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Effect of solid solution formation on densification of hot-pressed ZrC ceramics with MC (M = V, Nb, and Ta) additions

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Abstract

ZrC ceramics with additions of MC (M = V, Nb, and Ta) were prepared by hot pressing, and the effect of MC additions on densification was analyzed in terms of the solubility limit and kinetics of formation of MC solid solutions with ZrC. VC additions of 2.5–10 vol% (3.5–13.5 mol%), which is higher than its solid solubility limit of 1.3 vol% (1.8 mol%), effectively promoted the densification process and nearly fully dense ZrC ceramics were obtained by hot-pressing at 1900 °C. In contrast, both NbC and TaC additions, which can form unlimited solid solutions with ZrC, have no obvious contribution to ZrC densification. This is because formation of the solid solution of NbC and TaC with ZrC matrix requires higher temperature and longer time due to their stronger bonding energy, compared to VC. SEM observation demonstrated that the VC addition resulted in larger grains, compared to ZrC ceramics with NbC and TaC additions.

Keywords: Hot pressing; Sintering; Carbides; Solid solution; Structural applications

1. Introduction

The refractory carbides of group IV–V transition metals, such as ZrC, HfC and TaC, comprise a family of materials, which have the NaCl crystal structure. ZrC has a unique combination of properties, including a very high melting point (>3540 °C), low density, high hardness, good thermal shock resistance and low chemical reactivity.[1,2] As a result, ZrC is a potential candidate for applications such as next-generation rocket engines and hypersonic spacecraft working at 2200–3000 °C.[3] In addition, ZrC has low neutron absorption cross-section and resistance to the corrosion of nuclear fission products.[4,5] In the framework of the Generation-IV international project, ZrC is one of the promising inert matrix materials to be used for some fuel components of high temperature nuclear reactors such as the gas-cooled fast reactor and high temperature gas reactor.[6–8]

As with other ultra-high temperature ceramics, such as ZrB_2, HfB_2 and HfC, owing to the strong covalent bonding and low self-diffusion coefficient, very high temperature (2300–2600 °C) and external pressure are required to densify ZrC ceramics.[9–11] Besides the sintering temperature, time and pressure, the densification of ZrC is also affected by the character of the ZrC powders used, including (1) purity, particle size and particle distribution of the raw ZrC powders; (2) additives; and (3) carbon vacancies or oxygen atom substitution onto the carbon sites. Zirconium carbide can be a non-stoichiometric compound ZrC_{1-x} with the C/Zr ratio ranging from 0.493 to 1. The sintering activation energy of ZrC_{1-x} decreases with increase of x value. For example, the relative density of the ZrC_{1-x} ceramics hot-pressed at 2300 °C for 5 min increased from 91% to 97.8% when the x value increased from 0 to 0.35.[11] This is because the increase in carbon deficiency in the ZrC_{1-x} lattice enhanced the mass transport and consequently the densification was accelerated.[12,13] Meanwhile, the intergranular glide and dislocation motion caused by the external applied loads can also contribute to the densification. Gendre et al. studied densification mechanism of $ZrC_{0.94}O_{0.05}$ powders by spark plasma sintering under several applied loads (25, 50, 100 MPa) and revealed that at a low macroscopic applied stress (25 MPa), an intergranular glide mechanism dominates the densification process, while dislocation motion happened at a higher applied load (100 MPa).[14] Reductive additives such as B, C and B_4C can act as densification

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aids to remove the oxide impurities present on the surface of the ZrC_{1-x} particles to activate the densification.[12,15,16] Other additives, like Mo and $MoSi_2$ promoted the densification by a liquid phase formation.[2,17]

In addition, solid solution formation also can promote densification by enhancing mass transport. Huang et al. reported that addition of VC in WC can promote the densification due to formation of the (V,W)C solid solution.[18] Hu et al. reported that the addition of $TaSi_2$ contributed to the densification of ZrB_2–SiC and HfB_2–SiC composites. A probable reason is that Ta atoms from the decomposition of $TaSi_2$ dissolve into boride grains and cause the decrease of the activation energy for diffusion at boride grain boundaries.[19] MC (M = V, Nb, and Ta) have high melting points and the same crystal structure as ZrC. Because the difference in covalent radii between Zr (1.597 Å) and V (1.338 Å) exceeds 15%, VC forms a limited solid solution with ZrC. As the covalent radius of Nb and Ta was 1.456 Å and 1.457 Å, respectively, a smaller radius difference (<15%) between Nb, Ta and Zr leads to a continuous solid solution of Nb and Ta carbides with ZrC.[20] The phase diagrams of ZrC–VC, ZrC–NbC and ZrC–TaC systems as shown in Fig. 1 demonstrate this tendency.[21]

The aim of the present work is to investigate the effects of MC (M = V, Nb, and Ta) additives, which have different solid solubilities and dissolution kinetics in ZrC, on the densification and microstructural evolution of ZrC ceramics.

2. Experimental procedure

2.1. ZrC Powder synthesis

ZrC powder was synthesized by carbothermal reaction between ZrO_2 and C at 1700 °C in vacuum. The starting powders were ZrO_2 and graphite powders and their impurity content, average particle size and suppliers are listed in Table 1. The ZrO_2 and graphite powders with the molar ratio of 1:3 according to Eq. (1) were ball mixed with ethanol in a plastic bottle for 24 h using ZrO_2 media (12 mm in diameter).

$$ZrO_2 + 3C = ZrC + 2CO(g) \qquad (1)$$

After mixing, the slurries were dried in a rotary evaporator at 70 °C, and then the dried powder mixtures were pressed into pellets with dimensions of 30 mm × 37 mm × 5 mm under a pressure of 0.1 MPa to improve particle contact for promoting solid state reaction at high temperature. Several pellets (50 g batches) were then placed into a graphite crucible and heated to 1700 °C for 1 h in a graphite resistance furnace (ZT-18-22, Shanghai Chenhua Electrical Furnace Inc., Shanghai, China). The total pressure in the furnace chamber was kept below 5 Pa by a vacuum pump. After the reaction, the furnace was cooled down to room temperature naturally. The reacted pellets were crushed to powder in an agate mortar and then sieved through a 200-mesh screen. The produced ZrC had 99% purity and an average particle size of 1–3 μm. The oxygen content of the as-synthesized ZrC powder was determined by Oxygen-Azote mensuration equipment (TC600, LECO, USA). VC, NbC and TaC (99% purity, 2–5 μm, Beijing Mountai Technical Development Center for non-ferrous Metals, Beijing, China) were used as additives.

2.2. Sample preparation

The synthesized ZrC powder and designated amount (1–10 vol%) of MC additives were mixed by ball milling in ethanol in a plastic bottle for 24 h using Si_3N_4 media with a diameter of 10 mm. The weight ratio of the powders to the Si_3N_4 media was 1:3. After mixing, the slurry was dried at 70 °C using a rotary evaporator. The dried powder mixture cakes were sieved through a 200-mesh screen to form granules. The granules of ZrC powder, with or without additives, were compacted in a graphite die lined with a graphite foil coated with BN. The powder compacts were heated at 10 °C/min to 1450 °C and held for 30 min under a mild vacuum (<10 Pa) for out-gassing. After out-gassing, the furnace atmosphere was switched to flowing argon (>10^5 Pa). In order to densify the powder compacts of ZrC powder, with or without additives, the compacts in the graphite die were subjected to a uniaxial pressure of 30 MPa and were heated at the same rate to the designed densification temperatures ranging from 1800 °C to 2000 °C with 100 °C intervals. The compacts were sintered at the densification temperatures for 1 h. At the end of the holding time, the furnace was cooled at a rate of 30 °C/min to 1700 °C, then the applied pressure was removed, after which the furnace was cooled naturally to room temperature. The produced specimens had dimensions of 37 mm × 30 mm × 5 mm.

2.3. Characterization

The bulk densities of the sintered ZrC ceramics were measured using the Archimedes method. The relative densities were calculated by dividing the measured bulk density by the appropriate calculated theoretical density that was based on the composition. The phase present was determined by X-ray diffraction (XRD, *D*/max 2550 V, Tokyo, Japan). The lattice parameters were determined by XRD using a Guinier–Hägg focusing camera (XCD-1000, Sweden) with $CuK_{\alpha 1}$ ($\lambda = 1.5405981$ Å) radiation. Si powder (99.99% purity) was used as an internal standard. The obtained photographs were evaluated with a computerized scanner system.[22] The lattice parameter of each sample was determined by means of the PIRUM program based on Guinier–Hägg film data.[23] The amount of MC dissolved in ZrC to form solid solution was determined by Vegard's law (a linear relation), which is based on the assumption of an ideal crystal structure. Secondary electron images of fracture surfaces and acid etched polished surfaces were taken by scanning electron microscopy (SEM, Hitachi S-570, Tokyo, Japan). The chemical composition and backscattered electron (BSE) image of the hot-pressed specimens were analyzed using electron probe microanalyzer (JEOL JXA-8100F, Japan) along with energy-dispersive spectroscopy (EDS, Oxford INCA energy). Some hot-pressed samples were ground and polished with a diamond paste to 0.5 μm and chemically etched using an acid mixture of HF: HNO_3: H_2O (volume ratio = 1:1:2) for microstructural investigation. The