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14. ABSTRACT

Transition metal carbide (TMC) powders including TaC and ZrC with less than 300 nm in particle size have been successfully synthesized by a unique solvothermal approach. We have effectively modified the particle morphology of the TMC particles from round/irregular shapes to polyhedrons enclosed by {111} and {100} surfaces. We also report the formation of perfect/truncated nanocubes through the dual-effects of carbide diluent and transition metal doping. The TaC:Ni system demonstrated ~80% of morphological modification among the

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Tailored Carbide Morphologies: Materials by Design for Creep Resistance at Ultra-high Temperatures

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Summary

Transition metal carbide (TMC) powders including TaC and ZrC with less than 300 nm in particle size have been successfully synthesized by a unique solvothermal approach. We have effectively modified the particle morphology of the TMC particles from round/irregular shapes to polyhedrons enclosed by {111} and {100} surfaces. We also report the formation of perfect/truncated nanocubes through the dual-effects of carbide diluent and transition metal doping. The TaC:Ni system demonstrated ~80% of morphological modification among the particles evaluated. The governing mechanisms for Ni to have significant impact on morphological modification include (1) the selective absorption of Ni atoms onto {100} surfaces and (2) the molten Ni acts as diluent for carbon dissolution and diffusion. The effectiveness of the carbide diluent is attributed to its lowering of the maximum combustion temperature during reaction, which prevents particle surfaces from roughening and rounding, promoting exposure of facets.

1. Introduction

Transition metal carbides (TMCs) are ultra-high temperature ceramics (UHTCs) that have drawn great research attention as promising structural and functional materials for applications in harsh environments such as thermal protection of hypersonic vehicles and missiles, rocket propulsion components, high-temperature sensors, etc. Although TMCs possess extremely high melting temperatures (>3500°C), their use is still limited due to relatively poor oxidation resistance, degraded mechanical performance at elevated temperatures, as well as difficulties during sintering.

The crystal structure of Group IV-V TMCs, including TiC, VC, ZrC, NbC, HfC and TaC, is face-centered cubic (FCC, rocksalt), in which FCC lattices of transition metal and carbon atoms interpenetrate each other, filling up the octahedral interstitial sites. In general, the morphology control of these materials has received minimal attention. Grove *et al.* [1,2] investigated the particle morphology change of TiC and NbC nanoparticles synthesized using an arc discharge method using various types and amounts of gaseous carbon sources. They claimed that free organic molecules such as methane, ethylene and acetylene act as growth inhibitors for the {111} surfaces. Lower concentrations of methane resulted in the majority of TiC particles of cubic shapes, while higher methane concentrations resulted in cuboctahedrons. They attributed the change of morphology to the slowed growth rate of {111} surfaces in the presence of organic free radicals absorbed on the kink sites of the surfaces. Nie *et al.* [3] studied the morphology evolution of TiC particles synthesized by SHS in aluminum alloy melts and observed that the TiC particles have a cubic morphology when nickel is present in the melt compared to octahedral particles extracted mainly from non-Ni containing melts. They conjecture that Ni and other group VIII elements, i.e. Fe and Co, selectively absorb onto the {100} surfaces due to strong interactions between the metal 3*d* orbitals and the C 2*p* orbitals, reducing the surface energy of the {100} surfaces and resulting in a cubic particle morphology, where the {100} surfaces are exposed. Other researchers, such as Jin *et al.* [4], believe that carbon stoichiometry plays an important role in the final particle morphology. Low carbon stoichiometry usually leads to octahedral or truncated octahedral particles, while high carbon stoichiometry yields cubic particles.

In this project, we have explored the effect of dopant types and amounts, as well as several other secondary variables, on the preparation of cubic morphologies of TaC and ZrC during solvothermal synthesis of these materials.

2. Experimental

Tantalum(V) chloride [$TaCl_5$, 99.8%, Sigma-Aldrich] and zirconium(IV) chloride [$ZrCl_4$, 99.5%, Sigma-Aldrich] were used as the metal source for the preparation of TaC and ZrC. Dopant precursors were yttrium(III) chloride [YCl_3, 99.99%, Sigma-Aldrich], niobium(V) chloride [$NbCl_5$, 99%, Sigma-Aldrich], and nickel chloride [Purified, Spectrum Chemical]. For Ni-doped systems, pure Ni metal powder as a doping precursor was also evaluated in comparison to its chloride form. The tantalum and zirconium chlorides in some cases act as the dopants, i.e., tantalum carbide doped with zirconium (TaC:Zr) and zirconium carbide doped with tantalum (ZrC:Ta). Carbon black [>99.9%, Alfa Aesar] was used as the carbon source. According to the governing reactions involved in this solvethermal synthesis technique (**Eq. 1** and **Eq. 2**), granular lithium [Li, 99%, Sigma-Aldrich] was employed as the non-aqueous solvent and reductant:

$$TaCl_{5(s)} + C_{(s)} + 5Li \rightarrow TaC_{(s)} + 5LiCl_{(s)} \qquad \textbf{Eq. 1}$$

$$ZrCl_{4(s)} + C_{(s)} + 4Li \rightarrow ZrC_{(s)} + 4LiCl_{(s)} \qquad \textbf{Eq. 2}$$

The precursor powders were weighed and thoroughly mixed manually with mortar and pestle in an argon glovebox for 15 minutes. Granular Li was then added into the precursors and the powder-lithium mixture was transferred to a quartz test tube for preheating and ignition. Several samples were made with the addition of reaction diluents. For example, pre-synthesized TaC was added into the precursor mixture for the preparation of TaC powders. The mixture was rolled in the test tube for another 5 minutes to confirm that granular Li was completely covered by the precursor powders with no surfaces exposed. The test tube was brought out of the glovebox with a temporary para-film seal and fixed onto a tube clamp inside a fume hood. The volumetric external heating for initializing the reaction was provided by a stainless steel hollow cylinder wrapped with a dual-element high-temperature heating tape. The volumetric heating system was preheated to an inside temperature of ~400°C in order for the reaction to take place in a timely manner. Once ignited, the reaction for carbide formation is self-sustaining because of the large enthalpy of formation of the carbides. This is very similar to self-propagating high-temperature synthesis (SHS). The post-reaction test tube was air-cooled to room temperature. The reaction products were then rinsed with deionized water and washed with 15 vol.% hydrochloric acid solution two times, followed by another water wash and finally, an ethanol wash. The washed powders were dried in air for 24 hours prior to collection and characterization. All samples were subsequently analyzed by X-ray diffraction (XRD) on a Bruker D2 Phaser, and field-emission scanning electron microscopy (SEM) on a FEI XL30 SFEG UHR-SEM.

3. Results and Discussion

We studied the TaC:Y, TaC:Nb, TaC:Zr, TaC:Ni, ZrC:Ta, and ZrC:Ni systems. The amount of dopant was varied from 0 mol.% to 20 mol.%. It was previously demonstrated [5] that phase-pure TaC can be obtained through this unique solvothermal process. This is further confirmed by the present study with the addition of dopants. **Figure 1** illustrates the XRD patterns of undoped TaC and ZrC, as well as their general morphologies under SEM. The purity of both carbide phases is very high with only a minimal amount of residual graphite for the TaC sample and metallic Zr for the ZrC sample. The graphite impurity was completely eliminated in later synthesis by using an amorphous carbon source. The morphology for both TaC and ZrC particles is irregular in shape with particle sizes ranging from 50 to 100 nm.

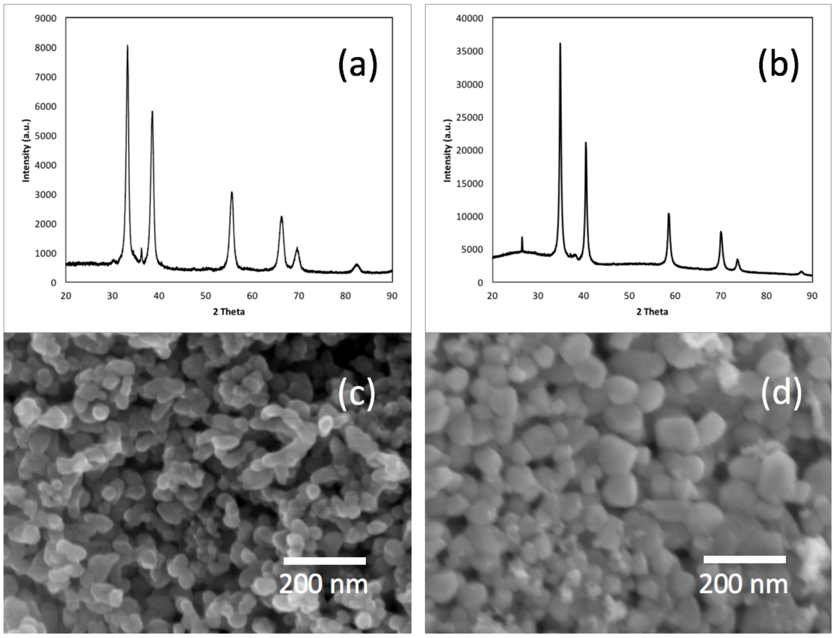

Figure 1. (a) XRD pattern and (c) particle morphology of undoped ZrC. (b) XRD pattern and (d) particle morphology for undoped TaC.

Yttrium as the dopant was first attempted. However, no significant morphological changes were observed for the TaC:Y system over the entire range of dopant amount. There is some level of promising morphological change in TaC:15Y sample (15 mol.% Y-doped), but the overall percentage of modified particles is very small. Only about 5% of the particles were modified. Less than 10% of the particles were modified in other systems, including TaC:Zr, TaC:Nb (without diluent) and ZrC:Ta, independent of the dopant amount. **Figure 2** illustrates typical morphologies of the TaC:Y, TaC:Zr, TaC:Nb (without diluent), and ZrC:Ta powders.

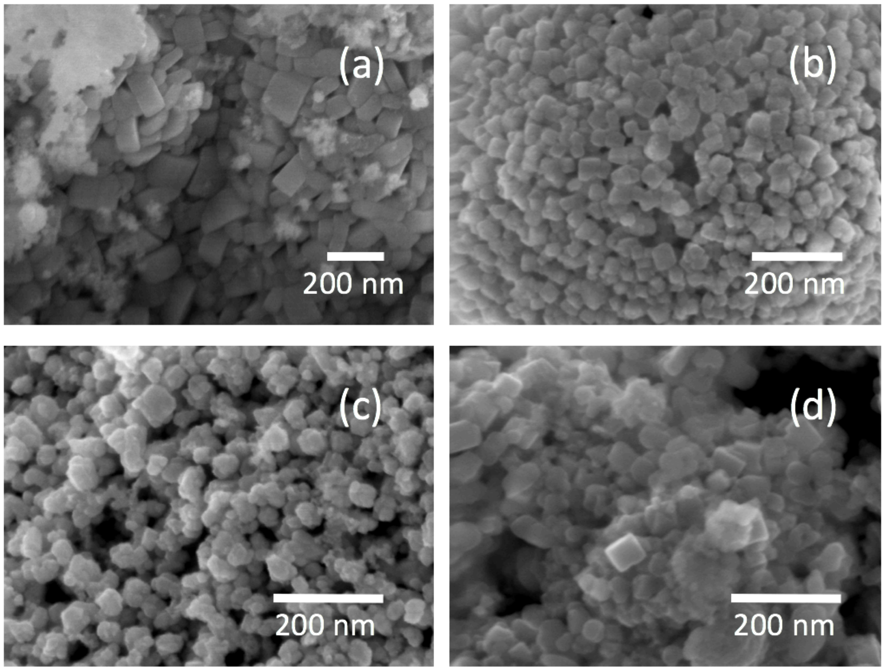

Figure 2. Morphologies of (a) TaC:15Y, (b) TaC:10Zr, (c) TaC:10Nb, and (d) ZrC:10Ta. Some faceted or even cubic particles are seen but the overall percentage is low (<10%) for these systems.

For high-temperature materials synthesized by SHS, reaction diluent is often used to control the microstructure of the particles formed. The diluent reduces the combustion temperature, preventing the particles from agglomerating. According to Jin *et al.* [4], the reaction temperature has a significant effect on the final particle morphology of TMCs. If the reaction temperature is high enough to exceed a critical temperature, surface roughening and rounding will occur, resulting in round and/or irregularly-shaped particles. We added 10 and 20 wt.% of previously synthesized undoped TaC product, with respect to the target weight of the new carbide product, together with the precursors (for a 3 g batch, this equals to 0.3 and 0.6 g of TaC diluent, respectively). **Figure 3** illustrates the general morphologies for each of the two compositions. It can be seen that the particles have more defined shapes compared to the undoped samples without diluent in **Figure 1**. Some particles exhibit truncated octahedral/cubic morphologies as the exposure of {100} surfaces becomes more pronounced, with about 20% of the particles exhibiting morphological changes. The effectiveness of TaC reaction diluent is believed to originate from reducing the combustion temperature. The surface roughening and rounding of ceramic particles at high temperature has been reported by many researchers and thermodynamic roughening is believed to dominate at high temperatures to reduce the Gibbs free energy [4,6,7,8]. **Figure 3(b)** illustrates an example of surface rounding. For those carbide particles synthesized without a diluent, surface roughening and rounding certainly plays a role in defining the final particle morphologies.

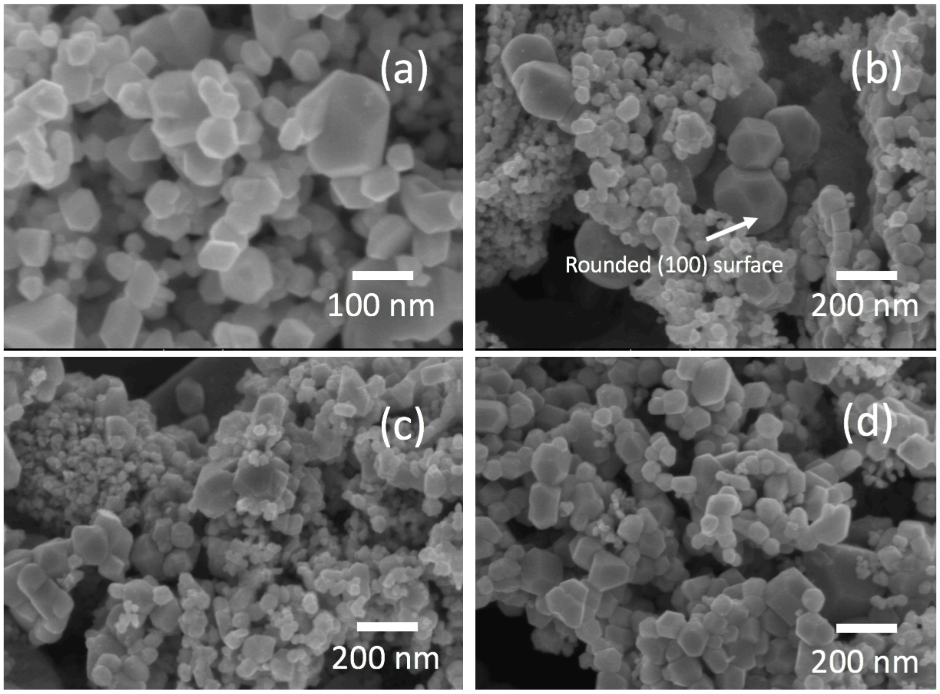

Figure 3. Undoped TaC particles synthesized with 10 wt% (a)(c) and 20 wt% (b)(d) TaC reaction diluent. Particles are seen in more defined shapes with a considerable amount (~20%) of particles enclosed by both {111} and {100} surfaces.

The effectiveness of the diluent is further confirmed in the TaC:Nb system. **Figure 4** illustrates cubic particles of TaC:10Nb synthesized using 10 wt.% TaC diluent. The percentage of morphologically-modified particles is increased to ~29%.

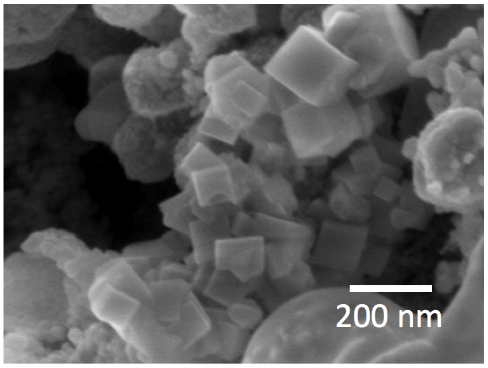

Figure 4. Cubic particles in TaC:10Nb with 10 wt.% TaC diluent added.

It has been reported by Nie *et al.* [3] that Ni is effective in modifying the morphology of TiC particles from octahedrons to cubes and, as previously discussed, they claimed that the selective absorption of Ni onto the {100} surfaces is the key factor for the morphological change. Thus, it is reasonable to expect that Ni will have a similar effect on other TMCs, including TaC and ZrC. TaC:5Ni was first produced by adding the corresponding amounts of $NiCl_2$ along with 20 wt.% TaC diluent. **Figure 5** illustrates the XRD pattern and SEM micrographs of the sample. The sample has excellent phase purity with just a minimal amount of oxide phases. In addition, over 70% of the particles are morphologically modified and enclosed by both {111} and {100} surfaces. Among these modified particles, ~10% can be classified as truncated cubes with {100} surfaces representing the majority of the surface area. This means that the growth rate of {100} surfaces in these particles has been significantly retarded by the combined effects of Ni doping as well as the TaC diluent. Polyhedrons equally enclosed by both {111} and {100} surfaces represent the morphology for most modified particles, meaning that during the formation of these particles, the growth rates of {111} and {100} surfaces are comparable.

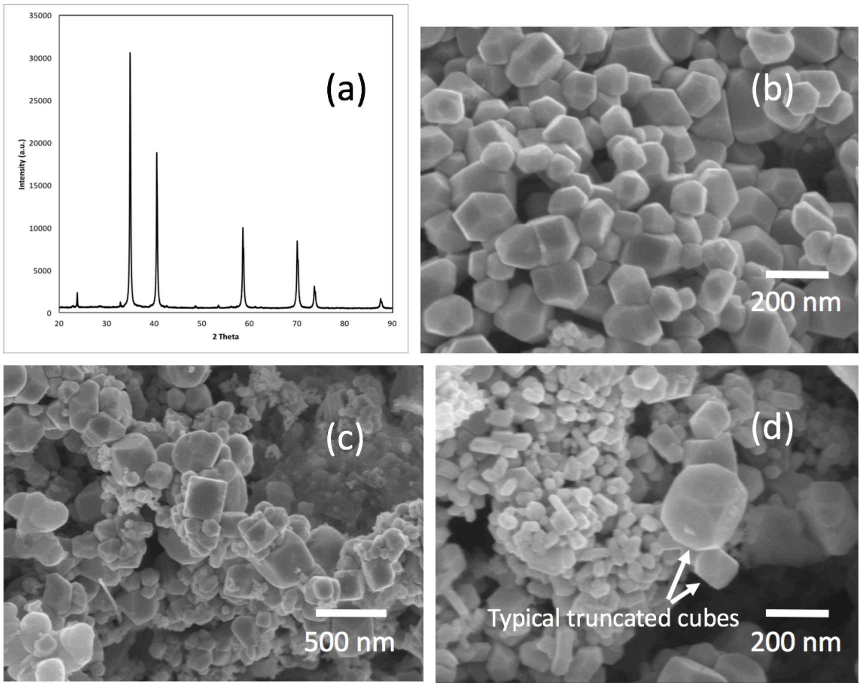

Figure 5. XRD pattern (a) and general morphologies (b)-(d) of TaC:5Ni using $NiCl_2$ as the doping precursor and 20 wt% TaC diluent. Over 70% of the particles have modified morphologies with ~10% of them being truncated cubes.

With just 5 mol.% of doping being this effective, one may think that increasing Ni content would ultimately lead to stronger modification effects. However, when the Ni content was increased to 10 and 20 mol.%, the percentage of particles modified decreased to ~65% and ~55%, respectively. While the exact reason behind this phenomenon is not yet confirmed, we believe the solubility limit of Ni in TaC matrix is responsible for this decrease. According to the mechanism proposed by Nie *et al.*[3], {111} surfaces in TMCs have alternating layers of metal and carbon atoms while {100} surfaces have continuous tiling of carbon atoms, Ni atoms therefore selectively attach to {100} surfaces due to strong interactions between the Ni 3*d* and C 2*p* orbitals. Assuming this is the only responsible mechanism for the morphological modification of TMCs, then there must be a critical Ni content which maximizes the doping effectiveness.

In an attempt to further increase the effectiveness of Ni doping, metallic Ni was used instead of $NiCl_2$ for the TaC:20Ni system. **Figure 6** illustrates the XRD pattern and particle morphology of the resulting sample. Again, the carbide phase is near pure with minor oxidation. The particles, on the other hand, show notable improvement with respect to the percentage of modification. Almost 80% of the particles are morphologically modified to polyhedrons enclosed by {111} and {100} surfaces. This number is considerably higher than the TaC:20Ni sample using the $NiCl_2$ precursor.

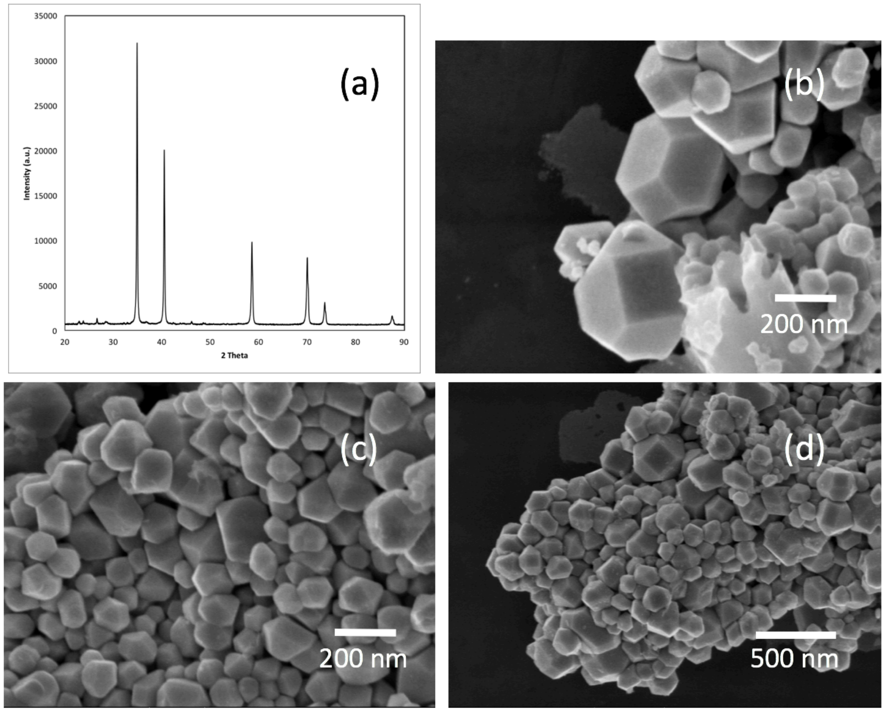

Figure 6. XRD pattern (a) and general morphologies (b)-(d) of TaC:20Ni using metallic Ni as the doping precursor and 20 wt.% TaC diluent. Approximately 80% of the particles have modified morphologies.

For FCC crystals in general, {111} and {100} are the two surfaces with the lowest surface energies and are supposed to dominate the final crystal morphology under equilibrium conditions. The actual shape of the particles depends on the relative growth rates of these two surfaces. Wulff's theorem states that the growth rates along the <111> and <100>

crystallographic directions are proportional to the surface free energies of the {111} and {100} surfaces, respectively [9]. For pure metallic FCC crystals, {111} has the lowest surface free energy due to the most close-packed atomic arrangement. Therefore, the morphologies of metallic FCC crystals are usually octahedrons or truncated octahedrons. However, for FCC crystals in rocksalt structures such as NaCl, the {111} surfaces are usually highly unstable because of the alternating layers of cations and anions along the <111> directions. In this case, the {111} surfaces have so-called high divergent electrostatic energy, which destabilizes the {111} surfaces and, thus, makes the crystal morphology cubic or truncated cubic [8,10]. In the case of TMCs, the bonding is a complex mixture of covalent, ionic and metallic. The covalent interaction between metal and carbon atoms is the strongest among these three types of bonding and it is highly directional along <100> directions. Therefore, once the activation energy barrier for Ti-C bond formation is overcome, the growth rate of the {100} surfaces surpasses the growth rate of the {111} surfaces and contributes to the formation of octahedrons at the initial stage of the combustion reaction because the adiabatic flame temperature is the highest to provide driving force for Ti-C covalent bond formation. In addition, during the initial stages of the reaction, the carbide seeds formed are usually highly sub-stoichiometric with a vast carbon deficiency. Correlating this to the situation in rocksalt crystals, in which the {111} surfaces are highly unstable due to strong charge transfer from cations to anions (strong ionicity), the newly formed carbide seeds have much more stable {111} surfaces simply because insufficient carbon atoms are present for metal atoms to provide charge transfer. As the combustion reaction moves forward, the temperature decreases and more carbon atoms start to diffuse into the lattice structure to increase the carbide stoichiometry. At this stage, the stability of {111} surfaces decreases due to increased ionicity along <111> directions and they begin to grow more quickly.

This results in a change of relative growth rates between the {111} and {100} surfaces. The metallic Ni, in our case, act as another path, aside from the molten Li, for carbon to diffuse and therefore help with exposure of the {100} surfaces. It should be noted that the solubility of carbon in molten nickel is quite large and even though the reaction temperature decreases from its peak, it is still high enough to keep Ni in molten form. Hence, it is reasonable to believe that the addition of metallic Ni helps destabilize the {111} surfaces by promoting carbon diffusion. On the other hand, although the percentage of cuboctahedrons is greater among all the particles evaluated for TaC:20Ni (metallic Ni) compared to TaC:5Ni ($NiCl_2$), the percentage of truncated cubes is lower in TaC:20Ni. Further verification is needed to better address this aspect. So far, we are able to draw preliminary conclusions that the effectiveness of Ni in morphological modification comes from two combined mechanisms: (1) Ni atoms selectively absorb onto {100} surfaces, reduce its surface free energy, and retard its growth; and (2) metallic Ni provides extra liquid phase for carbon dissolution and diffusion, increasing the surface free energy of the {111} surfaces and promoting their growth.

We have observed similar morphological modification in the ZrC:Ni system. **Figure 7** illustrates the XRD pattern and SEM micrographs of this sample. These powders contain some level of impurity phases of zirconium oxides, but the carbide phase is still predominant. It should be noted that for the ZrC:Ni system, LiCl salt was used as the reaction diluent and the Ni source is $NiCl_2$. The percentage of particle modification is around 30%. The results indicate that LiCl as a reaction diluent is not as effective as the host carbide counterpart.

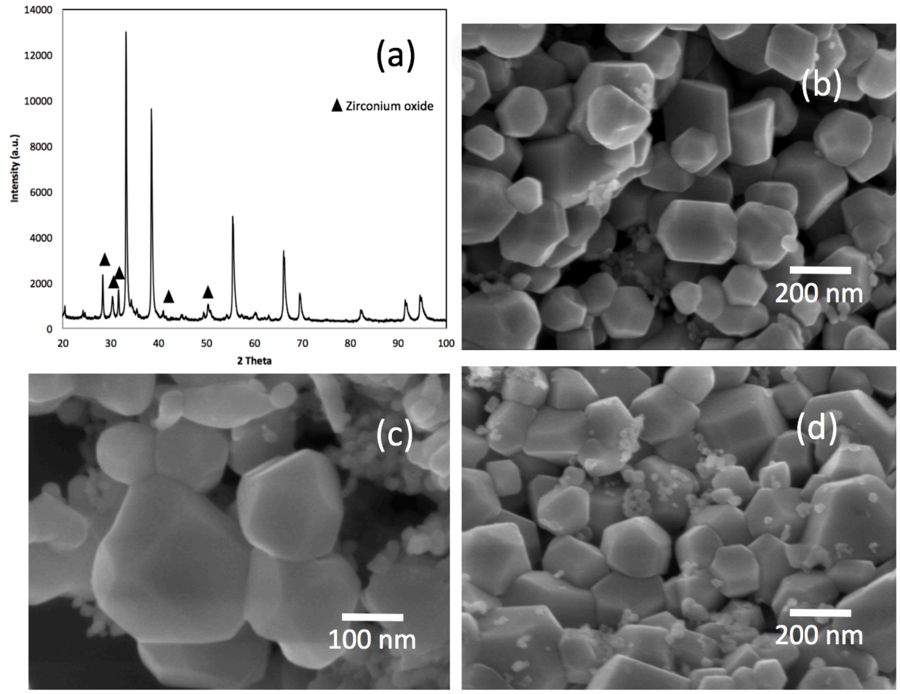

Figure 7. XRD pattern (a) and general morphologies (b)-(d) of ZrC:10Ni using $NiCl_2$ as the doping precursor and 10 wt.% LiCl diluent. Approximately 30% of the particles have modified morphologies.

Table 1 summarizes key statistics for the TaC:Ni and ZrC:Ni systems. Generally speaking, the increased amount of $NiCl_2$ dopant precursors lowers the percentage of particles modified in TaC:Ni system due to the solubility limit of Ni in the TaC lattice. There is no direct trend in the particle modification effectiveness for ZrC:Ni system with respect to the Ni content. For those TaC:Ni systems with high percentage of modification, the portion of perfect/truncated cubes are still small overall, but the ones with $NiCl_2$ as precursor have considerably higher percentage of perfect/truncated cubes compare to the one with metallic Ni.

4. Conclusions and Future Directions

We have successfully synthesized phase-pure near-stoichiometric undoped and doped TMCs including TaC and ZrC with less than 300 nm in size by a unique solvothermal technique that requires only moderate external heat input and simple experimental set-up. We have successfully modified the morphology of TMCs from round/irregular shapes to polyhedrons enclosed by {111} and {100} surfaces, truncated cubes with the majority of surfaces enclosed by {100} and even highly regular cubes. Among all the systems investigated, Ni dopant has the strongest impact on morphological modification of synthesized TMC particles.

Table 1. Summary of effectiveness of particle modification with Ni doping.

	Dopant Amount (mol%)	**Particles Evaluated**	**% Particles Modified**	**% Perfect/truncated cubes**
TaC:Ni (w/ 20 wt% TaC diluent)	5 ($NiCl_2$)	465	71.7	~10
	10 ($NiCl_2$)	432	64.9	~10
	20 ($NiCl_2$)	377	54.8	~7.7
	20 (Metallic Ni)	398	79.1	very rare
ZrC:Ni (w/ 10 wt% LiCl diluent)	5 ($NiCl_2$)	345	30.7	-
	10 ($NiCl_2$)	495	37	-
	20 ($NiCl_2$)	392	28	-

The governing mechanisms for Ni to affect morphology include:

1. Due to the strong interaction between the Ni 3*d* and C 2*p* orbitals, Ni selectively absorbs onto {100} surfaces by reducing their surface free energy and resulting in {100} surface exposures,
2. Metallic Ni provides extra molten phase during synthesis for carbon atoms to dissolve and diffuse into the host carbide lattices, shortening the time frame for increasing the carbon stoichiometry and destabilizing {111} surfaces due to increased ionicity along the <111> directions. The growth rate of {111} surfaces is therefore promoted, resulting in less {111} surface exposure and more {100} surface exposure.

The synthesized undoped carbides used as reaction diluents are shown to positively impact the final particle morphologies. We attribute this to less surface roughening/rounding of particles that occurs at the reduced maximum reaction temperatures with the addition of carbide diluents. Although the results are inspiring, there are still many unknown effects associated with the growth of TMC particles through this specific route that we will explore in future efforts.

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