Spectrochimica Acta Part B 63 (2008) 1183–1190

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

On-line monitoring of composite nanoparticles synthesized in a pre-industrial laser pyrolysis reactor using Laser-Induced Breakdown Spectroscopy ☆

Tanguy Amodeo [a,*], Christophe Dutouquet [a], François Tenegal [b], Benoît Guizard [b], Hicham Maskrot [b], Olivier Le Bihan [a], Emeric Fréjafon [a]

[a] Institut National de l'Environnement Industriel et des Risques (INERIS), Parc Technologique Alata, BP2, 60550 Verneuil-En-Halatte, France
[b] DEN/DMN/SRMA/LTMEx, CEA Saclay, 91191 Gif Sur Yvette, France

ARTICLE INFO

Article history:
Received 26 October 2007
Accepted 31 August 2008
Available online 18 September 2008

Keywords:
LIBS
On-line monitoring
Process control
Laser pyrolysis
Composite nanoparticles

ABSTRACT

Laser-Induced Breakdown Spectroscopy (LIBS) was employed for on-line and real time process monitoring during nanoparticle production by laser pyrolysis. Laser pyrolysis has proved to be a reliable and versatile method for nanoparticle production. However, an on-line and real time monitoring system could greatly enhance the process optimization and accordingly improve its performances. For this purpose, experiments aiming at demonstrating the feasibility of an on-line monitoring system for silicon carbide nanoparticle production using the LIBS technique were carried out. Nanosecond laser pulses were focused into a cell through which part of the nanoparticle flux diverted from the production process was flowed for LIBS analysis purposes. The nanoparticles were vaporized within the laser-induced plasma created in argon used as background gas in the process. Temporally-resolved emission spectroscopy measurements were performed in order to monitor nanoparticle stoichiometry. Promising results were obtained and on-line Si/C_x stoichiometry was successfully observed. These results put forward the possibility of real time correction of the nanoparticle stoichiometry during the production process.

1. Introduction

Over the last years, research in the field of nanostructured materials synthesis has become increasingly important. Such materials designed at a nanometric scale are expected to show new properties of great interest to a wide range of industrial applications. In this context, the development of nanoparticle-based materials has advanced rapidly and along with it the need for generic and safe nanoparticle production systems. Producing and commercializing nanoparticle-based materials for different applications (composites, cosmetics, catalysis, optics,…) require industrial equipments permitting large-scale production of a wide range of nanoparticles. Furthermore, these industrial lines are expected to produce nanoparticles with constant quality (size distribution, chemical composition).

For this purpose, the development of an on-line monitoring system allowing a real time analysis, both qualitative and quantitative, of some characteristics of the nanoparticles such as the chemical composition and the size is highly desirable. The monitoring of some of these characteristics will thus provide quasi instantaneous feedback for process control. This is of primary importance while the development of composite nanoparticles arouses a growing interest. These nanoparticles are elaborated from several elements with the aim of creating materials with advanced functionalities. The large number of elements these nanoparticles consist of has actually emphasized the need for on-line stoichiometry control. In addition to process control, production safety requirements could be satisfied by utilizing on-line monitoring systems to secure the installations producing, handling and integrating nanoparticles. A tool devised both for in-situ and real time chemical and physical identification of nanoparticles could detect their release in the ambient air and therefore could assure safety for the operating personnel and the surrounding environment.

Among all the methods known, the continuous nanoparticle synthesis processes are very interesting for nanoparticle production at industrial scale. Indeed, with these techniques, nanoparticles are produced continuously by injecting a continuous flow of reactants in a reactor leading to large daily production rates. Some of these methods are already developed at industrial scale for the production of metals or oxides nanoparticles (for example TiO_2 nanoparticles by the Aerosil® process of DEGUSSA) and the development of industrial processes for non-oxide nanoparticles is currently in progress. Laser pyrolysis is one of these promising techniques. Basically, its principle rests on the interaction between a continuous high-power CO_2 laser beam and a continuous flux of gaseous or liquid reactants. Reactant

☆ This paper was presented at the Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS 2007) held in Paris (France), 11–13 September 2007, and is published in the Special Issue of Spectrochimica Acta Part B, dedicated to that conference.

* Corresponding author. Tel.: +33 3 44 55 69 47; fax: +33 3 44 55 63 02.
E-mail addresses: tanguy.amodeo@ineris.fr (T. Amodeo), christophe.dutouquet@ineris.fr (C. Dutouquet), francois.tenegal@cea.fr (F. Tenegal), benoit.guizard@cea.fr (B. Guizard), hicham.maskrot@cea.fr (H. Maskrot), olivier.le-bihan@ineris.fr (O. Le Bihan), emeric.frejafon@ineris.fr (E. Fréjafon).

0584-8547/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2008.09.005

molecules absorb laser radiation which results in their dissociation. Afterwards, molecules recombine with one another within the pyrolysis flame to form nanoparticles. Thereby, a wide range of nanoparticles can be produced. The process yields a continuous high production rate of nanoparticles with a good control of their size, structure and chemical composition [1]. Furthermore, nanoparticles produced in this way are usually weakly agglomerated. In addition, the method is very efficient to produce composite nanoparticles which characteristics can be easily adjusted by varying some processing parameters such as the laser power density, the flow rate, the composition and dilution of the reactants.

Though this method assures a good control of compound stoichiometry, stoichiometry variations in the course of nanoparticle production are not to be neglected. Thus, the production rate of nanoparticle compounds with the right stoichiometry could be enhanced with an on-line and real time quality control. With this aim in view, the LIBS technique was selected. LIBS has been demonstrated to be a versatile, reliable analytical method for multi-elemental analysis of solid [2], liquid [3], gas [4,5] and aerosols [6,7] both for qualitative and quantitative measurements. It has the advantage of being non-intrusive and no sampling is required. Moreover, measurements can be performed at remote distances, in real time and in-situ without sample preparation. All these characteristics make LIBS a particularly well adapted tool to analyze materials which are not easily accessible or for which confinement is required.

The LIBS analysis method has already been utilized in diverse industrial applications. Its potential in the steel industry at different stages of the production chain has already been demonstrated [8,9]. For instance, the LIBS technique has been applied for on-line monitoring of molten steel in order to improve the steel quality and to obtain a better production gain. In the nuclear industry [10], LIBS has been selected as the most adequate technique when in-situ material analyses were required. It was the most practical method to implement in a hostile environment with high temperatures and level of radiation. Recently, concerns have been raised regarding particles of micrometric and submicrometric sizes emitted in ambient air (from different sources such as plants, engines….) and their possible hazard towards human health and environment. Several studies have demonstrated the LIBS potentialities for particle detection [11]. LIBS was therefore used for on-line monitoring of metal laden aerosols in industrial production, combustion processes [12–14], environmental purposes [15,16] and promising results were obtained. All these studies point out the advantages of LIBS for process control and particle detection both on-line and in real time.

In this paper, we report the results of a study coupling for the first time the LIBS technique and a laser pyrolysis reactor. The LIBS equipment was integrated into a laser pyrolysis unit developed by the French Atomic Energy Commission (CEA — Saclay, France) with the aim of monitoring on-line and in real time SiC_x composite nanoparticle stoichiometry. These nanoparticles are synthesized prior to nanostructured silicon carbide elaboration, the latter being a promising material for high temperature applications in the nuclear energy industry. Our main objective was centered on nanoparticle stoichiometry determination while the process was being operated. Stoichiometry calculation was achieved using temporally-resolved emission spectroscopy measurements followed by plasma analysis. The results obtained are reported and discussed.

2. Experimental set-up: Laser-Induced Breakdown Spectroscopy and laser pyrolysis

2.1. Instrumentation

2.1.1. Laser pyrolysis experimental set-up

The experimental set-up (Fig. 1) consists of a reactor equipped with an inlet nozzle at its bottom, an outlet duct at its top and many optical windows among which those for the laser beam passage and the pyrolysis flame monitoring. Reactants, namely SiH_4 and C_2H_2 for SiC_x

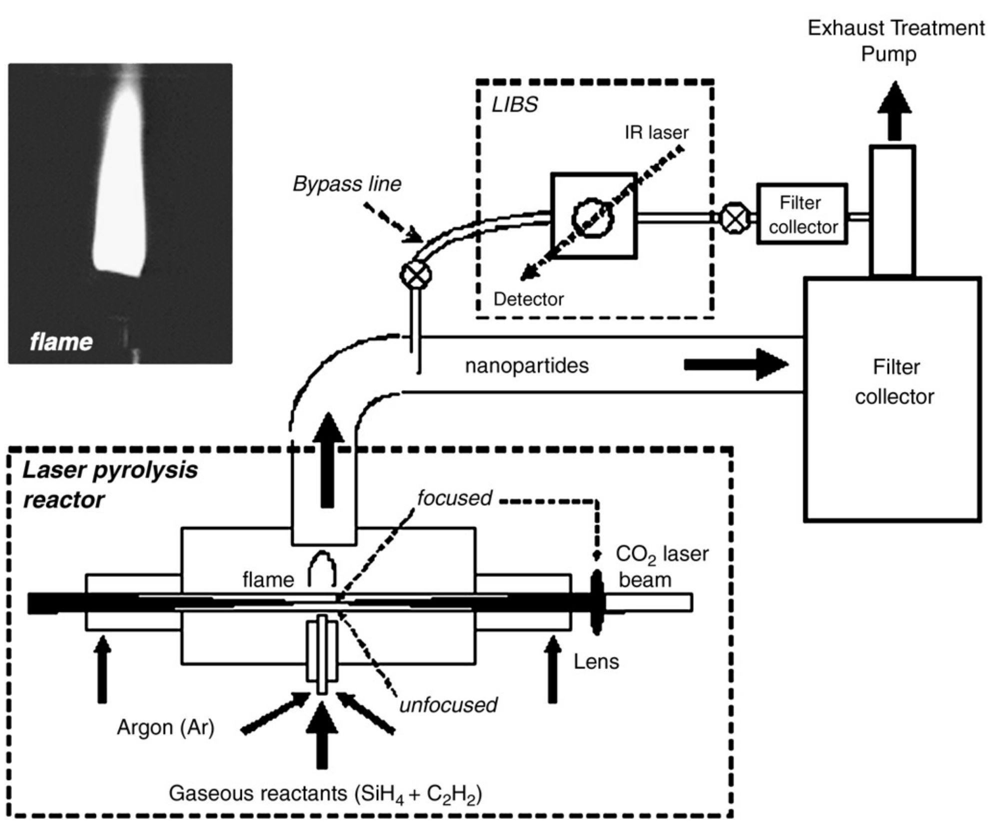

Fig. 1. Laser pyrolysis reactor experimental set-up including the LIBS unit.