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Direct synthesis of nanocrystalline tungsten carbide from scheelite ore by solid state reaction method

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Abstract

This article reports the synthesis of nanocrystalline tungsten carbide by solid state reaction method directly from its ore. Scheelite-an ore of tungsten was milled for 50 h and 100 h with activated charcoal in excess of stoichiometric ratio followed by calcination in the argon atmosphere at different temperatures. The 100 h milled sample showed complete reduction/carburisation of scheelite at 1025 °C. The calcined sample was then acid washed (1:1 HCl) followed by base washing (0.25 M NaOH) to remove impurities and undesired reaction products. The obtained powders were characterised by X-ray diffraction, scanning electron microscope, HRSEM and HRTEM. The final product contained single phase nanocrystalline tungsten carbide (WC) phase. This method can be scaled up for bulk manufacturing of nancrystalline WC directly from ore.

Keywords: Calcination; Milling; Tungsten carbide; X-ray methods

1. Introduction

Tungsten carbide (WC) possesses unique properties like high hardness and high bulk modulus of elasticity along with good oxidation and corrosion resistance. Tungsten carbide is extensively used in cutting tools, dies, wear resistance parts and as anvil material in high pressure instruments. These mechanical properties are further enhanced with reduced WC grain size [1]. Apart from these nanocrystalline WC shows good catalytic activity along with stability and is used as low cost substitute for precious metal catalysts. It is a promising material to replace platinum in fuel cell as it exhibits more resistance to CO poisoning than platinum (Pt) [2,3]. Recently various routes have been explored to synthesise nanocrystalline WC from different precursors of tungsten like (i) WO_3; using solid state reaction method [4,5], combustion synthesis [6], solvothermal method [7] (ii) elemental W; by mechanical alloying [8], electrical discharge machining [9], mechanochemically activated synthesis [10] (iii) H_2WO_4; by thermochemical processing [11,12] (iv) WCl_4; by urea glass route [13] (v) WCl_6; by co-reduction carbonization [14] (vi) $W(CO)_6$; using chemical vapour condensation process [15] and (vii) Ammonium tungstate $(NH_4)_2WO_4$; by combustion reaction [16]. However, extraction of tungsten from ore is a lengthy and costly process which involves multi step high temperature and pressure treatments [17–19]. Further cost is added when tungsten is converted to other precursors like $W(CO)_6$, WCl_6 and WCl_4. Any process which synthesise nanocrystalline WC directly from ore will be more economical.

There are two important ores of tungsten, namely scheelite ($CaWO_4$) and wolframite ($FeWO_4$). Scheelite becomes more important as $CaWO_4$ is also an intermediate product in the tungsten extraction process if the extraction is done from wolframite. The other intermediate products in the extraction sequence are tungstic acid (H_2WO_4), ammonium paratungstate (APT) and WO_3 [17,18]. Lastly WO_3 is reduced to W by hydrogen at high temperature. The elemental tungsten is then carburised at high temperatures (1200–1450° C) to get WC in conventional process. Any method which can convert ore directly into nanocrystalline WC by minimal treatment could be a technological breakthrough.

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Generally ore contains different impurities, and to remove impurities different processes are adopted which make the whole metal extraction process energy intensive and costly. The idea here is to use impurities as grain growth inhibitor to synthesise nanocrystalline WC. After synthesis of WC the impurities are washed out with dilute acid and base. So thereby requiring very less amount of acid/base, since only impurities are to be leached out from the product phase and not the entire ore which has to be digested with acid and base in conventional process [17–19]. Another major advantage is that it will generate lesser effluent than conventionl process. Moreover, the digestion of the ore itself is a complicated process which requires high temperature and pressure treatments [19]. In this article we report a simple synthesis method which is environment friendly besides being energy efficient and economical. There were few attempts to synthesis WC directly from scheelite [20–23], but none could lead to single phase WC. To the best of our knowledge, this is the first report of synthesis of *single phase nanocrystalline* tungsten carbide directly from the scheelite ore by solid state reaction method though some reports on synthesis of microcrystalline WC phase exists [21–22].

2. Experimental

The starting material consists of scheelite ($CaWO_4$) ore procured from North American Tungsten Corporation, Canada, and activated charcoal from SD Fine Chemicals, India. The major impurities in the ore were Fe (1.5–3.5%), SiO_2 (0.7–1.2%), Na (0.5%), S (0.2–1.0%), Al (0.1–0.2%), Bi (0.1–0.6), Mg (0.15–0.30%), Mn (0.15–0.30%), and rest impurities were at ppm level. The particle size of $CaWO_4$ was in the range of 100–400 μm (Fig. 1(a)). The procured scheelite ore was milled for 40 h to reduce the particle size (Fig. 1(b)). The ball to powder ratio (BPR) was kept as 10:1 and this powder is termed as milled scheelite in this article. The mixtures of milled scheelite and activated charcoal (1:2 weight ratios) were prepared. Powders were loaded and milled again in air in 250 ml capacity tungsten carbide jar and balls (Retsch PM 100). The charge to ball ratio was kept at 50:1. The mixtures were milled for 50 h and 100 h. These powders are termed as 50 h milled and 100 h milled samples in this article. After milling, the powders were taken out and pellets were made. The powders were loaded in a die of 15 mm diameter and a force of 10 t was applied on the plunger of the die. The pressure was maintained for one minute and after that pressure was released. These pellets were taken out and calcined in a tube furnace at different temperatures under flowing argon gas.

To find the phases present, the X-ray analysis was done on X'PERT PRO of PANalytical X-ray diffraction machine using characteristic wavelength of Cu (Kα) 1.54060 Å.The scanning of the samples was done at the rate of 5°/min and in the range of diffraction angle (2θ) 10–100°. Differential thermal analysis and thermo-gravimetric analysis were carried out in the heating cycle mode at 10° C/min using PerkinElmer, diamond TG thermal analyser. The spectrum was obtained in the temperature range of 50–1000° C in N_2 atmosphere. Commercial nitrogen of high purity was used for thermal analysis. The morphology of the powders was studied with scanning electron microscope (Jeol JSM 6510V) and FESEM (Jeol 7600F). Transmission electron microscopy (PHILIPS CM200) and HRTEM (JEOL-JM 2100F) was done by taking one drop of ethanol suspended powder on carbon coated copper grid. The solution was allowed to evaporate before investigation.

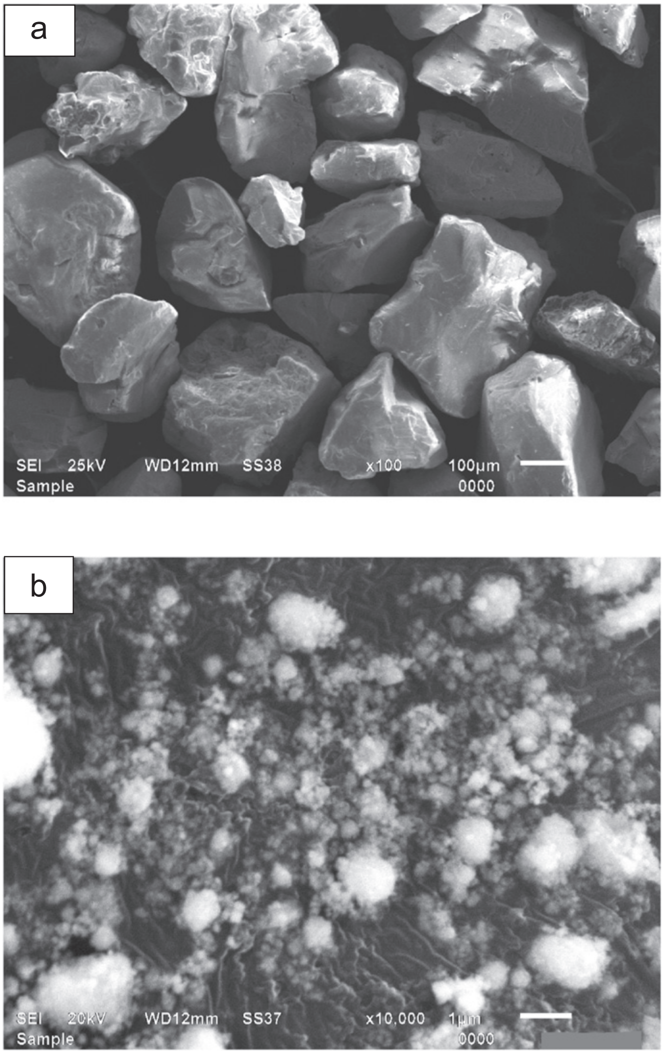

Fig. 1. Scanning electron micrograph of (a) raw scheelite (b) raw scheelite milled for 40 h.

3. Results and discussion

Fig. 2(a) and (b) shows the X-ray diffraction pattern of raw and milled scheelite (matched with ICDD card no. 01-072-1624). The broadening of the peaks in Fig. 2(b) can be attributed to reduced particle size and induced strain in the scheelite. Fig. 2(c) and (d) shows X-ray diffraction patterns of 50 h and 100 h milled samples. The X-ray diffraction of

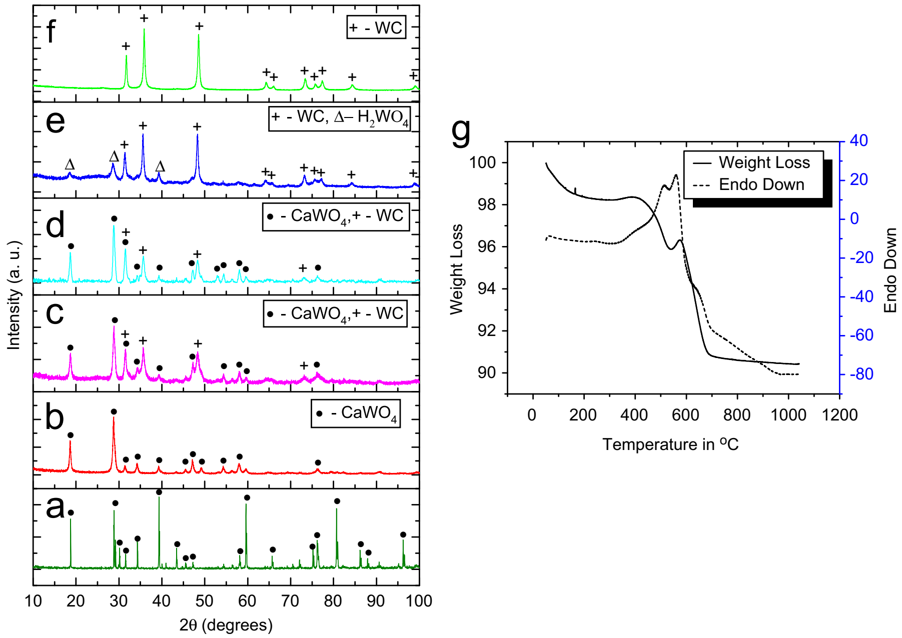

Fig. 2. X-ray diffraction pattern of (a) raw scheelite, (b) raw scheelite milled for 40 h, (c) 50 h milled sample, (d) 100 h milled sample, (e) sample (c) calcined (1025° C for 4 h) and leached, (f) sample (d) calcined (1025° C for 4 h) and leached and (g) DTA/TG curves of powder (d) calcined (1025° C for 4 h) without leaching.

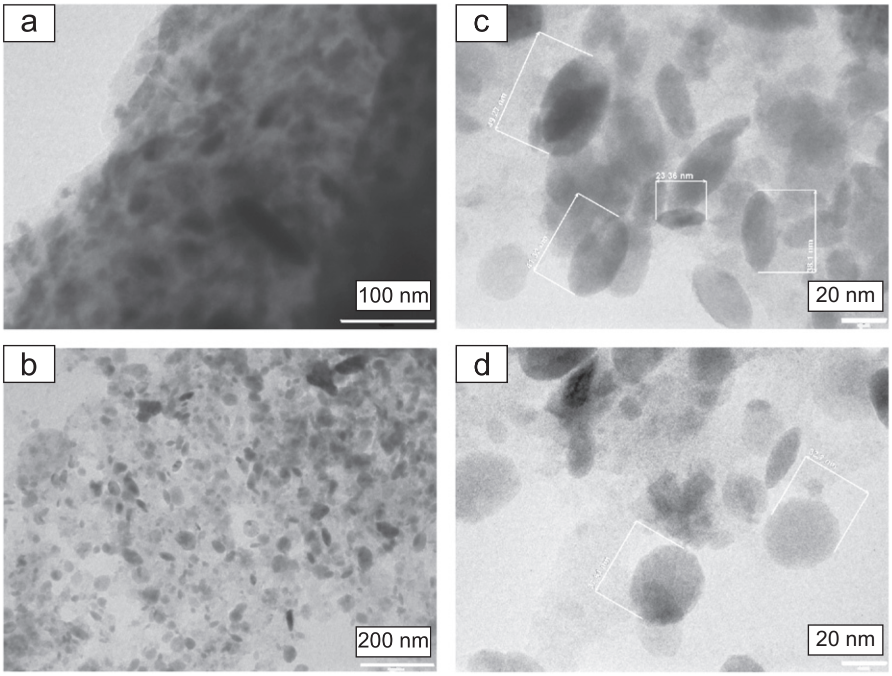

Fig. 3. Transmission electron micrograph of (a) 50 h milled sample (b) 100 h milled sample (c and d) nano sized capsule and sphere shaped $CaWO_4$ particles produced in 100 h milled sample.

50 h milled sample showed medium intensity peaks corresponding to WC phase and high intensity peaks of $CaWO_4$ phase. This indicates that some reduction has occurred during milling itself. The loading of the scheelite and activated charcoal powders in milling jar were done in air only. Some of the activated charcoal may have formed CO inside the jar during milling. The activated charcoal/CO might have reduced some scheelite particles to WC during milling operation. Similar results were also observed for 100 h milled powders as can be in Fig. 2(d). We found no substantial increase in the WC phase formation in comparison to 50 h milled sample.

Fig. 2(e) shows the X-ray diffraction pattern of 50 h milled and calcined (1025° C for 4 h) sample which was leached by acid (1:1 HCl) first then followed by base (0.25 M NaOH). Diffraction pattern could be indexed to WC and tungstic acid (H_2WO_4) phases. Tungstic acid peaks came from residual scheelite which got converted to H_2WO_4 during leaching with HCl. Fig. 2(f) shows the X-ray diffraction pattern of 100 h milled and calcined (1025° C for 4 h) sample which were subsequently acid and base leached. The peak position and intensities matched with WC (ICDD card no. 01-073-9874). The lattice constants calculated from X-ray diffraction peaks are $a=2.898$ Å, $c=2.835$ Å, which are close to reported values ($a=2.900$ Å, $c=2.831$ Å, ICDD card no. 01-073-9874) confirming the presence of nanocrystalline WC (hexagonal phase, space group P_6m2). To check the presence of residual carbon, thermal analysis of the unleached sample was done. Fig. 2(g) shows the DTA/TG curves of the 100 h milled and calcined (1025° C for 4 h) sample. There is around 8 wt% loss in the sample in two steps. The corresponding exothermic peaks indicate the burning of the carbon in the sample. The free carbon burns first and then wrapped carbon on the surface of WC. There is 0.5% weight increase from 540 to 570° C, this increase in weight may be due to oxidation of other impurities.

Fig. 3(a) shows transmission electron micrograph of 50 h milled sample. The scheelite particles were reduced to the nano range and their appearance is of agglomerated state. Because of the agglomerated state, some of scheelite particles were not reduced and got converted to tungstic acid during acid leaching. Fig. 3(b) shows TEM of 100 h milled sample. The major difference in comparison to the 50 h milled sample was that here particles are well distributed (not in agglomerate state). This might be the reason of complete reduction of scheelite particles in 100 h milled sample. The other interesting feature in 100 h milled powder is that scheelite particles were reduced to nano sized capsules and spherical shapes as can be seen in Fig. 3(c) and (d). Fig. 4(a) and (b) shows HRSEM of 100 h milled sample calcined (1025° C for 4 h) subsequently acid and base leached. Well faceted WC nanoparticles can be seen in the micrographs. Fig. 5(a) shows the HRTEM of 100 h milled sample, calcined (1025° C for 4 h) and subsequently acid and base leached. Well faceted nanocrystalline WC particles can be seen in the micrograph. Fig. 5(b) shows HRTEM of 35 nm size WC particle. Fig. 5(c) shows the corresponding diffraction pattern of single WC particle. The diffraction spots could be indexed to (200) and (002) planes of WC.

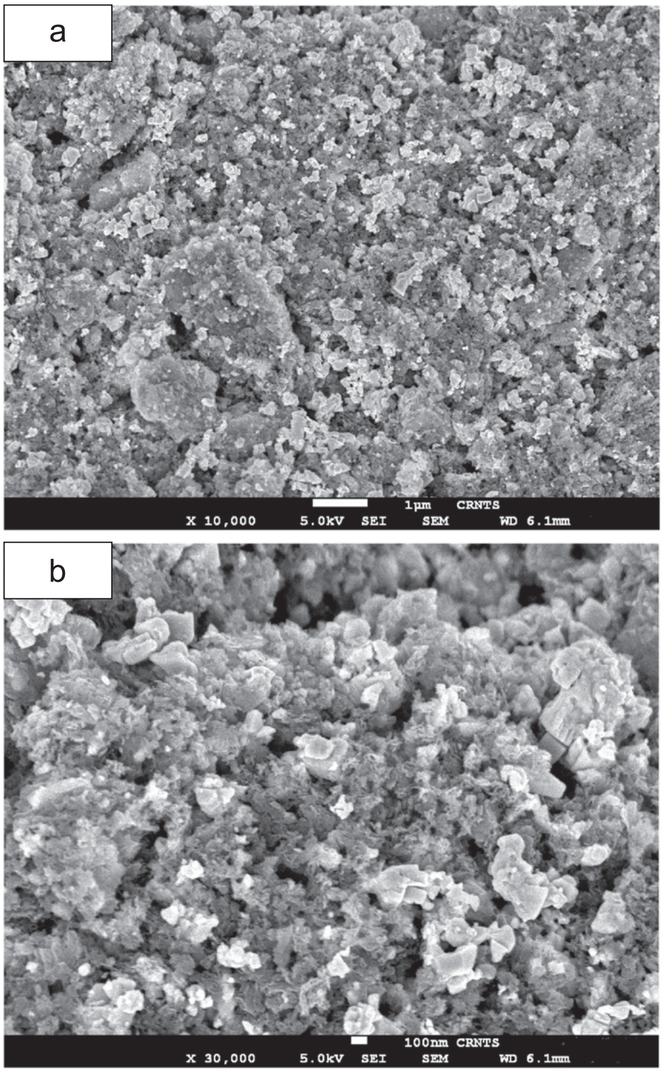

Fig. 4. (a) and (b) HRSEM of 100 h milled sample calcined (1025° C for 4 h) subsequently acid and base leached.

To find the mechanism of formation of nanocrystalline WC, series of experiments were conducted. Powders milled for 50 h were calcined at 700, 800, 900, 1000, and 1100° C. The X-ray diffraction patterns indicated that no reaction had occurred at 700, 800 and 900° C, rather reactant scheelite retained its initial state. Only two crystalline phases WC and $CaWO_4$ were observed at 1000° C and 1100° C. In order to find exact milling time and temperature for the reaction more calcination experiments were conducted with 50 h and 100 h milled samples each at 950° C and 1025° C. The best results were observed for 100 h milled samples calcined at 1025° C. The X-ray diffraction pattern of this sample showed traces of unreacted scheelite and a very low intensity single peak of calcium silicon oxide ($CaSiO_3$). This $CaSiO_3$ was formed by the following reactions:

$$CaWO_4+4C \rightarrow WC+CaO+3CO \tag{1}$$

$$CaO+SiO_2 \rightarrow CaSiO_3 \tag{2}$$

The scheelite ore consisted of SiO_2 as one of its impurity. This SiO_2 reacted with CaO (reaction 1) at 1025° C and formed $CaSiO_3$. These undesired products CaO, $CaSiO_3$ and other impurities were leached out by dilute HCl (1:1) followed by base leaching with 0.25 M NaOH solution. The above experiments revealed two interesting facts. Firstly the peaks of WC phase which were observed in 50 h milled powders of scheelite and activated charcoal disappeared when calcined at 700, 800 and 900 °C, implying that WC

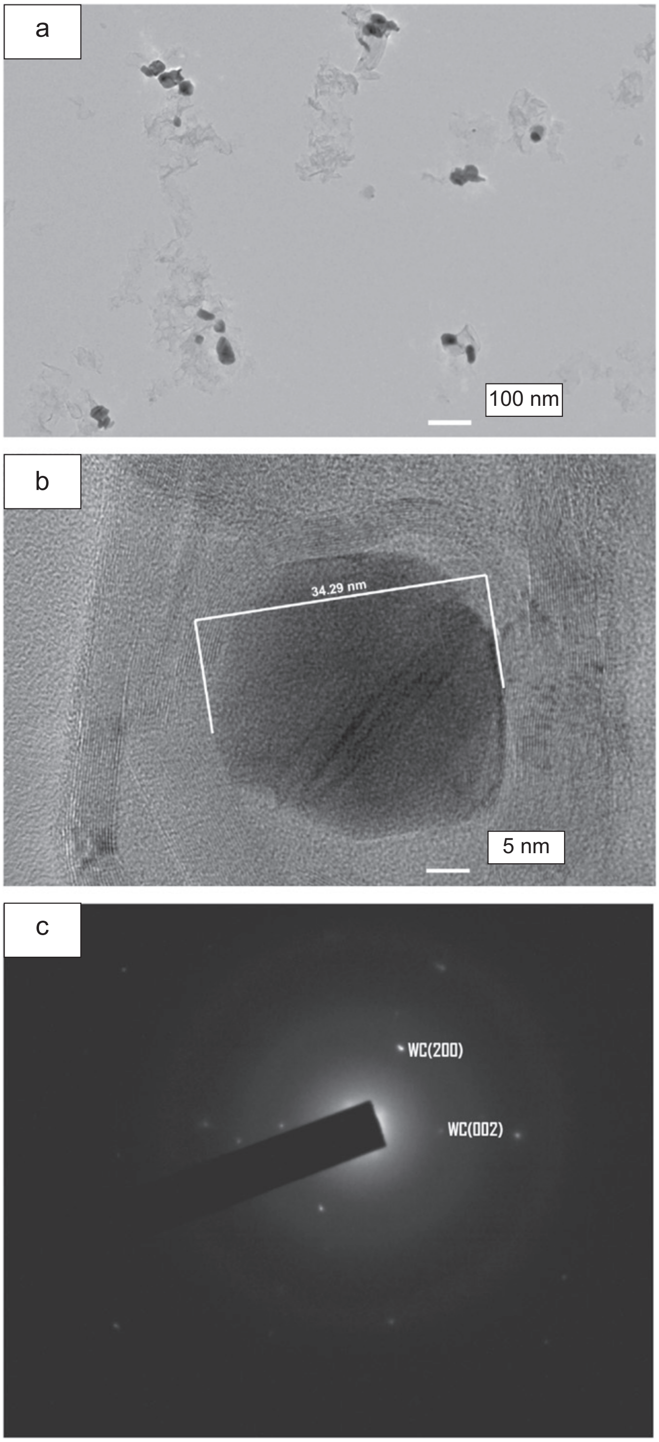

Fig. 5. HRTEM of (a) 100 h milled sample calcined (10251° C for 4 h) subsequently acid and base leached (b) single nanocrystalline WC particle (c) diffraction pattern of single nanocrystalline WC particle.

phase formed during milling was unstable as there was slight reduction on the outer surface of the some of the scheelite particles. Secondly no intermediate phase like W, W_2C and Ca_3WO_6 were observed in the calcined samples. Only two phases $CaWO_4$ and WC were observed when powders were calcined above 900° C. This behaviour was in contrast to the general solid state reactions which usually proceeds with the formation of intermediate phase followed by final product, whereas in our experiments final phase is formed directly without formation of intermediate products. The probable reason for this variation could be the existence of scheelite particles in nano range and its homogeneous mixing with activated charcoal. Further experiments are in progress to get large amount of WC nanoparticles by this route.

4. Conclusions

In summary, single phase nanocrystalline tungsten carbide has been synthesised from scheelite concentrate by simple solid state reaction method. Experiments have revealed interesting behaviour of nanoparticles of scheelite, forming final nanocrystalline WC without intermediate phases. Impurities present in the ore do not interfere in the synthesis of nanocrystalline WC. Impurities may act as grain growth inhibitor thus facilitating in synthesis of WC nanoparticles, which are leached out after synthesis. This method can be scaled up for bulk manufacturing of nancrystalline WC directly from ore-an ecofriendly, energy efficient and economical route.

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