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Growth model for nanomallets of zinc oxide from a catalyst-free combust-oxidised process

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Abstract

A growth model is proposed for a newly found nanostructure of zinc oxide, namely nanomallet, that is prepared via a catalyst-free combust-oxidised (CFCO) process (better known as the French process). In the CFCO process, molten zinc is vaporised and instantaneously oxidised in normal atmosphere to produce high purity zinc oxide. With the help of high-resolution field emission scanning electron microscope (FESEM) set at 15 kV incident electron energy, clear images of mallet-like nanostructure are observed. These polycrystalline structures can be classified into polyhedral and rectangular nanomallets. The polyhedral nanomallet has higher O/Zn relative atomic mol% ratio based on EDAX data and its *handle* tend to grow along [0002] direction. The quasi-rectangular nanomallet tend to grow along [10 $\bar{1}$ 0] direction for both the *head* and *handle*. Local temperature and oxygen partial pressure play a key role in determining the preferred nanostructures that include rectangular-like, polyhedral-like and taper-faceted structures.

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1. Introduction

The French process, a four decade-old industrial technology, can be considered as a catalyst-free combust-oxidised (CFCO) process. The majority of commercial ZnO is manufactured via CFCO process and it is employed in diversified applications that include electronics, rubber, paint, ceramics, pharmaceuticals, cosmetics and UV protection. The CFCO furnace (Fig. 1) consists of a graphite crucible placed inside a cylindrical firebrick furnace. The design is a muffle type whereby hot flame from a burner heats up the crucible by convection, and heat is transferred to the zinc ingots (inside the crucible) via conduction through the graphite lining. Zinc melts at 420 °C with heat of fusion 6.67 kJ/mol, boils at 907 °C with

heat of vaporization 114.2 kJ/mol and possesses a critical temperature of 3107 °C [1]. The crucible is covered with a graphite lid in order to pressurise the zinc vapour trapped inside the crucible where zinc vapour temperature rises as its pressure increases. Once the lid orifice is removed, the pressure difference causes the zinc vapour to purge out and it is instantaneously oxidised by ambient air. The zinc vapour has a nozzle temperature of 1100–1400 °C and a nozzle speed of about 8–12 m/s (calculated). An enclosure is sometimes built around the combustion chamber in order to control the oxygen-to-zinc ratio and to stabilise the temperature.

Zinc oxidation and crystal growth take place in the combustion area. An interesting feature of the crystallisation process is the sudden 1100–800 °C temperature drop (in seconds) between the crucible orifice and the top part of the conical suction hood (Fig. 1(a)). Despite the highly nonuniform crystallisation nature of this rapid *subminute* growth process, a large variety of one-dimensional nanostructures of ZnO can be formed which

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