Microstructure and Mechanical Properties of Ti-Zr-C-N System Compounds Prepared by Spark Plasma Sintering

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Chapter 1 Introduction

This chapter briefly introduced the Ti- and Zr-based non-oxide ceramics, such as carbides, nitrides and carbonitrides and their composites. Because of their high melting point, low densities, high hardness, excellent thermal stability and good corrosion resistance, Ti- and Zr-based non-oxide ceramics are promising as cutting tools, protecting coating, decorative coatings, jet engine parts, nose caps and leading edges re-entry space aircraft. However, low sinterability and poor fracture toughness of Ti- and Zr-based ceramics restrict their practical applications. TiC, TiN, ZrC and ZrN have an NaCl-type crystal structure and can form complete solid solutions as TiZrC, TiZrN, TiCN and ZrCN. The formation of solid solution may result in the modification of microstructure and enhancement in mechanical properties by solution strengthening. On the other hand, it is known that the TiC-ZrC and TiN-ZrN are immiscible at temperatures lower than 2400 K and 1610 K, respectively. By heat treatment of TiC-ZrC and TiN-ZrN solid solutions at a temperature lower than the consolute temperature, the solution decomposes into two phases and forms self-assembled nanoscale composites, yielding microstructure refinement. This process is attributed to spinodal decomposition that is a mechanism by which a solution of two or more components separate into distinct phases with distinctly different chemical compositions and physical properties without thermodynamic barrier to the growth of new phase. No research on the phase decomposition of Ti–Zr–C–N in the entire composition range was previously reported. The purpose of this thesis was to prepare TiC–ZrC, TiN–ZrN and TiCN–ZrCN composites by spark plasma sintering (SPS) and to investigate the effect of sintering temperature on the formation of complete solid solution, densification behavior and mechanical properties. Furthermore, the effect of subsequently heat treatment on the phase decomposition, microstructure evolution, mechanical properties of TiC–ZrC, TiN–ZrN and TiCN–ZrCN complete solid solution was investigated.

Chapter 2 Preliminary investigation
In this chapter, some physical, mechanical properties and preparation processes of the starting materials used in this study, such as TiC, ZrC, TiN, ZrN and TiCN (C: N = 3: 7, 1: 1 and 7: 3) powders were expatiated based on literature survey. All these Ti- and Zr-based carbides, nitrides, and carbonitrides have melting point over 3000 K, which are known as ultra-high-temperature ceramics, and have the same face-centered cubic crystal structures of an NaCl-type. Ti- and Zr-based carbides, nitrides, and carbonitrides all exist over a wide range of compositions due to the vacancies in the carbon or nitrogen sublattice. The Ti- and Zr-based ceramics have high hardness (TiC or ZrC: ~ 25 GPa; TiN or ZrN: ~ 21 GPa), whereas exhibit relatively low fracture toughness. To promote densification, Ti- and Zr-based ceramics are usually sintered with additives/binders, such as Ni, Co and Mo. The phase relationships in Ti−Zr−C−N systems were reviewed. The four quasi-binary systems of TiC−ZrC, TiN−ZrN, TiC−TiN and ZrC−ZrN all are complete solid solution systems. And at the same time, there is a miscibility gap in the TiC−ZrC and TiN−ZrN systems for phase decomposition. Therefore, TiC−ZrC, TiN−ZrN and TiCN−ZrCN can form a complete solid solution of (Ti, Zr)C, (Ti, Zr)N and (Ti, Zr)CN at high temperature and then the solid solution decomposes into Ti- and Zr-rich phases below the miscibility gap. The process of phase decomposition is spinodal decomposition, which is also discussed in this chapter. Spinodal decomposition differs from the classical nucleation: the phase separation by spinodal decomposition occurs uniformly throughout the material, not just at discrete nucleation sites. For compositions within the spinodal region, a homogeneous solution is unstable against microscopic fluctuations in density or composition, and there is no thermodynamic barrier to the growth of a new phase, i.e., the phase transformation is solely up-hill diffusion controlled. The precipitation by phase decomposition in the spinodal form usually showed a modulated fine microstructure and a substantial increase in physico-mechanical properties, which has been attributed to the isostructural decomposition and the resulting coherency strains between A- and B-rich domains. Most of the researches on spinodal decomposition have been performed mainly on the metallic alloy and oxide systems in the past several decades. The Ti−Zr−C−N system composites drew less attention and no research on the phase decomposition of Ti−Zr−C−N in the entire composition range was previously reported. The experimental procedure and characterization methods were generally described in this chapter. It is difficult to consolidate Ti- and Zr-based carbides, nitrides and carbonitrides by conventional sintering, because of the high melting temperatures, high degree of covalent bonding and low self-diffusion coefficients of the constituent elements of Ti- and Zr-based carbides, nitrides and carbonitrides. Spark plasma sintering (SPS) can be used to synthesize fully dense hard materials by applying a high-density direct pulsed current and load for a short time.
Chapter 3 Consolidation and phase decomposition of TiC−ZrC composites

In this chapter, results and discussion on consolidation of TiC−ZrC composites by SPS and phase decomposition by subsequent heat treatment are given. The TiC−ZrC composites were consolidated to form a solid solution by SPS at 1773–2473 K using TiC and ZrC powders as starting materials, and the effect of heat treatment temperature (1000–2273 K) and time (0.6−180 ks) on the phases, microstructure and mechanical properties of TiC−ZrC complete solid solution were also investigated.

For sintering, TiC−ZrC composites having TiC compositions above 60 mol% were densified to relative densities over 95% at sintering temperatures above 2073 K. In comparison, the densities of the Zr-rich composites with ZrC compositions above 80 mol% were below 90% relative density at 2373 K. At sintering temperatures below 2173 K, the sintered bodies were mixed phases of Ti- and Zr-rich (Ti, Zr)C. As sintering temperature increased, the lattice parameters of Ti- and Zr-rich (Ti, Zr)C increased and decreased, respectively, so that a single-phase (Ti, Zr)C formed with a uniform morphology. The single-phase (Ti, Zr)C and composites of Ti- and Zr-rich (Ti, Zr)C with TiC compositions above 80 mol% had relative densities greater than 97% and values of HV above 26 GPa.

For changing heat-treatment time from 0.6 to 180 ks, a 90TiC−10ZrC (mol%) composite was consolidated by SPS at 2373 K, resulting in the formation of a homogeneous (Ti, Zr)C solid solution. The heat treatment of (Ti, Zr)C at 1573 K caused phase decomposition into a Ti₀.₉₇Zr₀.₀₃C matrix and Zr₀.₉₄Ti₀.₀₆C nodules. The phase decomposition began from the grain boundary, and enlarged to the whole grain with increasing the heat-treatment time. The Zr₀.₉₄Ti₀.₀₆C nodules had widths of hundreds of nanometers and lengths of 0.5–3 μm and were dispersed in Ti₀.₉₇Zr₀.₀₃C matrix with the coherent orientation relationship of Ti₀.₉₇Zr₀.₀₃C {100} // Zr₀.₉₄Ti₀.₀₆C {100}. No evolution of the Zr₀.₉₄Ti₀.₀₆C nodules was observed after heat treatment for 36 ks. The HV and K IC increased with increasing heat-treatment time and reached 25.9 GPa and 3.3 MPa m¹/₂, respectively.

For changing heat-treatment temperature from 1000 to 2273 K in the entire composition range, the heat-treatment of TiC−ZrC at 10−70 mol% ZrC caused the decomposition into TiC-rich (Ti, Zr)C and ZrC-rich (Zr, Ti)C at 1473−2273 K for 3.6 ks. The heat treatment resulted in the formation of a nodular structure in the size of several tens to hundreds nanometers. With increasing the heat-treatment temperature, the lattice parameters of ZrC-rich (Zr, Ti)C and TiC-rich (Ti, Zr)C decreased and increased, respectively, and the average nodule length increased. TiC-rich (Ti, Zr)C and ZrC-rich (Zr, Ti)C showed coherent crystal orientation relationship of TiC-rich phase {100} // ZrC-rich phase {100} with lattice matching at the interface.
The highest $H_V$ and $K_{IC}$ were 26 GPa and 3.0 MPa m$^{1/2}$, for 80TiC–20ZrC heat-treated at 1873 K.

Chapter 4 Consolidation and phase decomposition of TiCN–ZrCN composites

In this chapter, results and discussion on consolidation of TiCN–ZrCN composites by SPS and phase decomposition by subsequent heat treatment are given. The TiCN (C: N = 1: 1)–ZrC composites were consolidated to form a solid solution (Ti, Zr)CN at 1773–2373 K by SPS using TiCN and ZrC powders as starting materials, and the effect of heat treatment on the phases, microstructure and mechanical properties of (Ti, Zr)CN complete solid solution were investigated. At last, the effect of C/N ratios on the phase decomposition of Ti–Zr–C–N system was also examined using starting powders of TiC, ZrC, TiN, ZrN and TiCN (C: N = 7: 3, 1: 1, 3: 7).

For sintering, TiCN–ZrCN solid solutions were densified to relative densities of 96–99% at sintering temperature above 2073 K. At sintering temperatures below 1973 K, the sintered bodies were mixed phases of Ti- and Zr-rich (Ti, Zr)CN. As the sintering temperature increased, the lattice parameters of Ti- and Zr-rich (Ti, Zr)CN increased and decreased, respectively. Single-phase (Ti, Zr)CN formed with a uniform morphology at sintering temperature above 2073 K. (Ti, Zr)CN at all compositions were fully consolidated with values of $H_V$ above 20 GPa. Comparing to the TiC–ZrC, the substitution of N for C reduced the critical sintering temperature of 200–300 K to form a single-phase solid solution and 1–2 GPa in the $H_V$.

For changing heat-treatment temperature for 3.6 ks, the heat-treatment of (Ti, Zr)CN at ZrC compositions of 20–80 mol% caused the phase-decomposition into TiCN-rich (Ti, Zr)CN and ZrCN-rich (Zr, Ti)CN at 1373–2173 K. The heat treatment resulted in the formation of a nodular or labyrinth-like structure in the size of several tens to hundred nanometers. TiCN-rich phase and ZrCN-rich phase showed coherent crystal orientation relationship of TiCN-rich phase \{100\} // ZrCN-rich phase \{100\}. The heat treatment resulted in an increase in the $H_V$ and $K_{IC}$ value of carbonitride system.

For the effect of C/N ratios on the phase decomposition, the sintering temperature for the formation of a single-phase solid solution increased from 1973 to 2473 K with increasing the C composition from 0 to 100 mol%. With increasing C composition, the lattice parameter of single-phase solid solution linearly increased from 0.431 to 0.441 nm, which was consistent with Vegard’s law. Ti–Zr–C–N complete solid solution by heat treatment decomposed into Ti- and Zr-rich phases at C compositions of 60–100 mol%, showing a nodular microstructure in the size of several hundred nanometers.

Chapter 5 Conclusions
This chapter concluded the current thesis.

In chapter 3 about TiC−ZrC, the sintered bodies were composed of Ti- and Zr-rich solid solutions at sintering temperature below 2173 K; at high temperature above 2273 K, a single-phase (Ti, Zr)C formed with a uniform morphology. TiC−ZrC at TiC composition above 60 mol% were densified to relative densities above 95% at sintering temperature above 2073 K and showed the highest Vickers hardness of 26.2 GPa. The single-phase (Ti, Zr)C at ZrC composition of 10–70 mol% was decomposed into TiC-rich and ZrC-rich phases by heat treatment at 1473–2273 K for 0.6−180 ks. The heat treatment resulted in the formation of a nodular structure in the size of several tens nanometers. The TiC-rich and ZrC-rich phases showed a coherent crystal orientation relationship of TiC-rich phase {100} // ZrC-rich phase {100} in the nodular structure formed by phase decomposition. The phase decomposition began from the grain boundary, and enlarged to the inside of the grain with increasing the heat-treatment time. With increasing heat-treatment time and temperature, $H_V$ and $K_{IC}$ were increased and reached 26 GPa and 3.0 MPa m$^{1/2}$.

In chapter 4 about TiCN−ZrCN, the sintered bodies comprised of Ti- and Zr-rich (Ti, Zr)CN at sintering temperature below 1973 K; at high temperature above 2073 K, single-phase (Ti, Zr)CN formed with a uniform morphology. The sintering temperature for the formation of a single-phase solid solution increased from 1973 to 2473 K with increasing the C composition from 0 to 100 mol%. TiCN−ZrCN was densified to relative densities of 96–99% above 2073 K and showed a maximum $H_V$ value of 22.5 GPa. The single-phase (Ti, Zr)CN at ZrC composition of 20–80 mol% was decomposed into TiCN-rich and ZrCN-rich phases by heat treatment at 1373–2173 K for 3.6 ks. The heat treatment resulted in the formation of a nodular or labyrinth-like structure in the size of several tens to hundreds nanometers. The TiCN-rich and ZrCN-rich phases showed coherent crystal orientation relationship of TiCN-rich phase {100} // ZrCN-rich phase {100}. The heat treatment resulted in an increase in the $H_V$ and $K_{IC}$ values of carbonitride system. Ti−Zr−C−N complete solid solution by heat treatment decomposed into Ti- and Zr-rich phases at C contents of 60−100 mol%, showing a nodular microstructure in the size of several hundred nanometers.