1 General Introduction

Zirconium carbide (ZrC) is the one of interest for ultrahigh temperature applications due to its high melting point (~3550 °C, respectively), solid-state phase stability, and good thermo-mechanical and thermo-chemical properties.[1] And it has typical faceted carbides with NaCl-type lattice structure, which exhibits many exceptional properties, such as high specific strength and hardness, high wear and corrosion resistance, as well as higher temperature tensile and creep strength. [2,3] Furthermore, these carbide particles are good obstacle for dislocation movement and can increase recrystallization temperature and hinder grain growth of tungsten matrix, which result in strength increment at elevated temperature.[4] Tungsten, due to its high melting point, is an ideal material for high temperature applications. In recent years, tungsten based composites with improved properties were developed. The W–ZrC composites present great erosion resistance and lower density. ZrC as the second phase in W–ZrC composite has some advantages, namely: (i) high melting point (3540 °C), (ii) its linear thermal expansion coefficient, (iii) its thermal conductivity is lower than tungsten [5], (iv) the density of ZrC is lower than W and (v) it can enhance the oxidation resistance of the composite because several reactions take place between hot gas and W–ZrC composite. Meanwhile, mechanical alloying (MA) of powder has been developed as a versatile alternative to other processing routes in preparing nanostructure materials with inert gas condensation, electro-deposition, rapid solidification, sputtering, crystallization of amorphous phase by annealing. And also MA is the commonly used method to synthesize nano-size materials. And from other study, nanocrystalline materials from mechanical alloying showed limited grain growth being strongly affected by the amount of lattice strain present due to the longer recrystallization time. [6] In the present study, grain size control by the amount of lattice strain in ZrC with MA. And finally we tried to determine the correlation between grain size and lattice strain during sintering of W-ZrC.

2. Preparation

ZrC and W-ZrC samples were prepared using commercial ZrC (<5µm, High Purity Chemicals) and W(~2.3µm High Taegutec). Mechanical milling was performed by dry planetary milling (Pulverisette 7, Fritsch, Germany). Tungsten carbide (WC-Co) balls were mixed with tungsten and ZrC mixture at a ball-to-powder ratio (BPR) of 40:1 by weight, and the milling was performed in WC-coated bowls at a speed of 250 rpm. SPS was performed at 1850°C for 0 min under vacuum at 30MPa pressure. All powders were analyzed by X-ray diffraction (M18XHF-SRA, Macscience, Japan) with Si as a standard. Crystallite size (L) and lattice strain (ε) were calculated from the FWHM broadening of the first five peaks of ZrC (111, 200, 220, 311, 222) and observed first three peaks of W (110, 200,211) in the 2θ range of 20-80° on sinθ, according to the Hall’s equation.
\[ \beta \cos \theta = \frac{K \lambda}{L} + 2 \sin \theta \]

where \( \beta \) was FWHM observed, shape factor K was assumed to be 0.9 and \( \lambda \) was a wavelength of CuK\( \alpha \) radiation (0.1540598\( \text{nm} \)). The microstructures of the sintered specimens were studied by scanning electron microscopy (JSM-6360, JEOL, Japan). The particle size distribution (PSD) was measured by laser analysis (Horiba LA920, Japan). The specific surface area was analyzed using the BET method (Micromeritics ASAP 2000 Analyzer).

3 Result

3.1 SPS of strained ZrC

Figure 1 shows the XRD results of as-received commercial ZrC powders as a function of milling time. XRD of the milled ZrC sample displayed peak broadening due to changes of the amount of lattice strain as a result of defects and particle size during milling. The ZrC phase has a relatively high thermal stability compared with other transition carbides of the same crystal structure. For example, TiC has a \( G_f \) of \(-162\) kcal/mol at 1700K, whereas ZrC has a \( G_f \) of \(-182\) kcal/mol at the same temperature. [7]

Thermal stability is related to bonding strength between transitional metal and carbon. Thus, ZrC has a much higher hardness (2600kg/mm\(^2\)) than other oxides, carbides, or nitrides. Previously, X-ray line broadening measurements showed that transition metal carbides can undergo heavy strains during high-energy ball milling. [8] Regardless of the high hardness and thermal stability, XRD peak broadening during milling showed that the planetary ball milling is enough to evaluate lattice strain in ZrC. The specific surface area and particle size distribution of the milled powder are shown in Figure 2 as a function of milling time. The average particle size of milled powders was determined by BET calculations to be around 200nm. The particle size differences between the calculated using the BET method and laser particle size analysis were interpreted as arising from agglomeration of tiny particles.

Figure 1. XRD data after planetary milling for (a) 5 hours (b) 10 hours (c) 20 hours (d) 40 hours.

Figure 2 (a) BET-calculated specific surface area and (b) particle size distribution of ZrC as a function of milling time. Measurements were made by laser technique.

So these results suggested that the milling time did not alter the particle size noticeably. The initial particle size was 5\( \mu \)m, and the particle size decreased dramatically until 10 hours milling, after which time the particle size stabilized. And the changes in the crystallite size and lattice parameter were monitored with respect to milling time (Figure 3). Those were calculated from the XRD peak broadening of the ZrC phase in Figure 1. using the Hall & Williamson method. The calculated results demonstrate that the crystallite size decreased with milling time, as shown in Figure 3(a). After 20 hours milling, the particle size decreased until it stabilized at \( \sim 2.0\) nm after 40 hours milling. Figure 3(b) shows that the lattice parameter increased with milling time, indicating an increase of disorder in the crystal
structure. The lattice parameter rapidly increased over the first 10–20 hours of milling. After 20 hours, the lattice parameter stabilized. The milling effect was apparently maximized at this time. In other words, the lattice structure of ZrC could not contain anymore, various defects such as vacancies, dislocations, and stacking faults beyond this point in the process. Therefore, the lattice parameter and crystallite size are showing the inverse proportion.

Figure 3(a) Crystallite size and (b) the lattice parameter as a function of milling time

Figure 4 shows the results of the lattice strain and microstructure after spark plasma sintering. In contrast with the results described above, the lattice strain increased during the first 10 hours then, decreased rapidly. This trend has been similarly reported previously. [9] The reason of decrease in strain was an offset between dislocations when the number of defects exceeded the maximum during mechanical milling. Also, milling can cause an increase in temperature due to the heat generated by collisions and due to friction between balls and particles. In a separate experiment, the temperature of the milling vessel increased to near 400°C. Although the covalent and metallic bonds in ZrC were strong, lattice structural changes may be introduced under such conditions. The average particle size of the powder before sintering was less than 200 nm. After sintering, the average ZrC particle size was 5–10 µm. Considering, that the pulverized fine powder contained agglomerates of less than 100 nm in size, the growth is significantly fast. It is normally explained by coalescence and coarsening of transition metal carbides [10] It is to be noted that the microstructures of the sintered specimens appeared to be correlated with the lattice strain trends, as shown in Figure 4.

The reason of this microstructure difference is thought to arise mainly under the applied lattice strain, because the powder particle size did not vary significantly, as shown in Figure 2. Previous studies have reported that lattice strain can inhibit grain growth in nanomaterial systems. [9,11-13] When this strained system receive some kind of energy, then the lattice is recovered, and recrystallization observed. The correlation between grain growth and decrease of strains leads to the conclusion that the reduction of strain is caused by the recrystallization process. Grain growth can start after a certain amount of lattice strain has been released. [12] This phenomenon is more obvious particularly under SPS conditions because the heat effects are least and the sintering times are relatively short. In conventional sintering, the heating and holding times are very long, so these phenomena are usually not observed. Short sintering times with maximum lattice strain enabled the control of grain growth.

3.2 SPS of strained W-ZrC composite
The SPS was conducted on the W-ZrC powders milled each time. The microstructure of commercial W-ZrC which means non-milled powder is showed in Figure 5. Dark side in this picture means ZrC ceramic particles. Huge agglomerate of tiny ceramic grains can be seen. The reason of this behavior is aggressive grain growth of W which can be shown in Figure 5(b). This grain growth drives ceramic particles into the triple junction point of W. It makes huge ZrC ceramic particle (~70µm). It can be one of reason to decrease density, mechanical properties and so on. Grain growth of W can be impeded by lattice strain too.

Figure 6 is XRD result with milling time. Although WC contamination is observed but peak broadening of W can be seen due to particle size and lattice strain effect during milling.

From this XRD result, we can determined lattice strain as seen in Figure 7. The black line (ZrC) is same with Figure 4, we can expect W has similar trend but we cannot calculate lattice strain of W after 20hours due to the too low intensity. After sintering, we can get homogeneous microstructure in fig 8. It has significantly uniform dispersion of ZrC in W matrix too. The unexpected microstructure is observed after 10hour milling due to the relatively high strain.

**4. Conclusion**

1. The change in the grain size of ZrC was investigated by sintering strained ZrC powder using
the SPS technique after applying a high-energy ball milling process. High energy ball milling increases lattice strain in ZrC crystal structure. The amount of strain can be controlled by milling time. High strain causes longer time to eliminate all strain and finally less grain growth. But general sintering requires long sintering times, which facilitate lattice structure healing and allow the initiation of grain growth. In contrast, we can decrease sintering time using the SPS method. The final average grain size in fully dense specimens was 3–5µm, and the lattice strain and particle size were controlled by applying the milling time and sintering method.

2. To suppress grain growth of tungsten in W-ZrC composite, we changed the amount of lattice strain with high energy ball milling too. Finally we can get uniformly dispersed ZrC in W matrix.

References