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Corrosion of pressureless sintered ZrB_2–$MoSi_2$ composite in H_2SO_4 aqueous solution

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Abstract

The corrosion behaviour in closed system of a pressureless sintered ZrB_2–20 vol% $MoSi_2$ composite was studied in 1.8 M H_2SO_4 solution at RT, 40 and 70 °C up to 90 h. The corrosion resistance is quite poor because of the easy leaching of ZrB_2 phase. $MoSi_2$ phase and secondary phases such as ZrO_2 and Mo_5Si_3 are less affected by acidic corrosion. After corrosion at RT and 40 °C, both the weight losses and the microstructural features indicate that the corrosion is not uniform through the specimens' volume. The weight gain data are greatly influenced by the amount of preferential corrosion sites on the samples surfaces (pores or scratches remaining after polishing). At 70 °C, the leaching of ZrB_2 is very fast and gas evolution occurs. Pourbaix diagrams indicate that at 70 °C ZrB_2 phase is less stable than $MoSi_2$ and the formation of Zr^{4+} cations.

Keywords: Composites; Corrosion; Borides; $MoSi_2$

1. Introduction

Diborides and carbides of zirconium and hafnium belong to a class of materials with extremely high melting temperatures, recently defined ultra-high-temperature ceramics (UHTCs). These compounds are of particular interest because of their properties such as, besides the highest refractoriness, high electrical and thermal conductivity, chemical inertness against molten metals or non basic slags and superb thermal shock resistance.[1] These properties make them attractive candidates for high-temperature applications where resistance to corrosion, wear and oxidation is demanded. However, due to their high melting point and high vapour pressure, the complete densification of pure borides and carbides powder mixtures needs extremely high sintering temperatures. The addition of $MoSi_2$ helps sintering ZrB_2 also under pressureless condition,[2] moreover $MoSi_2$ is an excellent structural and electroconductive ceramic that fulfils many of the requirements for high-temperature application.[3]

Literature is very scarce about aqueous corrosion of structural ceramic composites.[4–9] Previous studies on monolithic ZrB_2[6] and ZrB_2–SiC composite[7] demonstrated that the addition of SiC as secondary phase did not modify the corrosion behaviour of the ZrB_2 phase in aqueous environments. However, the addition of a secondary phase was found to influence the overall corrosion of ceramic composites because of its individual and specific corrosion characteristic, such as $MoSi_2$ in AlN–SiC and Si_3N_4 matrices.[8,9]

In this study, the corrosion behaviour of a pressureless sintered ZrB_2 + 20 vol% $MoSi_2$ composite was investigated in 1.8 M sulphuric acid aqueous solution at room temperature, 40 and 70 °C up to 90 h.

2. Experimental procedure

The dense ceramic composite, with the composition ZrB_2–20 vol% $MoSi_2$, was prepared by pressureless sintering in argon atmosphere at 1830 °C for 30 min. Rectangular plates 12.0 mm × 8.0 mm × 1.0 mm were cut and polished up to 6 μm. The specimens were sealed in a polyethylene tube containing 50 ml of 1.8 M H_2SO_4 solution (pH 0.13), previously thermostated at the test temperature in a stirred water bath. The free rotation of the PET bottles in the bath induced the stirring of the corrosive solutions. The corrosion tests were performed at room temperature (∼20 °C), 40 and 70 °C up to 90 h. After the tests, the specimens were rinsed in boiling deionized water, dried at 100 °C and then weighted to calculate the weight loss.

The microstructure of the corroded specimens were analysed through X-Ray diffraction, scanning electron microscopy (SEM) and microanalysis EDS.

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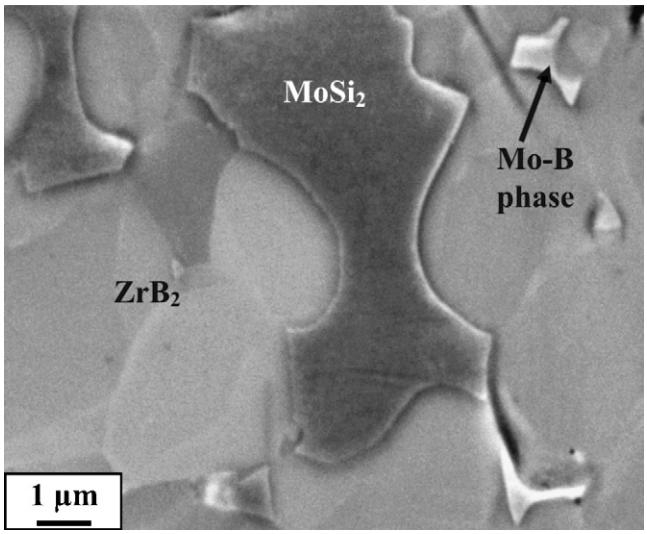

Fig. 1. SEM micrograph of the polished surface of the as-sintered ZrB_2–$MoSi_2$ composite.

Pourbaix diagrams (Eh versus pH) are calculated by HSC software package[10] to study the corrosion in acidic aqueous environment of the each phase.

3. Results and discussion

3.1. The as-sintered material

Detailed microstructural analyses of the pressureless sintered composite are described in ref.[2] The most important features are herewith summarized.

The final relative density of the ZrB_2–20 vol% $MoSi_2$ composite is 99.7%. The microstructure of the as-sintered material is represented in Fig. 1. The polishing procedure with colloidal silica produces different material removal rate on the various phases[2]: the globular grains are ZrB_2 phase (which appear to undergo preferential removal by polishing), while the phase appearing in relief is $MoSi_2$. The different contrast exhibited by ZrB_2 grains is due to their different crystallographic orientation. The following crystalline phases were identified on the XRD patterns: hexagonal ZrB_2, tetragonal $MoSi_2$ and traces of $Mo_{4.8}Si_3C_{0.6}$ (carbon is present as impurity in ZrB_2 raw powder and also in the sintering atmosphere). Detailed EDS analyses show the presence of Mo-rich phases with different composition in Mo–Si–C, Mo–Si–B and Mo–B systems and ZrC phase[2]: the estimated amount of these secondary phases is 3% in volume.

Table 1
Ratio R between the heights h of the $MoSi_2$ (1 0 3) and the ZrB_2 (1 0 1) peaks, after corrosion tests

Permanence (h)	$R_{MoSi_2(103)/ZrB_2(101)}$		
	RT	40 °C	70 °C
15	0.16	0.23	0.3
25	0.17	0.24	–
50	0.16	0.30	–
70	0.23	0.58	–
90	0.23	0.64	8.

3.2. The corrosion behaviour

After corrosion in the selected acidic environment, the sample surface exhibits extensive pitting (Fig. 2a), particularly ZrB_2 particles are preferentially corroded (Fig. 2b). Residual acicular shaped ZrB_2 crystals evidences the progressive leaching of that grains. Globular forms of Zr–B–O–Mo–Si phases are present on ZrB_2 particle after the leaching at both RT and 40 °C, while C traces are always detected after all corrosion test.

XRD patterns detected on the surfaces of the corroded samples show a progressive increase of the ratio R (1) between the intensities h of the $MoSi_2$ (1 0 3) and of the ZrB_2 (1 0 1) peaks:

$$R = \frac{h_{MoSi_2}}{h_{ZrB_2}} \quad (1)$$

R increases from 0.06 in the as-sintered material up to 0.3 and up to 8, respectively, after 15 and 90 h of exposure to H_2SO_4 solution at 70 °C (Table 1). This means that in the corroded sample surfaces, the amount of ZrB_2 decreases more than molybdenum disilicide. Moreover, the removal of the ZrB_2 phase allows to clearly reveal, by XRD, other secondary phases such as ZrO_2 and Mo_5Si_3 (Table 2). These phases are pre-existing, but not detectable by XRD in the original composite because of their very low amount in respect with ZrB_2 phases. However, the increment of ZrO_2 is caused also by the electrochemical corrosion of ZrB_2 phase. As reported in a previous work on ZrB_2 corrosion in acidic aqueous solutions,[6] in presence of sulphate

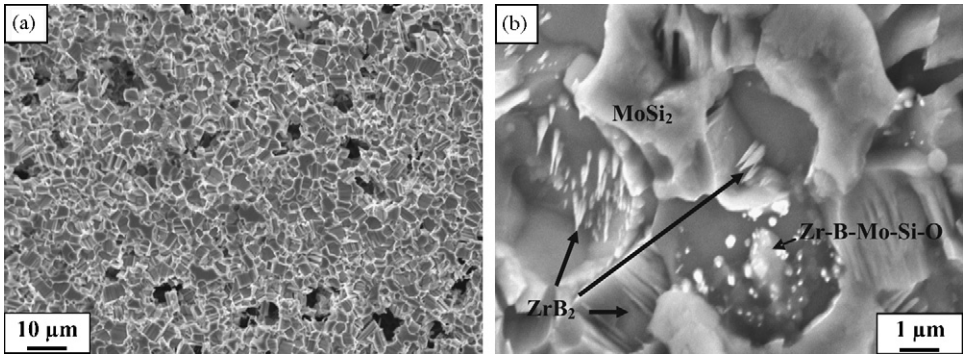

Fig. 2. SEM micrographs of specimens surfaces corroded at RT for: 90 h (a) and 50 h (b).

Table 2
Additional crystalline phases detected by XRD after corrosion tests

Phases	RT					40 °C					70 °C	
	15 h	25 h	50 h	70 h	90 h	15 h	25 h	50 h	70 h	90 h	5 h	90 h
Mo_5Si_3	–	–	–	x	x	x	x	x	–	x	x	x
ZrO_2	–	–	–	–	–	–	–	x	x	x		x

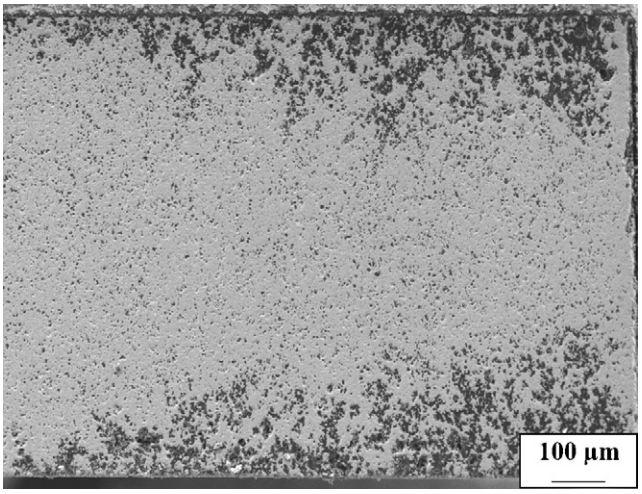

Fig. 3. SEM micrographs of the cross section of the specimen after a corrosion cycle of 50 h at 40 °C.

anions both soluble and insoluble products, such as boric acid, ZrO_2 and soluble complex of Zr(IV) are formed as follows:

$$ZrB_2 + 8H_2O \rightarrow ZrO_2 + 2H_3BO_3 + 10H^+ + 10e^- \quad (2)$$

$$ZrO_2 + 2SO_4{}^{2-} + 2H^+ \rightarrow [ZrO(SO_4)_2]^{2-} + H_2O \quad (3)$$

The penetration of the corrosion is deeper at the sample edges than in the middle of the samples as shown in Fig. 3. The analyses of the microstructure after the corrosion tests at room temperature and 40 °C give explanations of why the weight loss data do not clearly fit a definite law kinetic. In Fig. 4 a linear law is indicated, together with the experimental weight loss data: the regression coefficients are quite low as the corrosion is not uniform through the whole sample's volume. This is probably do to a different amounts of preferential corrosion sites, that concentrate particularly in the correspondence of pores or scratches consequent to the sample preparation and remaining, after polishing, especially at the sample edges. In these areas, enhanced corrosion is observed.

During the corrosion tests at 70 °C, a conspicuous gas evolution is detected inside the closed system. The leaching of ZrB_2

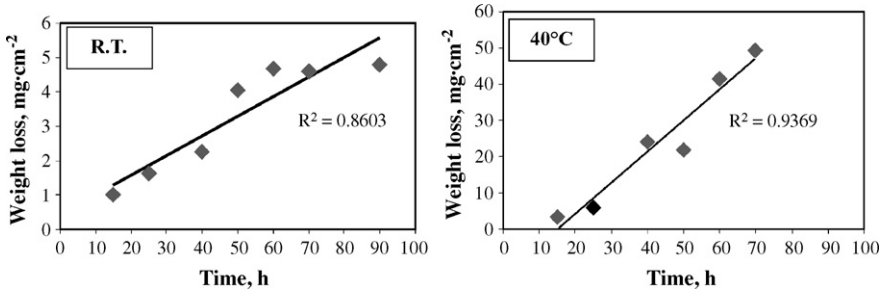

Fig. 4. Weight loss against time at room temperature and at 40 °C.

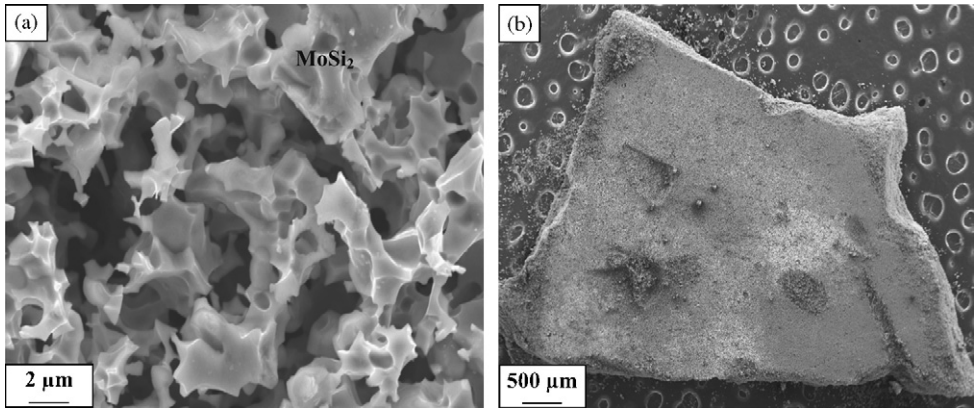

Fig. 5. SEM micrographs of the surface (a) and of the whole sample (b) after corrosion at 70 °C for 90 h.

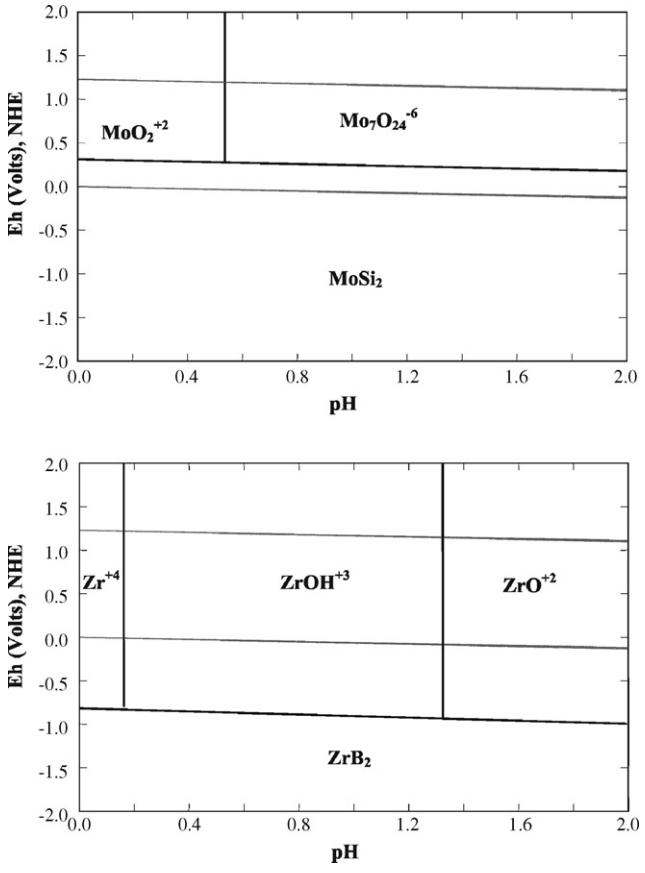

Fig. 6. Eh vs. pH plots of Mo–Si–H_2O and Zr–B–H_2O systems at 70 °C.[10]

is very fast and penetrates very deeply into the bulk material destroying the sample and leaving a $MoSi_2$ skeleton (Fig. 5).

Eh versus pH plots (Pourbaix diagrams) of the Mo–Si–H_2O and Zr–B–H_2O systems at 70 °C[10] are reported in Fig. 6. They indicate that, at low pH values, ZrB_2 phase is a less stable phase than $MoSi_2$ and the formation of Zr^{4+} cations. Tests carried out under deareated conditions at 45 °C and pH 1 showed that under free corrosion the cathodic reaction consists in oxygen reduction.[6] However, under more aggressive test conditions (pH < 0.2, higher temperature (70 °C)) and long exposure times in a closed system, the cathodic reaction is supposed to be the hydrogen reduction. This is consistent with the conspicuous formation of gas.

4. Conclusions

The chemical stability in of zirconium diboride in 1.8 M H_2SO_4 solution is quite low at RT and at 40 °C, and it is very low at temperature above 70 °C. Pourbaix diagrams at 70 °C indicate that the secondary phase $MoSi_2$ is more stable than ZrB_2. Thus, the ZrB_2–20 vol% $MoSi_2$ composite have a very poor corrosion resistance in acidic aqueous solutions, mainly because of the diboride matrix. The corrosion sites are strongly dependent on surface defects like pores, scratches, microcracks.

Acknowledgements

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