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Interface reactions in the system sialon–Cu–Cu_2O

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The interface reactions between an α/β-sialon ceramic and Cu, Cu_2O or a Cu–Cu_2O mixture have been studied. A fully dense sialon ceramic material prepared by pressureless sintering at 1775° C with 6 wt% Y_2O_3 as sintering aid, were coldpressed together with Cu, Cu_2O or Cu–Cu_2O mixtures into cylindrical tablets. These samples were heat treated at 700, 850 and 1000° C in evacuated silica tubes. The reaction zones formed between the sialon and the powder compacts were studied in a SEM equipped with an EDS system. No reaction between copper and sialon ceramic could be detected in spite of prolonged heat treatment at 1000° C. Cu_2O reacted with the ceramic at 850 and 1000° C to form a glass containing copper and all the other sialon components. The interaction between the sialon material and the Cu–Cu_2O powder compacts was characterized by a redox reaction. The sialon was thus oxidized to SiO_2 and N_2 while Cu_2O was reduced to copper. A glass phase containing silicon, aluminium, yttrium and copper was also formed in the reaction.

1. Introduction

Silicon nitride, Si_3N_4, and related high-performance ceramic materials like sialon have for some time been considered as suitable materials for many high-temperature engineering applications, where high strength and wear resistance are required. The covalent character of the bonding in these ceramics yields a desirable combination of mechanical, thermal and chemical properties, making them interesting candidates as materials in wear resistant forming tools, especially for non-ferrous metal processing. One such application is the use of sialon ceramics in wire- or tube-forming dies for copper-based alloys.

The corrosion of silicon nitride-based ceramics in various metallic melts and in molten salts has been studied previously [1–5] but there are no reports concerning the interaction between sialon ceramics and solid metals or between sialon and solid metal oxides at elevated temperatures. This paper describes such a study of the solid state interaction between a sialon ceramic and Cu, Cu_2O and mixtures of Cu–Cu_2O at 700, 850 and 1000° C.

2. Experimental details

Pure silicon nitride is very difficult to fabricate into dense components with normal sintering procedures. Addition of aluminium oxide, aluminium nitride and/or yttria to the silicon nitride powder prior to the sintering makes it possible, however, to fabricate dense components via a pressureless sintering process. The sialon ceramics thus formed typically contain one or two crystalline phases and minor amounts of grain-boundary phases. The two most commonly found crystalline phases have the same structure as α- and β-Si_3N_4 and are consequently called α-sialon and β-sialon, respectively. The composition of the α-sialon phase can be written as $Me_x(Si, Al)_{12}(O, N)_{16}$ and the β-sialon phase can be represented by the formula $Si_{6-z}Al_zO_zN_{8-z}$ with $0 < z < 4.2$.

The sialon ceramic used in the present study was prepared with 6 wt% Y_2O_3 as sintering aid. The overall composition of the starting material was $Y_{0.1}Si_{3.6}Al_{0.6}O_{0.5}N_{5.2}$. The fully dense material was characterized by its X-ray powder diffraction pattern and by examining the obtained microstructure in a SEM. Three phases were found to be present: (i) a β-sialon phase with a x value of 0.53; (ii) an α-sialon phase with a x value of 0.3; (iii) an yttria-containing intergranular glassy phase. The analysis of the X-ray pattern showed 71 vol% of the crystalline phases present to be β-phase and 29% α-phase; in addition, an evaluation of the SEM micrographs revealed that the glassy phase constituted approximately 14% of the total volume. Further details concerning the preparation and properties of the used sialon material are given in [6] where it is called Grade 2.

Pieces of the sialon ceramic of approximately $3 \times 3 \times 3\,mm^3$ in size were cold-pressed together with copper, Cu_2O or mixtures of Cu–Cu_2O. The following Cu–Cu_2O molar ratios were used: 25–75, 50–50 and 75–25. The cold-pressed tablets were placed in quartz tubes which were evacuated to 10^{-3} torr and sealed. The tubes were then heated at 1000, 850 and 700° C from 2 h up to 20 days. In the case of the Cu–sialon system the heat treatments at 850 and 700° C were omitted as no reaction was observed at 1000° C. After the heat treatment the tablets were embedded in bakelite and cut so as to expose a cross-section of the sialon–Cu–Cu_2O matrix. The cross-section was carefuly polished with a submicrometre diamond

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paste, and finally a thin layer of carbon was evaporated onto the surface. The cross-sections were studied in scanning electron microscopes (Jeol JSM 820 and JSM 880) equipped with energy-dispersive X-ray analysers (A Link QX200 EDS-system allowing detection of elements with $Z > 4$.) In this connection it can be noted that we have found it very difficult to detect nitrogen in Si_3N_4-based ceramics especially in sialon materials. Thus, for instance, for pure β-sialon materials, $Si_{6-z}Al_zO_zN_{8-z}$, the peak in the EDS-spectra associated to nitrogen was clearly resolved for lower z values but not for higher ones. This means that we cannot expel the possibility that the phase studied might contain some nitrogen even though we have not been able to detect any nitrogen. The micrographs presented below are obtained with backscattered electrons. The reaction products were characterized by their X-ray powder patterns obtained in a Guinier–Hägg focusing camera Cu Kα_1 radiation and with silicon as internal standard.

3. Results and discussion

3.1. Interaction between sialon and copper metal

The reaction zone of a sialon sample heat treated at 1000° C during 20 days in contact with copper metal is shown in Fig. 1. The microstructure of the α/β-sialon material is seen in the upper part of the micrograph. The β-sialon crystals appear as dark areas while the α-sialon crystals are grey. The lightest parts between the sialon grains represent to the yttria-containing intergranular glassy phase. The bright zone adjacent to the sialon material consists of metallic copper. As seen in the micrograph there is no observable reaction between the two materials and the EDS analysis showed that none of the elements forming the sialon could be traced in the copper matrix and nor could any copper be found in the sialon material.

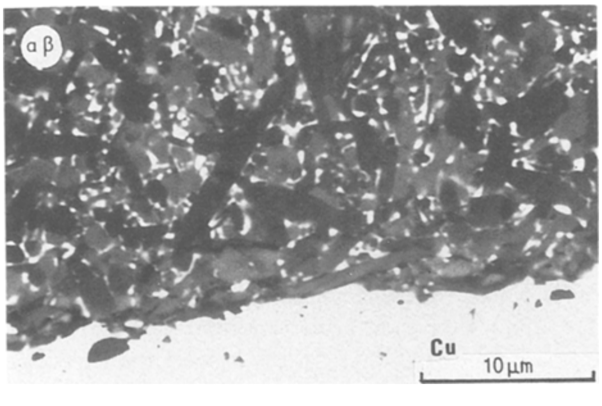

Figure 1 A micrograph of the copper–sialon interface after heat-treatment at 1000° C for 20 days. The EDS analysis showed that no copper enters the sialon and nor silicon or aluminium could be detected in the copper matrix. Three different phases are recognized in the sialon: black B-sialon crystals, grey α-sialon crystals and a white intergranular phase.

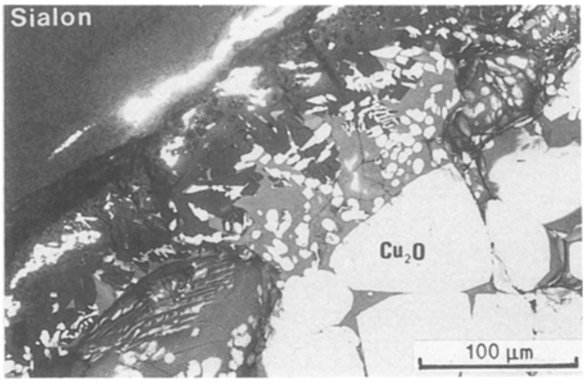

Figure 2 The reaction zone formed between the sialon ceramic and Cu_2O after 7 days of heat treatment at 1000° C. The dark areas closest to the sialon consist of SiO_2 and the adjacent grey parts are a glass phase containing all elements present in the system e.g. Cu, Al, Si, Y, O and N. The white grains are unreacted Cu_2O. The light areas at the edge of the sialon piece is caused by charging by the electron beam.

3.2. Interaction between sialon and Cu_2O

In contrast to pure copper metal, Cu_2O reacts with the sialon matrial. A typical rection zone from a Cu_2O–sialon tablet, heat-treated for 7 days at 1000° C is seen in Fig. 2. The sialon is recognized in the upper left-hand corner of the micrograph (the very bright fields at the edge of the sialon area originate from charging by the electron beam) and the dark grey area next to the sialon consists of SiO_2 according to the X-ray and EDS analysis. Traces of aluminium were also detected in the SiO_2 layer. An enlargement of this layer is seen in Fig. 3 and the area closest to the sialon contains a large number of cavities. (The origin of these cavities will be discussed below.) The large bright grains at the bottom right-hand corner of Fig. 2 consist of Cu_2O and in between these grains a grey phase is observed. The same type of phase is also found between the Cu_2O grains some distance further out in the matrix of the copper oxide, which indicates it to be a low-viscosity liquid at the reaction temperature. The EDS analysis of this phase revealed all the metals present in the system studied, e.g. yttrium, silicon, aluminium and copper. The phase also contains oxygen and since no redox-reaction was observed, as in the system described below, it ought to contain nitrogen as well. The relative amounts of metals present were found to vary somewhat from area to area, but typically the Si : Al : Y : Cu ratio was found to be around 53 : 25 : 5 : 17, thus, we did not observe any significant compositional variation of this grey phase with, for instance, the distance from the sialon matrix. Finally, it can be noted that we

Figure 3 An enlargement of the reaction zone closest to the sialon in the Cu_2O–sialon system. The micrograph shows the occurrence of cavities in the SiO_2 matrix.

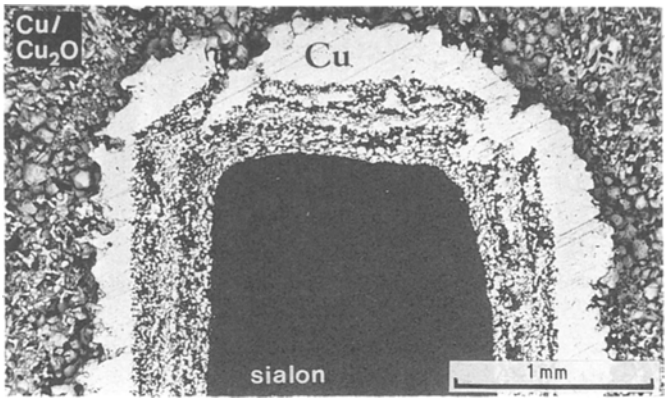

Figure 4 An overview of the reaction between sialon and a 50 : 50 mol % mixture of copper and Cu_2O after 7 days heat treatment at 1000° C. A part of an almost continuous band of copper has developed around the sialon piece is shown. Various reaction products have formed between the copper band and the sialon.

found small undissolved grains of Cu_2O completely enclosed by a larger area of the amorphous grey phase.

The X-ray powder pattern of material from the reaction zone showed to contain only SiO_2 and Cu_2O as crystalline phases, implying that the grey phase must have been a liquid at high temperatures, which upon cooling formed a glass.

Almost the same reaction pattern was found for tablets heat treated at 850° C. The reaction seems, however, to proceed much slower at 850° C than at 1000° C, and another difference is that one also can observe traces of an yttrium-rich silicate phase embedded in the SiO_2 phase. At 700° C, finally, this sialon ceramic seems to be inert against Cu_2O, as no reaction was observed after heat treatment at this temperature for 14 days.

3.3. Interaction between sialon and Cu–Cu_2O mixtures

The chemical attack in this system is severe, as seen in Fig. 4. This micrograph originates from a tablet containing sialon and a 50 : 50 mol % Cu–Cu_2O mixture, heat treated at 1000° C for 7 days. A band of copper is formed around the piece of sialon, and inside this copper band a variety of phases have formed as described below. An enlargement of the reaction zone is shown in Fig. 5, where the sialon is found in the right-hand part of the micrograph and the copper-band is seen in the left-hand part. The reaction zone is about 300 μm thick and Fig. 6 is a further enlargement of this area. EDS analysis shows that the very light areas in this micrograph consist of pure copper, the dark parts are SiO_2, while the grey areas contain silicon, aluminium, yttrium and copper as well as oxygen. The relative amounts of the metals vary somewhat from area to area, but average around 67(Si) : 20(Al) : 1(Y) : 12(Cu). The copper content of this phase is thus lower than that of the one discussed above. In the sialon ceramic we were able to detect the presence of nitrogen, but not in the grey phase in Fig. 6. Due to the difficulties of detecting smaller amounts of nitrogen (see above), we cannot, however, exclude the possibility that the grey phase does not contain some nitrogen.

The absence of any Cu_2O and the occurrence of relatively large amounts of copper in the reaction zone, however, strongly suggests that parts of the Cu_2O has partly been reduced to copper. The only species that can be oxidized is the Si_3N_4-based ceramic which mainly forms SiO_2 and N_2. Cavities that might contain part of the released nitrogen were found in the reaction zone, especially next to the sialon. In this connection, it can be noted that only the reaction between Cu–Cu_2O mixtures and sialon yielded an overpressure in the silica tubes. This reaction route will be further discussed below. Besides these phases the EDS analysis revealed the presence of two more phases, one of them an yttrium silicate (small amounts) and the other a Cu–Al oxide.

The X-ray powder patterns of materials from the reaction zone exhibit sharp reflexions originating from copper and from the α-cristobalite modification of SiO_2 and some rather diffuse reflections which can be ascribed to $CuAlO_2$. This implies that the grey phase above must be X-ray amorphous.

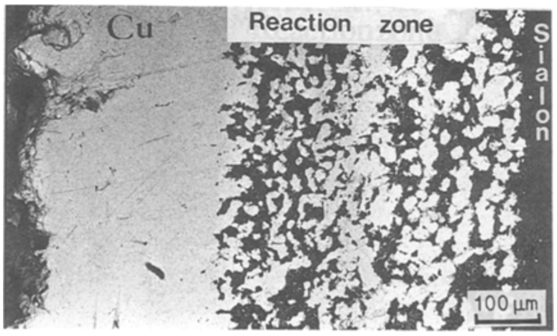

Figure 5 An enlargement of the reaction zone in Fig. 4 with the copper band on the left and the sialon on the right. The light areas inside the copper band are copper.

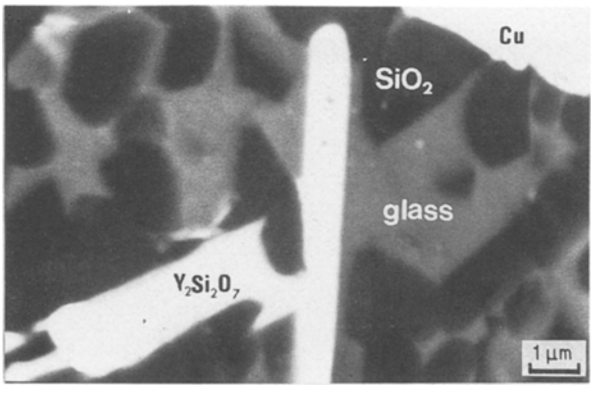

Figure 6 An enlargement of the grey area in the reaction zone in Fig. 5. Four different phases can be observed: SiO_2, Cu, a glass phase containing Si, Al, Cu, Y and O and $Y_2Si_2O_7$ (only a few fragments have been observed).

The observations described are typical for a 50 : 50 mol % mixture of copper and Cu_2O. The same reaction products were found for the 25 : 75 and 75 : 25 mixtures of copper and Cu_2O. In the 75 : 25 case a rather thick coherent layer of copper around the sialon piece is easily formed, and this band prevents Cu_2O from diffusion into the reaction zone from the outer parts of the tablet. As shown above, copper does not interact with the sialon material, implying that in the present case the reaction ought to cease when all Cu_2O inside the copper band has been consumed. We do in fact observe an approximately 50 μm wide reaction zone independent of the time of heat treatment. When, however, a 25 : 75 mixture of copper and Cu_2O is used, a thin non-coherent copper band is formed and the chemical attack on the sialon material is expected to continue, in agreement with the experimental observations.

Finally, the same reaction pattern is observed for tablets heat treated at 850 and 700° C, but the reaction seems to be much slower. The microstructure of the reaction zone is different, however. A substantially more fine-grained structure is observed in these cases, and in samples heat treated at 700° C separate phases in the SEM can hardly be distinguished.

4. Concluding remarks

This study has shown that the sialon material is inert against metallic copper even for prolonged heat treatment at 1000° C. Cu_2O, however, reacts with the sialon forming an amorphous phase which besides copper also contains silicon, aluminium and yttrium. It ought to be an oxynitride phase as we have not observed any redox-reaction. This phase shows a clear tendency to diffuse into the Cu_2O matrix, and we have not been able to detect any significant variation in the composition from one area to another. The average composition expressed as the Si : Al : Y : Cu ratio was found to be 52 : 25 : 5 : 17. Corresponding ratio for the sialon material is 83 : 14 : 3 : 0. The silicon to aluminium ratio in the copper-containing amorphous phase is thus substantially smaller than that in the sialon material. This implies that, besides the copper-containing phase, a silicon oxide or a silicon-oxynitride phase must be formed. Experimentally we have also found SiO_2 located in a layer close to the sialon. Al and Y are thus depleted from this layer, implying that the volume of the remaining SiO_2 is smaller than that of the reaction zone, which explains the observed cavities next to the sialon (see Fig. 3). As the reaction proceeds the number of cavities must increase, which will slow down the process and finally cause it to end.

As mentioned above, we believe that in the sialon–Cu–Cu_2O system the Si_3N_4-based ceramic is oxidized to SiO_2 and N_2 under formation of a glass phase containing copper, silicon, aluminium and yttrium, while Cu_2O is reduced to copper (minor amounts of $Y_2Si_2O_7$ and $CuAlO_2$ have also been found). It thus seems that copper metal promote a redox reaction to take place when Cu_2O is present simultaneously but not otherwise. Thus in the absence of copper as in the sialon–Cu_2O system one cannot observe any redox process involving the sialon material.

The results described above indicate that this sialon material can be used in forming dies for wires or tubes of pure copper, but to the extent that Cu_2O is present or is formed during the process the dies will be seriously corroded.

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