KME
CONSORTIUM MATERIALS TECHNOLOGY for demonstration and development of thermal energy processes

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KME-505

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# Preface

The project has been performed within the fifth framework of the material technology research programme KME.

KME, Consortium Materials technology for demonstration and development of thermal Energy processes, was established in 1997 on the initiative of the Swedish Energy Agency. In the consortium, the Swedish Energy Agency, seven industrial companies and 18 energy companies participate. The programme stage has been financed with 60.2 % by participating industrial companies and with 39.8 % by Swedish Energy Agency. The consortium is managed by Elforsk.

The programme shall contribute to increasing knowledge to forward the development of thermal energy processes for various energy applications through improved expertise, refined methods and new tools. The programme shall through material technology and process technology developments contribute to making electricity production using thermal processes with renewable fuel more effective. This is achieved by

- Forward the industrial developments of thermal processes through strengthen collaboration between industry, academy and institutes.
- Build new knowledge and strengthen existing knowledge base at academy and institutes
- Coordinate ongoing activities within academy, institutes and industry

KME’s activities are characterised by long term industry relevant research and constitutes an important part of the effort to promote the development of new energy technology with the aim to create an economic, environmentally friendly and sustainable energy system.

# Abstract

The flexure strength of $(Mo_{0.9}Cr_{0.1})Si_2$+15% $ZrO_2$ at 1200°C and fracture toughness at room temperature are similar to those of $Si_3N_4$. Cr-enriched silicide in the sintered surface allows a fast formed glassy protective scale up to 1500°C. However, oxidation resistance of the composite was destroyed by the high Cr addition under thermal cyclic oxidation (TCF) conditions at 1200 and 1300ºC. It is encouraging that $(Mo_{0.94}Cr_{0.06})Si_2$+15% $ZrO_2$ composite with medium Cr addition showed promising properties in both high temperature isothermal and TCF tests, since stable thermal cyclic property is one of important criterions for the hot components in turbine applications. Apparently, further optimization at lower Cr side and material testing is required for the alloyed silicide matrix composite. Excellent HT oxidation and thermal cyclic resistance of bulk $MoSi_2$+15vol% $ZrO_2$ composite has been proved in the same tests. But, these intrinsic properties were degraded by Si depleted Mo-Zr-Si silicide layer (~ 100 µm) on the as-sintered surface as a result of low oxygen sintering atmospheres. The reduction and formation of this silicide surface layer can be controlled by adjusting the oxygen partial pressure in sintering gases.

# Sammanfattning

För att öka turbineffektiviteten och minimera skadliga utsläpp hos framtida biokraftenergisystem strävar industrin ständigt efter högre temperaturer. Högsmältande keramer och intermetaller har potential att ersätta konventionella material. $MoSi_2$-baserade kompositer är en av kandidaterna på grund av dess högre oxidationsmotstånd än hos Ni- baserade superlegeringar. Syftet med KME-505 är att tillämpa $MoSi_2$-baserade material i högeffektiva kraftsystem för biomassa. KME-405 har visat att kompositen $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ har ett högt oxidationsmotstånd vid 1400°C och anmärkningsvärd sintringsbarhet. Vi har utvecklat en keramisk tillverkningsmetod för tillverkning, baserad på blandning/granulering - CIP – CNC - bearbetning - trycklös sintring (PLS), och har tagit fram en värmeskölds-prototyp för gasturbinen SGT800B i nämnda kompositmaterial.

Projekt KME-505 har som mål att utvärdera mekaniska och termiska utmattningsegenskaper hos denna Cr-legerade komposit jämfört med kommersiella keramiska material (t.ex. $Si_3N_4$). Fysikaliska egenskaper hos materialet har mätts, eftersom dessa data krävs för komponentdesign. Studier har gjorts på $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ och olegerade $MoSi_2$+15 vol% $ZrO_2$. I KME-505 deltog två industriföretag och ett universitet: Sandvik Materials Technology (Kanthal) som materialtillverkare; Siemens Industrial Turbomachinery AB som slutanvändare; och Chalmers tekniska högskola.

Resultat från 4-punktstest visade att $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol % $ZrO_2$ har en brottgräns på 200 resp. 320 MPa vid 1200°C resp. RT. Brottsegheten vid rumstemperatur uppmättes till 4.7 $MPa\cdot m^{1/2}$ enligt en standardmetod. Hårdheten för kompositen (HV10) var 8.2 GPa De mekaniska egenskaperna hos dessa Cr-legerade kompositer ligger nära publicerade data för liknande material. Under isoterma ugnsexponeringar mellan 1000 och 1500°C i upp till 1000 h uppvisade denna komposit parabolisk viktökning. Vid termisk cykling vid 1200 och 1300°C uppvisade materialet dåliga resultat, vilket möjligen kan tillskrivas fasövergången hos tillsatsen $ZrO_2$ som sker vid temperaturer lägre än DBT temperaturen hos $MoSi_2$. $(Mo,Cr)Si_2$+15 vol% $ZrO_2$ med lägre Cr-halt uppvisade förbättrade egenskaper i både isoterma och cykliska tester. $MoSi_2$+15 vol% $ZrO_2$ uppvisade utmärkt motstånd vid cyklisk oxidation och god värmebeständighet, jämförbar med ren $MoSi_2$. Vid sintring bildas ett Si-utarmat ytskikt (100 μm) bestående av Mo-Zr-Si, pga. reduktion av sintringsgasen. Detta skikt är mycket skört och resulterar i en porös yta som har negativa effekter på oxidationsprestanda.

Det har framkommit av KME-505 att: (1) $(Mo_{0.9}Cr_{0.1})Si_2$ +15 vol% $ZrO_2$ tillverkad med PLS har måttlig hållfasthet vid 1200°C och måttlig brottseghet vid rumstemperatur. Den kan användas med en låg belastning i oxiderande miljöer upp till 1500°C, men är inte lämplig vid cykliska oxidations-förhållanden. (2) en lägre Cr-halt verkar lovande då en kompromiss fås mellan legeringseffekt på den sintrade ytan och bulken. (3) $MoSi_2$+15 vol% $ZrO_2$ har utmärkt beständighet upp till 1500°C och cyklisk oxidations-beständighet upp till 1300°C. Kompositen är lämplig för komponenter som används i cyklisk oxidation, men det ogynnsamma Si-utarmade ytskiktet bör undvikas. En möjlig lösning skulle kunna vara att justera syrehalten i sintringsgasen eller att tillämpa lämplig föroxidering efter sintring.

Enligt resultaten av KME-505 föreslås det att fokusera på att minska Cr-halten i matrisen, och att anpassa den sintrade ytan i $MoSi_2$+15 vol% $ZrO_2$. Denna

teknik kan tillämpas för att ta fram $MoSi_2$-kompositer som produceras med PLS.

**Nyckelord**: molybdendisilicid, kompositer, mekanisk provning, termisk cyklisk utmattning, oxidation vid hög temperatur, varmkorrosion.

# Summary

In the light of increased gas turbine efficiency and minimised hazardous emission of future biomass-fuelled energy converting system, industries are constantly looking forward to high temperature ceramics and intermetallics to replace conventional materials. $MoSi_2$-based composite is one of the candidates due to its higher temperature capability and oxidation resistance superior to superalloys. The goal of our investigation is to find the application of $MoSi_2$-based materials in the high power-to-heat ratio biomass power generation systems. Our KME-405 project has evidenced that $(Mo_{0.9}Cr_{0.1})Si_2$ +15vol% $ZrO_2$ composite has high oxidation resistance at 1400°C and remarkable sinterability, and we have developed ceramic manufacturing method of mixing/granulation - CIP – pre-sintering – CNC matching – pressure-less sintering (PLS) to produce a prototype of SGT800B turbine heat shield.

The project KME-505 aimed at the evaluation of mechanical and thermal cycle fatigue properties of the Cr-alloyed composite compared with commercial candidate materials (e.g. $Si_3N_4$). Physical properties of the material were measured, since these data are required for component design. Investigations have been carried out on Cr-alloyed composite $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ and un-alloyed composite $MoSi_2$ +15 vol% $ZrO_2$. KME-505 project was supported by two industrial companies and a university: Sandvik Materials Technology (Kanthal) as material manufacturer; Siemens Industrial Turbomachinery AB as end-user of the materials; and Chalmers University of Technology.

4-point bending tests resulted in a fracture strength for $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ of 200 and 320 MPa at 1200°C and RT, respectively. Room temperature fracture toughness was 4.7 $MPa{\cdot}m^{1/2}$, measured with standard 4-point SEVNB method. Hardness (HV10) was 8.2 GPa The mechanical properties of the Cr alloyed composite are close to published data of similar materials. As-sintered +15 vol% $ZrO_2$ displays parabolic weight gain in isothermal oxidation exposures at 1000 – 1500°C for 1000 h. However, this composite exhibited degraded performance in thermal cycling exposures (TFC) at 1200 and 1300°C, which was possibly attributed to martinsite phase transformation of $ZrO_2$ at lower temperature than DBT of the silicide, and the reduced E modulus in the Cr-alloyed matrix. The composite $(Mo_{0.94}Cr_{0.06})Si_2$+15 vol% $ZrO_2$ with lower Cr addition showed promising properties in both isothermal and cyclic testing. On the other hand, excellent HT oxidation and thermal cyclic resistance of $MoSi_2$+15 vol% $ZrO_2$ composite has been proved in the same tests, being comparable to that of monolithic $MoSi_2$. These intrinsic properties are, yet, influenced by a Si depleted Mo-Zr-Si silicide layer (~ 80 µm) on the as-sintered surface formed by the reduction by the sintering gas. The Mo-Zr-Si silicide layer at as-sintered surface is very brittle and leads to porous surface, which gives detrimental effects on HT oxidation and HT mechanical properties.

It is concluded through KME-505: (1) As-sintered $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ composite produced by PLS has moderate strength at 1200°C and fracture toughness at room temperature. It can be used with low loading in isothermal condition in oxidizing environments up to 1500°C, but is not suitable in cyclic oxidation conditions. (2) Alloyed silicide matrix composite with a lower Cr addition is very promising to compromise the alloying effect on sintered surface and bulk. (3) $MoSi_2$+15 vol% $ZrO_2$ possesses excellent intrinsic oxidation resistance up to 1500°C and thermal cyclic oxidation resistance up to 1300°C. The bulk of this composite is suitable for high temperature components used at cyclic oxidation conditions, but the detrimental Si-depleted silicide formed at $MoSi_2$+15 vol% $ZrO_2$ surface has to be avoided. The possible solution could be adjustment of oxygen content in the sintering gas, and applying suitable pre-oxidation post sintering treatment.

According to the results of KME-505, it is advisable to focus the activity on lowering the Cr addition in $MoSi_2$ matrix, and tailoring the sintered surface of $MoSi_2$ + 15 vol% $ZrO_2$. The achieved technique can be applied to the development of related $MoSi_2$ based materials produced by PLS technique.

**Keywords**: molybdenum disilicide, composite, mechanical testing, thermal cyclic fatigue, high temperature oxidation, hot corrosion.

# Table of contents

# 1 Introduction

## 1.1 Background

The biomass gasification IGCC (integrated gasification combined cycle) systems together with gas turbines are regarded as high power-to-heat ratio biomass power generation systems and therefore attractive. The biomass gasification process produces fuel gas (a mixture of CO + $H_2$ and others) at a high temperature 800-1000°C. The product gas is then converted into a relatively cleaned liquid gas to feed the combustor of a gas turbine. The liquid gas is fired with air, generating combustion products at high temperature and pressure in conventional gas turbines. In such systems, a large amount of hazardous compounds such as $H_2S$, K, HCl, exists in the gas, leading to an increased risk of corrosion attack on blading materials in the gas turbines. In currently existing systems, the fuel gas is cooled down to below the dew-point of alkali compounds to minimize degradation, but heat losses are un-avoidable. The system efficiency can be increased if the as-synthesised gas would be used in biomass gasification systems.

Regarding with the encountered challenge, there are two technical approaches, 1) using hot corrosion resistant material, and 2) increasing material temperature to minimize salt deposition on material surface. The currently used materials are Ni-alloys and TBC coatings. However, oxidation damage of the metal substrate has been found, which limits temperature and life time of the components (around 1100°C). The prototypes within the project should be aimed at burner nozzles for boilers, guide vanes and heat shields for IGCC gas turbines as well as heat exchangers.

As a known high temperature heating element material, $MoSi_2$-composites are the promising materials that have higher temperature and oxidation resistance capability than Ni-alloys and could fit into both approaches mentioned above. The structural application of the materials has been hindered by its brittleness below 1000ºC (room temperature toughness, and degraded strength and creeping resistance above 1200°C. During the last 20 years, great efforts have been made on reinforcing $MoSi_2$ [1] by (i) in situ reinforcement with silicide/carbide, (ii) ductile-phase toughening, (iii) dispersion reinforcement with continuous fibres, whiskers, and ceramic particles, e.g., $Si_3N_4$ SiC, $ZrB_2$, $TiB_2$ and $ZrO_2$. A special attention was paid to the $ZrO_2$-additives due to the transformation toughening mechanism. The highest fracture toughness (Kc) values of 8 MPa√m has been published in $MoSi_2$-$ZrO_2$ composites reinforced with un-stabilized $ZrO_2$ particles [2].

## 1.2 Description of the research field

For the application of high temperature turbine components, both high room temperature toughness and good oxidation resistance at high temperature are specially required for the $MoSi_2$ – base composites. Through the last four periods of KME projects, extensive researches have been carried out on molybdenum silicide based composites. The developed composite systems include $MoSi_2$+SiC, $MoSi_2$+$ZrO_2$, $MoSi_2$+$ZrO_2$+MoB,

$MoSi_2$+$ZrO_2$+MoB+SiC, $MoSi_2$+$ZrO_2$+MoB+C, $MoSi_2$ alloyed with Al, Cr, Nb and Re alone or in combination, and composite of Cr alloyed $MoSi_2$ matrix with un-stabilized $ZrO_2$ particles. The creeping rate of $MoSi_2$+$ZrO_2$+MoB+SiC composite has been reduced 1 order compared with $MoSi_2$ at 1200°C RT, and the room temperature toughness of $MoSi_2$+$ZrO_2$ composite has been increase 2 time of that of $MoSi_2$. With the optimized Cr-alloying content of $(Mo_{0.9}Cr_{0.1})Si_2$–15vol%$ZrO_2$ (designated as Cr10-$ZrO_2$), a low oxidation rate constant close to that of $MoSi_2$ has been achieved in this composite at 1400°C. A ceramic manufacturing method has been developed to produce components with high sintering density, using mixing/granulation - CIP – pre-sintering – CNC matching – pressure-less sintering (PLS). During KME-405 project, a prototype of SBT800B turbine heat shield 1 has been successfully developed using this technique (Fig. 1).

Fig. 1 The prototype of turbine heat shield manufactured with Cr10-$ZrO_2$ composite, the front side and back side of the prototype (15 x 7 x 3 cm).

## 1.3 Research task

The task of KME-505 project is aiming at the evaluation of mechanical properties at ambient and high temperature, thermal cyclic and physics properties of Cr10-$ZrO_2$ composite, in comparison with commercial candidate materials ($Si_3N_4$). The results will yield input to further optimisation for improvements in toughening and oxidation/corrosion properties.

## 1.4 Goal

The goal of the project is to find the application of $MoSi_2$-based materials in the high efficiency biomass power generation systems, and the composite prototypes in the project could be burner nozzles for boilers, guide vanes and heat shields for IGCC gas turbines, as well as for heat exchangers.

## 1.5 Project organisation

### Project participants:

KME-505 project was supported by two industrial companies; they are Sandvik Heating Technology AB (Kanthal) as the materials producer and Siemens Industrial Turbomachinery AB (Siemens) as the end-user of the materials. The project participants are included:

Yiming Yao, Department of Materials and Manufacturing Technology, Chalmers University of Technology

Erik Ström, R & D, Sandvik Heating Technology AB

Xing-Hai Li, Siemens Industrial Turbomachinery AB

Qin Lu, R & D, Sandvik Heating Technology AB

Niclas Åberg, Siemens Industrial Turbomachinery AB

Chalmers University is in charge of project management, high-temperature mechanical testing (via NPL UK), toughness measurement, HT dilatometer, TG-TAG, microstructure characterization.

Sandvik is responsible for material processing, density and specific surface measurements, XRD analysis, specimen preparation/matching for TCF and mechanical tests, HT isothermal oxidation tests.

Siemens is responsible for physical property measurement, HT TCF cyclic oxidation tests, calculation of possible component applications, prototype design and machining.

### Reference group:

Robert Pompe, Swerea IVF AB

### Present total project budget

800 kkr for 4 years

### Project have been financed by KME

800 kkr in 4 years

Contribution from Sandvik Thermal Technology: 600 kkr in 4 years

Contribution from Siemens Industrial Turbomachinery: 600 kkr in 4 years.

# 2 Actions

According to the contrast, the actions of KME-505 were focused on evaluations of mechanical, physical, HT oxidation resistance, TCF properties of the Cr-alloyed composite. Extensive investigations were also carried out reactions on the sintered surfaces, as well as a pre-study on optimizing $ZrO_2$ additive dispersion.

a) 4-point flexure strength tests for $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ composite at 1200°C and ambient temperatures. Room temperature fracture toughness was measured with standard 4-point SEVNB method. Above tests were performed on a commercial $Si_3N_4$ as a reference material.

b) Physical properties of thermal capacity, diffusion coefficient, thermal conductivity, and thermal expansion were measured for $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol% $ZrO_2$ composite. Thermal expansion coefficients from 200 – 1400°C were measured for Cr-alloyed and un-alloyed silicide matrix and composites.

c) Isothermal oxidation tests at 1000 – 1500°C for 1000 h were conducted on a wide range of materials, including $(Mo_{1-x}Cr_x)Si_2$ matrixes and $(Mo_{1-x}Cr_x)Si_2$+15vol% $ZrO_2$ (x=0.6, 0.8, 1,0, 1.2) composites, $MoSi_2$ and $MoSi_2$+15vol%, $Si_3N_4$, KS1700, ER, (Mo, Re)$Si_2$. Two different surface conditions of as-sintered (AS) and grounded surface (GS) were both tested for each material.

d) TFC exposures at 1200 and 1300°C up to 900 cycles were conducted on $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol%$ZrO_2$, $(Mo_{0.94}Cr_{0.06})Si_2$+15vol%$ZrO_2$, $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol%$ZrO_2$, $Si_3N_4$, KS1700, ER, (Mo, Re)$Si_2$ materials.

e) Thermal analyses investigation TG and TAG were performed to investigate the reactions at sintered surfaces in Ar for $(Mo_{0.9}Cr_{0.1})Si_2$+15 vol%$ZrO_2$ and $MoSi_2$+15 vol%$ZrO_2$ powder mixtures.

f) Microstructure investigations (XRD, fractography, metallography, SEM) were carried out on the materials before and after HT mechanical testing, isothermal oxidation, TCF, and so on.

g) A pre-study on optimizing $ZrO_2$ additive dispersion was conducted for increasing toughness.

# 3 Results

## 3.1 Mechanical testing

Mechanical properties at 1200°C and ambient temperature were measured using 4-point bending method at NPL (UK). The results are summarized in Table 1 and Table 2:

**Table 1 Flexural strength testing at 1200°C**[*]

| Material | Cross-head speed | $\sigma_f$ (MPa) | $\sigma_y$ (MPa) (at 0.2% strain) | E (GPa) |
|---|---|---|---|---|
| A2[#] | 0.2mm/min ($3.6x10^{-5}s^{-1}$) | 200.1 ± 27.0 | 215 | 220 |
| $Si_3N_4$ | 0.2mm/min ($3.6x10^{-5}s^{-1}$) | 294.1 ± 29.1 | - | 161 |

[*] All testing pieces were chamfered.

[#] A2 is Cr10-$ZrO_2$ composite bar, dispersed/mixed at IVF, CIPed and sintered at Sandvik (Kanthal), sintering density $\rho$ = 6.00 g/$cm^3$ (96%T.D.).

**Table 2 Flexural strength testing at RT**

| | Chamfered | $\sigma_f$ (MPa) | E[&] (GPa) | KIC (MPa.$m^{1/2}$)[*] | Kc (MPa.$m^{1/2}$)[@] | HV10 (GPa) |
|---|---|---|---|---|---|---|
| A2[#] | yes | 274.6 ± 36.1 | 309.2 ± 0.1 (thickness);<br>323.4 – 327.6 ± 0.1 (longitudinal) | 4.7 ± 0.3 | 6.4 ± 0.4 | 8.0 ± 0.1 |
| A2[#] | no | 292.5 ± 24.5 | - | 4.7 ± 0.3 | 6.4 ± 0.4 | 8.0 ± 0.1 |
| $Si_3N_4$ | yes | 629.3 ± 24.4 | 295.9 ± 0.4 | 5.2 ± 0.1 | 5.0 ± 0.3 | 13.5±0.5 |

[#] A2 is Cr10-$ZrO_2$ composite bar, dispersed/mixed at IVF, CIP, and sintered in Ar at Sandvik (Kanthal), sintering density $\rho$ = 6.00 g/$cm^3$ (96%T.D.).

[&] Young's modulus was measured with impact excitation technique.

[*] Fracture toughness KIC is measured with 4-piont single edge V notch beam (SEVNB) method.

[@] Fracture toughness Kc by indentation fractures (IF) method with loading 10 kg, calculated with Anstis equation [3].

a). Flexural strength of the Cr10-$ZrO_2$ composite at 1200 °C is comparable to the published data for hot pressed $MoSi_2$-$ZrO_2$ composites [4], which is slightly lower than that of hot pressed $Si_3N_4$ (SN). The composite is capable of plastically deforming at a strain rate of about $3.6 \times 10^{-5}s^{-1}$ at this temperature, while the SN remains substantially brittle. More plasticity was facilitated at slower strain rates with lower stresses to achieve greater strains, and no cracking was observed with a strain rate $9 \times 10^{-7}s^{-1}$ at 1200 °C. Irregularly spaced micro-cracks with length of 100 - 200 µm were observed on the as-sintered surface, and the failure was always found initiating from the chamfered edges, most likely at those surface cracks. These surface defects was originated from a layer of Si-depleted (Mo,Zr,Cr) silicides during sintering, which will be discussed in later sections.

b). Kc of $Si_3N_4$ measured from indentation fracture method (IF) calculated using Anstis equation was well agreed with that from the KIC dada from SEVNB, indicating that IF method is reliable for brittle ceramics. But, if we assume that KIC result from SEVNB is the true value, the fracture toughness Kc is overestimated for Cr10-$ZrO_2$ composite by IF method that is dependent on the crack length *c* generated from the corner of a Vickers indenter (Fig. 2). Anstis fracture module for brittle materials does not valid to a multi-cracking mode presenting in Cr10-$ZrO_2$ composite. Multi-cracks with shorter length are found to along the whole Vicker's indenter edges in Cr10-$ZrO_2$ instead of from the four individual corners of the indent (Fig. 2), which led underestimating for the crack length.

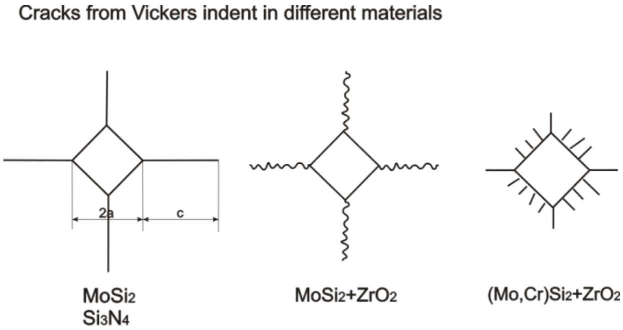


Fig. 2 Scheme of cracking modes of different materials created during Vickers indentation.

c). Biaxial flexure strength (FS) or "pin-on-disc" technique is popular ceramic materials with a small specimen size. Kc of Cr10-$ZrO_2$ was measure using FS by making an indent in the centre of a disc shaped specimen with dimension of $\phi$19 x 1.5 mm. Different indent loadings (15, 20, 30, 40, 50 kg) were applied for the correlation of fracture strength $\sigma_f$ and loading P. An $\sigma_f$ - P correlation was obtained as a power law function of $\sigma_f \sim P^{0.177}$. The calculated Kc value was 7 – 8 MPa.$m^{1/2}$ for Cr10-$ZrO_2$ using a published equation ($Kc= 0.88(\sigma_f.P^{1/3})^{3/4}$) [5], which was still too high compared with the KIC value, partially due to that the Kc equation was deduced from 4-p bending flexure strength for brittle ceramics. A calibration from 4-p bending and pin-on-disc tests is needed for Kc measurement with FS method.

## 3.2 Physical properties

For estimating the requirements of the mechanical strength of the composites, physical properties of thermal diffusivity, specific heat Cp were measured using laser flash method and differential scanning calorimeter. Thermal conductivity and temperature response was calculated from measured data of thermal diffusivity and specific heat (Fig. 3). Thermal expansion and coefficient of thermal expansion (CTE) was measured using a NETZSCH dilatometer.

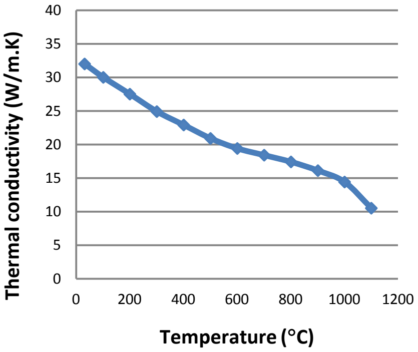


Fig. 3 Thermal conductivity of Cr10-$ZrO_2$ as a function of temperature.

Fig. 4 shows temperature dependence of CTE (alpha) of matrix materials of Cr10, Cr06, $MoSi_2$ and composites of Cr10-$ZrO_2$, Cr06-$ZrO_2$ and $MoSi_2$+15vol%$ZrO_2$. One can see that the CTE change is very small in $MoSi_2$ with currently used Cr-alloying. In contrast, contraction appears in present of $ZrO_2$ additives at 1130°C during heating, expressed as a peak in alpha curves. The expansion occurs during cooling between 800 – 500°C that is lower than that of DBT temperature of $MoSi_2$, expressed as peaks in the cooling alpha curves. The behaviour of thermal expansion hysteresis is reversible and confirmed by the repeated measurements. According to the temperature, it is believed that the variation in CTE is originated from phase transformation of $ZrO_2$ (monoclinic – tetragonal).

It is know that a large volume change (~ 4 vol%) is involved in un-stabilized $ZrO_2$ phase transformation at 1170°C, which is indicated in the heating curves of the composites. The thermal expansion hysteresis during cooling might be explained as that the volume increasing of monoclinic $ZrO_2$ particles required by the transformation is constricted by the silicide matrix. Thus the transformation is detained to lower temperatures. The position and amplitude of the distinct peaks in the alpha curves might reflect the $ZrO_2$ particle/particle cluster size and dispersion in the bulks. The deformation could be elastic and residual stress creates in the matrix around a small particle/cluster. For a larger particle/particle cluster, microcracks might be formed at particle-matrix interface at lower temperature than DBT of $MoSi_2$. It is noticed that the change in both thermal expansion and CTE is much smaller in $MoSi_2$+15vol%$ZrO_2$ and Cr06-$ZrO_2$ than in Cr10-$ZrO_2$. Indeed, microcracks were observed around $ZrO_2$ particles in Cr10-$ZrO_2$, but not in Cr06-$ZrO_2$ and $MoSi_2$-$ZrO_2$. The difference could explain why the thermal cyclic performance of $MoSi_2$+$ZrO_2$ and Cr06-$ZrO_2$ composites is better than that of Cr10-$ZrO_2$, shown in following sections. Further measurements in $ZrO_2$ particle size distribution and residual stress are needed to prove above hypothesis.

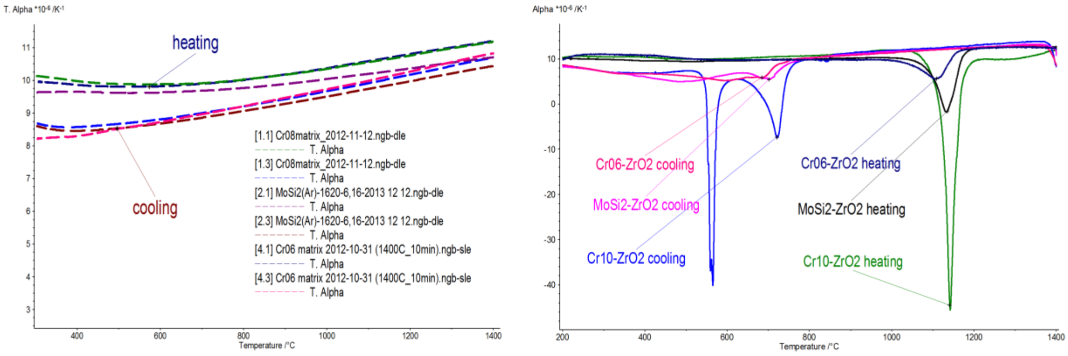


Fig. 4 CTE curves of heating and cooling as a function of temperature. The left figure is CTE of matrix materials of Cr08, Cr06 and $MoSi_2$, the right figure is CTE of the composite materials of Cr06-$ZrO_2$, Cr10-$ZrO_2$ and $MoSi_2$-$ZrO_2$.

## 3.3 Isothermal oxidation tests from 1000 – 1500°C for 1000 h

$MoSi_2$+15vol%$ZrO_2$ and $Mo_{1-x}Cr_xSi_2$-$ZrO_2$ composites with Cr-contents from x = 0.00, 0.06, 0.08, 0.10, 0.12, 0.15, (designated as $MoSi_2$-$ZrO_2$, Cr06-$ZrO_2$, Cr08-$ZrO_2$, Cr10-$ZrO_2$, Cr12-$ZrO_2$ and Cr15-$ZrO_2$) were prepared and isothermally oxidized between 1000 and 1500°C for 1000 h in ambient air. Specimens with as-sintered and ground surfaces were placed on $MoSi_2$-based supports. Kanthal Super 1700 (which is $MoSi_2$ containing ~12 vol.-% aluminosilicate), $Si_3N_4$ were taken as reference materials. Fig. 5 shows mass change versus exposure time at different temperatures.

At 1000°C the total weight gain for Cr10-$ZrO_2$ was in the order of 1 mg/cm$^3$ after 1000 h. At 1200°C, the total weight gain was ~1.2-2 mg/cm$^3$ for the same composition, Samples that were lower in Cr had ~0.6 mg/cm$^3$ in total weight gain over 1000 h. Higher Cr-content seemed to result in higher total weight gain and a slightly steeper slope of the weight gain curve could be observed.

Samples run at 1300°C for 1000 h were ground prior to oxidation in order to remove the as-sintered surface, as this layer had been observed to be depleted in Si as a result of sintering in inert atmosphere. Removal of the surface layer seemed to have a negative impact on oxidation behavior as the total weight gain was higher for ground samples at 1300°C than for as-sintered samples tested at 1400°C. The total weight gain after 1000 h oxidation for Cr10-$ZrO_2$ was 5-9 mg/cm$^3$ and 1.5-2.2 mg/cm$^3$ respectively for ground samples at 1300°C and as-sintered samples at 1400°C.

The first 1400°C -test evaluated Ar vs. $H_2$ sintering of the composites. Ar-sintered samples seemed to perform better in oxidation, indicated with lower weigh gain and thinner oxide scales. Another 1400°C-test aimed at confirming the good oxidation behavior in the as-sintered condition of Ar-sintered composites with different Cr contents (x = 0.06, 0.08, 0.10, 0.12) (Fig. 6). The composites with higher Cr contents presented with higher weight gains. However, both Cr08-$ZrO_2$ and Cr10-$ZrO_2$ deviated from previous results as they showed weight loss instead of parabolic weight gain. Both of them were sintered from test coupons that had been exposed to air for approx. one year. The sintered densities were lower than for freshly granulated powder, so it is indicated that density has large impact on oxidation behavior. Total weight gain after 1000 h exposure at 1400°C varied between 0.5 mg/cm$^3$ (Cr06-$ZrO_2$) and 13 mg/cm$^3$ (for Cr08-$ZrO_2$). The fact that such large variations occurred in samples having Cr content similar to each other and that the weight gain curves were not always parabolic indicate unstable oxidation properties especially for Cr06-$ZrO_2$. Furthermore, reference samples $MoSi_2$-based (KS-1700) and $MoSi_2$–$ZrO_2$, respectively, were evaluated (Fig. 7). $MoSi_2$-$ZrO_2$ samples with as-sintered surface presented with erratic weight loss at beginning stage, in the irrespective of whether sintering gases of Ar or $H_2$, especially for the specimens with low sintering density (Fig. 7).

Samples run at 1500°C for 1000 h were ground prior to oxidation. Composites with lower Cr-content seemed to have formed a thick $SiO_2$ surface coating, whereas those having higher Cr-content had a dull appearance. It is indicated that this temperature is too high for Cr-containing composites, as the material containing the lowest amount of Cr06-$ZrO_2$ showed an unstable weight change curve (Fig. 5).

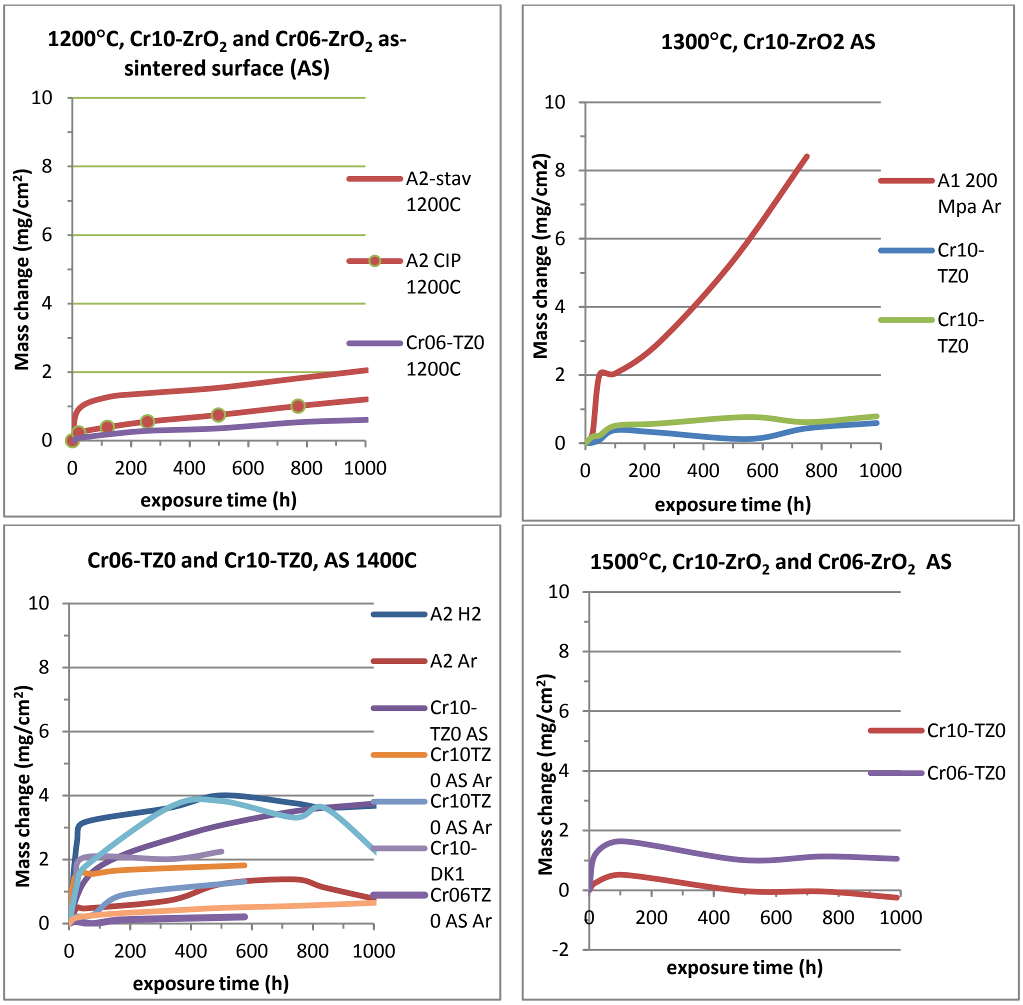


Fig. 5 Mass change versus exposure time at 1200-1500°C of Cr06-$ZrO_2$

and Cr10-ZrO$_2$ composites with as-sintered surface in H$_2$ and Ar. Cr06-ZrO$_2$ presents lower mass gain than that of Cr10-ZrO$_2$, and the composites with sintered in H$_2$ present with higher with gains than that in Ar.

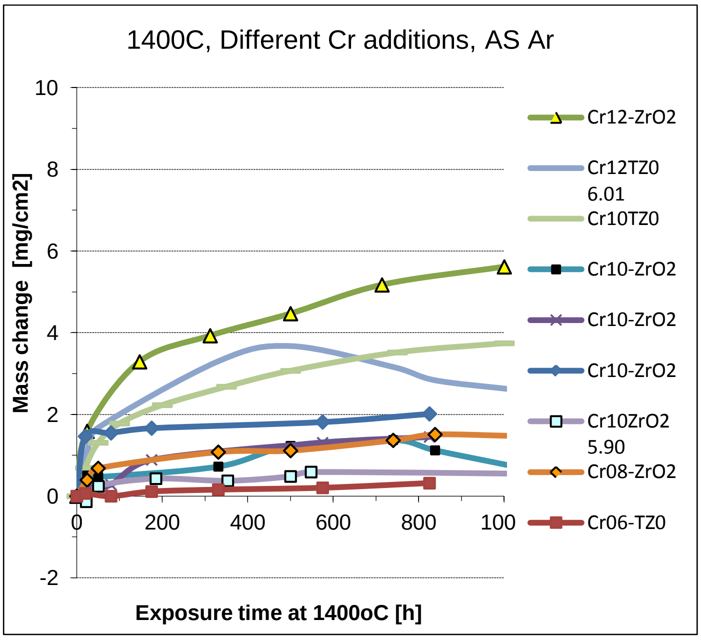


Fig. 6 Mass change of Cr-alloyed composites with different Cr-additions (x = 0.06, 0.08, 0.10, 0.12) sintered at 1400°C in Ar.

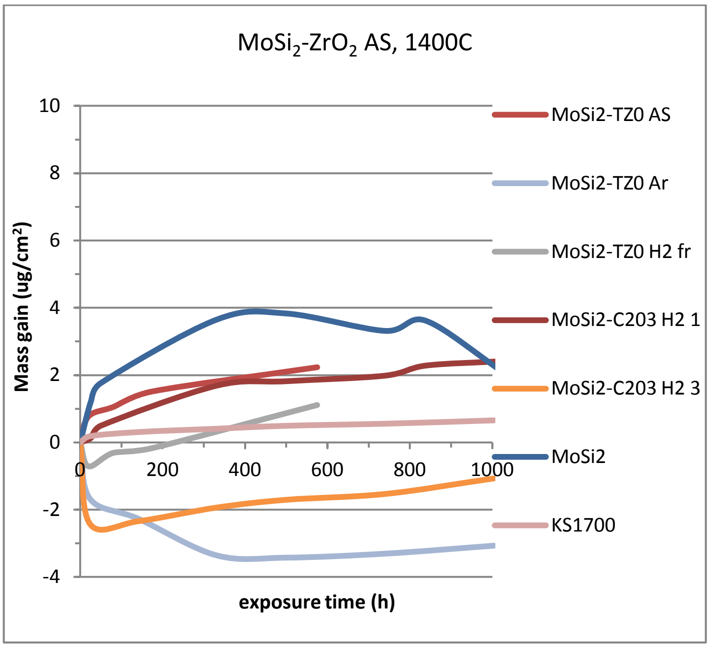


Fig. 7 Mass change of MoSi$_2$-ZrO$_2$ composites sintered at 1400°C in H$_2$ and Ar.

In order to investigate the effect of the reduced silicide phase at the sintered surfaces on the oxidation property, the tested specimens were ground and tested at 1300, 1400 and 1500°C (Fig. 8). It seems that $MoSi_2$–$ZrO_2$ performs very well under all the testing temperatures if the sintered surface was removed, but Cr-containing composites, especially for high Cr-contents.

So far, the materials showing reasonable behavior were $MoSi_2$-$ZrO_2$ and Cr06-$ZrO_2$ that had been ground to fine surface finish, and showed total weight loss of 3 $mg/cm^3$ or less after exposure for 1000 h at 1400°C. Also, their mass change curves were in principle parabolic except for an initial weight loss for samples having as-sintered surfaces.

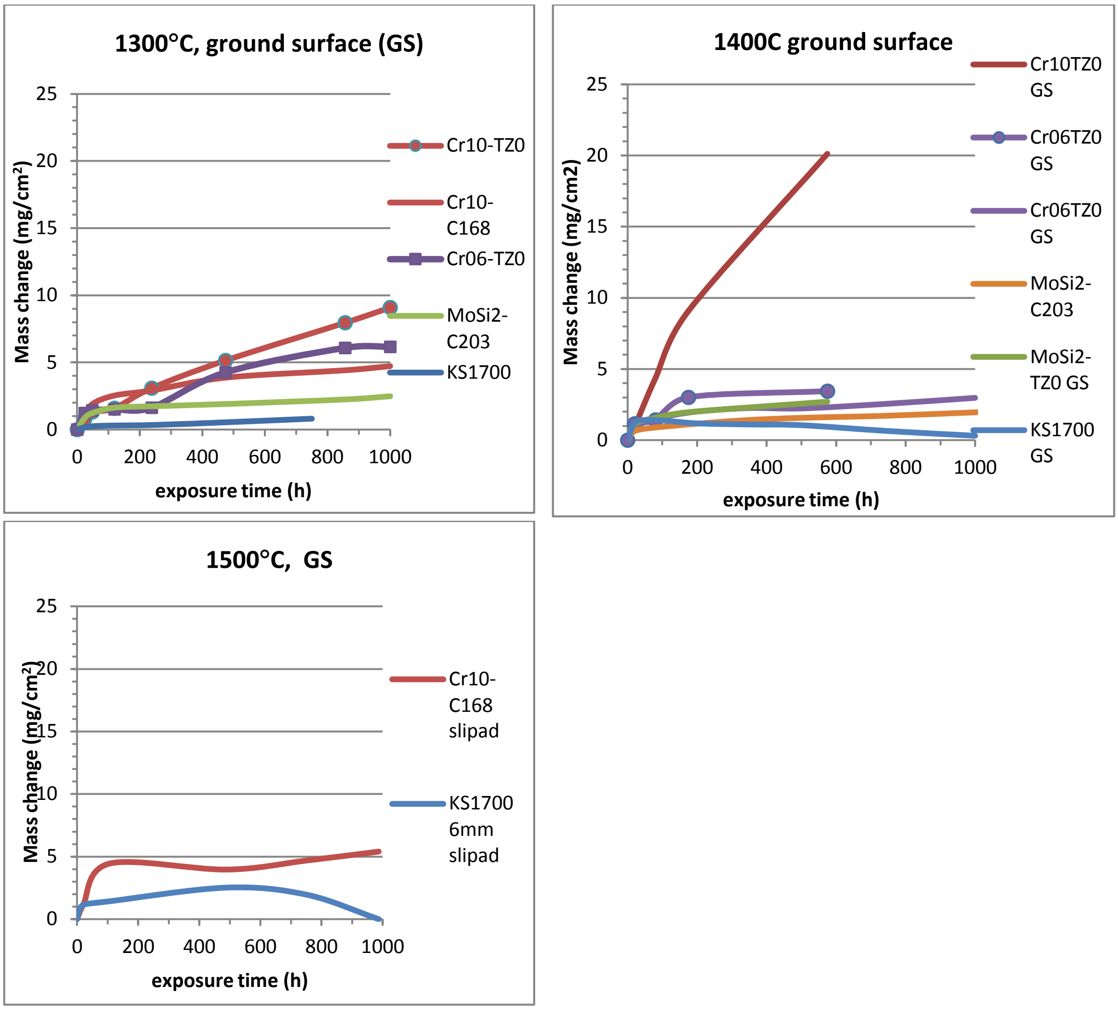


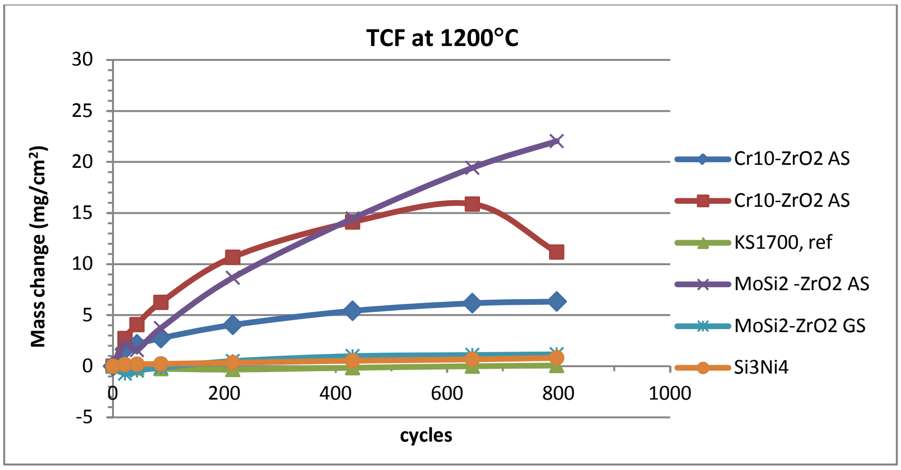
Fig. 8 Weight changes of materials with ground surfaces.

## 3.4 Thermal cyclic test (TCF) at 1200 and 1300°C

Cyclic oxidation tests were run over 900 cycles at 1200 and 1300°C, respectively, using a standard industry method at Siemens. Each cycle consisted of heating up to the temperature and keeping for 1 h, followed by forced air cooling to 100°C in 10 minutes. KS1700 and hot pressed $Si_3N_4$ materials were tested as references (Fig. 9).

After 926 cycles to 1200°C, the Cr10-$ZrO_2$ composite samples showed total weight gains of >20 $mg/cm^3$, i.e., a ten-fold increase compared to the weight gain for isothermally tested materials. The sample was deformed and cracked considerably at 76 cycles at 1200°C. The reference materials KS1700, $Si_3N_4$ and $MoSi_2$-$ZrO_2$ (ground prior to testing) exhibited low weight gains and structural stability; no cracks and damages were found 926 cycles at 1200°C. $MoSi_2$-$ZrO_2$ with as-sintered surface upon testing gained 5 $mg/cm^3$ after completion of the test at 1200°C (Fig. 9). However, the microscopy showed that this sample was internally oxidized through. Micro-cracks in non-protective oxide were observed at the surface, and oxidation went through in the bulk along grain boundaries.

The samples that withstood the thermal cycling at 1300°C were KS1700, ground $MoSi_2$, ground $MoSi_2$–$ZrO_2$ and Cr06-$ZrO_2$, exhibiting total weight gains below 2 $mg/cm^3$ after 540 cycles (Fig. 9). It is noticed that Cr06-$ZrO_2$ presented with a low mass gain (< 3 $mg/cm^2$) at 1300C after 700 cycles from both as-sintered and ground specimens (Fig. 10). The microstructure of these samples has to be examined. $MoSi_2$–15vol%$ZrO_2$ in as-sintered condition and $Si_3N_4$ as well as Cr10-$ZrO_2$ had total weight gains of 5-22 $mg/cm^2$. The cracks were observed on as-sintered C10-$ZrO_2$ after 25 cycles. The ground composite $MoSi_2$+15vol%$ZrO_2$ kept no crack/damage after 263 cycles, but, the as-sintered $MoSi_2$-$ZrO_2$ was suffered by the oxidation through surface micro-cracks, while, the $Si_3N_4$ was subjected to severe oxidation in the same extension.



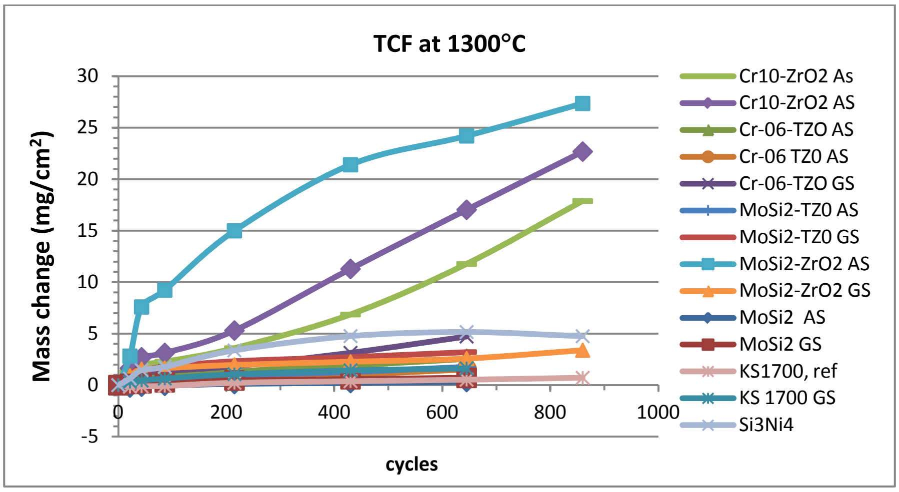


Fig. 9 Mass change from TCF tests at 1200 and 1300°C.

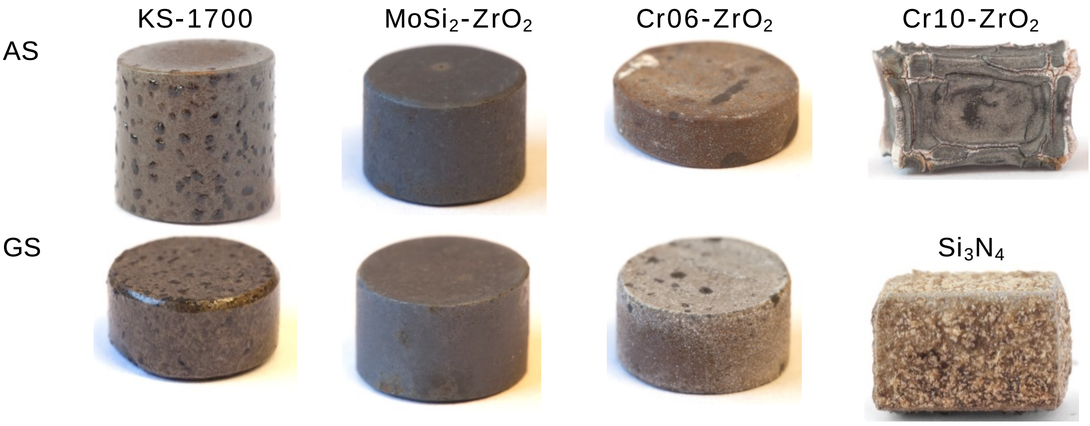


Fig. 10 Tested Materials after TCF at 1300C for 700 cycles.

## 3.5 Microstructure characterization

In order to explain the HT oxidation behaviour of the composites, microstructure on the as-sintered and oxidized surfaces of $MoSi_2$-$ZrO_2$ and Cr10-$ZrO_2$ and Cr06-$ZrO_2$ were investigated using XRD and SEM. Isothermal oxidation tests from 1000 – 1500°C for 1000 h have convinced that the intrinsic oxidation property of $MoSi_2$ - $ZrO_2$ composite (with ground surface) is excellent up to 1400°C. But, as sintered $MoSi_2$ -$ZrO_2$ composite presents with weight loss at initial stage, and white oxide product was characterized as $ZrSiO_4$. . The outer layer of as-sintered $MoSi_2$ -$ZrO_2$ consists of Si depleted (Mo, Zr) silicide with high amounts of Zr (~15 at% Zr, with a unknown crystal structure) (Fig. 11). This Mo-Zr-Si silicide outer layer (30-80 µm) results from the reduction of $ZrO_2$ by $H_2$ and evaporation of Si in $H_2$ and Ar sintering gas. The Mo-Zr-Si silicide was severely decomposed and oxidized into $ZrSiO_4$ fine particles to form a porous and loose structure at the surface during initial oxidation stage. A protective and adhesive $SiO_2$ scale was gradually formed when the top Mo-Zr-Si silicide layer was removed by oxidation. In additional to weight loss, the cracks were formed in the brittle Mo-Zr-Si silicide surface layer during cyclic exposure, which caused extensive oxidation through grain boundaries into the inner bulk.

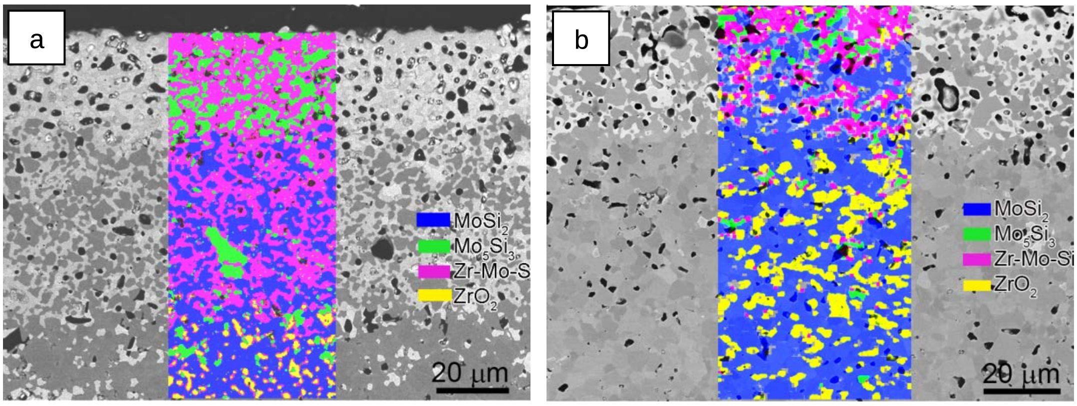


Fig. 11 SEM images and EDS phase maps at as-sintered surface areas of $MoSi_2$-$ZrO_2$ composite sintered a) in $H_2$, and b) in Ar.

In contrast, an outer layer on as-sintered Cr10–$ZrO_2$ surface consists of Si depleted (Cr-Mo-Zr) silicide with high amounts of Cr and Zr (Fig. 12). Cr content in the surface silicide phase was changed with different sintered gas (Table 2). It is believed that the Cr-enriched Cr-Mo-Zr-Si silicide layer can aid fast formation of a protective silica scale; therefore, the Cr-alloyed composite can avoid weight loss at initial oxidation. However, the oxidation resistance property of the Cr10-$ZrO_2$ composite will be lost if this Cr-Mo-Zr-Si silicide surface silicide layer is removed, which results in an un-protective scale in terms of fast outwards diffusion of Cr from subsurface region. In the case of lower Cr-addition, stable oxidation behaviour present in Cr06-$ZrO_2$ composite in both as-sintered and ground surface (Fig. 5, 6, 8, 9 and 10), indicating that the outer diffusion of Cr from the subsurface area was much weaker than that of Si. It was also found that oxidation property of Cr-alloyed composites was also strongly affected by sintering density.

The mechanism of Cr in the oxidation is not completely understood. It is believed that the Cr-Mo-Zr-Si silicide can be oxidized faster and form glassy layer at relative lower temperature because $Cr_2O_3$ starts to evaporate at 900°C. A competition of weight loss and gain must exist in the initial oxidation stage before the formation of a stable scale.

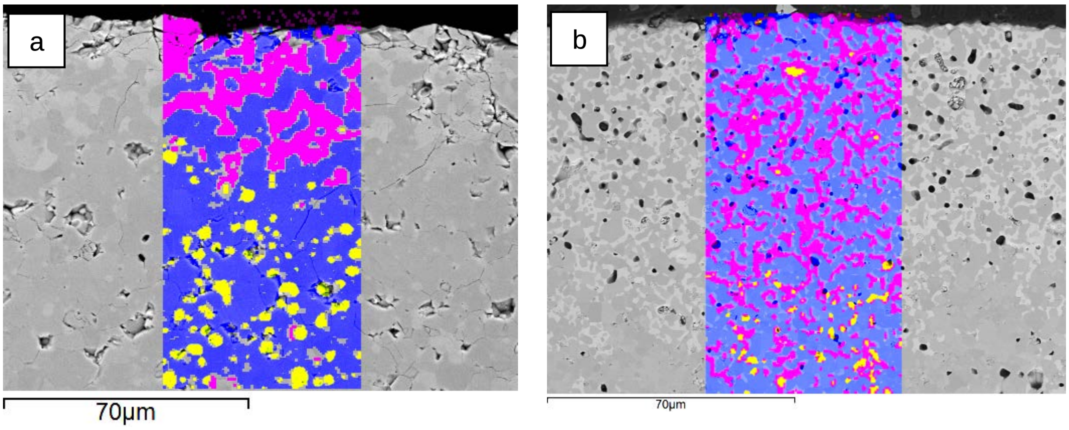


Fig. 12 SEM images and overlapped EDS maps at as-sintered surface of Cr10-$ZrO_2$ composites sintered a) in $H_2$, and b) in Ar (blue – $MoSi_2$, pink – Mo-Zr-Si silicide, yellow – $ZrO_2$ particles).

**Table 2 Cr contents in Cr-Mo-Zr-Si silicide in surfaces layer (at%)**

| | Si | Cr | Zr | Mo |
|---|---|---|---|---|
| Cr10-$ZrO_2$, $H_2$ | 45 | 23.2 | 11 | 21 |
| Cr10-$ZrO_2$, Ar | 44 | 5.2 | 17 | 35 |
| Cr06-$ZrO_2$, Ar | 48 | 5.1 | 14 | 34 |

* Cr-content in Cr10 matrix is 2.6 at%

## 3.6 Reactions at surface in sintering gases

In order to understand the reaction on the sintering surface, thermal gravimetric analysis (TG) was conducted for the powders of $MoSi_2$, $ZrO_2$, $MoSi_2$-$ZrO_2$ in Ar and Ar+50%$H_2$. The powders were analysed with XRD before and after TG. A powder pre-sintered at 900°C in Ar was also tested for comparison. The weight loss in $MoSi_2$ powders below 500°C was due to the evaporation of lubrication regents. The TG curve (Fig. 13) shows a weight loss reaction in all the powders at around 1200°C, which is related to the formation of $Mo_5Si_3$ according to XRD analysis (Fig. 14), No products or phases were found from the reactions between $MoSi_2$ and $ZrO_2$ up to 1300°C. That means that $ZrO_2$ is still stable with $MoSi_2$ in Ar and $H_2$ at $\leq$1300°C, i.e. the silicidation of $ZrO_2$ should occur at higher temperature. Higher temperatures TG and thermal analysis are needed for investigation of $ZrO_2$ silicidation in different gases.

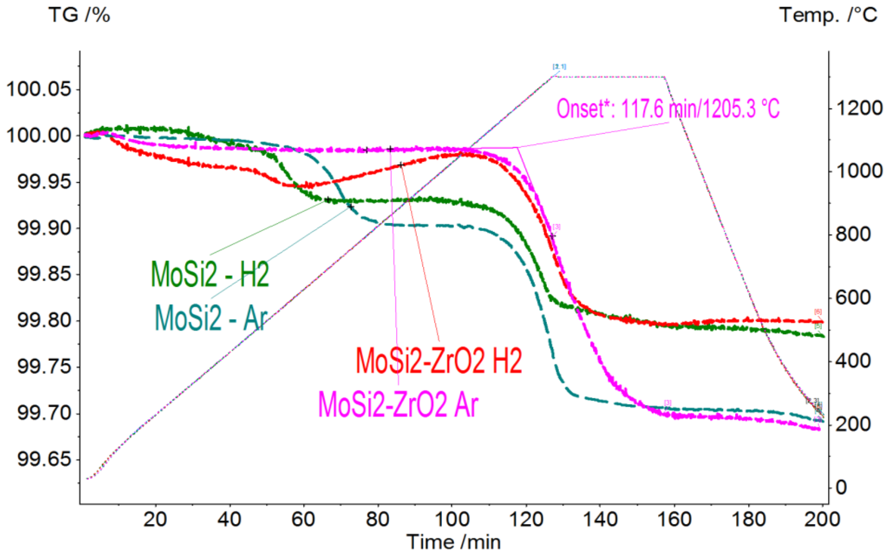


Fig. 13 TG analysis of $MoSi_2$ and $MoSi_2$+15 vol% $ZrO_2$ powders in Ar and Ar+50vol%$H_2$ gases.

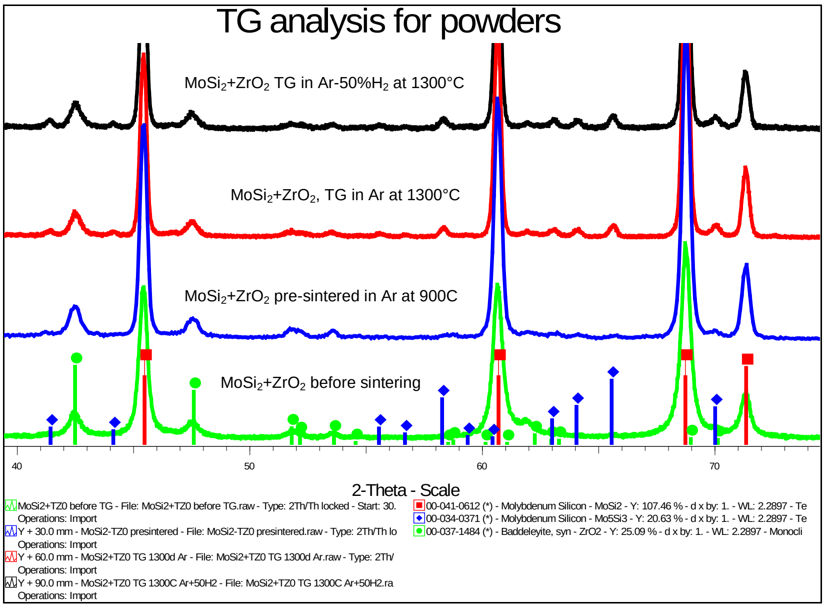


Fig. 14 XRD of the powders $MoSi_2$+15 vol% $ZrO_2$ after TG analysis at 1300°C

## 3.7 Experiment of sintering density via milling time

$MoSi_2$ having BET 1.70 $m^2/g$ was mixed with Tosoh TZ-0 (BET 14.3 $m^2/g$) in a Mo-lined vial using Mo-balls in order to achieve a well-dispersed powder mixture. The mixture was then CIPed and pre-sintered in Ar for 1 h at 600-800°C on a Mo support. After final sintering in Ar at 1620°C for 1 h, the density was only ~5.80 g/cm$^3$ with 94.5%T.D (theoretic density). Theoretical density of $MoSi_2$+15vol%$ZrO_2$ is 6.14 g/cm$^3$ based on a rule-of-mixtures calculation. To find out the impact of BET of $MoSi_2$ starting powder on sintered density, the aforementioned powder mixture was additionally milled up to 140 h and subsequently sintered at 1620°C for 1 h in Ar and $H_2$, respectively. For reference, BET of the initial powder mixture was measured. The BET of starting powders and resultant sintering density is shown in Fig. 15. The result showed that expanding milling time was efficient in increasing BET of the powders and sintering density. BET is lineally increasing with milling time, while the sintering density increase reaches to a saturated value of 6.10 g/cm$^3$ (99.3%T.D.) after milling for 100 h. However, the increased density by expanding milling time did result in the toughness improvement Kc of the composite. Detailed investigation is needed for effects of dispersion/particle size of $ZrO_2$ additives on fractured toughness.

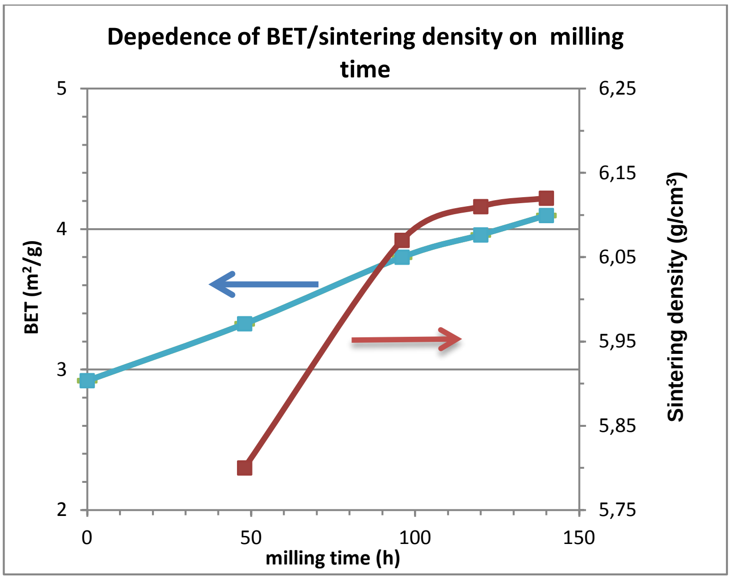


Fig. 15 BET of starting powder and sintering density as function of milling time.

# 4 Analysis of the results

The excellent intrinsic oxidation property of $MoSi_2$+15 vol% $ZrO_2$ composite has been proved, which is close to those of the monolithic disilicide. However, these properties are sheltered by a Si depleted $(Mo,Zr)_5Si_3$ layer (~100 µm thick) on the as-sintered surface originating from reduction/evaporation at 1200°C in sintering gas with low oxygen partial pressure. Oxidation of this Zr enriched 5-3 silicide surface layer results in weight loss at the initial oxidation stage and severe internal oxidation through surface cracks during cyclic oxidation. The microcrack defects in the brittle silicide surface layer are also the crack origins during bending mechanical testing. Therefore, the degraded oxidation and mechanical performance of $MoSi_2$-$ZrO_2$ composite might actually arise from the as-sintered surface, and it is not practical to remove the hard outer layer using mechanical grinding for components having complex geometries in future application. We consider solving the problem using pre-oxidation treatment after final sintering to remove the surface layer. It is also possible to eliminate the surface 5-3 silicide by means of adjusting $O_2$ level in the sintering gas.

Cr alloying can partly solve the problem confronted by $MoSi_2$-$ZrO_2$, in terms of forming a Cr-enriched silicide at as-sintered surface, which allows a fast formed glassy scale up to 1400°C. However, for a high Cr addition, this oxide scale is not stable and self-healing due to strong outward diffusion/evaporation of Cr. A thick $Cr_2O_3$ sub-layer will grow beneath the silica scale, which causes de-bonding and cracking of the scale and unstable oxidation properties in a long term exposure. The mechanical test showed the flexure strength of Cr10-$ZrO_2$ similar to that of $Si_3N_4$ at 1200°C. This result could be underestimated due to the crack defects existing in the as-sintered surface containing brittle Cr-Mo-Zr-Si silicide.

Regarding the Cr-alloying effect on the properties of the silicide matrix, the amount of $SiO_2$ particles was reduced by 50% in the Cr-alloyed silicide matrix by means of decreasing native $SiO_2$ on $MoSi_2$ powder surfaces, which will benefit the HT creep resistance. But, if Cr addition amounts are too high $Cr_5Si_3$ secondary phase with lower melting temperature will be present at the grain boundaries. The thermal expansion of silicide matrix is not affected by Cr-addition up to $Mo_{0.92}Cr_{0.08}Si_2$. But, larger CTE variation and volume expansion from $ZrO_2$ phase transformation has been evidenced in Cr10-$ZrO_2$, which might explain the difference in cyclic performance of Cr10-$ZrO_2$ and Cr06-$ZrO_2$.

It is very interesting that as-sintered and bulk Cr06-$ZrO_2$ composites with medium Cr content exhibit good oxidation resistance in both isothermal and TCF cyclic tests. It indicates that Cr-surface silicide plays a positive role on oxidation resistance, and outer diffusion of Cr from sub-surface region is reduced compared with Cr10-$ZrO_2$. In brief, it is promising to optimize Cr-addition at lower Cr side, so that we can take the advantage of the surface modification with Cr-addition, and eliminate the detrimental effects on the $MoSi_2$ matrix.

Based on the technique developed for Cr alloyed and $MoSi_2$+15vol%$ZrO_2$ composites, we feel that it is worth to re-examine the HT oxidation property of the patented $MoSi_2$-$ZrO_2$-MoB-SiC composites developed in Kanthal in 1997. High fracture toughness and high creep resistance of this composite system has been proved in KME-105. The developed technique of sintered surface modification for $MoSi_2$–$ZrO_2$ can be applied to this composite. The HT oxidation resistance and cyclic oxidation properties of the composites should be re-evaluated.

# 5 Conclusions

Through the investigations during this project period, we have gained profound knowledge on HT oxidation, mechanical, physical and thermal properties of the PLSed molybdenum disilicide composites. The excellent intrinsic properties of $MoSi_2$+15 vol% $ZrO_2$ composite have been proved in HT oxidation and cyclic oxidation, which are close to those of the monolithic disilicide. These properties can be cancelled by Si depleted Mo-Zr-Si silicide surface layer (~ 100 µm) reduced in sintering gases with low oxygen partial pressure at 1200°C. It is not practical to remove the hard outer layer using mechanical grinding for component applications in future. To solve the problem, we consider pre-oxidation treatment after final sintering, and adjusting the $O_2$ level in the sintering gases.

Cr alloying can partly avoid the difficulty confronted in $MoSi_2$+15 vol% $ZrO_2$, since Cr additions allow for a fast formed glassy scale up to 1400°C. However, this oxide scale becomes unstable in TCF conditions for Cr10-$ZrO_2$ with high Cr additions. The mechanical test has showed the flexure strength of Cr10-$ZrO_2$ similar to that of $Si_3N_4$ at 1200°C. This result could be underestimated due to the presence of crack defects at the as-sintered surface, containing Cr enriched brittle silicide. As-sintered and bulk Cr06-$ZrO_2$ composite with medium Cr addition exhibits good oxidation resistance in both isothermal and cyclic tests, since stable thermal cyclic property is one of important criterions for the hot components in turbine applications. It is very promising to optimize Cr-addition at the lower Cr side, so that we can take advantage of the surface modification with Cr-addition, and eliminate the detrimental effects on the $MoSi_2$ matrix.

# 6 Goal fulfilment

We have fulfilled the planned tasks for KME 505, i.e. evaluation of mechanical properties at ambient and high temperature, thermal cyclic and physics properties of Cr10-$ZrO_2$ composite, in comparison with commercial candidate materials ($Si_3N_4$). The effort of optimizing $ZrO_2$ dispersing has been made for improving toughening and oxidation/corrosion properties.

In additional, it is advisable to stop the work on high Cr-alloyed composite (Cr10-$ZrO_2$), according to the thermal cyclic oxidation test results. A test of $SiO_2$ coating on $MoSi_2$+15 vol% $ZrO_2$ was conducted using infiltrating $SiO_2$ slurry on a low density pre-sintered sample surface. The result showed that the deposited $SiO_2$ on the surface actually assisted the silicidation of $ZrO_2$ under a low oxygen atmosphere. In order to improve TCF property of the composites, investigation on reactions at composite surfaces in sintering gases has also been initiated for better understanding the effects of surface products on oxidation behaviours.

The goals of the project are to find the application of $MoSi_2$-based materials in the high efficiency biomass power generation systems in terms of suitable components prototypes used in boilers and gas turbines.

We have found the practical method to produced high quality and complicatedly shaped prototype of $MoSi_2$ based composite using economic PM and PLS techniques. We have evidenced that $MoSi_2$-$ZrO_2$ composite possesses similar oxidation and mechanical properties at 1200°C to $Si_3N_4$, but superior to $Si_3N_4$ at 1300°C. We have found the suitable material for the structural and hot corrosion component application above 1200C and the method to manufacture it. By this means, we have fulfilled the project goal.

The next step of work is to solve the problems of detrimental as-sintered surface, and improve the TCF property of the as-manufactured product by PLS. The creeping resistance of $MoSi_2$-$ZrO_2$ composite has to be verified, and low temperature toughness has to be improved.

# 7 Suggestions for future research work

Further investigation is needed of reduction mechanisms on the $MoSi_2$ – $ZrO_2$ composite surface in sintering gases. Thermal analysis and sintering experiments should run in Ar with different oxygen levels controlled by dew points, and the formed phases will be identified using XRD. The sintering gas and process will be optimized to eliminate the formation of Si depleted silicide on the surface, therefor, more detailed thermal dynamical calculations and thermal analysis works are required. The samples will be characterized and tested with TCF.

According to the results from Cr06-$ZrO_2$ composite, lower Cr addition will be optimized. The samples will be characterized and tested with TCF and high temperature mechanical testing.

Better understanding is necessary for the relationship of $ZrO_2$ additive size/dispersion on fracture toughness and hysteresis behaviour in CTE, which might give an important impact on TCF property of the composites.

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# 9 Publications

List of publications resulting from the project:

Yao, Yiming; Ström, Erik; Li, Xin-Hai: EFFECT OF SINTERING ATMOSPHERE ON SURFACE AND. *International Conference on Innovative Technologies, IN-TECH 2012, Rijeka, 26 – 28 September 2012*, ISBN/ISSN: 978-953-6326-77-8

# Appendices

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