSi_2$+15 vol.% ZrO_2 after isothermal exposure at 1400˚C for 1000h; mass change as function of exposure time at 1400˚C (lower).

The photos of the specimen after TCF at 1200 and 1300˚C after 100 cycles are shown in Fig. 2. The brownish colour on the specimen surface resulted from contamination by the supporting material in the furnace. No cracks were observed in the surface of the FS composite samples. The protective oxide on the FS sample surface withstood the TCF test for at least 100 cycles at 1300˚C. In contrast, the AS samples were oxidized to certain extension. Fig. 3 shows the weight changes in TCF tests at 1200 and 1300˚C. The oxidation and thermal chock resistance of the FS $MoSi_2$+15 vol.% ZrO_2 material was superior to the as-sintered counterpart. The thermal shock resistance of this material is similar to KS 1700 material, which was proved in KME-505.



As-sintered at 1620˚C in Ar | As-sintered at 1620˚C in H_2 | Final sintered at 1715˚C for 5 min



As-sintered at 1620˚C in Ar. | As-sintered at 1620˚C in H_2. | Final sintered at 1715˚C for 5 min.

Fig. 2 Sample appearance after TCF test (10 min heating/10 min cooling) for $MoSi_2$+15 vol.% ZrO_2 with different surface conditions; 1200˚C for 100 cycles (upper row); 1300˚C for 100 cycles (lower row). The brownish colour on the specimen surface resulted from the contamination from the sample holder.

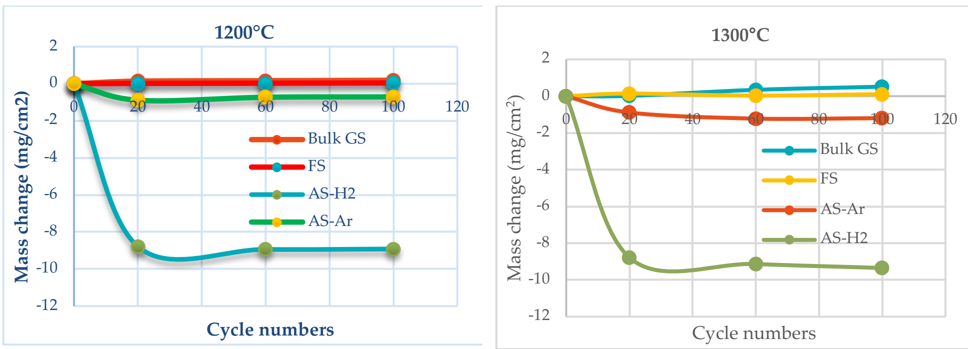


Fig. 3 Weight changes of $MoSi_2$+15 vol.% ZrO_2 with different surface conditions in TCF tests at 1200˚C (left), and at 1300˚C (right).

Hardness, 4-p bending fracture toughness K_{IC}, and 4-p flexure strength were measured at RT. The room temperature flexure toughness K_{IC} of the FS composite was 4.36 MPa·m$^{1/2}$, which was 1.5 times greater than that of monolithic $MoSi_2$. Flexure strength was measured with 4-p bending at 1200˚C for both AS and FS specimens (Fig. 4). AS sample bars were obviously oxidized during the test compared with the FS samples. Final sintered material had 427 MPa flexure strength at 1200˚C, which was 28% higher than that in the as-sintered material. Especially, the material exhibited plastic deformation of 2.6% strain without fracture at this temperature (Fig. 4). High temperature creep resistance was evaluated by sag tests in air. The FS $MoSi_2$+15 vol.%

ZrO_2 composite retained its shape at 1600˚C, and the creep deformation was in the same level as for state-of-the-art KS HT at 1700°C (Fig. 5).

Above experiments and tests indicate that final sintering is a necessary process for PLSed $MoSi_2$-ZrO_2 components. The pre-oxidation process gives positive influences to the PLSed $MoSi_2$-ZrO_2 composite on HT oxidation, HT strength, and creep resistance in terms of efficiently removing the Mo_5Si_3 surface layer formed during PLS.

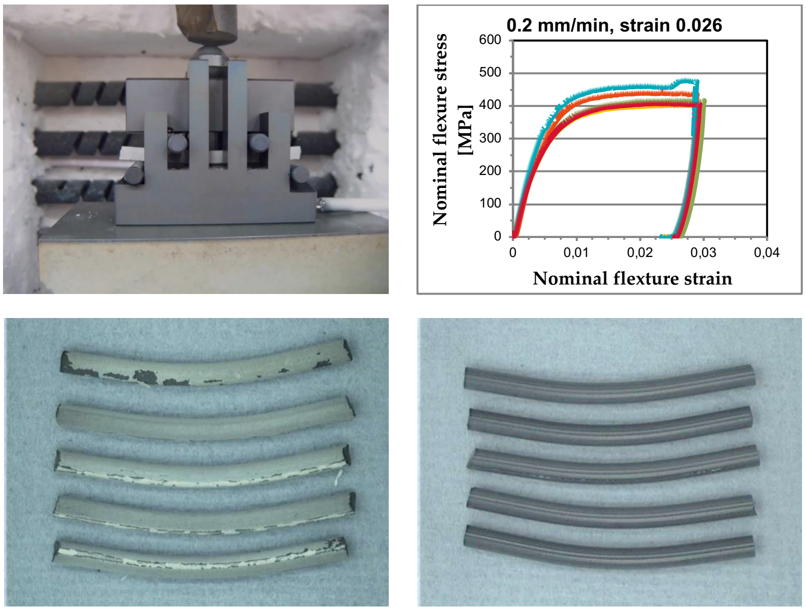


Fig. 4 Four-point bending flexure strength was tested at 1200˚C for AS and FS $MoSi_2$+15 vol.% ZrO_2 (upper left); the plot of stress-strain curves of the FS composite indicates consistent fracture strength for all samples, and 2.6% strain without fracture (upper right); the AS and FS specimens after testing at 1200˚C (lower left and right), respectively. AS sample bars were severely oxidized during the test compared with the FS samples.

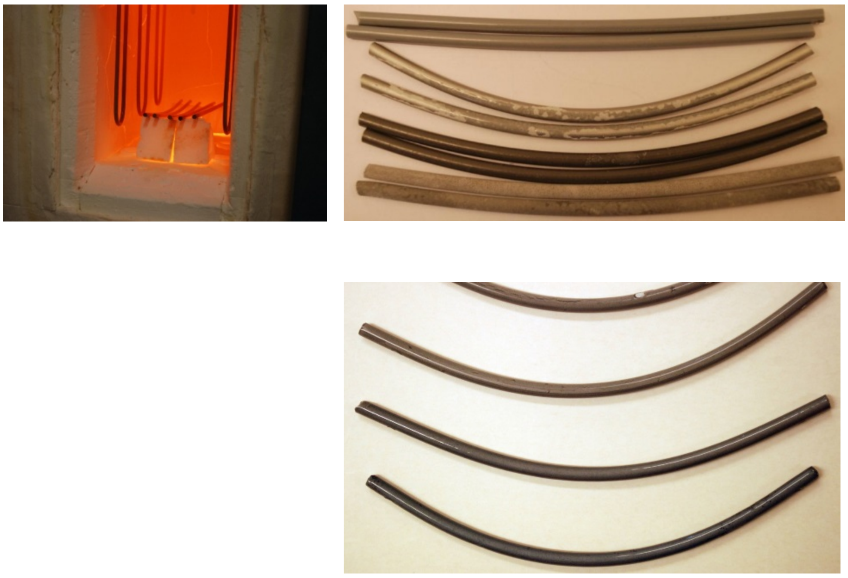


Fig. 5 Sag tests in air at 1600 and 1700˚C for 100 h; the sag testing setup (left), testing bars of different materials after sagging at 1600˚C (upper right); testing bars sagged at 1700˚C.

2.2 PRE-OXIDATION (FS) TREATED MOSI$_2$-SIC AND MO(SI,AL)$_2$-SIC COMPOSITES

SiC particles reinforced composites $MoSi_2$-SiC and $Mo(Si,Al)_2$-SiC were produced with SiC additive contents of 5, 10, 15 vol.%. The materials were sintered at 1620˚C in H_2 and 1700˚C in Ar, respectively. Sintered densities up to 97% of theoretical were achieved. SiC plays a positive role in protecting the sintered surface from formation of Mo_5Si_3 in H_2 and Ar sintering atmospheres. Mo_5Si_3 surface layers were absent in both $MoSi_2$-SiC (Fig. 6) and $Mo(Si,Al)_2$-SiC composites. The fracture toughness Kc was not affected by SiC additives, but hardness HV was low due to the low sintered density. Isothermal oxidation exposure was performed at 1400˚C for 1000 h. Thin protective SiO_2 scales were formed directly on as-sintered $MoSi_2$-SiC samples, and the thickness of the oxide layer increased with SiC content (Fig. 6). The oxidation behaviour at 1400˚C showed parabolic weight gains for all $MoSi_2$-SiC samples. The oxidation kinetics of the as-sintered $MoSi_2$+5% SiC and $MoSi_2$+10% SiC were as good as for ground (GS) and FS $MoSi_2$+15 vol.% ZrO_2, which was comparable to that of KS1700 material (Fig. 7). High weight gain was noticed for $MoSi_2$+15% SiC, which was reflected by the thicker surface oxide layer as shown in Fig. 6. Long-term exposure at 1400˚C resulted in further sintering and increased density. Consequently, an increase in hardness HV and fracture toughness Kc was observed for the $MoSi_2$-SiC composites.

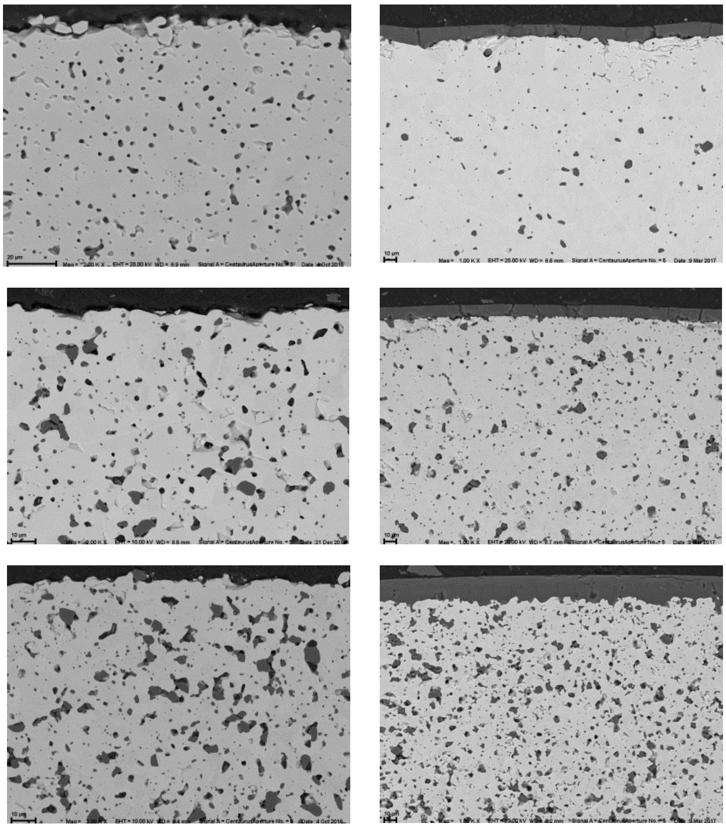


Fig. 6 Surface sections after sintering (left column) and after isothermal oxidation at 1400˚C for 1000 h (right column) of $MoSi_2$-SiC composites; 5 vol.% SiC (upper row); 10 vol.% SiC (middle row); 15 vol.% SiC (lower row). Mo_5Si_3 surface layers were not observed in any of the AS sample surfaces, as opposed to those in the as-sintered $MoSi_2$-ZrO_2 composite. A thicker oxide layer was noticed in the 15% SiC sample.

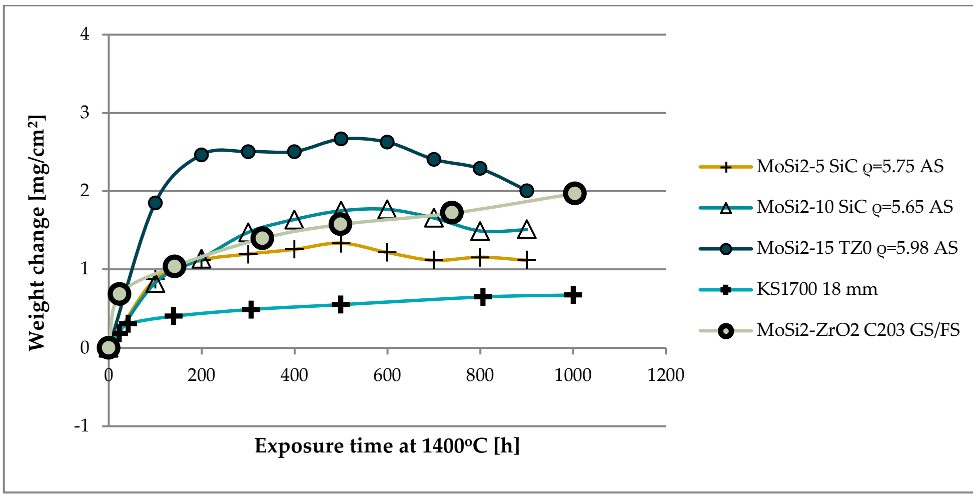


Fig. 7 Weight changes in isothermal oxidation exposure of $MoSi_2$-SiC composite at 1400˚C for 1000 h.

Sag test was performed on $MoSi_2$-SiC composites at 1700˚C in air for 100 h. The result showed that MoSi-SiC had low deformation and retained its shape at this temperature (Fig. 8). The creep resistance of $MoSi_2$-SiC ($MoSi_2$+10 vol.% SiC) was comparable to Kanthal HT material, which is superior to $MoSi_2$-ZrO_2 composite, which is indicated in the comparison of deflections in Fig. 8. However, it was also found that SiC additives were decomposed at 1700˚C, which created glass bubbles and pores on the surface, probably due to the released gaseous products from the decomposition. All the PLSed $Mo(Si,Al)_2$-SiC materials were severely oxidized and behaved brittle in all the oxidation exposures in air due to the formation and spallation of non-protective and thick (Al,Si)- and Al-oxide scales.

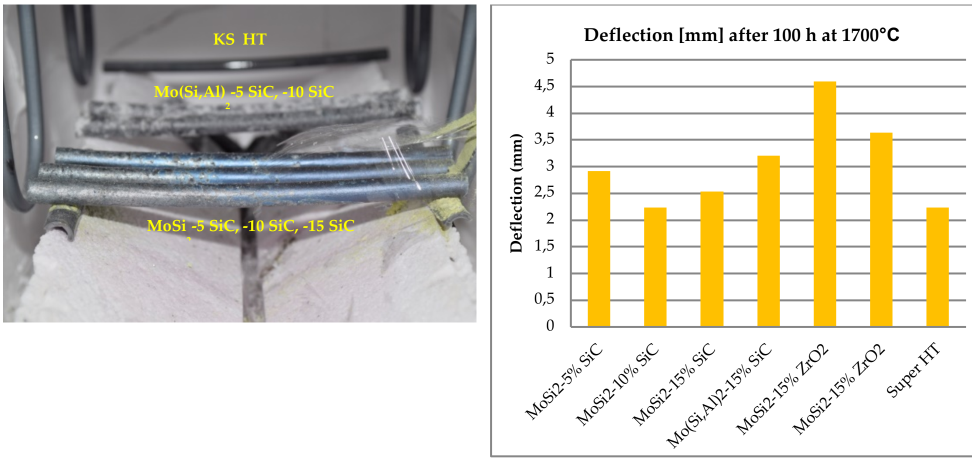


Fig. 8 Sagging test was taken at 1700°C for 100 h in air (left); deflection of $MoSi_2$+SiC and $Mo(Si,Al)_2$+SiC composites after sagging 100 h at 1700˚C (right).

2.3 SINGLE EDGE V-NOTCH BEAM (SEVNB) TECHNIQUE

Micro-notch polishing and Single Edge V- Notch Beam (SEVNB) measurement technique was developed for cylindrical specimens during KME-705. SEVNB is a standard method for toughness testing of brittle materials, in which 3-point or 4-point bending testing is performed on a testing beam with a pre-cracked sharp V-notch, and the fracture toughness can be deduced from the fracturing strength in the formula (1):

$$K_{IC} = \sigma\sqrt{\pi a} \cdot M_b \qquad (1)$$

where *a* is the notch depth, and *r* is bar radius.

The ASTM standard for SEVNB usually requires a rectangular shape testing bar. The root radius of the V-notch in a micron-scale (Equation (1) of smaller than 20 nm is required to insure the measurement accuracy, which is difficult to machine for the hard and brittle materials. A round testing bar geometry is much easy in this a point of view, which is readily obtained from extrusion-PLS products of the silicide composites. However, two challenges were faced in the innovation. First of all, the calibration factor *Mb* in formula (1) for a round bar geometry has to be defined. An approximation and a full analytic formulation were found of stress intensity factor calibration factor *Ft* (*Mb*) in Equation (2) was found for the round-bar geometry by National Physics Laboratory (NPL, UK). The Mb was calculated used (2) for each measurement. The plot in Fig. 8 shows a reasonable match between the modelling and experiment results [11, 12].

$$Mb = 1.04 - 3.64\left(\frac{a}{2r}\right) + 16.86\left(\frac{a}{2r}\right)^2 - 32.59\left(\frac{a}{2r}\right)^3 + 28.41\left(\frac{a}{2r}\right)^4 \ldots \qquad (2)$$

where a is the notch depth, and r is bar radius.

Another challenge was that pre-cracking for SEVNB required a V-notch with root radius <20 μm on a cylindrical silicide specimen, and a high demand for the testing fixture alignment of the notched beam. Therefore, a precise notch polishing machine, and special fixtures for 3-piont and 4-point bending tests were made in the project (Fig. 9). Notches within the specification were produced with the polisher. High accuracy of K_{IC} results was obtained for the FS $MoSi_2$+15 vol.% ZrO_2 composite at IMS Chalmers, compared with reference tests performed at NPL, UK (Table 1) (with an accuracy difference of 0.7%). This technique can be directly applied to as-manufactured cylindrical shaped specimens without further machining. A higher deviation value was noticed. It was believed that is was attributed to the too high loading scale of the loading cell and instability in the fixtures for large metallic specimens currently used in the lab. This should be improved in future work.

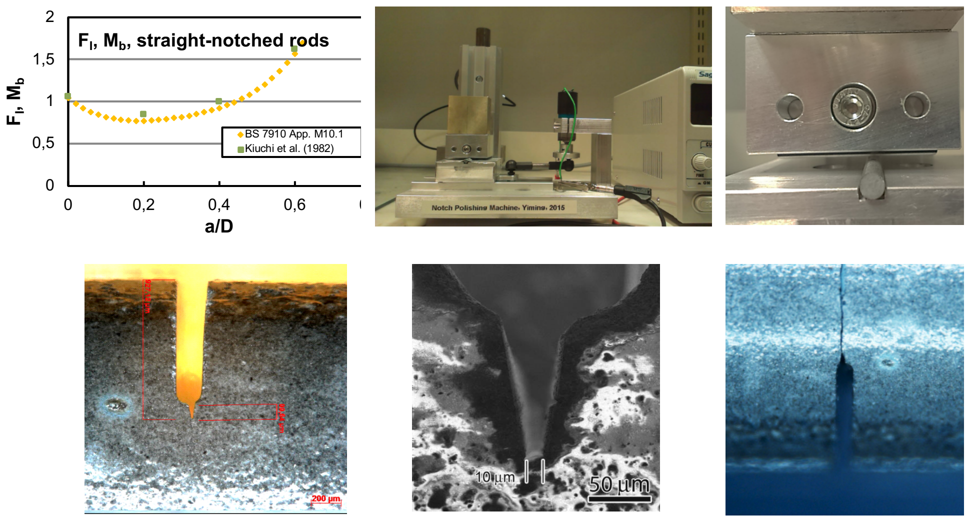


Fig. 9 Single Edge V- Notch Beam (SEVNB) measurement technique and micro-notch polishing for round bars was developed in IMS Chalmers during KME-705; the plot (upper left) shows a reasonable match between the modelling and experiment results; a precise notch polishing machine was made (upper middle and right), and notches with root radius of 10 μm were produced for the FS $MoSi_2$+15 vol.% ZrO_2 composite bars used for the K_{IC} measurements (lower left, middle and right).

Table 1 K_{IC} measurements averaged from 5 specimens

	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)	3.04 ± 0.47 (on radial direction)	n.a.	4.36 ± 0.12
	9.03 ± 0.09 (on longitudinal)	4.41 ± 0.53 (on longitudinal)		
MoT Chalmers	9.55 ± 0.52 (on radial direction)	3.14 ± 0.24 (on radial direction)	5.05 ± 0.55	4.39 ± 0.52
	9.11 ± 0.08 (on longitudinal)	4.51 ± 0.32 (on longitudinal)		

3 Analysis of the results

The results of tests and analyses during KME 705 have shown the benificial effect of final sintering heat treatment on PLSed $MoSi_2$-ZrO_2 composite in terms of removing the Mo_5Si_3 enriched surface layer. Final sintering considerably improved the high temperature oxidation resistance, thermal shock resistance, and mechanical properties of PLS produced $MoSi_2$-ZrO_2 composite. High density $MoSi_2$+15 vol.% ZrO_2 produced by PLS and FS process can be used for structural components at 1200˚C in oxidation environments, and for oxidation protection of components up to 1600˚C.

It was proved in KME-705 that a reasonable sintered density (97%T.D.) could be obtained using PLS for $MoSi_2$-SiC composite with SiC content lower than 10 vol.%. Even higher density can be achieved using Hot Isostatic Pressing (HIP) after a primary PLS sintering to further reduce porosity and defects. As-sintered $MoSi_2$-SiC composites (SiC additive < 10 vol.%) with high oxidation resistance and creep resistance can be used for air oxidation, and potentially for CO+H_2 corrosion components below 1600˚C, since the composites were sintered in H_2 and Ar at high temperatures. It was revealed in KME 705 that carbon solubility in the silicide of $MoSi_2$-SiC reached 2.6% when sintered in H_2 at 1600˚C, which allowed the composites to exhibit resistance to both dry, reducing gases and oxidation at high temperature. Therefore, the $MoSi_2$-SiC and $Mo(Si,Al)_2$-SiC composites and composite coatings on medium and high carbon steels could potentially be an alternative, and obviously there is a fundamental and technical interest in the corrosion of C/Al- containing $MoSi_2$ composite coatings. The corrosion resistance of the composites in H_2, CO, CO_2, CH_4, N_2 gases needs to be investigated. Meanwhile, coating processes such as plasma spray or laser cladding [9] should be developed and compared with the properties of aluminide coatings.

It has been found in the study of other KME groups that alumina forming materials such as Kanthal APM and aluminide coatings have excellent corrosion resistance in lab and field exposure tests in biomass and synthesis gas (H_2, CO, CO_2, CH_4, N_2) at 450-1100°C, contrasted to standard stainless steels and Ni-based materials that must be protected. $Mo(Si,Al)_2$ composite is one of the potential choices to compete with APM and aluminides under synthesis gaseous environment. In KME 705, it was proved that the $Mo(Si,Al)_2$-SiC composites are not suitable for high temperature applications in air environments. These composites could be more promising for applications in reducing atmospheres, under high gas velocities (as Al_2O_3 is not volatile such as SiO_2), and potentially in dry combustion gases.

Regarding manufacturing the high temperature component, $MoSi_2$+15 vol.% ZrO_2 and $MoSi_2$+10 vol.% SiC composite materials are promising. However, room temperature toughness is still insufficient for these materials regarding manufacturing and engineering requirements even though it is improved by ZrO_2 reinforcement. Additive Manufacturing (AM) could be a solution. Successful net-shape manufacturing of brittle materials and ceramics using AM techniques, e.g. Selective Laser Melting (SLM), Selective Laser Sintering (SLS) and other surface manufacturing techniques, e.g. thermal spray and laser cladding, have attracted wider attention in the ceramic community in recent years [10]. One can consider to apply these techniques to molybdenum disilicide based composite materials and find potential applications in gas turbine and aerospace industries. The work taken place in KME-705 undoubtedly provided valuable data for future development of silicide matrix composite materials for high temperature applications.

4 Conclusions

From the results of KME 705, two groups of PLS produced silicide composites (oxide and carbide additives) i.e. final sintered $MoSi_2$+15% ZrO_2 and as-sintered $MoSi_2$+10% SiC can be recommended for applications in high temperature corrosion resistant components, which can allow to increase the efficiency of the engines in terms of increasing the operating temperature by 100-200˚C and reducing cooling. It is suggested that high density $MoSi_2$+15 vol.% ZrO_2 produced by PLS and FS process can be used for structural components at 1200˚C in oxidation environments, and oxidation protection components up to 1600˚C; and as-sintered $MoSi_2$+10 vol.%SiC composite with high corrosion and creep resistance can be used for oxidation environment, and potentially be used for dry and CO+H_2 corrosion components below 1600˚C.

An accurate SEVNB technique for fracture toughness measurements on cylindrical samples was developed in KME 705. The innovation is not only a breakthrough for the K_{IC} measurement technique in the project, but is also valuable during the development of ceramics and intermetallic materials.

5 Goal fulfilment

KME-705 has fulfilled the project tasks in the agreement with Energimyndigheten. According to the project plan, the TCF/isothermal exposure in H_2-containing atmosphere at 1200˚C, and toughness K_{IC} testing were not conducted for the Mo(Si,Al)Si_2-SiC composites. One of the reasons was poor oxidation behaviour of the composites in air, which might result from too high Al addition to the base Mo(Si,Al)$_2$ silicide. Another reason was the unavailability of high temperature exposure device for the H_2+CO atmosphere at high temperature. As a substitution, the $MoSi_2$-SiC composites with different SiC contents (5, 10, 15, 20 wt%) were, therefore, produced and tested at high temperatures. The results were described in this report.

6 Suggestions for future research work

Additive manufacturing (AM) or functionally graded materials (FGM)utilising the composite materials studied within this project could be considered to improve currently used high temperature corrosion resistant materials even further.

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8 Publications

Yiming Yao, Erik Ström, Xin-Hai Li, Qin-Lu, Property and Oxidation Behaviours of (Mo,Cr)Si_2+ZrO_2 Composite Produced by Pressure-Less Sintering, Journal of Materials Science and Chemical Engineering, 4 (2016) 15-21.

MOSI2 MATRIX COMPOSITES FOR COMBUSTION COMPONENTS EXPOSED TO HIGH TEMPERATURE OXIDATION AND HOT CORROSION

$MoSi_2$ based material is the soundest heating element material owing to its high melting point, excellent oxidation resistance, high thermal conductivity and thermal stability. Applying $MoSi_2$ matrix composites for hot corrosion components can potentially increase the efficiency of a gas turbine by increasing its operation temperature by 100–200˚C.

The oxidation resistance of Final Sintered $MoSi_2$+15 vol.% ZrO_2 composite was comparable to that of Kanthal Super 1700 heating element material in cyclic exposures at 1200 – 1300˚C and isothermal exposure at 1400˚C. Creep resistance was close to state of the art KS HT material in sag testing at 1600˚C; four-point flexure strength was 427 MPa at 1200°C. The oxidation behaviour of as-sintered $MoSi_2$-SiC composite at 1400˚C was comparable to that of KS1700 and FS $MoSi_2$-ZrO_2 composite; the creep resistance at 1600 and 1700˚C was comparable to that of Kanthal HT and superior to $MoSi_2$+ZrO_2 composite.

Single Edge V- Notch Beam toughness measurement technique was developed for cylindrical shaped specimens. The technique can be directly applied to as-manufactured testing pieces without machining. High accuracy of K_{IC} data were obtained compared to references from National Physics Laboratory, UK. The innovation provides reliable K_{IC} measurement on ceramics and intermetallic-based materials.