

Reaction-assisted sintering and platelet growth by adiabatic heating in WC–Si cermets

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Received 30 July 2013; accepted 23 September 2013

Available online 30 September 2013

Enhanced densification is observed between 1323 and 1573 K during the sintering of nanometric WC powders with Si addition. Microstructural observations and thermodynamics suggest that the exothermicity of a silicidation reaction that can lead to a temperature excess of nearly 500 K is probably the cause. At higher temperatures, the adiabatic heat of reaction prompts the recombination-climb of existing $1/6\langle 11\bar{2}13 \rangle$ partials from the prismatic to the basal planes, resulting in sudden platelet growth by 2-D nucleation on the $\{11\bar{2}0\}$ planes.

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Keywords: Tungsten carbide; Dislocation climb; Abnormal grain growth; Adiabatic heating

Dense nano scale tungsten carbide (n-WC) is currently being investigated for use as the preform or mould in the near net shape fabrication of flat aspheric lenses used in DVDs and cellular phones. High temperature coarsening and oxidation are consistent problems in the powder compaction of n-WC. These manufacturing hurdles are now overcome by resorting to activated sintering methods like spark plasma sintering (SPS) or microwave sintering, or by the addition of an elemental metal or compound that behaves as a sintering enhancer, leading to rapid densification even at sub-solidus temperatures [1,2]. Sometimes the high temperatures achieved with SPS, microwave or laser sintering can lead to a secondary reaction which may be self-sustaining in nature due to the exothermicity of the reaction (called self-propagating high temperature synthesis). The local temperatures can exceed the ambient by several hundreds of degrees; sometimes a partial transformation can also be effected leading to reactive sintering [3]. This report discusses certain specific traits that are observed in the activated sintering of n-WC with 1 wt.% Si and the mechanism of sintering enhancement and microstructural growth in the compacts.

Commercially purchased n-WC powder (70 nm by BET analysis and containing <0.4% oxygen) was ball

milled with 1 wt.% of Si powder (2–5 μm and 99.9% purity) in a planetary ball milling unit for 30 min. SPS was carried out in a Dr. Sinter Lab instrument fitted with a dilatometer (0.01 mm resolution) and a pyrometer focused on the graphite die for monitoring the linear shrinkage and temperature of the specimen during sintering. All samples were first compressed at 50 MPa, then ramped up to 873 K and held for 3 min for temperature stabilization; next, a set of samples were heated to various temperatures (1323, 1423, 1523, 1573 and 1673 K) at 50 K/min and held isothermally for 30 min; at the end of sintering, they were allowed to cool down inside the evacuated chamber to room temperature. Grain size measurements using a FESEM were conducted on cut, polished and etched cross-sections of the specimens. Two samples – one sintered at 1323 K and the other sintered at 1673 K – were chosen for transmission electron microscopy (TEM) analysis. TEM foils were prepared by polishing, dimpling and ion milling at 4 kV. For electron backscatter diffraction (EBSD) analysis, cross-sectioned specimens of the 1673 K sintered sample were polished successively by diamond paste with particle sizes of 1 and 0.25 μm and finally with ultrafine alumina.

Figure 1a,b compare the densification and coarsening the agglomeration-induced intermediate of n-WC–Si and pure n-WC. Apparently, trajectories density plateau [4] is significantly shortened with the addition of Si and the densification rate sharply increases thereafter up to

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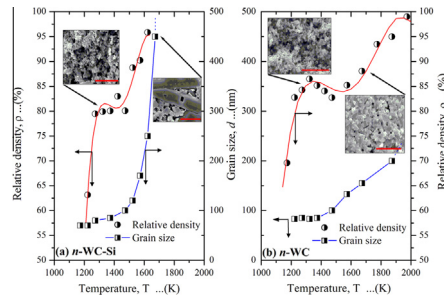


Figure 1. A sintering map showing the variation of measured density and grain size with temperature in (a) n-WC–Si and (b) n-WC. Distance markers in the inset images represent 1 μm .

1673 K, when the final density of $\approx 96\%$ pth is reached. The coarsening trajectory, on the other hand, was rapid above 1573 K for n-WC–Si, while pure n-WC showed restricted coarsening even at higher temperatures. In effect, to reach a final relative density of 95%, the sintering temperature is lowered by 250 K with the addition of Si. This sinter-enhancing step occurs between 1423 and 1673 K, but prior to the melting of Si at 1693 K. The highest linear densification rate in a continuous ramp experiment at 50 K min^{-1} was increased threefold by the addition of Si: the maxima in the $\dot{\epsilon}$ curve occurred at 0.12 min^{-1} between 1473 and 1573 K in the case of n-WC–Si, while pure n-WC under exactly similar SPS conditions showed two peaks, one at 0.042 min^{-1} occurring at $\sim 1373\text{ K}$ and another at 0.04 min^{-1} at $\sim 1850\text{ K}$. These macroscopic sintering observations point to a mechanism of sintering enhancement in a comparatively narrow temperature range with the addition of Si.

This change in sintering rate by Si addition was probed by analysing samples interrupted at various temperatures. X-ray diffraction (not shown) revealed that a silicidation reaction, leading to the formation of WSi_2 , was initiated at 1323 K and persisted until the end of sintering [5]. However, the fraction of the silicide, calculated from the normalized intensity ratios of the WC and WSi peaks after background reduction, was found to be very minor ($<3\%$), suggesting that, at low temperatures, the reaction could be spatially limited to regions very near the Si particles.

TEM investigations of the 1323 K sintered sample showed excessive planar defects lying on the prismatic planes, clearly evident by strong streaking along $g = \langle 10\bar{1}0 \rangle$. By conventional tilt experiments based on the invisibility criteria, it was found that these stacking faults (SFs) were bound by partial dislocations of the type $1/6\langle 12\bar{1}3 \rangle$, in accordance with dislocations commonly reported in sintered and deformed samples [6,7]. The origins of these defects were traced back to the powders, since such SFs were found in the raw powders too, manufactured by a chemical route of decomposing methane over pure tungsten (Figure 2a and b). Interestingly, pockets of amorphous carbon and graphite were also detected (diffraction from these regions showed diffuse ring patterns), and no WSi_2 could be detected in the WC matrix. In stark contrast, the sample sintered at 1673 K to $\sim 95\%$ relative density showed large abnor-

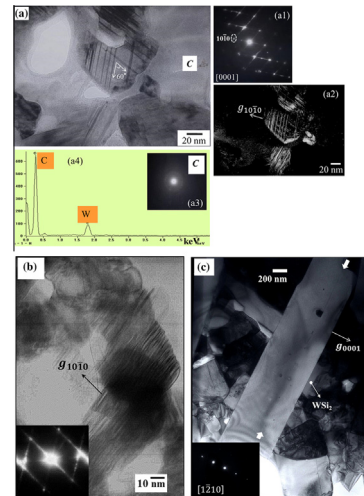


Figure 2. (a) TEM micrograph of an n-WC–Si sample sintered at 1323 K, showing SFs on the prism planes in the carbide grains and the occurrence of amorphous carbon (marked as C) in the microstructure. (a1) A diffraction pattern showing clear streaking along $\langle 10\bar{1}0 \rangle$; (a2) a dark-field image from one of the spots in (a1); (a3) the diffraction from the carbon, showing a diffuse ring; (a4) the X-ray energy-dispersive spectroscopy spectrum from region C, showing the strong presence of carbon. (b) TEM micrograph and diffraction pattern of ball-milled n-WC–Si powder showing prism plane SFs. (c) TEM image of a platelet from an n-WC–Si sample sintered at 1723 K, showing a thin fault line (denoted by thick arrows). The inset shows the diffraction pattern from the platelets.

mally grown platelets, constituting nearly 30 vol.% of the microstructure and small faceted grains. All of the platelets were invariably characterized by thin defect lines only on their basal planes; the prismatic planes, surprisingly, were found to be devoid of any defects (Figure 2c). This transformation in microstructure was abrupt and occurred at $\approx 1673\text{ K}$, when the W–Si eutectic phase is expected to form [5].

The results of the EBSD analysis confirmed that the platelets were mostly oriented along either the $\langle 10\bar{1}0 \rangle$ or $\langle 2\bar{1}\bar{1}0 \rangle$ long axis and the $\langle 0001 \rangle$ short axis. The GB misorientation angle chart obtained after a clean-up routine indicated two clear peaks, one at $\leq 5^\circ$, corresponding to low-angle grain boundaries (LAGBs), and another at $\approx 90^\circ$ which are high-angle grain boundaries (HAGBs) (Figure 3a–c). While this preferential clustering of faceted grains into two specific regions in misorientation angle space has often been reported in WC–Co cermets [8], in this case the LAGBs occurred almost three times more frequently than the HAGBs. Unlike the HAGBs, which are $\Sigma 2$ coincident site lattice (CSL) boundaries formed by a $\{0001\}$ – $\{1\bar{1}00\}$ pair [8], the LAGBs do not represent any specific orientation pair but rather point to a particle rearrangement mechanism occurring immediately after the formation of the liquid phase at around 1673 K [5]. While the high temperature microstructure is clearly a case of abnormal grain growth, what is interesting is that the low temperature partial dislocations seem to spontaneously climb over to the basal planes at the eutectic temperature. Intuitively the dislocation climb velocities, which are functions of the diffusion coeffi-

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