Pergamon

Scripta Materialia, Vol. 36, No. 9, pp. 1075-1080, 1997
Elsevier Science Ltd

1359-6462/97 $17.00 + .00

PII S1359-6462(96)00481-2

HIGH-TEMPERATURE REACTIVITY IN THE ZrW_2O_8-Cu SYSTEM

C. Verdon and D.C. Dunand
Department of Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge MA 02119, USA

(Received December 18, 1996)

Introduction

Zirconium tungstate (ZrW_2O_8) exhibits the unusual property of a negative coefficient of thermal expansion (CTE) over a wide range of temperature, from 0.3 to 1050 K. This property was reported about thirty years ago (1), but only recently were the structure of this compound solved, the low-temperature CTE measurement performed and a physical explanation for the negative CTE proposed (2). Zirconium tungstate, which is stable between 1105°C and 1257°C (3), is metastable at room temperature and decomposes into the base oxides ZrO_2 and WO_3 when heated above 750°C in air (4). Beside the fundamental physical interest of a negative CTE, the material is of great technological interest for low thermal expansion applications. However its complicated synthesis, which includes many days of heating at temperature above 1200°C, has prevented its large-scale use in engineering applications. The recent discovery of a more rapid precursor approach to the synthesis (2) is likely to change this situation.

As a reinforcement in a composite, zirconium tungstate can reduce the overall thermal expansion of the composite much more effectively than a ceramic with positive CTE. If a metallic matrix is used, the resulting composite will also exhibit high thermal conductivity, with applications such as heat sink for microelectronics devices (CTE matching that of silicon or alumina) or high precision optical elements subjected to thermal fluctuation (zero CTE) (5). As a matrix, copper is prime candidate, because it has the second highest thermal conductivity of all metals after silver, and because it can be easily processed within the temperature window imposed by the metastability of ZrW_2O_8. Moreover, copper is already widely used in electronics industry and can be easily soldered.

In the present work, we investigate the stability of ZrW_2O_8 when hot-isostatically pressed with copper, in order to explore the processing feasibility of a low thermal expansion, high conductivity ZrW_2O_8-Cu composite.

Experimental

Copper powders (99.5% pure, with size between 45 μm and 63 μm, from Cerac Inc. Milwaukee, WI) were blended with 23.5 wt% (33 vol%) zirconium tungstate powders (from Teledyne Wah Chang, Albany, OR) which had been crushed and sieved to match the size of the copper powder. The mixture was poured and compacted under a 300 MPa uniaxial stress into a low carbon steel can, which had been previously electrochemically coated with copper and lined with a copper foil to avoid contamination from the can. The evacuated can was subjected to hot isostatic pressing (HIPing) for 3 hours under a pressure of 103 MPa at a temperature of 600°C. As a control experiment, the above powder mixture was heat-treated for 3 hours at 600°C within an evacuated quartz tube gettered with titanium.

The initial powders, the processed composite, as well as the extracted ceramic phase from the composite (dissolution in 10% HCl solution), were examined by optical microscopy and X-ray diffraction. Thin foils were prepared by ion milling and observed in the transmission electron microscope (TEM, Jeol 200CX operated at 200 kV) and in an analytical scanning TEM (VG HB603) outfitted with an energy dispersive spectrometer (EDS).

Results

As shown by its XRD pattern (Fig. 1a), the as-received ZrW_2O_8 powder is almost pure. It contains only traces of other phases such as tungsten oxides. After heat treatment of ZrW_2O_8-Cu mixture at 600°C under vacuum and no stress, the ceramic is partially decomposed (Fig 1b). While a large fraction of the ZrW_2O_8 is retained, decomposition products include zirconium oxide and various tungsten oxides (6), including WO_3. This decomposition in vacuum at 600°C (below the literature decomposition temperature in air of 750°C(4)) is probably induced by an oxygen loss experienced by ZrW_2O_8, as suggested by the blue color of the titanium getter indicative of sub-stochiometric TiO_2 (7).

In contrast, the HIPed composite does not contain any ZrW_2O_8 (Fig 1c). The XRD pattern of the extracted ceramic shows that one or several new phases have appeared during HIPing, as a result of a reaction between copper and zirconium tungstate. The extracted powder has a dark-gray color different from

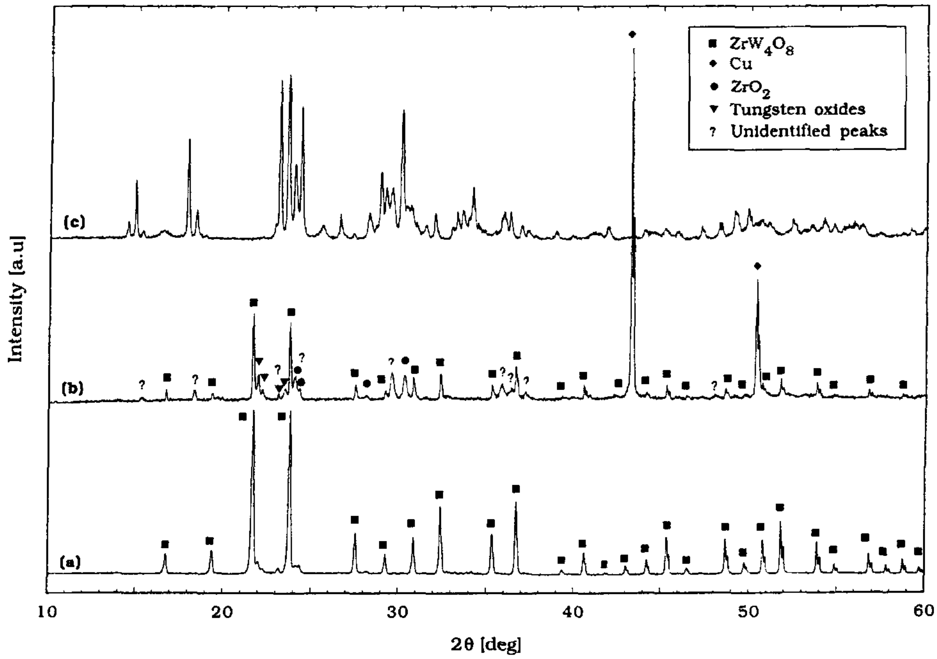

Figure 1. X-ray diffraction spectra: (a) as received ZrW_2O_8 powder, (b) ZrW_2O_8 and Cu powders, heat treated under vacuum at 600°C for 3 hr, (c) ceramic extracted from the HIPed sample (at 600°C for 3 hr); the latter spectrum is not indexed. Intensities are not directly comparable.

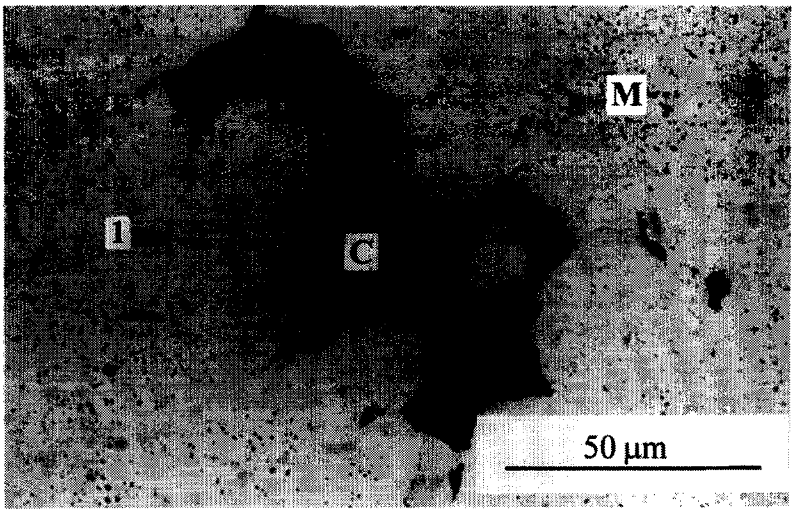

Figure 2. Optical micrograph of a polished section of the HIPed sample. The reacted and crushed ceramic powder (C) is embedded in the copper matrix (M) which contains Cu_2O precipitates. (1) indicates a native layer of copper oxide on a copper grain.

the white-greenish color of the original ceramic. Except for WO_3, the peaks recorded do not correspond to any compound listed in the ICDD data base (8) including the elements present i.e. W, Zr, Cu, O.

After HIPing the sample is fully compacted (Fig 2). A thin native oxide layer decorates the boundary of some of the powder original surfaces. The ZrW_2O_8 powder grains, which had originally blocky shape and a porous, sponge-like structure, were crushed between the Cu powders during the pressing operations. As a result, the reacted ceramic phase is discontinuous and is located in the gaps between the original copper powders. Most of the cavities and cracks in the crushed ceramic were filled with extruded copper. Despite some residual porosity, the density of the composite measured by water displacement (7.95 g/

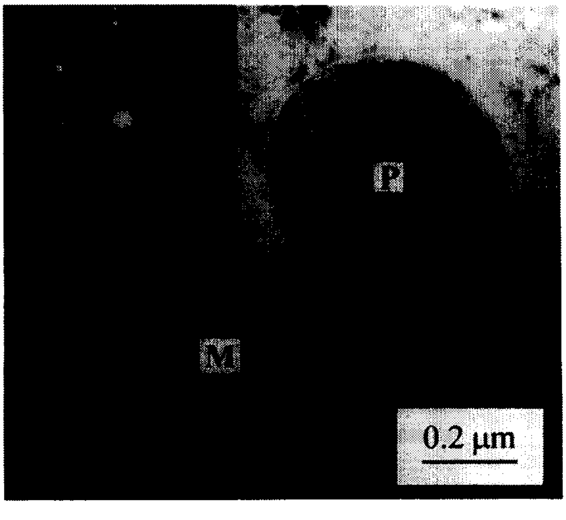

Figure 3. Bright field TEM image of a Cu_2O precipitate (P) embedded in the copper matrix (M). In insert, SAD diffraction of the precipitate indexed as Cu_2O.

cm^3), is above the theoretical value (7.63 g/cm^3) calculated from a simple rule of mixture with densities of copper (8.9 g/cm^3) and ZrW_2O_8 (5.072 g/cm^3) (4). This indicates that the compounds formed are on average denser than ZrW_2O_8.

Precipitates (Fig 2) with size less than 2 micron are present in the copper matrix with a non-uniform distribution. The regions directly surrounding the ceramic phase show only a few much smaller precipitates. These precipitates were identified as Cu_2O by selected area diffraction (SAD) in TEM. Figure 3 shows one of these spherical precipitates embedded in the copper matrix which contains a high dislocation density (probably resulting from the high strain undergone by copper during processing). On the insert, the SAD pattern is indexed as the [2,1,5] zone axis of Cu_2O. The few extra spots correspond to the copper matrix. Furthermore, EDS measurements in STEM confirmed that these precipitates contain oxygen, unlike the surrounding matrix, which was also found to be free of tungsten or zirconium.

In the ceramic phase, a precipitation in epitaxy with the matrix can be observed (Fig. 4). The EDS measurements revealed that both phases contain Zr, W, Cu and O. While a quantitative analysis was impossible because the peaks recorded are from both K and L types, very little difference in the peak intensities was found, indicating that the two phases in Figure 4 have a similar chemical composition.

Discussion

Figure 5 presents a schematic of the possible mechanisms explaining the experimental observations. At the early stage of HIPing (Fig 5 (a)), the two unreacted phases are in contact (the powder character is not represented here). Except for the pressure applied, HIPing is equivalent to a heat treatment under vacuum. Zirconium tungstate probably experiences oxygen loss (Fig 5(b)) under these conditions which is followed by decomposition. This fact was already reported for a temperature of 500°C (9), but in that case the gray-black product formed was found to revert to the stochiometric oxide (ZrW_2O_8) upon heating in air and no decomposition was found. As a consequence of the high coefficient of diffusion of oxygen in copper ($2.15 \cdot 10^{-10}$ m^2/s at 600°C (10)), the oxygen liberated by the decomposition of ZrW_2O_8 diffuses readily

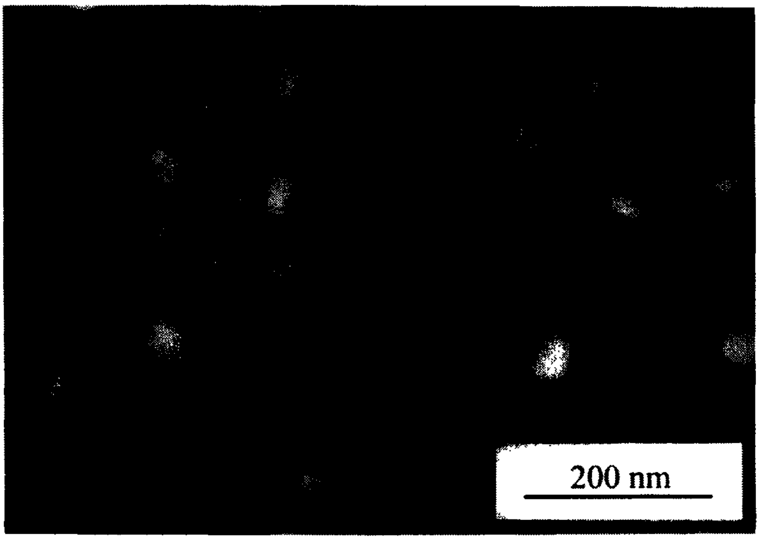

Figure 4. Bright field TEM image of the reacted ceramic showing precipitation of a second phase in epitaxy. Both phases contain W, Zr, Cu and O and have almost the same chemical composition.

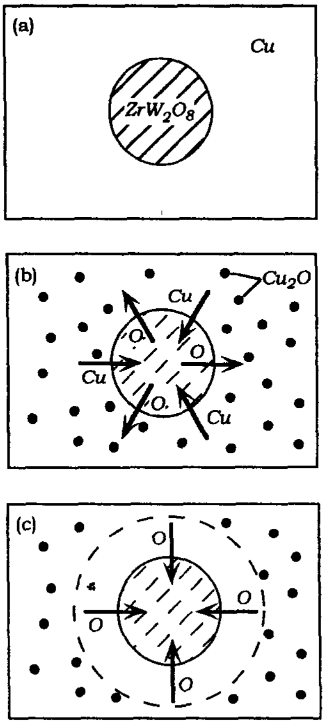

Figure 5. Schematics of proposed reaction mechanisms in the ZrW_2O_8-Cu system during HIPing. (a) early stage; (b) later stage; (c) cooling stage.

through copper (Fig. 5(b)). The time needed to travel a typical diffusion distance ($\sqrt{Dt}$), corresponding to the mean free path between ceramic particles, is about 100 s. Therefore, at the time scale of the processing, the oxygen concentration is constant throughout the matrix. At 600°C, this dissolved oxygen is in equilibrium with the lowest copper oxide Cu_2O (10). Copper thus acts as a oxygen sink and the oxygen partial pressure needed to stop the decomposition of ZrW_2O_8 is never reached. When the compaction of the powders provides an intimate contact between the two phases, copper diffuses into the ceramic phases. Because the species involved diffuse more slowly, this reaction occurs slower than the Cu_2O precipitation. In agreement with our EDS measurements, little diffusion of zirconium or tungsten is expected in the copper matrix, since the binary phase diagrams Cu-W (11) and Cu-Zr (12) show virtually no solubility of tungsten and zirconium in copper.

The precipitate-free zones observed around the ceramic suggest that some oxygen dissolved in the matrix diffuses back into the ceramic (Fig 5(c)), probably because the oxide formed needs more oxygen. These zones are unexpected since, as pointed out before, the diffusion of oxygen in copper at 600°C is very fast so that all the precipitates should dissolve at the same rate. It can thus be concluded that the back-diffusion of oxygen happened under cooling, when the coefficient of diffusion of oxygen is low enough to become rate-limiting.

The formation of Cu_2O during this experiment indicates that Cu_2O is more stable than ZrW_2O_8. There are only few oxides which are less stable than Cu_2O, namely those of noble metals, which can hardly be considered as a matrix for a composite because of their high price. Therefore kinetic control of the reaction must be used to successfully manufacture a ZrW_2O_8-Cu composite. This can be achieved by reducing processing temperature and time, a strategy currently in investigation in our laboratories. On the other hand, the reaction observed in this system can be useful. Indeed, depending on the temperature of processing, high residual stresses can develop at room temperature in the composite, since the phases have a very large CTE mismatch, and these stresses can lead to a delamination of the ceramic particles from the matrix and a concomitant increase in composite CTE. A controlled reaction could thus be used to enhance the bonding between ZrW_2O_8 and copper.

Conclusion

Blended copper and ZrW_2O_8 powders were hot-isostatically-pressed at 600°C for 3 hours. Reaction between the two phases resulted in a composite consisting of complex oxides (containing Cu, Zr and W) within a copper matrix with Cu_2O precipitates. We believe that two concurrent processes are taking place. First the ceramic loses oxygen and decomposes due to heating under low oxygen partial pressure, leading to the formation of Cu_2O within the matrix. Second copper diffuses into the ceramic to form new oxides which absorbs some oxygen upon cooling.

Acknowledgments

The authors acknowledge the support of the Swiss National Fund for Scientific Research (in the form of a post-doctoral scholarship for C.V.) and AMAX (in the form of an endowed chair at M.I.T. for D.C.D.). They are also grateful to Dr J.C. Haygarth from Teledyne Wah Chang for supplying ZrW_2O_8 powders.

References

1. C. Martinek and F.A. Hummel, J. Am. Ceram. Soc., **51**, 227 (1968).
2. T.A. Mary, J.S.O. Evans, T. Vogt and A.W. Sleight, Science, **272**, 90 (1996).
3. L.L.Y. Chang, M.G. Scroger and B. Phillips, J. Am. Ceram. Soc., **50**, 211 (1967).
4. Zirconium Tungstate Data Sheet, Teledyne Wah Chang, Albany, OR, (1996).
5. T.W. Clyne and P.J. Withers, An Introduction to Metal Matrix Composites, Cambridge University Press, 469 (1993).
6. Gmelins Handbuch der anorganischen Chemie, Wolfram Nr 54 B2, Springer-Verlag, 94 (1979).
7. Gmelins Handbuch der anorganischen Chemie, Titan Nr 41, Verlag Chemie, 214 (1951).
8. Powder Diffraction File PDF 2, International Center for Diffraction Data, Pennsylvania, (1994).
9. J. Graham, A.D. Wadsley, J.H. Weymouth and L.S. Williams, J. Am. Ceram. Soc., **42**, 570 (1959).
10. Smithells Metals Reference Book - 7th ed., Edited by E.A. Brandes and G.B. Brook, Butterworth Heinemann Ltd., 13-80 (1992).
11. P.R. Subramanian and D.E. Laughlin, Phase Diagrams of Binary Tungsten Alloys, Edited by S.V. Nagender Naidu and P. Rama Rao, Indian Institute of Metals, Calcutta, 76 (1991).
12. D. Arias and J.P. Abriata, Bulletin of Alloy Phase Diagrams, **11**, 452 (1990).