High-temperature oxidation behavior of ZrO$_2$-ZrSiO$_4$/NiCr composites and its applicability for functionally graded materials

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Abstract. In the present study, high-temperature oxidation behavior of pressurelessly sintered ZrO$_2$-ZrSiO$_4$/NiCr8020 samples with different volume fractions of ceramic is investigated with the aim to develop oxidation resistant ZrO$_2$-ZrSiO$_4$/NiCr functionally graded materials out of them. Sintered samples with 0, 25, 50 and 75 vol% ceramic were oxidized at 1000 °C for 36 h in synthetic air. The oxidation kinetics depends strongly upon the phase connectivity of NiCr in the ceramic matrix, which also governs the crack pattern formed due to the volume expansion of NiCr particles. While nearly full oxidation of the NiCr particles occurs in the 75 vol% ceramic composite with a relatively low phase connectivity of NiCr, the 25 vol% ceramic composite with a highly percolative NiCr phase exhibits a metal-like oxidation behavior and its overall oxidation was limited to the surface near area.

1. Introduction

Functionally graded materials (FGMs) have the potential for multifunctionality combining different materials and providing a spatial variation in composition, structure and properties that cannot be achieved by conventional homogeneous materials [1]. Metal-ceramic FGMs are promising candidates for future high-temperature applications, with the ceramic component offering thermal barrier effects and protecting the metal from melting, corrosion and oxidation, while the FGMs are toughened and strengthened by the metallic component [2]. ZrO$_2$/NiCr FGMs are typical FGMs of thermal barrier type and they have already received fairly intensive study [3-8] in the recent 20 years. However, to the best knowledge of authors, few studies [3,4] have dealt with the high-temperature oxidation behavior of this type of FGM. Moreover, we have found no reports yet concerning the characteristic oxidation behavior of individual constituent layers of such FGMs.

Borchert [3] found that the oxidation resistance of ZrO$_2$/NiCr FGMs is able to be improved significantly by adding a relatively low volume fraction of ZrSiO$_4$ in the ZrO$_2$ matrix as inclusion. In order to develop oxidation resistant ZrO$_2$-ZrSiO$_4$/NiCr FGMs, high-temperature oxidation behavior of ZrO$_2$-ZrSiO$_4$/NiCr composites with different volume fractions of ceramic is investigated based on their oxidation kinetics and microstructure in the present study.

2. Experimental

2.1. Starting materials
Ceramic powders used in the present study were 8 mol% yttria-stabilized zirconia powder (TZ-8YS, \(D_{50}=0.54 \text{ µm}\), Tosoh, Japan) and \(\text{ZrSiO}_4\) powder (\(D_{50}=0.85 \text{ µm}\), Helmut Kreutz GmbH, Germany). The \(\text{ZrO}_2\) powder was delivered in the form of spray-dried granules. The applied metal powder was irregularly shaped NiCr8020 powder (\(D_{50}=13.80 \text{ µm}\), H.C. Starck, Germany) with 20 wt% Cr as alloying element. Fig. 1 shows the typical microstructure of the starting materials.

![Figure 1. SE images of starting materials: (a) TZ-8YS; (b) \(\text{ZrSiO}_4\); (c) NiCr8020.](image)

### 2.2. Sample preparation

For the high-temperature oxidation experiments, \(\text{ZrO}_2-\text{ZrSiO}_4/\text{NiCr}\) samples with different volume fractions of ceramic were fabricated via die and isostatic pressing followed by pressureless sintering. In the fabrication process, 5 vol% \(\text{ZrSiO}_4\) was selected as the inclusion phase to be added into the respective \(\text{ZrO}_2\) matrix. Metal-ceramic powder mixtures with 75, 50 and 25 vol% \(\text{ZrO}_2-\text{ZrSiO}_4\) (5 vol%) ceramic, respectively, were firstly prepared by weighing the powders according to their volume ratios and mixing them by planetary ball milling for 3 h using ethanol as solvent. Pure NiCr powder (0 vol% ceramic) was mixed with an aqueous PVA solution (5 wt%) in order to improve the green strength of the sample. After drying, the mixtures were sieved through a screen with a mesh size of 200 µm to crush the soft agglomerates. Subsequently, they were filled into a steel die with an inner diameter of 8 mm and compacted just with hand as pre-compaction. After demoulding, green bodies were pressed cold-isostatically under 300 MPa as post-compaction, followed by pressureless sintering at 1350 °C for 3 h under argon in a high-temperature alumina tube furnace (Thermal Technology, USA).

### 2.3. High-temperature oxidation

Sintered samples had a dimension of about 7 mm (Φ) × 2.5 mm. A hole with a diameter of 1 mm was drilled in the center of the samples, so that they can be hung on a platinum wire as shown in Fig. 2, in order to ensure a homogeneous oxidation of the samples. Subsequently, they were heated with 5 °C/min up to 1000 °C under nitrogen followed by oxidation at this temperature for 36 h under
flowing synthetic air (N₂/O₂ 80/20), with a gas flowing rate of 40 ml/min. Weight gain of the samples during the oxidation was registered by using a TG/DSC analyzer (STA 499 C/4/G, Netzsch, Germany).

Figure 2. Sample arrangement for the oxidation experiments.

2.4. Characterization
Relative densities and porosities of the as-sintered samples were determined by the Archimedes’ method. Specific surface area of the composite samples was measured using a physisorption analyzer (ASAP 2010, Micromeritics, Germany). In order to improve the measuring accuracy, at least 10 identical samples were used for each individual measurement. However, surface area of the pure metal samples was still too low to be measured correctly by the physisorption method. Thus, specific surface area of the pure metal sample was deduced by fitting the initial linear portion of the measured parabolic oxidation curve with that taken from the literature [9], in which Ni-19.4 %Cr samples were oxidized at 1000 °C in static air. Additionally, microstructure and element distribution of the oxidized samples were studied by using a scanning electron microscope (JSM-840A, Jeol, Japan) equipped with a dispersive X-ray spectrometer (Oxford Instruments, UK).

3. Results

3.1 Sintered samples prior to oxidation
In the present study, ZrO₂-ZrSiO₄/NiCr samples with 75 to 0 vol% ceramic are termed as 75C to 0C. Table 1 shows the basic properties of the as-sintered samples. We note that the samples exhibit similar relative densities ranging from 86.40 to 90.41 %. Specific surface areas of the metal-ceramic composite samples are comparable among each other, whereas that of the pure metal sample is significantly lower than those of the composite ones.

Table 1. Basic properties of the as-sintered non-FGM samples.

| Phase | Relative density (%) | Porosity (%) | Open porosity (%) | Specific surface area (cm²/g) |
|-------|----------------------|--------------|-------------------|-----------------------------|
| 75C   | 86.40                | 13.60        | 6.59              | 1517                        |
| 50C   | 90.41                | 9.59         | 5.12              | 843                         |
| 25C   | 88.94                | 11.06        | 9.31              | 711                         |
| 0C    | 87.73                | 12.27        | 9.29              | 9                           |
Microstructure of the sintered samples with different volume fraction of ceramic is shown in Fig. 3. We note that NiCr particles are distributed homogeneously in all the composite phases. As the volume fraction of metal increases from 25 to 75 vol%, matrix phase of the composite transits gradually from ceramic matrix with dispersed NiCr particles to metal matrix with an interpenetrating ceramic network. For the 0C sample, several small dark gray spots can be observed. These spots are composed of Ni–Cr,Cy [10], which was formed due to an incomplete debindinging.

Figure 3. SE and BSE images of the ZrO2-ZrSiO4/NiCr samples.

3.2 Samples after oxidation
Since all the samples were still porous after sintering, their surface area can vary substantially during the oxidation process, thus application of the parabolic law assuming a constant surface area during oxidation for data analysis is not suitable for this case. Instead, we use the degree of oxidation to describe the oxidation kinetics, which was calculated by dividing the weight gain of the sample by the total weight gain, when the sample is totally oxidized. Fig. 4 shows the degree of oxidation as a function of oxidation time for the different ZrO2-ZrSiO4/NiCr samples. We note that for all the phases the degree of oxidation increases with increasing oxidation time, although the increase for 0C is difficult to be identified from the figure. During the first 10 h of oxidation, the three composite phases exhibit similar degrees of oxidation. From t=10 h up to the end of the process, the degree of oxidation decreases with increasing volume fraction of metal at a certain oxidation time. Additionally, it is noteworthy that 75C was oxidized almost completely after an oxidation time of 36 h.
Figure 4. Influence of time on degree of oxidation for the ZrO$_2$-ZrSiO$_4$/NiCr samples.

Fig. 5 shows the kinetic constants of oxidation for the ZrO$_2$-ZrSiO$_4$/NiCr samples. In the first five hours, kinetic constants of the composite phases decrease rapidly from about 8.5 to 2.5 % h$^{-1}$, while that of 0C is much smaller and it decreases from 0.93 to 0.05 % h$^{-1}$. Afterwards, kinetic constant of 75C increases intensively to 5.17 % h$^{-1}$ at t=15 h, decreases then rapidly again to a minimum value of 0.17 % h$^{-1}$ at t=35 h, agrees well with its degree of oxidation reaching nearly 100 % at t=36 h as shown in Fig. 4. Similarly, kinetic constant of 50C increases slightly to 2.79 % h$^{-1}$ at t=10 h, decrease then gradually to a value of 0.91 % h$^{-1}$ at t=35 h. For the metal-rich phases, kinetic constant of 25C decreases monotonically up to 0.21 % h$^{-1}$ at t=35 h, while that of 0C remains nearly constant at a low value of ~0.01 % h$^{-1}$ up to the end of the process.

Figure 5. Kinetic constants of oxidation for the ZrO$_2$-ZrSiO$_4$/NiCr samples.

Fig. 6 shows microstructure and element mapping obtained from the center of the oxidized 75C sample. We observe from Fig. 6(a) and (b) that all the NiCr particles were oxidized and voids were generated in most of the particles, indicating that the whole sample has been oxidized almost completely. In addition, a network of oxide interpenetrating in the ceramic matrix can be observed. When comparing the element mapping in Fig. 6(c) and (d), we note that Cr in the NiCr particles has been depleted completely and a dense Cr$_2$O$_3$ scale is formed around each NiCr particle. Nickel phase...
of the metal particles was also strongly oxidized since oxygen was able to be detected over the whole particles. When comparing Fig. 6(d), (e) and (f), we may deduce that the interpenetrating network of oxide is composed of NiO, even though no network of oxygen could be identified from Fig. 6(c) due to the presence of oxygen detected from the \( \text{ZrO}_2-\text{ZrSiO}_4 \) (5 vol%) matrix.

![Microstructure and element mapping](image)

**Figure 6.** Microstructure and element mapping obtained from the center of the oxidized 75C sample: (a) SE image; (b) BSE image; (c) oxygen (red); (d) chromium (green) (e) nickel (blue) (f) zirconium (white). All elements were recorded from their K\( \alpha \) line.

Fig. 7 shows microstructure of the oxidized 50C sample, which was obtained from near the surface and the center of the sample, respectively. The subsurface zone where the NiCr particles were strongly oxidized reaches a thickness of \(~620\ \mu\text{m}\). From Fig. 7(b), we observe that a relatively finer network of NiO than that in 75C was formed in this zone. In contrast, the center of the sample was just slightly oxidized, with a thin oxide scale around each metal particle and the inside of the particles remaining unoxidized (Fig. 7(c) and (d)). Additionally, no network of NiO was found in the ceramic matrix.
Microstructure of the oxidized 50C sample with (a) SE and (b) BSE images obtained near the surface and (c) SE and (d) BSE images obtained from the center of the sample.

Microstructure of the oxidized 25C sample is shown in Fig. 8. The strongly oxidized subsurface zone reaches a thickness of about 110 µm. A finer network of NiO than that in 50C can also be observed in the subsurface zone, with the amount of the NiO-network significantly less than those in 75C and 50C. Dissimilar to the 75C and 50C samples as described above, a continuous dense oxide scale along the surface of the sample was formed, which can reduce the surface area and protect the sample from further oxidation effectively. From the EDX result (spectrum 1 in Fig. 8(a)) with 43.69 at% oxygen and 56.31 at% nickel, we may deduce that this oxide scale is also composed of NiO.

Figure 7. Microstructure of the oxidized 50C sample with (a) SE and (b) BSE images obtained near the surface and (c) SE and (d) BSE images obtained from the center of the sample.

Figure 8. Microstructure of the oxidized 25C sample: (a) SE image; (b) BSE image.

Fig. 9 shows microstructure of the oxidized 0C sample. We note that after the oxidation process all the open pores near its surface were blocked by oxide scales, which are dark gray and marked by using arrows in Fig. 9(a). Moreover, a continuous oxide scale along the surface of the sample was formed. EDX results detected on the light gray and dark gray phases are listed in Table 2. In spectrum 1, the
element Cr and O have a mol ratio of about 2:3 with the Ni content of only 0.92 at%, indicating that the dark gray phase is mainly composed of Cr$_2$O$_3$. In spectrum 2, no oxygen was detected and the elements Cr and Ni have a mol ratio of about 1:9, lower than the nominal ratio of the NiCr8020 alloy, indicating that the light gray phase is the unoxidized NiCr phase with reduced content of Cr. Fig. 9(b) shows the microstructure obtained from the center of the 0C sample. Expect for several dark gray spots composed of Ni-Cr$_x$C$_y$ as mentioned above, no oxide scales can be observed.

**Figure 9.** Microstructure of the oxidized 0C sample with (a) SE image obtained near the surface and (b) SE image obtained from the center of the sample. Blocked open pores near the surface are marked by using arrows.

**Table 2.** EDX results detected on the cross section of the 0C sample.

| Element (at%) | O   | Cr  | Ni  |
|--------------|-----|-----|-----|
| Spectrum 1   | 54.19 | 44.89 | 0.92 |
| Spectrum 2   | 11.02 | 88.98 |       |

4. Discussion

Although dispersed NiCr particles are observed from the microstructure of 75C and 50C (Fig. 3), a percolative network of NiCr was formed in both samples. Percolation theory [11] tell us that a random distribution of inclusions form branching clusters of touching inclusions and at a critical volume fraction (percolation threshold) of ~0.16, one of the clusters forms a percolative network of inclusions that spans the entire volume of the specimen. For elongated inclusions, the percolation threshold can be dramatically reduced [12]. Lange et al. [13] found that more than 95% of the inclusions will be part of the same network when the volume fraction of inclusion reaches 0.20. After sintering, volume fractions of NiCr particles based on the total volume in 75C, 50C and 25C were 21.60, 45.21, 66.71 vol%, respectively, indicating that a percolative network of NiCr was formed in all the composite samples, but the phase connectivity of NiCr still increases with increasing volume fraction of metal, as shown in Fig. 3.

In the first 5 h of the oxidation process, the composite phases exhibit similar degrees of oxidation and kinetic constants. Their kinetic constants decrease from about 8.5 % h$^{-1}$ to 2.5 % h$^{-1}$ in this period, which can be attributed to the oxidation of Cr near the surface of the samples by inward diffusion of oxygen through both open pores and oxygen ion-conducting ZrO$_2$ matrix. Simultaneously, the oxidation of Cr resulted in a volume expansion of the metal particles, since the volume of Cr$_2$O$_3$ is about twice as large as that of Cr according to the Pilling-Bedworth ratio [14]. However, due to the
relatively low content of Cr of 20 wt% in each metal particle, volume expansion during this period is considered to be relatively slight without crack formation in the ceramic matrix, since existing pores in the ceramic matrix can help to accommodate slight volume expansion of metal particles [15]. Additionally, surface areas of the composite phases were probably reduced to a certain extent by the volume expansion of NiCr particles. For the pure metal phase, kinetic constant of 0C also decreases during this period from 0.93 to 0.05 % h\(^{-1}\), indicating that oxide scales were formed and they grew gradually in the open pores near the surface of the sample, resulting in a reduction of the surface area. The kinetic constant of 0C is much smaller than those of the composite phases, since the latter exhibit significantly higher specific surface areas as compared to the former after sintering.

After depletion of Cr near the surface of the composite samples, nickel phase in the NiCr particles near the surface began to be oxidized. Since Ni is the dominant element in each metal particle and the volume ratio between NiO and Ni reaches a relatively high value of 1.65 [14], the oxidation of Ni can thus give rise to a more intensive volume expansion of NiCr particles than that of Cr. Moreover, nickel cations diffuse more quickly through oxide scales than oxygen anions [14], i.e. NiO tends to grow outwards with voids generated inside the NiCr particles, which further enhances the effect of volume expansion. When internal stress intensity caused by the volume expansion reached the fracture toughness \(K_{IC}\) of the ceramic matrix, cracks were initiated from several sides of each metal particle, propagated in the ceramic matrix and were arrested by adjacent metal particles. Cracking of the ceramic matrix led to an increase in the surface area and an improved oxidation kinetics. An increase in the kinetic constants of the 75C and 50C samples was thus observed after an oxidation time of 5 h (Fig. 5), whereas the extent of increase for 50C is much lower than that for 75C. From the microstructure of oxidized 75C and 50C (Fig. 6 and 7), we note that the cracks in 50C is also much finer than that in 75C. These observations can be attributed to the higher phase connectivity of NiCr and resulting higher fracture toughness of 50C than those of 75C. Kinetic constant of 25C decreases monotonically during this period of time. Moreover, it exhibits the lowest extent of cracks in 25C among the composite phases. The reason is, on the one hand, the phase connectivity of NiCr in 25C is the highest among the composite phases. On the other hand, the simultaneous formation of a continuous NiO scale on the surface helps to reduce the surface area and to improve the oxidation resistance, as shown in Fig. 8.

After cracks were initiated, remaining unoxidized nickel cations diffused outwards through oxide scales into the cracks and filled the cracks with NiO, resulting in the formation of an interpenetrating network of NiO in the ceramic matrix, which reduced the surface area and the oxidation kinetics again. For the 0C sample, its kinetic constant keeps at a nearly constant value of only about 0.01 % h\(^{-1}\) from t=5 h up to the end of the process, indicating that all the open pores near the surface had been blocked by the formation of oxide scales. The porous 0C sample began to be oxidized like a dense metal from this point of time.

From the high-temperature oxidation behavior of the ZrO\(_2\)-ZrSiO\(_4\)/NiCr samples with different volume fraction of ceramic, we may conclude that in order to improve the oxidation resistance of ZrO\(_2\)-ZrSiO\(_4\)/NiCr FGMs processed by powder metallurgy, high relative density and low surface area are very beneficial on the one hand. On the other hand, fracture toughness of the ceramic-rich side of FGM should be improved, by for example adding high-temperature resistant fibers or applying elongated NiCr particles to increase the phase connectivity of metal.

5. Conclusions
High-temperature oxidation behavior of pressurelessly sintered ZrO\(_2\)-ZrSiO\(_4\)/NiCr samples with different volume fractions of ceramic is investigated in the present study. The oxidation kinetics depends strongly upon the phase connectivity of NiCr in the ceramic matrix, which also governs the crack pattern formed due to the volume expansion of NiCr particles. In order to obtain an oxidation resistant ZrO\(_2\)-ZrSiO\(_4\)/NiCr FGM, fracture toughness of the ceramic-rich side of FGM should be improved.
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