

# Synthesis and Characterization of ZrC Nano-Powder and its Potential Role to Increase the Cladding Material Properties

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**Abstract:** Nanocrystalline powders of ZrC were prepared by mechanochemical synthesis of elemental Zirconium (Zr) and Carbon (C) powder. Two different Process Control Agents (PCA's), i.e. Toluene and n-Hexane were used to avoid the agglomeration of the nanoparticles. For the purpose of the present study, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) have been employed. A complete single phase of fcc-ZrC was obtained after 165 ks of milling time. No impurity other than oxygen was detected in the samples. n-Hexane compare to toluene was observed to inhibit the agglomeration more efficiently. ZrC nanoparticles were successfully synthesized indigenously, using mechanochemical synthesis. This can be used as a potential coating agent in indigenous industry specially the nuclear power industry.

**Keywords:** Mechanochemical Synthesis, Nanocrystalline ZrC, Process Control Agents (PCA), Indigenous Industry Applications

## 1. Introduction

Over the last years nanomaterials; materials with grain sizes less than 100 nm have received much attention as advance engineering materials with improved physical and mechanical properties [1],[2]. Among the other synthesis techniques, Mechanochemical Synthesis involves a popular technique for fabrication of several amorphous, metal carbides, metal nitrides, alloys and nanocomposite materials, has been considered a useful technique for synthesizing numerous nanocrystalline materials [3]. Recently, the MA process has become a popular method to fabricate nanocrystalline materials due to its simplicity and inexpensive equipment, comparatively low cost raw materials and high yield [4]. Zirconium carbide (ZrC), like other carbides of the transition metals of Groups IV, V, and VI, exhibits an unusual combination of properties that are appealing for refractory applications. These carbides combine the cohesive properties of covalently-bonded ceramics -high melting point, high strength

and hardness - with the electronic properties of metals - high thermal and electrical conductivity, metallic slip systems [7], [8].

ZrC belongs to the family of Ultra high temperature ceramic (UHTC) compounds that include the Group IVB carbides along with Ta and W, and is a promising material for ultra-high temperature applications due to its high melting point (~3550 °C), solid-state phase stability, and good thermo-mechanical and thermochemical properties. Zirconium carbide (ZrC) is among the hardest known compounds with microhardness value of ~ 2600 kg/mm<sup>2</sup> and high electrical conductivity and it could be reasons of various applications such as cutting tools, wear-resistant components, thermophotovoltaic radiators, field emission arrays and as a diffusion barrier coating on UO<sub>2</sub> particles in the nuclear industry. ZrC also exhibits high emissivity and high current capacity at elevated temperatures. Thus, zirconium carbide is a promising material for use in thermophotovoltaic radiators and field emitter tips and arrays [9], [10].

## 2. Potential Role of ZrC to Increase the Cladding Material Properties

Owing to its amazing properties mentioned earlier, such as good thermal conductivity, reasonable coefficient of thermal expansion (CTE), high melting point (thermal Stability), Phase Stability, high mechanical strength, good irradiation stability, resistance to fission product attack, low neutron absorption cross-section, ZrC potentially can be used to improve the cladding material performance. The idea was to employ nanocoating of ZrC on Zr-4 cladding. This will enhance cladding material properties like tolerance against fission product attack, oxidation resistance capability, hydrogen embrittlement. The properties of ZrC which may make it a suitable choice as coating material are reported in literature. Y. Kato et al [17] and H. F. Jackson et al. [18] have reported a detail review of the currently available literature on these properties. Their results are summarized in Table 1. These properties shows reasonable compatibility with those of Zr-4. So ZrC can potentially be used as a coating material on Zr-4, however, detail study is required to finalize ZrC as a coating material. Before switching towards the application of ZrC as a coating material, the main problem we had the availability of ZrC nanopowder. Unfortunately ZrC nanopowder is not available in Pakistan commercially, so we decided to synthesize it indigenously.

**Table 1:** Some properties of ZrC as reported in literature [17], [18]

Property	Value	Behaviour
Thermal Conductivity	20-40 W/m.K	<ul style="list-style-type: none"> <li>Increases with increasing Temperature</li> <li>Depends upon C/Zr</li> </ul>
Thermal Expansion	$6.5 \times 10^{-6}/K - 7.4 \times 10^{-6}/K$	<ul style="list-style-type: none"> <li>Slightly increases with increasing temperature</li> <li>Depends upon C/Zr</li> </ul>
Oxidation	Oxidize in air at 500-900 K	<ul style="list-style-type: none"> <li>Depending on temperature, porosity, partial pressure of oxidative and reductive gas species (from the reaction), carbon content, and impurities</li> </ul>
Fission product retention	Good	<ul style="list-style-type: none"> <li>Good resistance to: Cesium (Cs-137), Palladium (Pd-46), Europium (Eu-154), Cesium (Ce-144), ruthenium (Ru-103), barium (Ba-140) and niobium(Nb-95).</li> <li>The release of xenon-133 from is reported to depend strongly on the C/Zr ratio and temperature</li> </ul>

On the industrial scale production of  $ZrC_x$  have been reported by the reactions of zirconium, zirconium hydrides ( $ZrH_2$ ), and zirconium dioxides ( $ZrO_2$ ) with carbon [11],[12],[13],[14],[15], using the methods listed in Table 2 [16]. Accordingly high cost of preparation is the disadvantages of these methods.

**Table 2:** Methods for fabrication of  $ZrC$  via the technique of Powder Metallurgy

Method	Reaction
Direct reaction between metallic elements and graphite	$Zr + C \rightarrow ZrC$
Direct reaction between metallic hydrides and graphite	$ZrH_2 + C \rightarrow ZrC + H_2$
Reduction of the metal oxide by graphite under vacuum or inert gas	$ZrO_2 + 3C \rightarrow ZrC + 2CO$

Owing to the difficulty of mixing the reactants on a fine scale (e.g., molecular-scale mixing), these synthesizing processes generally require relatively high reaction temperature, ranging between 2000 to 2300 K and long soaking time of several hours or more. The high synthesizing temperature usually leads to the fast growth of the  $ZrC_x$  grains, making it difficult to obtain the  $ZrC_x$  products with grains in nano or ultrafine scales. Mechanochemical synthesis or mechanical alloying is potential synthesizing process for nanoparticles of the transition-metalcarbides without external heat source [6]. During the high energy milling process the constituent powder are repeatedly welded, fractured, and rewelded. The powder particles have the tendency to reweld together soon after they are fractured [5]. Generally, cold-welding is hard to be avoided in the process of directly milling Zr with carbon, which makes it difficult to obtain the  $ZrC_x$  nanoparticles with a uniform distribution of size. In the mechanically milling process, process control agents (PCAs) can be used to avoid cold-welding and improve the pulverization of the materials [6].

### 3. EXPERIMENTAL

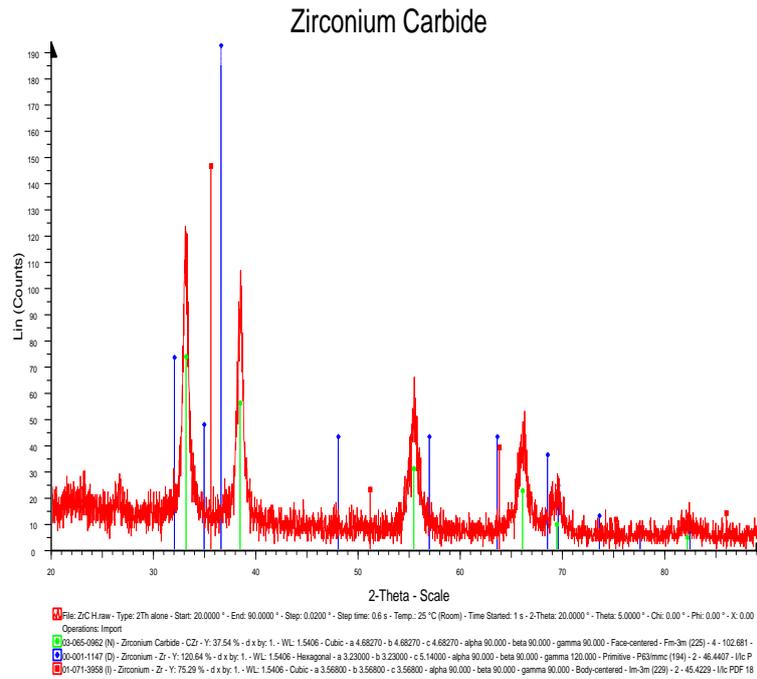
The Elemental Zr- and C- powder were used as starting materials. Mechanochemical synthesis technique was chosen as a synthesis route during this study because of its various advantages, such as:[11] for its simplicity, low cost of raw material, high yield and not requiring any external source. From the above two figures we concluded that n-Hexane compare to toluene is a better PCA to assist the carburization for the synthesis of a complete fcc-ZrC phase and inhibit the agglomeration of the nanoparticles during the milling process to be 11:1. The jars (50 ml in volume) and the balls (10mm in dia.) used were made of Tungsten carbide (WC). The two jars were then clamped, sealed and loaded into the planetary ballmill (Model: Retch, PM 200). The machine was set at a speed of 300 rpm, in dual mode .i.e. both forward and reverse milling after each three minutes (i.e. interval of 3 minutes) , with a break time of 5 seconds. The planetary ball mill was run at these parameters for one hour to test the machine is working properly. In the next phase the machine was set at a speed of 250 rpm, in dual mode with interval of 5 minutes and break time of 1 minute as in Figure 1. The milling was performed for two days, thus total milling time of ~ 46 hrs (~165ks). The jars were opened and to extract the powder Alcohol and Acetone were added to the jars containing Toluene and n-Hexane, respectively. The powders were extracted and left to dry for about 7 days at room temperature.

## 4. Results and Discussion

### 4.1. XRD Analysis

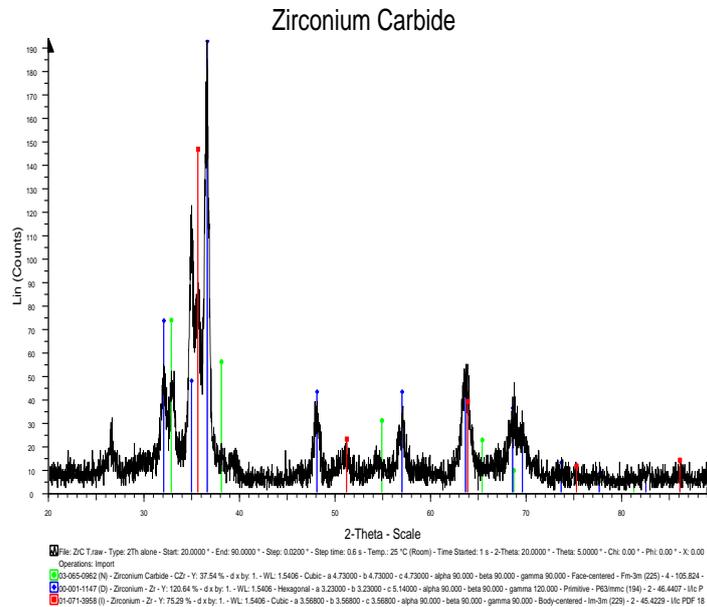
The XRD analysis were made to identify the different phases present in the samples. The XRD patterns of the two samples synthesized using n-hexane and toluene as PCA's are shown in Fig.1 and

Fig. 2, respectively. Fig.1 shows formation of fcc- ZrC phase, with Fm-3m (space group, 225) crystal structure as reported in the literature.



**Fig. 1 - XRD pattern of the ZrC sample synthesized using n-Hexane as PCA.**

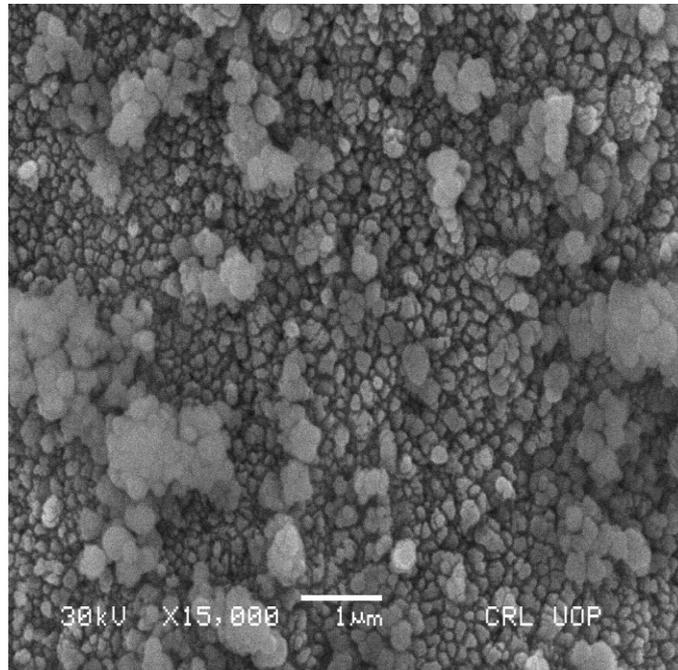
Figure 2 shows some peaks matching with zirconium and carbon peaks indicating the existing of free Zr and C in the sample. There are some peaks matching with ZrC, confirming the formation of ZrC phase. From the above two figures we concluded that n-Hexane compare to toluene is a better PCA to assist the carburization for the synthesis of a complete fcc-ZrC phase and inhibit the agglomeration of the nanoparticles during the milling process.



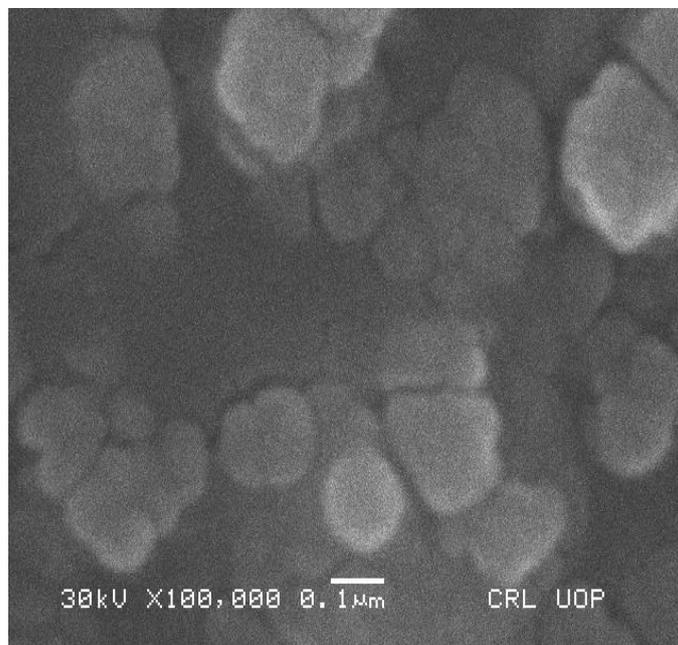
**Fig. 2 - XRD pattern of the ZrC sample synthesized using Toluene as PCA.**

#### 4.2. SEM Analysis

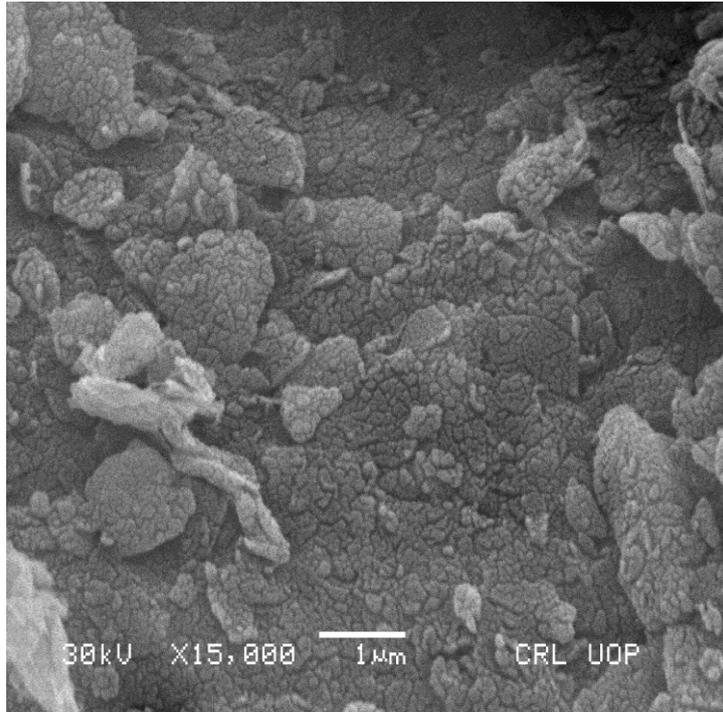
The SEM analysis were made to identify the grain morphology of the two samples. The SEM micrographs of the two samples are shown in Figure 3 and Figure 4. From the figure it is clear that, in the sample synthesized using n-Hexane, powders are mixed more properly than the one synthesized using toluene as PCA. Figure 5 and Figure 6 shows the SEM images of the two samples taken at a higher magnification, showing grain (cluster) sizes up to 100 nm. The comparison of the two images shows that n-hexane compare to toluene is more efficient in inhibiting the agglomeration of the nanoparticles. The grain size seems to be coarse in case of n-Hexane in comparison of that using toluene. Thus n-hexane is more efficient in grain size refinement compare to toluene.



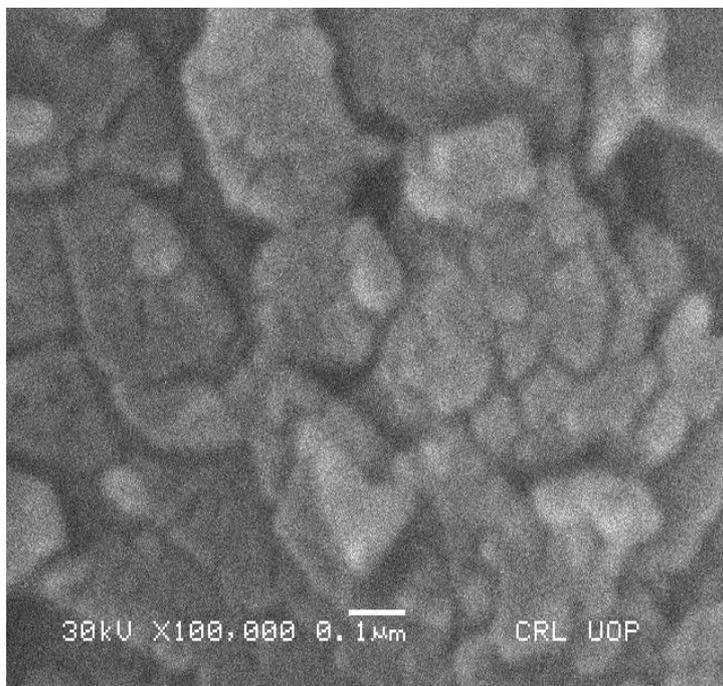
**Fig. 3 - SEM image of the ZrC sample synthesized using n-Hexane as PCA**



**Fig. 4 - SEM image of the ZrC sample synthesized using n-Hexane as PCA.**



**Fig.5 - SEM image of the ZrC sample synthesized using toluene as PCA.**

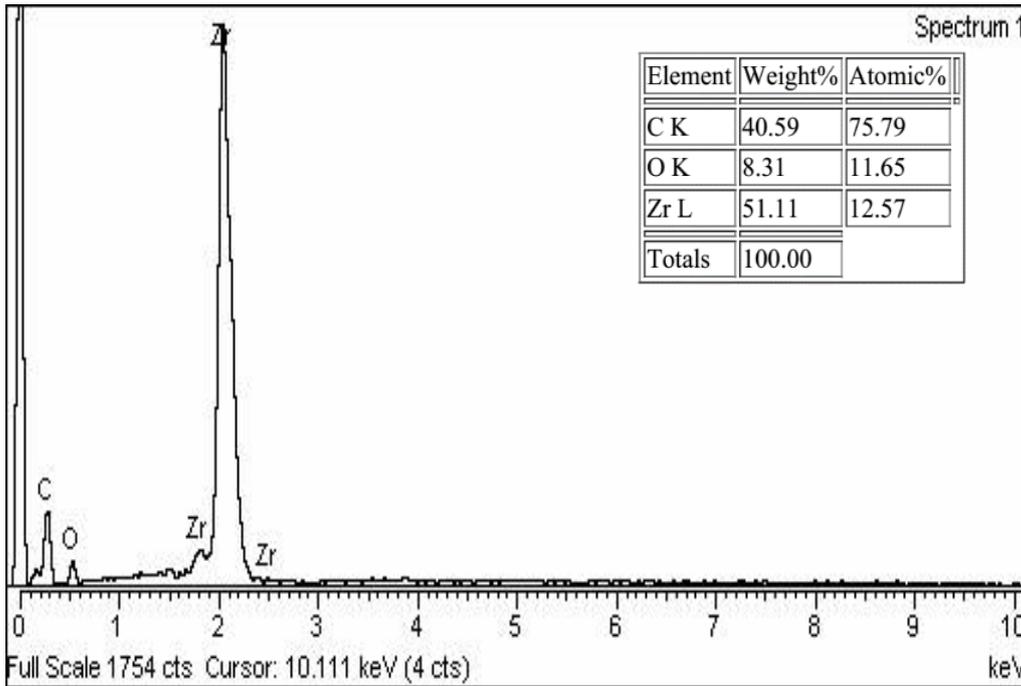


**Fig.6 - SEM image of the ZrC sample synthesized using toluene as PCA.**

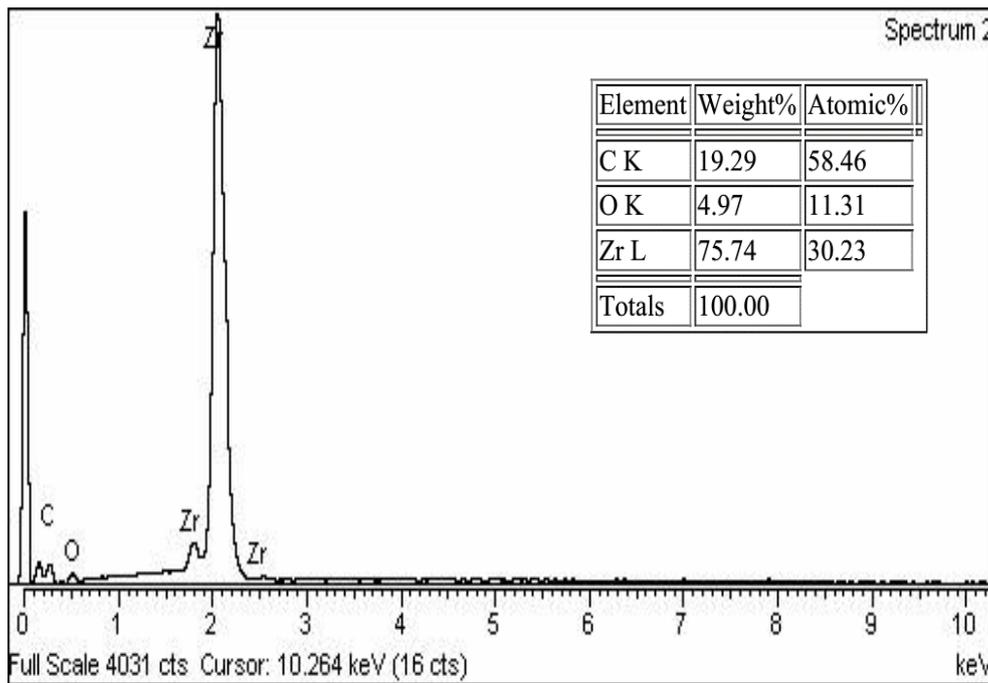
#### **4.3. EDX Analysis**

To find the elemental composition of the samples EDS analysis was performed. The result are shown in Figure 7 and Figure 8. In both the samples oxygen impurity was detected. This was because during the milling process no control environment was maintained and the milling was performed under

normal environment. There was possibility that air might ingress into the samples during the loading and unloading of the powders into the jars. Using a control environment such as vacuum or inert atmosphere, like argon or helium gas this problem may be avoided.



**Fig.7 - EDS spectrum of the ZrC sample synthesized using n-Hexane as PCA**



**Fig.8 - EDS spectrum of the ZrC sample synthesized using toluene as PCA.**

Table 3 shows the chemical analysis of the two samples. In both samples oxygen contents were detected. It is because the loading and unloading of powders into the jars is done in normal

environment, so there was great possibility that air might ingress into the samples. This difficulty can be avoided using control environment such as vacuum or inert gas like argon or helium.

**Table 3:** Chemical analyses of the as prepared samples, using n-Hexane and toluene as PCA's.

Sample	Zr content (at.%)	C content (at.%)	O content (at.%)
ZrC (n-Hexane)	30.23	58.46	11.31
ZrC (Toluene)	12.57	75.79	11.65

## 5. CONCLUSION

Within the domain of nanoparticle synthesis, the meticulous application of mechanochemical synthesis has yielded successful production of ZrC nanoparticles. Significantly, in the pivotal phase of averting agglomeration, it has been discerned that n-Hexane surpasses Toluene in efficacy. The selection of a solvent in nanoparticle synthesis assumes a paramount role in preventing undesirable aggregation, thereby underscoring the critical significance of n-Hexane within the mechanistic intricacies of the synthesis process. Moreover, scrutiny into the elemental composition of the synthesized ZrC nanoparticles has unveiled the presence of oxygen. To circumvent this inherent challenge, the contemplation of employing an inert environment or vacuum conditions has been posited. These measures, rooted in a scrupulous comprehension of the synthesis environment, are believed to assuage the inadvertent incorporation of oxygen, thereby ensuring the purity and integrity of the ZrC nanoparticle samples. Expanding the purview to potential applications, an exhaustive literature survey has elucidated the auspicious potential of ZrC as a coating agent. While extant studies lay a foundational groundwork for this prospective application, a nuanced and exhaustive investigation becomes imperative to comprehensively assess the feasibility and efficacy of ZrC nanoparticles as a coating material. This research underscores the imperativeness of not solely optimizing synthesis but also undertaking a profound exploration of the functional applications of the synthesized nanoparticles. In doing so, it contributes substantively to the burgeoning body of knowledge within the realm of nanomaterial science.

In summation, the synthesis of ZrC nanoparticles through mechanochemical means has unveiled the nuanced role of solvents, with n-Hexane emerging as a preeminent choice in mitigating agglomeration. In addressing the challenge of oxygen incorporation, the proposition of employing an inert environment or vacuum conditions is advanced. The exploration of ZrC's potential as a coating agent, while promising, necessitates further meticulous investigations to unlock its full spectrum of applications. This research not only augments the repertoire of nanoparticle synthesis methodologies but also propels the understanding of ZrC nanoparticles toward practical applications, representing a noteworthy advancement in the domain of nanomaterial research.

## 6. RECOMMENDATIONS

To make nanoparticles better, we need to carefully choose a special ingredient called a process control agent (PCA). This PCA not only helps prevent the particles from sticking together but also speeds up the milling process. Picking the right PCA is crucial for making nanoparticles using

mechanical methods, and exploring different options could make the process even better. To deal with the problem of oxygen getting into the nanoparticles when making ZrC, we should do it in a special environment. Creating a vacuum or using gases like Argon or helium can help keep the nanoparticles pure. This controlled environment is crucial to stop unwanted chemical reactions, especially the mixing of oxygen, and it improves how we make the nanoparticles. While ZrC seems good for coating things, we still need more detailed research to make sure it's a great choice. We have to look closely at the structure and chemicals in ZrC to see if it works well for coating and figure out the best conditions for a good coating. Looking ahead, using thermal spray methods to coat things with ZrC looks promising. These methods are known for being good at coating various materials efficiently. Studying how these methods work, including their settings and how they affect the coating quality, could open up new practical uses for ZrC nanoparticles.

In short, future research should focus on finding better ingredients for making nanoparticles, figuring out how to stop oxygen from messing up the process, understanding if ZrC is the best for coating, and exploring thermal spray methods for coating. These steps create a clear plan for learning more and finding useful applications for ZrC nanoparticles in different areas.

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### References

1. Rose, M., Balogh, A. G., & Hahn, H. (1997). Instability of irradiation induced defects in nanostructured materials. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 127, 119-122.
2. Sherif El-Eskandarany, M., Omori, M., Hirai, T., Konno, T. J., Sumiyama, K., & Suzuki, K. (1998). Syntheses of full-density nanocrystalline titanium nitride compacts by plasma-activated sintering of mechanically reacted powder. *Metallurgical and Materials Transactions A*, 29, 1973-1981.
3. Mahday, A. A., El-Eskandarany, M. S., Ahmed, H. A., & Amer, A. A. (2000). Mechanically induced solid state carburization for fabrication of nanocrystalline ZrC refractory material powders. *Journal of alloys and compounds*, 299(1-2), 244-253.
4. Yadav, T. P., Yadav, R. M., & Singh, D. P. (2012). Mechanical milling: a top down approach for the synthesis of nanomaterials and nanocomposites. *Nanoscience and Nanotechnology*, 2(3), 22-48.
5. Suryanarayana, C. (2001). Mechanical alloying and milling. *Progress in materials science*, 46(1-2), 1-184.
6. Xiang, J. Y., Liu, S. C., Hu, W. T., Zhang, Y., Chen, C. K., Wang, P., ... & Liu, Z. Y. (2011). Mechanochemically activated synthesis of zirconium carbide nanoparticles at room temperature: A simple route to prepare nanoparticles of transition metal carbides. *Journal of the European Ceramic Society*, 31(8), 1491-1496.

7. Jackson, H. F., Jayaseelan, D. D., Clegg, W. J., Reece, M. J., Inam, F., Manara, D., ... & Lee, W. E. (2010). Microstructure of Laser-Melted Zirconium Carbide Ceramics. *Advances in Materials Science for Environmental and Nuclear Technology*, 222, 113-125.
8. Jackson, H. F., & Lee, W. E. (2012). Properties and characteristics of ZrC. *Comprehensive nuclear materials*, 2, 339-372.
9. Ang, C., Williams, T., Seeber, A., Wang, H., & Cheng, Y. B. (2013). Synthesis and evolution of zirconium carbide via sol–gel route: features of nanoparticle oxide–carbon reactions. *Journal of the American Ceramic Society*, 96(4), 1099-1106.
10. Seo, M., Kang, S., Kim, Y., & Ryu, S. S. (2013). Preparation of highly dispersed ultra-fine ZrC by combination of carbothermal reduction of ball-milled ZrO<sub>2</sub> and C mixture and bead milling. *International Journal of Refractory Metals and Hard Materials*, 41, 345-350.
11. Norton, J. T., & Lewis, R. K. (1963). Advanced Metals Research Corp. Somerville, Massachusetts, N63-18389.
12. Ando, Y., & Uyeda, R. (1981). Preparation of ultrafine particles of refractory metal carbides by a gas-evaporation method. *Journal of Crystal Growth*, 52, 178-181.
13. Ruff, O., & Wallstein, R. (1923). Reduktion anorganischer Halogenide III. 1) Die Reduktion des Zirkontetrachlorids. *Zeitschrift für anorganische und allgemeine Chemie*, 128(1), 96-116.
14. Maitre, A., & Lefort, P. (1997). Solid state reaction of zirconia with carbon. *Solid State Ionics*, 104(1-2), 109-122.
15. Dong, J., Shen, W., Liu, X., Hu, X., Zhang, B., Kang, F., ... & Chen, N. (2001). A new method synthesizing the encapsulated ZrC with graphitic layers. *Materials research bulletin*, 36(5-6), 933-938.
16. Schwartzkopf, P., Kieffer, R., Leszynski, W., & Benesovsky, F. (1953). *Refractory hard metals: borides, carbides, nitrides, and silicides. The basic constituents of cemented hard metals and their use as high-temperature materials.* Macmillan.
17. Katoh, Y., Vasudevamurthy, G., Nozawa, T., & Snead, L. L. (2013). Properties of zirconium carbide for nuclear fuel applications. *Journal of Nuclear Materials*, 441(1-3), 718-742.
18. Jackson, H. F., & Lee, W. E. (2012). Properties and characteristics of ZrC. *Comprehensive nuclear materials*, 2, 339-372.