Thermal and corrosion properties of silicon nitride for copper die casting components

Iyas Khader^{* a,b}, Alexander Renz^b, Andreas Kailer^b, Daniel Haas^c

^a Department of Industrial Engineering, German Jordanian University, P.O. Box 35247, 11180 Amman, Jordan

^b Fraunhofer Institute for Mechanics of Materials IWM, Woehlerstr. 11, 79108 Freiburg, Germany

^c FCT Ingenieurkeramik GmbH, Gewerbepark 11, 96528 Frankenblick, Germany

Abstract

Due to the high melting temperature of copper and copper alloys, conventional die-steel components used in pressure die casting these materials exhibit short service lifetimes and undergo thermal fatigue. Thermal and corrosion properties of silicon nitride were studied to assess the material's applicability in substituting conventional die-steels in casting copper and copper alloys. In this study, experiments were conducted to test the thermal shock resistance and corrosion behaviour of a commercial silicon nitride in contact with molten pure copper. The results did not indicate any corrosive reaction between silicon nitride and pure copper. However, the presence of copper oxides at high temperatures accelerated the oxidation of the ceramic resulting in considerable loss of material. The thermal shock behaviour of silicon nitride proved to be adequate for the application.

Keywords: Silicon nitride; copper casting; die casting; oxidation; corrosion

1. Introduction

Pressure die casting is a fabrication process commonly used to manufacture magnesium and aluminium alloys. The process is economically feasible and its technological importance is continuously growing due to its capability of producing complex alloyed parts with outstanding quality and due to the growing demand for light-weight structures. The process is characterised by pressure-assisted rapid die filling and subsequent rapid cooling and solidification of the metal in the mould. It starts by pouring the melt into a relatively cold "shot sleeve" before being forced through gates and hot runners into the mould.

Despite the advances achieved in material engineering, the actual lifetime of dies, shot sleeves and hot runners is still insufficient. Conventional materials show inadequacy when corrosive alloys or alloys with high melting temperatures are processed [1]. A clear example manifests itself in pressure die casting copper alloys (such as brass and bronze) for the production of various parts, and pressure die casting pure copper for the production of copper

Corresponding author: Iyas Khader

E-mail address: iyas.khader@iwm-extern.fraunhofer.de

Phone: +49 (0)761 5142 429, Fax: +49 (0)761 5142 510

rotors in electrical motors [2]. The high melting point of pure copper (T_m =1083.4 °C) results in very rapid deterioration of steel dies due to cyclic thermal loading. An alternative fabrication process to manufacture the aforementioned parts other than pressure die casting is infeasible; hence, the selection of thermal shock and wear resistant materials is decisive.

Thermal fatigue cracking, decarburisation, softening and formation and dissolution of intermetallic layers are the principle failure mechanisms of die casting tooling components (i.e., shot sleeves, hot runners, dies and moulds) [3-6]. Thermal fatigue cracking, also known as heat checking (Fig. 1), results from the rapid cyclic expansion of the surface material in contact with the molten metal and the expansion constraints imposed by the much cooler bulk material. During cooling, the temperature of the surface falls down below that of the bulk resulting in high surface tensile stresses that may exceed the strength of the material causing crack formation. Such extreme surface thermal loading causes early tool damage, which may be even exacerbated by chemical attack of the melt.



(a)

(b)

Figure 1. Stereo-microscope images of a steel die-insert hot runner showing (a) thermal fatigue induced cracks; (b) a close-up of the damaged surface and residues of molten material ($CuZn_{16}Si_4$ -C) in the crack openings (Breuckmann GmbH & Co. KG)

Steel alloys and tungsten based alloys show inadequacy for casting copper [1,2] and copper alloys [6]. On the other hand, ceramic materials, such as silicon nitride, sustain high temperature strength and show high resistance to thermal shock. Increasing the lifetime of these parts considerably reduces production cost and maintenance delays; furthermore, preventing heat checking improves the surface quality of the product, which eliminates the need for subsequent extensive machining.

There is general agreement that refractories are eroded by copper more than ferrous alloys, despite the lower casting temperature of the former [7]. Kurushima and Ishizaki [7] investigated in detail the reaction of copper and copper oxides with nitride based ceramics. It was shown that CuO accelerates the oxidation of silicon nitride, especially if the partial pressure of oxygen in the reaction environment increases. The oxidation of silicon nitride was

extensively investigated in numerous works. Of the relevant studies worth mentioning are the works of Babini and Vincenzini [8], Stern [9], Gogotsi et al. [10], Cinibulk and Kleebe [11] and Nickel [12].

Sangiorgi et al. [13] and Klein et al. [14] separately studied the behaviour of silicon nitride in contact with pure copper in vacuum; a non-wetting behaviour was established in both studies.

Khader et al. [15] recently studied the corrosion of silicon nitride rolls in contact with copper in wire rolling, which requires high temperatures and high mechanical loading. It was shown that silicon nitride rolling tools undergo considerable tribochemical wear assisted by the high adhesion affinity between Cu and the SiO_2 layers formed on the surface of the ceramic at high temperatures. The adhesion affinity was studied by calculating the work of separation between Cu and SiO_2 atomically clean surfaces.

In this study the thermal properties and corrosion behaviour of silicon nitride with special regard to copper casting is addressed. The test conditions were selected according to the expected process parameters proposed by Breuckmann GmbH, Germany, for pressure die casting to investigate the extent of material degradation and to evaluate the applicability of silicon nitride as a material for shot sleeves, hot runners and mould inserts.

2. Experimental procedure

2.1 Materials and specimens

The ceramic specimens were prepared from a commercial grade of silicon nitride powder (Si₃N₄, FCT Ingenieurkeramik, Germany). The material, labelled "FSNI", was produced by cold isostatic pressing (CIP), sintering and subsequent machining by FCT Ingenieurkeramik GmbH, Germany. FSNI contains ~6 wt.% Al₂O₃ and ~4 wt.% Y_2O_3 as sintering additives. The microstructure consists mainly of β -grains with a secondary phase of silica and sintering additives. The specimens were sintered and machined to final dimensions of $4.0 \times 3.0 \times 65.0$ mm³ and their edges were chamfered to minimize stress concentration, whereas, no surface polishing was performed.

Preliminary tests were carried out to characterise basic ceramic material properties. Fig. 2 shows the elastic modulus and four-point bending strength as a function of temperature. The measurements were carried out at room temperature, 700, 1000 and 1200 °C.



Figure 2. (a) Temperature dependent elastic modulus of FSNI; error bars indicate the standard deviation for at least five specimens, the lines connecting the dots represent linear interpolation; (b) four-point bending strength; error bars indicate the standard deviation for at least five specimens

Fig. 3 shows the thermal conductivity, specific heat and coefficient of thermal expansion as a function of

temperature.



Figure 3. (a) Temperature dependent thermal conductivity and specific heat; (b) Temperature dependent coefficient of thermal expansion. Lines connecting the dots represent linear interpolation

Grade-A cathode copper (Boliden Mineral AB, Sweden) was used in the experiments. A summary of the impurity content provided by the supplier is shown in Table 1.

Table 1. Impurities in ppm typically found in Grade-A cathode copper as provided by the supplier (Boliden Mineral AB, Sweden)

Ag	As	Bi	Pb	Sb	Se	Ni	Те
15	0.3	0.05	0.5	0.5	0.3	1.0	0.3

2.2 Cyclic thermal loading experiments

Thermal shock experiments were carried out to evaluate the resistance of the ceramic material to cyclic heating and cooling. Two sets of experiments were carried out; firstly, the specimens were heated in a furnace to 1200 °C, held for 200 s then removed from the furnace and left to cool in air at room temperature (21 °C) for 200 s. This procedure was repeated for 50, 500, 1000 and 10,000 cycles. A similar procedure was carried out with a second set of specimens, wherein the cooling portion of the cycle was accelerated by submerging the specimens in water at room temperature (21 °C) for 200 s; in this case, the specimens underwent 200 and 10,000 heating and cooling cycles.

Subsequently, the specimens were inspected for cracks and alteration of surface integrity in addition to fracture surface inspection. Residual four-point bending strength measurements were conducted on the air cooled specimens and ceramographic cross-sectional specimens were prepared and studied.

2.3 Corrosion experiments

These experiments were conducted under ambient pressure to study the corrosion behaviour of silicon nitride in contact with molten copper. The surrounding atmosphere was varied by conducting the experiments in inert gas (mixture of Ar and N_2) and in air. These conditions enabled investigating the corrosion behaviour in ideal and realistic conditions (oxygen-rich environment).

The molten copper was held at 1200 °C in Al_2O_3 crucibles in air atmosphere. Al_2O_3 is already present in the silicon nitride material system as sintering agent, which eliminates any possible contamination with foreign species that might react with the melt. On the other hand, to reduce the amount of oxygen, as much as possible, graphite crucibles were used to hold the melt when carrying out the experiments in inert gas atmosphere.

Single cycle tests were conducted by partially submerging and holding the specimens in the melt for 10, 30, 60 and 300 s. Cyclic experiments were conducted by partially submerging and holding the specimens in the melt for 60 s, removing from the melt and holding in the furnace at 1200 °C for 200 s. This procedure was repeated for 10 and 100 cycles. Following the experiments, surface and ceramographic cross-sectional analyses were conducted to inspect the specimens.

3. Results

3.1 Thermal loading: Natural convection in air

The specimens did not show any signs of colouration or pitting after running the experiments, additionally, no visible macrocracking was observed. Scanning electron microscopy (SEM) showed distinct morphological changes to the surface of the specimens and the formation of a network of minute microcracks as shown in Figure 4.



(a)

(b)

Figure 4. SEM image of the surface of FSNI in (a) its virgin state; (b) after 10,000 cycles in air at 1200 °C/ air at RT

Energy-dispersive X-ray spectroscopy (EDX) analysis of the surface showed high content of oxygen in addition to higher levels of aluminium and yttrium compared to the bulk, indicating the formation of an oxygen-rich layer of SiO_2 , Al_2O_3 and Y_2O_3 . The absence of nitrogen on the surface is also worth noticing (see Table 2).

Element	Su	face	Bulk		
Element	Wt. %	Atom %	Wt. %	Atom %	
0	42.3	63.5	2.7	3.7	
Al	10.9	9.6	4.2	3.4	
Si	24.4	20.8	62.4	48.8	
Y	22.4	6.1	3.1	0.8	
Ν			27.6	43.3	
Total	100.0	100.0	100.0	100.0	

Table 2. Summary of EDX quantitative analysis after 10,000 heating and cooling cycles in air

SEM/EDX cross-sectional analysis of the specimens after 10,000 heating and cooling cycles clearly showed the formation of an oxide layer on the surface (Fig. 5a). Moreover, this surface oxide layer appeared to be composed of different phases (Fig. 5b).



Figure 5. Cross-sectional SEM image after 10,000 cycles in air at 1200 °C/ air at RT (a) formation of silicon oxide layer; (b) detailed view showing different phases within the oxide layer

Analysis of the chemical composition indicated higher concentrations of Y in the utmost outer brighter layer (40% O; 30% Y; less than 15% Si). The darker inner region was mostly composed of silica (52% O; 38% Si; less that 2% Al).

3.1.1 Residual strength

Four-point bending tests were carried out on specimens that had undergone 10,000 cycles of thermal loading and cooling in air. The residual strength measured at 1200°C showed considerable increase compared to the initial strength values. In a second set of tests, the residual strength was measured at room temperature after 1000 thermal loading cycles only. The change in strength was negligible in this case. The results are summarised in Table 3.

Table 3. Summary of 4-point bending residual strength measurement after thermal loading

4-point bending test temperature	Initial strength prior to cyclic thermal loading	No. of thermal loading cycles 1200°C air/21°C air	Residual strength after cyclic thermal loading	Difference in strength
1200 °C	203.5±17.2 MPa	10,000	423.4±31.0 MPa	+108.1%
RT	695.1±65.0 <mark>MPa</mark>	1000	687.6±75.2 <mark>MPa</mark>	-1.1%

3.2 Thermal loading: Quenching in water

The specimens quenched in water at 21°C showed a different behaviour; cracks initiating at the edges and propagating towards the centre of the specimens appeared on the surface after a low number of cycles (e.g., 150 cycles in Fig. 6a). By reaching 10,000 cycles most of the specimens have undergone complete fracture (Fig. 6b).



Figure 6. Crack formation due to thermal shock (a) after 150 cycles in air at 1200 $^{\circ}$ C / water at RT; (b) after 10,000 cycles in air at 1200 $^{\circ}$ C / water at RT; fracture surface appears shiny due to the formation of silicon oxide

The fracture surfaces appeared shiny, as shown in Fig. 6b, EDX analysis showed high oxygen content indicating silica build-up. The re-crystallisation of the glassy intergranular phase in the form of yttrium-containing needle-shaped particles was also observed on the surface (Fig. 7).



Figure 7. SEM of the fracture surface after 10,000 cycles air at 1200 $^{\circ}$ C / water at RT showing re-crystallisation of secondary phase (EDX results: needle-shaped particles: Y, O; glassy surface: Si, O)

Microcracks and micropores also formed on the surface as shown in Fig. 8a. A more detailed inspection of these pores showed voids formed at crack coalescence nodes (Fig. 8b). It is also noticeable that round shaped holes appeared in regions of thick oxide layers around the crack openings (Fig. 8a).



Figure 8. Fracture surface after 150 cycles in air at 1200 $^{\circ}$ C / water at RT showing (a) formation of silicon oxide, microcracking and recrystallisation of secondary phase; (b) formation of micropores at crack coalescence points

3.3 Determination of thermal shock parameters

In order to achieve a better understanding of the thermal shock behaviour for this grade of silicon nitride, the following parameters were calculated:

$$R = \frac{\sigma_{4p}(1-v)}{E\alpha} \tag{1}$$

and

$$R' = \frac{\sigma_{4p}(1-\nu)\lambda}{E\alpha}, \beta = \frac{hL_c}{\lambda}$$
(2)

Where σ_{4p} denotes the four-point bending strength at a certain temperature, ν is the Poisson's ratio, E the elastic modulus, α the coefficient of thermal expansion, λ the thermal conductivity, β the dimensionless Biot number, h the film coefficient and L_c the characteristic length of the specimen.

The parameter *R* is applicable for instantaneous change in surface temperature for conditions of rapid heat transfer. This resembles quenching in water as explained in Section 3.2. The parameter *R'*, on the other hand, applies to low Biot numbers (β <2) for conditions of slow heat transfer [16], which resembles slow cooling rate by natural convection in air (Section 3.1). A summary of the thermal shock parameters is given in Fig. 9.



Figure 9. Thermal shock parameters for FSNI

3.4 Contact with copper in air atmosphere

The specimens submerged in molten copper in air atmosphere showed distinct signs of corrosions. An example of a specimen partially submerged for 30 s only is shown in Fig. 10.



Figure 10. Overview and cross sections of a silicon nitride specimen after only 30 s of partial submersion in molten copper in air atmosphere A cross-sectional analysis of the specimen shows that the section closest to the surface of the molten metal, where a thick layer of slag builds up, was mostly affected by corrosion and material loss. The parts of the specimen fully submerged in copper showed significantly less corrosion, thus, less change in dimensions.

Cyclic submersion in the molten copper resulted in blunting the edges of the specimen despite the short contact period (Fig. 11).



Figure 11. Blunted edges of a specimen partially submerged in molten copper at 1200 °C in air for 10 cycles each lasted 20s; blunted edges as a result of cyclic submersion

SEM cross-sectional analysis and EDX analysis of the near surface zone revealed the formation of different

material layers as shown in Fig. 12.



Figure 12. Surface layers of a specimen after submersion in molten copper at 1200 °C for 30s in air atmosphere; notice the formation of gas bubbles at the interface

Worth noticing is the formation of large voids due to a chemical reaction resulting in the discharge of gas bubbles. An EDX mapping of the near surface zone was conducted to identify the composition of the different layers (Fig. 13).



Figure 13. EDX mapping at the near-surface zone of a specimen; three zones are identified: (i) lower – consists mainly of pure silicon nitride; (ii) middle – Si-rich oxide phase, (iii) upper – bright regions: Cu-rich oxides, dark regions: Si-rich oxides

Through EDX mapping it was possible to identify four distinct regions in terms of chemical composition. As shown in the SEM image (Fig. 13), the bottom region was identified as silicon nitride, showing peaks of Si, N, O, Al and Y (first region from the left shown in Fig. 12). The phase in the middle shows high concentrations of Si and O indicating a silicon-rich oxide phase (second region from the left in Fig. 12); peaks of Al and Cu were also identified in lesser quantities (51.2 wt.% Si, 46.0 wt.% O, 1.8 wt.% Cu and 1.0 wt.% Al). The upper region showed two distinct phases: a bright phase which appeared as isolated islands or patches, showing Cu and O signals (91.8 wt.% Cu and 8.9 wt.% O), and a darker phase (silica) surrounding the islands. Under higher magnifications a mixed phase with high content of Cu, O and Si (33.7 wt.% Cu, 32.4 wt.% O, 17.4 wt.% Si, 5.6 wt.% Al and 4.6 wt.% Y) was also identified. A detailed SEM image is shown in Fig. 14.



Figure 14. Isolated islands of a copper oxide phase surrounded by a thin layer of silicon oxide phase and a mixture of both phases



A summary of the identified phases is shown in Fig. 15.

Figure 15. SEM showing the development of oxidation and corrosion zones. The mixed region is shown in Fig. 14 in higher magnification; notice the formation of gas bubbles at the Si_3N_4/SiO_2 interface

A subsequent Raman spectroscopy confirmed these results. Fig. 16 shows an SEM image of the various phases labelled 1-4; wherein the region marked by number four is shown in higher magnification in Fig. 14.



Figure 16. SEM image showing the near-surface zones; the numbers indicate the Raman spectra shown in Fig. 17. The region marked with number "4" is shown in Fig. 14 in higher magnification

The Raman spectra shown in Fig. 17 and summarised in Table 4 correspond to the zones specified in Fig. 16.



Figure 17. Raman spectra corresponding to the zones specified in Fig. 16

It should be noted that Raman spectroscopy is not able to detect pure metallic phases such as Cu.

Spectrum	Main identified chemical composition
Point 1	Silicon nitride
Point 2	Cristobalite SiO ₂ , peak at 600 cm ⁻¹ may also indicate the formation of SiO ₂ ·nH ₂ O
Point 3	Cuprite Cu ₂ O, Tenorite CuO
Point 4 (see Fig. 14)	Cuprite Cu ₂ O, Tenorite CuO, Cristobalite SiO ₂ ; peak shift around 5 cm ⁻¹

Table 4. Summary of the Raman spectra shown in Fig. 17

3.5 Contact with copper under inert gas

After being submerged in the melt under inert gas atmosphere, the specimens showed no signs of corrosion or wetting with copper. The near surface zones of the specimens showed signs of oxidation (Fig. 18a) and higher content of sintering additives were detected on the surface. The oxide layer here also appeared to be composed of different phases (Fig. 18b). No signs of fracture were detected on the surfaces of the specimens.



(a)

(b)

Figure 18. (a) Near-surface zone of a specimen submerged in molten copper at 1200 $^{\circ}$ C in Ar and N₂ atmosphere for 100 cycles each lasted 60 s; (b) detailed view showing the oxide layer and different phases

4. Discussion

When heated up to around 700 °C, sintered silicon nitride starts building amorphous SiO_2 layers, which tend to crystallise to cristobalite at around 1000 °C [7,8]. The reaction between Si_3N_4 and O_2 releases N_2 and/or oxides of nitrogen. Upon further heating (in our case up to 1200 °C), the sintering additives may even start forming a variety of products [8].

In addition to the changes observed in the surface texture (Fig. 4b), the chemical composition of the surface layer showed higher concentrations of sintering additives compared to the bulk (Table 2). The most likely reason is a phase separation and accumulation of additive-rich oxides in direct contact with the melt and/or atmosphere. These yttrium-containing phases may include Y_2O_3 or $Y_2Si_2O_7$ [17],[18]. Considering the amounts of secondary-phase elements found in the oxide layer (refer to Table 2), there is no conclusive evidence that the glassy intergranular phase is leached out from the un-oxidised bulk material into the oxide layer. The oxide layers appeared inhomogeneous; brighter regions showed higher concentrations of yttrium (Fig. 5b), whereas the darker layer mostly contained silica. This phase separation and possible formation of oxynitride phases (e.g., Si₂ON₂) may influence oxidation significantly by affecting oxygen diffusion [19]. A detailed analysis of the reaction kinetics is, however, beyond the scope of the present study.

The formation of crystalline yttrium-containing products was observed on the examined fracture surfaces after quenching the specimens in water (Fig. 7). A similar observation was documented in [17] following an oxidising heat treatment and in [20] after post-sintering heat treatment of Y_2O_3 -Al₂O₃ containing silicon nitride ceramics. The high cooling rates also lead to crack formation and premature fracture of the specimens before even completing the 10^4 cycles. Crack formation and material resistance to thermal shock are directly related to the thermal shock parameter *R* (equation 1) due to the high cooling rate. In addition to the macrocracks visible in Fig. 6, which indicate typical thermal shock fracture patterns that start at the edges; microcracks were also visible throughout the silica covered fracture surfaces (Fig. 8) due to the different expansion and contraction strains undergone by the surface and the bulk.

The low number of undergone thermal cycles (10^4) has little, if any, fatigue degradation effect on the material. On the contrary, the observed increase in residual strength (see Table 3) might indicate a crack healing process (cf. [18]), which can be attributed to the formation of silica (cristobalite) due to the oxidation of Si₃N₄. The formation of oxide layers causes closure of natural flaws on the surface, especially if these flaws are small enough. This observation corroborates the findings of Harrer et al. [20], which indicated a significant increase in the characteristic strength of silicon nitride by 300-500 MPa following heat treatment and the formation of a glassy oxide layer on the surface. A more plausible cause is the melting of the glassy intergranular phase (compare Fig. 4a and Fig. 4b) which in turn, causes crack tip blunting. Cyclic thermal loading, on the other hand, causes relaxation of compressive residual stresses resulting from machining (cf. [21]). Such stresses ideally should increase the strength of the material.

The silica layer formed during oxidation acts as a passivation layer that protects the ceramic from further oxidation or corrosion (second layer from the left in Fig. 12). In the absence of tribological and/or mechanical loading, the formation of an oxide layer on the surface of silicon nitride will help protect the surface from further exposure to copper oxide and hence hamper possible further reaction (Khader et al. [15]). SiO₂ in a Si-Cu-O system (refer to **Raman spectroscopy shown in Fig. 17 and summarized in Table 4**), however, starts melting at around 1150 °C according to the phase diagram proposed by Uet'yantsev et al. [22]. The high temperature of molten copper (~1200 °C) causes the silica layer to melt leaving the surface of silicon nitride exposed and therefore, permitting further oxidation (compare the silica layers in Fig. 12 and Fig. 15). The gases released in this oxidation process will also try to escape (or diffuse) through the formed superficial oxide layers. The formation of N₂ bubbles as a result of the oxidation of Si₃N₄ was thoroughly discussed by Luthra [23] and considered in the implementation of a mathematical model for the growth rate of porous oxide layers on Si₃N₄ by Galanov et al. in [24]. Both Fig. 12 and Fig. 16 show voids formed due to gas entrapment between the reaction layers. Under these conditions the reaction of Si_3N_4 with copper is highly improbable.

It was proposed by Uet'yantsev et al. [22] that Cu^{2+} acts as a mineraliser (a substance that affects – in this case reduces – the crystallisation temperature and the formation of minerals) in the crystallisation of cristobalite at low temperatures. In other words, copper oxide functions as an accelerator to the oxidation of Si₃N₄ [7]. In casting copper and copper alloys in an oxygen-rich environment, copper oxide is readily present as slag at such high temperatures.

Copper (II) oxide (CuO) is widely used as a catalyst because of its high activity and selectivity in oxidation and reduction reactions [25]. It can be seen from the work of Schmidt-Whitley et al. [26] that unless special precautions are taken during the cooling of cuprous oxide (Cu₂O) from high temperatures – at which it is prepared – certain reactions will occur. One of the obvious reactions is the surface oxidation of cuprous oxide (Cu₂O) to cupric oxide (CuO).

When brought into contact with CuO (Fig. 15 and 16), the oxidation temperature of Si_3N_4 is lowered by around 100 °C [7]. The transformation of the oxide layer (SiO₂) covering the surface of silicon nitride from α -quartz to α -cristobalite above 1100 °C also accelerates the aforementioned oxidation process [7]. The thermal dissociation of silicon nitride occurs by the reaction of silicon with free oxygen atoms, which substitute the silicon nitride with silicon oxide. This reaction between silicon nitride and oxygen occurs at temperatures above 950 °C [27] as follows:

$$\operatorname{Si}_{3}\operatorname{N}_{4}+6\operatorname{O}_{2} \xrightarrow{\operatorname{CuO}} 3\operatorname{SiO}_{2}+2\operatorname{N}_{2}$$

whereas, CuO appears on the reaction arrow to emphasize its catalytic effect.

Fig. 10 clearly depicts that the middle section of the specimen, which was at the same level with the surface of the melt (i.e., in contact with the slag) suffered the most from corrosion and material loss, whereas the lower portion of the specimen, which was fully submerged in copper showed much less corrosion effects.

5. Conclusions

Thermal and corrosion properties of silicon nitride were studied to assess its applicability in copper casting. No corrosive reaction between silicon nitride and pure copper was detected in inert atmosphere. The corrosion of silicon nitride by continuous oxidation of Si_3N_4 and melting of the formed oxide phase was accelerated by the presence of copper oxide.

In order for silicon nitride to be successfully used in copper casting, a flow of inert gas should be supplied to inhibit copper oxidation.

6. Acknowledgment

The authors acknowledge the financial support of the German Federal Ministry of Economics and Technology BMWi under the AiF ZIM-KOOP program (Grant No. KF2294002CK9).

Many thanks are also due to Volker Breuckmann, Marco Grube, Wolfgang Zdanewitz and Thomas Prystaw from Breuckmann GmbH & Co. KG for their cooperation and support. The assistance provided by the Fraunhofer IWM staff is highly appreciated.

7. References

- [1] Peters DT, Cowie JG, Brush Jr. EF, Midson SP. Use of high temperature die materials and hot dies for high pressure die casting pure copper and copper alloys. Trans. of the North Amer. Die Casting Assoc. Congress, Rosemont, IL; 2002.
- [2] Peters DT, Cowie JG. Die-cast copper motor rotors: Die materials and process considerations for economical copper rotor production. Department of Energy, Washington DC: Report No.(s) DE2003-811913; Avail: National Technical Information Service (NTIS); 2003.
- [3] Benedyk JC, Moracz DJ, Wallace JF. Thermal fatigue behavior of die materials for aluminum die castings. Trans. of SDCE 1970; Paper No. 111.
- [4] Joshi V, Srivastava A, Shivpuri R. Intermetallic formation and its relation to interface mass loss and tribology in die casting dies. Wear 2004;256:1232-1235.
- [5] Klobčar D, Tušek J, Taljat B. Thermal fatigue of materials for die-casting tooling. Mater. Sci. Eng., A 2008;472:198-207.
- [6] Mellouli D, Haddar N, Köster A, Ayedi H-F. Thermal fatigue failure of brass die-casting dies. Eng. Fail. Anal. 2012;20:137-146.
- [7] Kurushima T, Ishizaki K. Reaction of copper and copper oxides with nitride ceramics (AlN, SiAlON, Si₃N₄) and oxide additives (Al₂O₃, Y₂O₃, SiO₂, MgO). J. Ceram. Soc. Jpn. 1992;100:955-959.
- [8] Babini GN, Vincenzini P. Oxidation kinetics of hot-pressed silicon nitride. Mater. Chem. 1982;7:773-785.
- [9] Stern KH. Oxidation of Silicon, Silicon Carbide (SiC) and Silicon Nitride (Si₃N₄). Naval Research Laboratory: NRL Memorandum Report 5774; 1986.
- [10] Gogotsi YuG, Grathwohl G, Thümmler F, Yaroshenko VP, Herrmann M, Ch. Taut, Oxidation of yttria- and alumina-containing dense silicon nitride ceramics. J. Eur. Ceram. Soc. 1993;11:375-386.

- [11] Cinibulk MK, Kleebe H-J. Effects of oxidation on intergranular phases in silicon nitride ceramics. J. Mater. Sci. 1993;28:5775-5782.
- [12] Nickel KG. Corrosion of Non-Oxide Ceramics. Ceram. Int. 1997;23:127-133.
- [13] Sangiorgi R, Muolo M, Bellosi A. Wettability of hot-pressed silicon nitride materials by liquid copper. Mater. Sci. Eng., A 1988;103:277-283.
- [14] Klein R, Desmaison-Brut M, Ginet P, Bellosi A, Desmaison J. Wettability of silicon nitride ceramic composites by silver, copper and silver copper titanium alloys. J. Eur. Ceram. Soc. 2005;25:1757-1763.
- [15] Khader I, Hashibon A, Albina J-M, Kailer A. Wear and corrosion of silicon nitride rolling tools in copper rolling. Wear 2011;271:2531-2541.
- [16] Aksel C, Warren P. Thermal shock parameters [R, R^{'''} and R^{''''}] of magnesia–spinel composites. J. Eur. Ceram. Soc. 2003;23:301-308.
- [17] Ziegler A, McNaney JM, Hoffmann MJ, Ritchie RO. On the effect of local grain-boundary chemistry on the macroscopic mechanical properties of a high-purity Y₂O₃-Al₂O₃-containing silicon nitride ceramic: Role of oxygen. J. Am. Ceram. Soc. 2005;88:1900-1908.
- [18] M. Nakatani, K. Ando, K. Houjou, Oxidation behaviour of Si₃N₄/Y₂O₃ system ceramics, and effect of crackhealing treatment on oxidation. J. Eur. Ceram. Soc. 2008; 28;1251-1257.
- [19] Klemm H, Taut C, Wötting G. Long-term stability of nonoxide ceramics in an oxidative environment at 1500 °C. J. Eur. Ceram. Soc. 2003;23:619-627.
- [20] Harrer W, Danzer R, Morrell R. Influence of surface defects on the biaxial strength of silicon nitride ceramic
 Increase of strength by crack healing. J. Eur. Ceram. Soc. 2012;32:27-35.
- [21] Pfeiffer W, Hollstein T. Influence of grinding parameters on strength-dominating near-surface characteristics of silicon nitride ceramics. J. Eur. Ceram. Soc. 1997;17:487-494.
- [22] Uet'yantsev VM, Sudakova LP, Bessonov AF. Zh. Neorgan. Khim. 1966;11:1177-1182, Russ. J. Inorg. Chem. (English transl.) 1966, 631.
- [23] Luthra KL. Some new perspectives on oxidation of silicon carbide and silicon nitride. J. Am. Ceram. Soc. 1991;74:1095-1103.
- [24] Galanov BA, Ivanov SM, Kartuzov EV, Kartuzov VV, Nickel KG, Gogotsi YG. Model of oxide scale growth on Si₃N₄ ceramics: nitrogen diffusion through oxide scale and pore formation. Comput. Mater. Sci. 2001;21:79-85.
- [25] Pike J, Chan S-W, Zhang F, Wang X, Hanson J. Formation of stable Cu₂O from reduction of CuO nanoparticles. Appl. Catal. A 2006;303:273-277.

- [26] Schmidt-Whitley RD, Martinez-Clemente M, Revcolevschi A. Growth and microstructural control of single crystal cuprous oxide Cu₂O. J. Cryst. Growth 1974;23:113-120.
- [27] Billy M. Annales de Chimie 1959, 795.

Figure 1. Stereo-microscope images of a steel die-insert hot runner showing (a) thermal fatigue induced cracks; (b) a close-up of the damaged surface and residues of molten material ($CuZn_{16}Si_4$ -C) in the crack openings (Breuckmann GmbH & Co. KG)

Figure 2. (a) Temperature dependent elastic modulus of FSNI; error bars indicate the standard deviation for at least five specimens, the lines connecting the dots represent linear interpolation; (b) four-point bending strength; error bars indicate the standard deviation for at least five specimens

Figure 3. (a) Temperature dependent thermal conductivity and specific heat; (b) Temperature dependent coefficient of thermal expansion. Lines connecting the dots represent linear interpolation

Figure 4. SEM image of the surface of FSNI in (a) its virgin state; (b) after 10,000 cycles in air at 1200 °C/ air at RT

Figure 5. Cross-sectional SEM image after 10,000 cycles in air at 1200 °C/ air at RT (a) formation of silicon oxide layer; (b) detailed view showing different phases within the oxide layer

Figure 6. Crack formation due to thermal shock (a) after 150 cycles in air at 1200 $^{\circ}C$ / water at RT; (b) after 10,000 cycles in air at 1200 $^{\circ}C$ / water at RT; fracture surface appears shiny due to the formation of silicon oxide

Figure 7. SEM of the fracture surface after 10,000 cycles air at 1200 $^{\circ}$ C / water at RT showing recrystallization of secondary phase (EDX results: needle-shaped particles: Y, O; glassy surface: Si, O)

Figure 8. Fracture surface after 150 cycles in air at $1200 \,^{\circ}\text{C}$ / water at RT showing (a) formation of silicon oxide, microcracking and recrystallization of secondary phase; (b) formation of micropores at crack coalescence points

Figure 9. Thermal shock parameters for FSNI

Figure 10. Overview and cross sections of a silicon nitride specimen after only 30 s of partial submersion in molten copper in air atmosphere

Figure 11. Blunted edges of a specimen partially submerged in molten copper at 1200 °C in air for 10 cycles each lasted 20s; blunted edges as a result of cyclic submersion

Figure 12. Surface layers of a specimen after submersion in molten copper at 1200 °C for 30s in air atmosphere; notice the formation of gas bubbles at the interface

Figure 13. EDX mapping at the near-surface zone of a specimen; three zones are identified: (i) lower – consists mainly of pure silicon nitride; (ii) middle – Si-rich oxide phase, (iii) upper – bright regions: Cu-rich oxides, dark regions: Si-rich oxides

Figure 14. Isolated islands of a copper oxide phase surrounded by a thin layer of silicon oxide phase and a mixture of both phases

Figure 15. SEM showing the development of oxidation and corrosion zones. The mixed region is shown in Fig. 14 in higher magnification; notice the formation of gas bubbles at the Si_3N_4/SiO_2 interface

Figure 16. SEM image showing the near-surface zones; the numbers indicate the Raman spectra shown in Fig. 17. The region marked with number "4" is shown in Fig. 14 in higher magnification

Figure 17. Raman spectra corresponding to the zones specified in Fig. 16

Figure 18. (a) Near-surface zone of a specimen submerged in molten copper at 1200 $^{\circ}$ C in Ar and N₂ atmosphere for 100 cycles each lasted 60 s; (b) detailed view showing the oxide layer and different phases





Fig1b Click here to download high resolution image





















Fig6b Click here to download high resolution image









Fig9 Click here to download high resolution image



Fig10 Click here to download high resolution image



Fig11 Click here to download high resolution image



Fig12 Click here to download high resolution image





















Ag	As	Bi	Pb	Sb	Se	Ni	Te
15	0.3	0.05	0.5	0.5	0.3	1.0	0.3

Table 1. Impurities in ppm typically found in Grade-A cathode copper as provided by the supplier (Boliden Mineral AB, Sweden)

Table 2. Summary of EDX quantitative analysis after 10,000 heating and cooling cycles in air

Flomont	Su	rface	Bulk	
Element	Wt. %	Atom %	Wt. %	Atom %
0	42.3	63.5	2.7	3.7
Al	10.9	9.6	4.2	3.4
Si	24.4	20.8	62.4	48.8
Y	22.4	6.1	3.1	0.8
Ν			27.6	43.3
Total	100.0	100.0	100.0	100.0

Table 3. Summary of 4-point bending residual strength measurement after thermal loading

4-point bending test temperature	Initial strength prior to cyclic thermal loading	No. of thermal loading cycles 1200°C air/21°C air	Residual strength after cyclic thermal loading	Difference in strength
1200 °C	203.5±17.2 MPa	10,000	423.4±31.0 MPa	+108.1%
RT	695.1±65.0 MPa	1000	687.6±75.2 MPa	-1.1%

Table 4. Summary of the Raman spectra shown in Fig. 17

Spectrum	Main identified chemical composition
Point 1	Silicon nitride
Point 2	Cristobalite SiO ₂ , peak at 600 cm ⁻¹ may also indicate the formation of SiO ₂ ·nH ₂ O
Point 3	Cuprite Cu ₂ O, Tenorite CuO
Point 4 (see Fig. 14)	Cuprite Cu ₂ O, Tenorite CuO, Cristobalite SiO ₂ ; peak shift around 5 cm ⁻¹