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Microstructure Analysis of Fibrous Material Manufactured by Plasma Spray Method

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This paper presents an investigation of the fibrous material manufactured by plasma spray technique employing non-equilibrium plasma spray technology at atmospheric pressure. Waste catalyst of oil refinery and petrochemical industries was used as raw material for fibrous material production. The influence of the plasma spray regimes on microstructure of the formed material was analyzed. Annealing of the fibrous material was performed in the temperature range from 900 °C up to 1200 °C for study of crystallization process and each time the crystallite size of the material was calculated. Crystallization of the fibrous material with formation of mullite phase started at 900 °C. Formation of cristobalite was observed after annealing at 1000 °C for 12 hours. SEM and XRD techniques were applied to examine the morphology, microstructure and composition of the samples.
Keywords: waste catalyst, plasma spraying, fibrous material, microstructure, crystallization.

1. INTRODUCTION

Strong interest is demonstrated in utilization of waste catalyst produced by petrochemical industry. It may be reused as a fine additive in grouts for various purposes as castables, concrete mixing, bricks and other compositions [1 – 3]. The researchers [4, 5] suggest reusing them for making new catalysts. Also waste catalyst can be recycled into the fibres using thermal plasmas. Plasma spray technique has unique advantages such as high enthalpy to enhance the reaction kinetics, high chemical reactivity, atmosphere in accordance with required chemical reactions and rapid quenching to produce chemical non-equilibrium materials [6, 7].

In particular, fibres generate great interest in certain industry segments, where alternative materials are characterized by limited performance or much higher unit prices. Ideally, the structural materials should be lightweight, strong, chemically and thermally stable; they should possess good mechanical properties and be relatively cheep. Fibre reinforced composites can fulfil many of the named requirements. The reinforcement of ceramic materials by ceramic long fibres is a promising way to achieve tough and damage-tolerant ceramics [8]. Thermal stable basalt fibres can serve as reinforcement of fibrous composites manufactured by means of additional heat treatment of a polymer matrix composite, which yields a ceramic matrix composite [9]. Alkali-resistant glass fibre is used as micro-reinforcement in concrete-like composites because of its stability in high alkali environments, to improve compressive and flexural strengths and toughness [10]. Furthermore there is an optimum fibre length for the best effect on the composite. For example, small diameter oxide fibres are excellent reinforcements for composites used in high temperature applications.

Mullite is one of the outstanding ceramic materials, noted for its refractory properties, high temperature strength and retention modulus, creep resistance, chemical stability and low thermal conductivity. An important potential application of mullite is fiber reinforcement in high temperature ceramic-matrix-composites. The superior structural properties of composite materials made by the incorporation of mullite fiber reinforcements into various ceramic matrix materials have received much attention from the military and civilian aircraft industries [8].

There are several methods for manufacturing of fibers in the SiO_2-Al_2O_3 system. Directionally solidified mullite fibers can be grown by a laser heated float-zone method. The successful method for preparation of polycrystalline mullite, mullite-alumina fibers is a sol-gel process [11–12]. Textured mullite fibers were formed by heat treatment of polycrystalline fibers using quadrupole lamp furnace [13]. An alternative fiber preparation technique can be so called internal crystallization method [14]. Each of them has advantages and disadvantages and depends on the properties has to be reached.

Fibrous material manufactured by plasma spray technique was studied in this research. Waste catalyst of oil refinery and petrochemical industries was used as raw material for fibrous material production. The influence of the plasma spray regimes as well as annealing temperature on microstructure of the formed fiber was analyzed. SEM and X-ray diffraction technique were applied to study morphology and composition of the fibers.

2. EXPERIMENTAL

The prime material for this work was powder of waste oil-cracking catalyst with following chemical composition [mass %]: Al_2O_3 – 40.9, SiO_2 – 55.2, Fe_2O_3 – 0.9, TiO_2 – 1.4, CaO – 0.5, MgO – 0.49, Na_2O – 0.2. The particle size was approximately 50 μm, density – 830 $kg \cdot m^{-3}$, ignition loss – 5.4 %.

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Plasma sprayed fibrous material was produced employing non-equilibrium plasma spraying technology at atmospheric pressure [15 – 16] suitable for various engineering applications.

For investigations plasma chemical reactor of two types were used. Experimental set-up, plasma spray parameters and four regimes had been depicted in detail elsewhere [17].

Scanning electron microscopy (JEOL, JSM 5600) was used to characterize the morphology and the microstructure of the as-formed and sintered fibrous material. The diameter changes of separate fibers before and after sintering were measured using optical microscope (OLYMPUS BX51TF) with software "QCapture Pro".

X-ray diffraction (XRD) profiles were obtained using Cu-K_α radiation (DRON-UM1) source to determine the crystallinity of fibrous material and to identify the existing phases by the commercial search match program. The crystallite size of fibers was determined using XFIT program by fitting XRD data using Fundamental Parameters Approach [18].

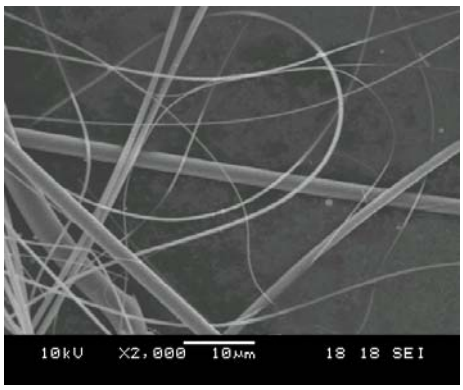
3. RESULTS AND DISCUSSION

Fibrous material manufactured by plasma spray method looks like a net of long (up to 150 mm) fibers of different diameters which vary in a range from 0.2 μm up to 20 μm. The calculated average diameter of fiber is (3.88 ±0.1) μm.

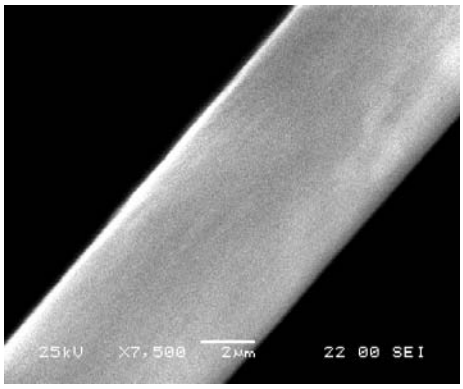
Figures 1 and 2 show typical SEM micrographs of as-produced fibrous material. It was observed that as-produced material can be divided into two groups according dimensionless parameter (l/d), where l is length of reactor and d is outlet diameter of reactor. The waste catalyst's particles were exposed longer in the plasma chemical reactor when (l/d) < 20. In this case more homogeneous state of melt was reached and material with smooth and fine fibers was formed (Fig. 1). Contrary, at (l/d) > 20 relatively high flow rate determined formation of fibrous material together with micro granules and agglomerates of sub microns particles (Fig. 2).

X-ray analysis showed that the fibrous material produced by four plasma spray regimes had only amorphous phase (not depicted). The obtained samples were annealed at various temperatures and different time for study of crystallization process of the material. Figure 3 shows the XRD patterns of the heat treated fibrous material. The amorphous phase partially transforms to crystalline mullite phase after annealing at relative low temperature 900 °C for 2 hours (Fig. 3, a). It is pointed out [19] that mullitization temperature decreases with increasing mixing scale at molecular level. Longer heat treatment of fibrous material up to 12 hours did not reduce amorphous phase and no changes in XRD patterns were observed. The formation of cristobalite was noticed after annealing at 1000 °C for 12 hours (Fig. 3, b). Complete crystallization of fiber occurred after calcinations at 1200 °C for 1 hour (Fig. 3, c).

Transformation temperature of SiO_2 depends on grain size as well as order of the structure. Formation of cristobalite

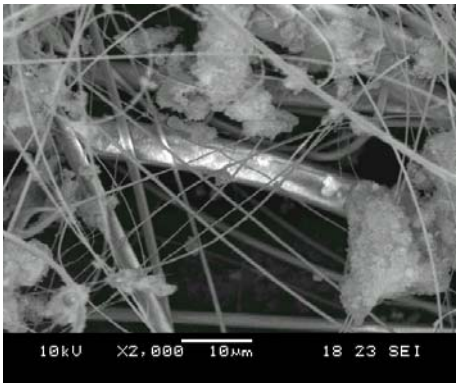


a



b

Fig. 1. Typical SEM views of as-produced fiber at (l/d) < 20 at various magnifications: a – ×2000, b – ×7500



a

b

Fig. 2. Typical SEM views of as-produced fiber at (l/d) > 20 at various magnifications: a – ×2000, b – ×6000

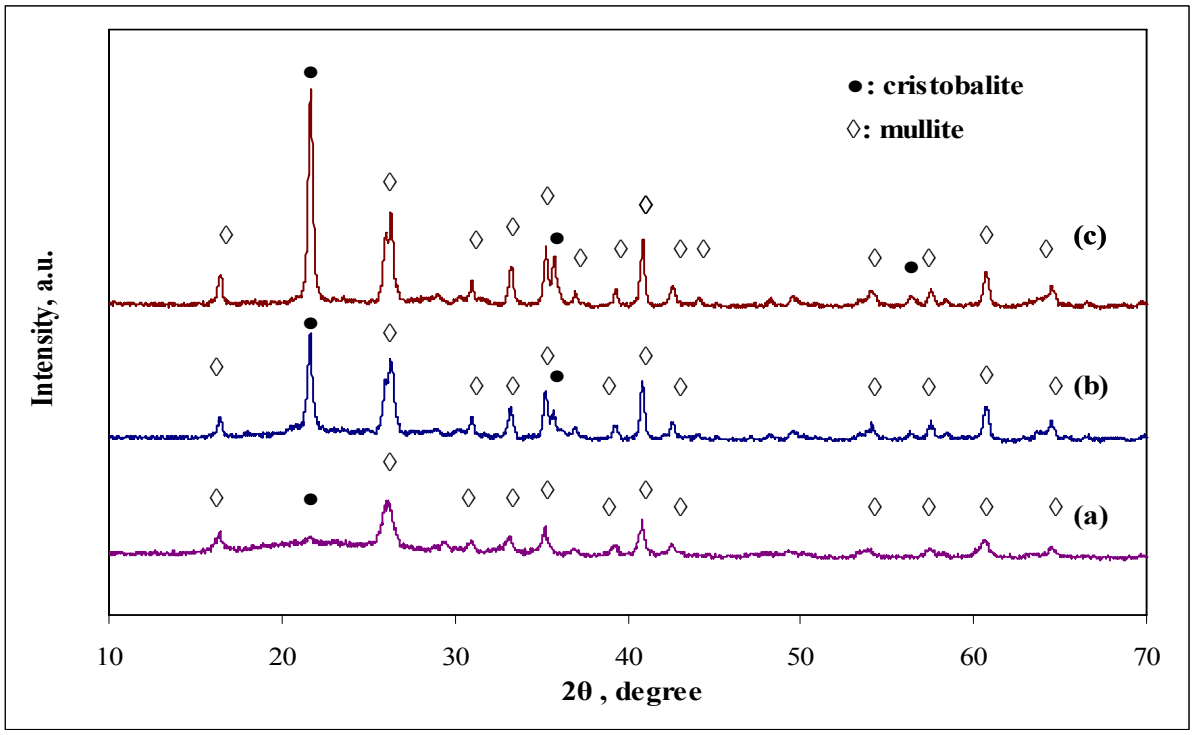
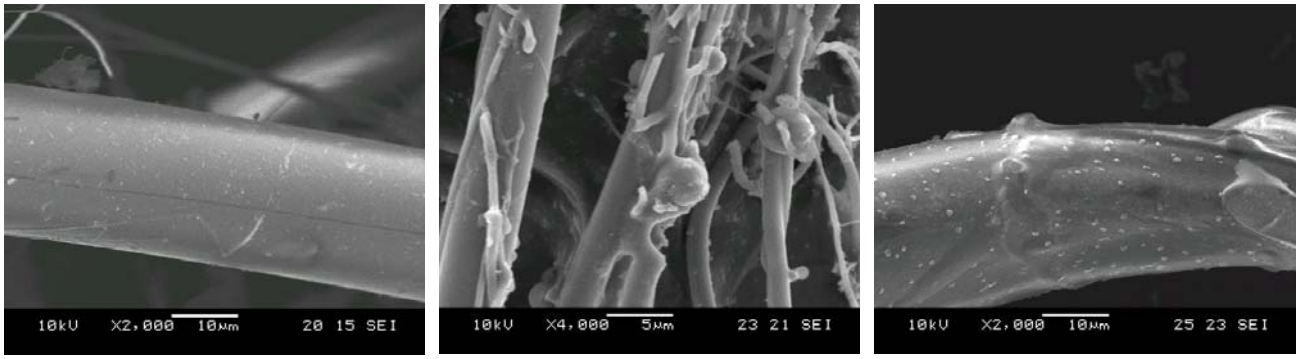


Fig. 3. XRD patterns of fiber heat treated: a – at 900 °C for 2 h, b – at 1000 °C for 12 h and c – at 1200 °C for 1 h



a b c

Fig. 4. SEM view of annealed fiber: a – at 900 °C for 2 h [(*l*/*d*) < 20], b – at 1000 °C for 12 h [(*l*/*d*) > 20], c – at 1200 °C for 1 h

takes place at 1200 °C ÷ 1400 °C when grain size is lower and crystallinity of material is higher [20]. However, cristobalite is detrimental to the mechanical properties and diminishes thermo stability of the fiber [20].

Thermal shrinkage and fragility of the fibrous material was observed after annealing at 1000 °C. It was due to mainly phase change and consolidation of the network of the fibers (Fig. 4, b). Shrinkage was evaluated by measuring diameter of separate fibers before and after thermal treatment at different temperatures. Results (Table 1) are in good agreement with literature [21] where was noted that thermal shrinkage of the aluminosilicate fiber increases with the increase of temperature and as long as amorphous phase is present.

The calculated mean diameter of crystallites (Table 1) as well as XRD results (Fig. 3) pointed out crystallization of the fibers with increasing temperature or annealing time which was also observed by others [13].

Figure 4 shows SEM micrographs of the annealed fiber. After annealing at 900 °C for 2 h, when formation of mullite phase was found, no essential differences in the morphology of fibers were observed excepting the appearance of small grains on the surface of fiber (Fig. 4, a). The surface of the fibers was fused after annealing at 1000 °C for 12 hours and was visible at (*l*/*d*) > 20 (Fig. 4, b).

Table 1. Diameter shrinkage and calculated crystallites size

Temperature, °C	Annealing time, h	Shrinkage, %	Crystallite size, nm
900	2	–	16.3
900	12	1	18.4
1000	12	5	25.4
1000	48	15	40.0
1200	1	15	56.1

Heat treatment at higher 1200 °C temperature determined growth of grains or belike new crystallization products of the fiber produced both at (*l*/*d*) > 20 and at (*l*/*d*) < 20 (Fig. 4, c).

4. CONCLUSIONS

Plasma spray method was used to form fibrous material from waste catalyst. It was observed that geometry of plasma chemical reactor and flow rate had influence on formation of two groups of fibrous material. Material with smooth and fine fiber was formed at $(l/d) < 20$, and at $(l/d) > 20$ fiber with micro particles was produced.

It was determined that crystallization of the fibrous material with formation of mullite phase started at 900 °C. Formation of cristobalite was observed after annealing at 1000 °C for 12 hours as well as fusion of the fibers. Shrinkage of the fibers had reached the highest value up to crystallization of the fiber occurred.

It was determined that crystallites size of the fiber increases with increasing annealing temperature and sintering time.

Acknowledgments

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