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Synthesis and characterization of β′-sialon whiskers prepared from the carbothermal reaction of silica fume and α-Al_2O_3

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β′-sialon whiskers were synthesized from silica fume and α-alumina via the carbothermal reduction reaction under nitrogen flow. The growth of whiskers was found to be conducted by the vapour–solid–liquid crystal growth mechanism involving SiO, $FeCl_3$ and other vapour species. SEM observation and EDAX reveal that the changing morphology of whiskers: branching, varying size, shape and growing direction, is a result of variations in vapour composition.

1. Introduction

Ceramic whiskers, such as SiC, Si_3N_4 whiskers, have received much attention, due to their advantages of high melting points, low densities and high moduli when used as reinforcing materials in composites. The most widely used and studied ceramic whiskers are silicon carbide whiskers [1–6]. Studies on the formation of Si_3N_4 whiskers [7] and β′-sialon whiskers [8] have been reported. β′-sialon whiskers were always formed in the synthesis of Si_3N_4 whiskers [8, 9], whereas efforts at synthesizing pure sialon whiskers have not been seen in the literature. Sialon powders can be obtained from various sources [10–14], of which agricultural and industrial by-products have attracted considerable attention. In our early work, β′-sialon powders were successfully produced by the carbothermal reduction reaction of alumina with silica fume, a silica waste in the silicon–ferroalloy industry, under nitrogen flow. The main objectives of the present paper are to investigate the synthesis and the characterisation of β′-sialon whiskers obtained in a similar process and to report the further understanding of the formation mechanism of sialon whiskers.

2. Experimental procedure

2.1. Whisker synthesis

The synthesis of β′-sialon whiskers was performed in a graphite crucible placed in a vertical tube furnace with a nitrogen flow through the bottom of the crucible, as schemed in Fig. 1. The compositions of starting materials are listed in Table I.

A small amount of $FeCl_3$ (c.p. grade, > 99.5%) was added to the batch as a catalyst for the formation of β′-sialon. The pellets ($\varnothing 3 \times 10$ mm) of the mixture were loaded into the crucible to 1/3 its volume. The nitrogen flow (99.0% purity) with a flow rate of 1000 cc min^{-1} was then introduced through the crucible. All reactions were carried out at 1450 °C for 6 h.

2.2. Whisker characterization

The resulting products, i.e. the pure wool-like whiskers and the base, where they grew from, were respectively identified by X-ray diffraction (XRD) using a Be window specimen holder for the wool-like whiskers and bulk base samples. The morphologies and the compositions of whiskers were investigated by scanning electron microscopy (SEM) and energy dispersion analysis of X-rays (EDAX). The specimens were coated with gold in the SEM observations and EDAX.

3. Results and discussion

Whiskers formed around the upper wall of the graphite crucible, mainly concentrated on the inside and outside of the crucible open area (Fig. 1). White wool-like whiskers grew from the crucible wall about 1 cm long with diameters of 0.2–2 μm. The surface layer of the crucible became rather loose and could be easily stripped off after the growth of whiskers. Short whiskers also formed on the pile of pellets. X-ray diffraction patterns of whiskers and the base are shown in Fig. 2. The X-ray diffraction patterns of β′-sialon powders produced with the same batch composition and identical processing but with different reaction parameters, especially the nitrogen flow rate, are also displayed in Fig. 2 for comparison. It indicates that the resultant whiskers, as well as the base, are in the form of β′-sialon, similar to the powders synthesized. The intensities of diffraction peaks for the whiskers and the base are different from that of the powders because wool-like and bulk specimens, instead of powders, were used in the XRD, resulting in an orientation effect. Fig. 3 shows the SEM observations of whiskers and the base, indicating both are fibrous materials, but with different morphologies due to different growth conditions. Some of the whiskers show globules with various surface morphologies at their tips (Fig. 4), that differ from the β′-sialon whiskers ob-

TABLE I Compositions of starting materials (wt %)

	SiO_2	Al_2O_3	Fe_2O_3	MgO + CaO	$Na_2O + K_2O$	TiO_2	C	LOI
Silica fume	91.50	0.10	0.51	2.50	0.90			4.50
α-Al_2O_3		92.0		1.50	1.0	3.0		0.05
Carbon black							> 99.0	

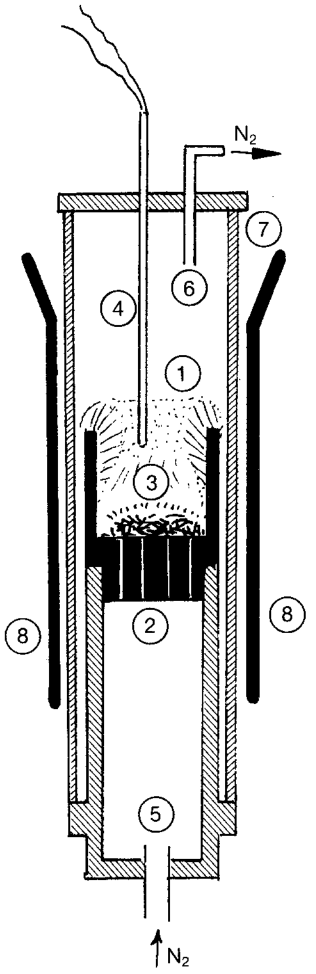

Figure 1 Scheme of the equipment for synthesis of β′-sialon whiskers: (1) sialon whiskers; (2) crucible bottom with pin holes for N_2 flow; (3) pile of raw material pellets with short whiskers; (4) thermal couple; (5) nitrogen inlet; (6) nitrogen outlet; (7) SiC tube; (8) heating elements.

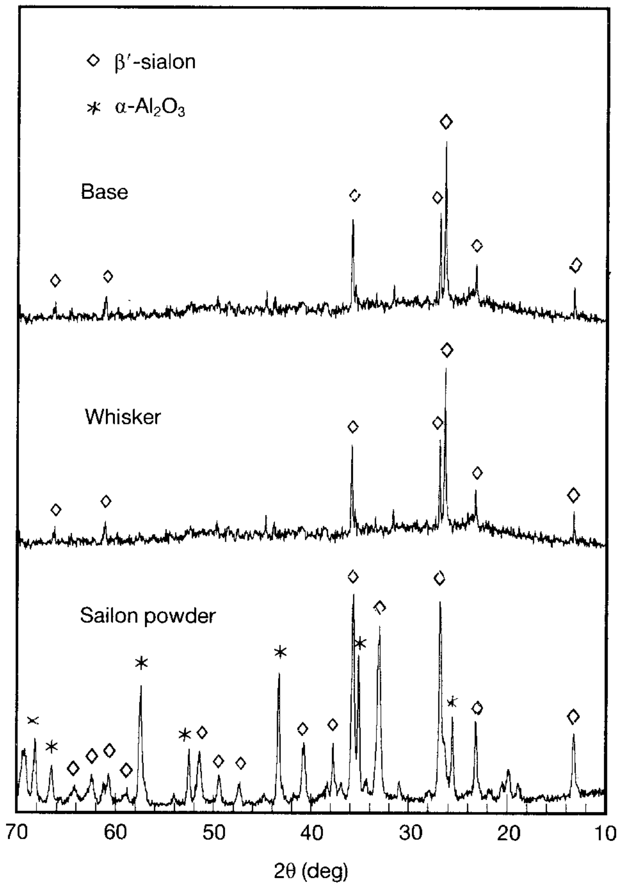

Figure 2 X-ray diffraction patterns of sialon whiskers, the base from which the whiskers grew and sialon powders.

tained in [9], but are consistent with a vapour–liquid–solid (VLS) related crystal growth mechanism [10]. The EDAX of one globule indicated a composition enriched with iron catalyst in a silicate solution (Fig. 4b). Very fine crystallisation features on the surface layer of the droplet can be clearly seen (Fig. 4a, c), which provide further evidence of the VSL growth mechanism dominating the synthesis of the whiskers [10]. Short whisker formation at some spots on the droplet at the whisker tip may also provide the possibility of a VS growth mechanism in some critical case (Fig. 4c). Most of the whiskers have rectangular cross sections, however some show varying size and a branching shape (Figs 5 and 6). The composition of the whisker trunk was analyzed by EDAX, as indicated in Fig. 5b, with a ratio of Si/Al = 97.91/2.09 (wt) and a low chlorine content. However, the whisker composition at the branching location shows considerably higher impurity levels, i.e. Na, K, Ca and a remarkably high chlorine content (Fig. 5c). The smooth branching of the whiskers implies a continuous composition variation from minor impurity content in the trunk to high impurity content in the joint. Fig. 6 shows another form of branching in which the whiskers could not form a branch but instead rapidly changed its growing direction. The fluctuation of whisker size and shape might also indicate a variation of composition near the joint location, as has been seen in Fig. 5.

Efforts were made to investigate the roots of the whiskers. Typically, a polycrystalline was found at the root from where the whisker grew, as shown in Fig. 7a. The whisker composition at the root is notable as having no chlorine content, compared with that of the trunk and the branching locations (Fig. 7b).

From the above observations, β′-sialon whisker formation most probably was conducted by a VLS growth mechanism, i.e. a liquid layer, in which the crystal material itself (or its compounds) is soluble, is situated between the vapour and the growing crystal.

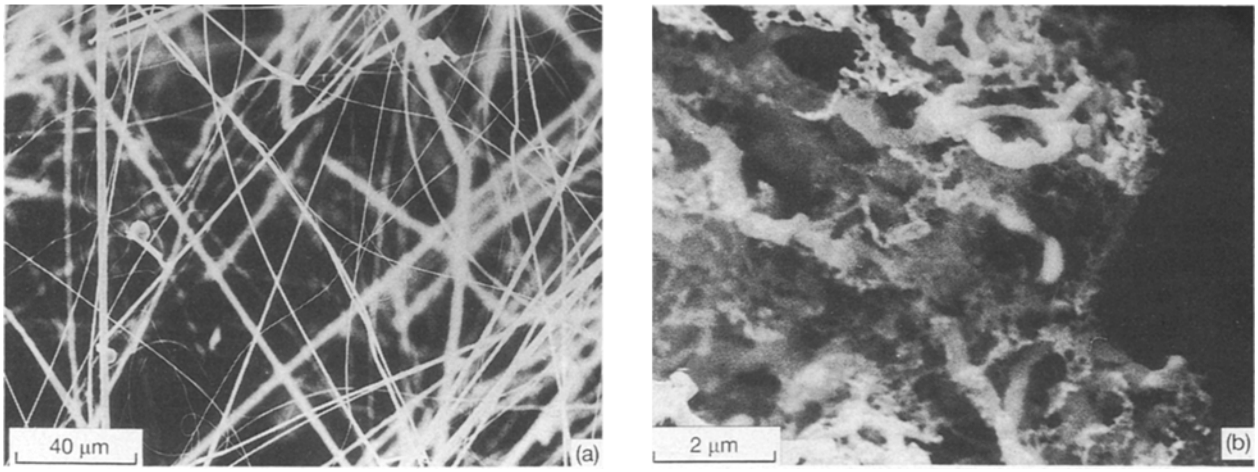

Figure 3 SEM micrographs of β′-sialon whiskers and the base: (a) whiskers; (b) base.

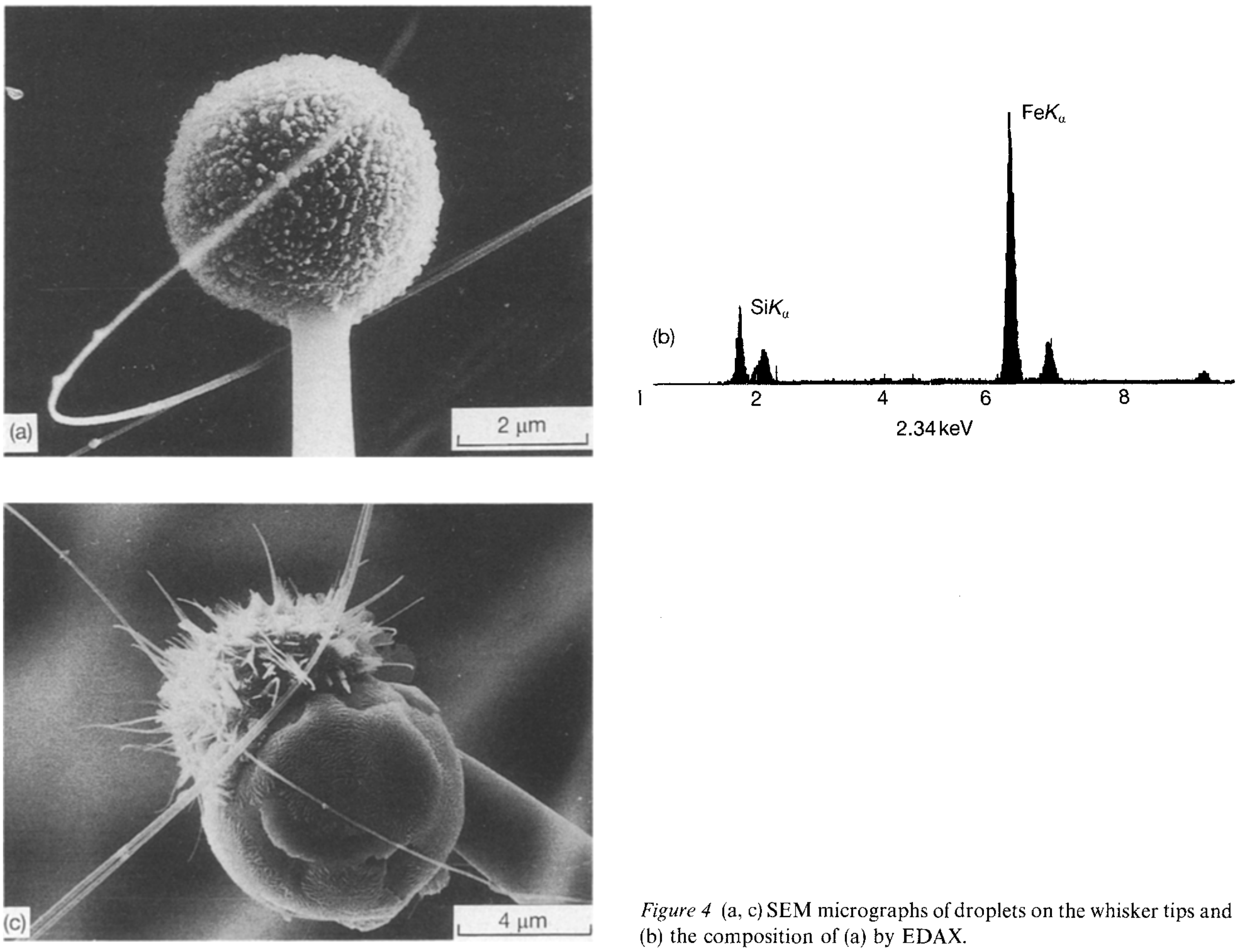

Figure 4 (a, c) SEM micrographs of droplets on the whisker tips and (b) the composition of (a) by EDAX.

The surface of the liquid is a preferred site for deposition of the soluble components from the vapour, and so once the liquid becomes supersaturated with the reacting species, crystal growth occurs by precipitation at the solid–liquid interface. The occurrence of droplets enriched with iron at the whisker tips was evidence that the growth of β′-sialon whiskers synthesized in the present work occurred by the VSL mechanism. A common observation for all VSL catalysts was the presence of a defective crystalline outlayer of varying thickness surrounding the bulk of the catalyst [10]; this was also observed in the present work for the droplets on the whisker tips (Fig. 4). The fact that the majority of whiskers formed on the open area of the graphite crucible implies that some vapour phases deposited on the crucible wall to form a liquid layer first, and then the others dissolved into that layer, making it supersaturated and a preferential site

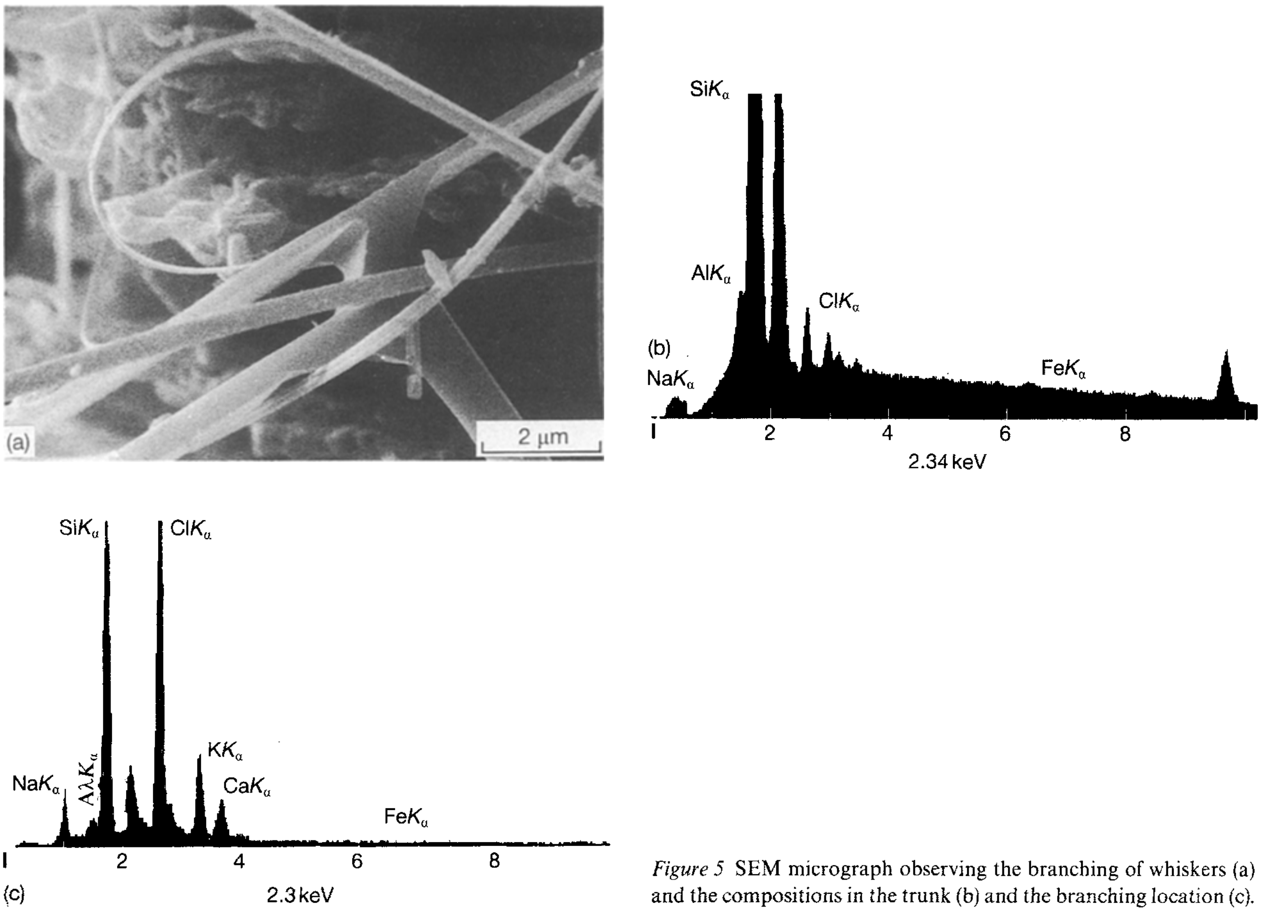

Figure 5 SEM micrograph observing the branching of whiskers (a) and the compositions in the trunk (b) and the branching location (c).

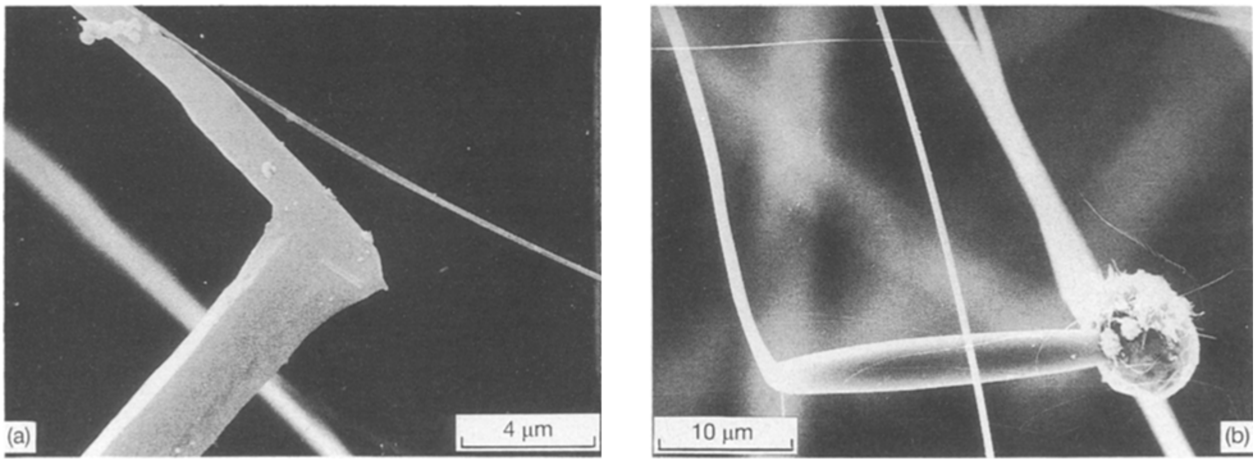

Figure 6 SEM micrographs of another form of whisker branching.

for the growth of whiskers. The liquid layer became a droplet on the whisker tip when growth of the whisker started. Dissolution of the vapour species into the droplet continued to supply the further whisker growth. The most important vapour phase in this reaction was SiO formed by the reaction:

$$SiO_2(S) + C(S) \rightarrow SiO(g) + CO(g)$$

The existence of SiO vapour in the reaction zone was confirmed by analyzing the deposit on the alumina outlet by X-ray diffraction and X-ray fluorescent spectrum analysis, shown in Fig. 8. It shows an amorphous substance having an X-ray diffraction pattern similar to that of silica fume and containing 42.0 wt % Si, which was close to the 46.6 wt % Si in SiO_2, and a small amount of Al, which was believed to be contamination from the alumina tube where the specimen for the analysis was collected. This was proved to be the product of SiO reoxidation in air. The occurrence of SiO vapour in carbothermal reductions involving silica has also been proved by others [9, 11, 12].

Another important vapour phase was the catalyst $FeCl_3$. Iron has long been known to be an effective catalyst for VLS whisker growth [13–18]. Due to its low boiling point, iron chloride possibly evaporated from the starting pellets, followed by reaction with

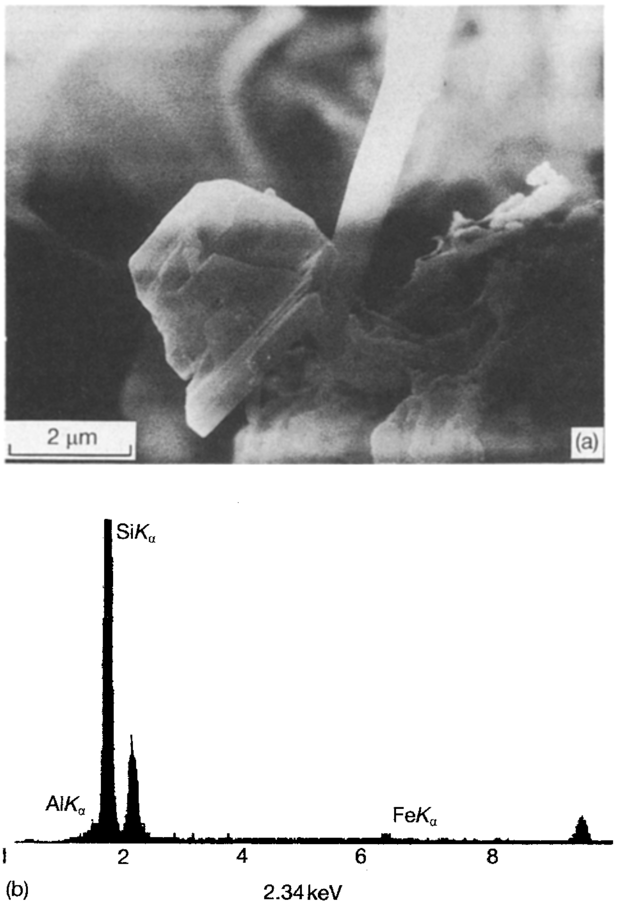

Figure 7 (a) SEM micrograph of whisker root and (b) its composition by EDAX.

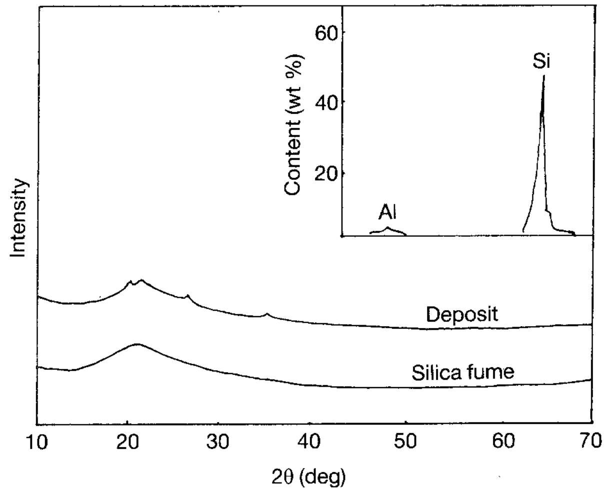

Figure 8 X-ray diffraction pattern of the deposit on the N_2 outlet and its composition by X-ray florescent analysis.

SiO to form iron silicate, resulting in a rise in its melting point and formation of a liquid layer on the graphite crucible wall. That liquid layer provided the site for further dissolution of SiO, N_2 and other evaporating substances that generally increased the viscosity of the liquid until it reached a value high enough that the surface tension of the solution could no longer keep the liquid in globular form as the whiskers grew. This resulted in a spinodal extending from the droplet as seen in Fig. 6b. It could be observed that the impurities Na, K and Ca in the silica fume or in the graphite binder, along with Cl from the catalyst, transformed into whiskers resulting in branching. It may suggest that whisker morphology could be monitored by controlling the vapour phase composition.

4. Conclusions

1. β′-sialon whiskers can be synthesized from silica fume and α-alumina via a carbothermal reduction reaction.
2. The formation of β′-sialon whiskers is proved to occur by a VSL growth mechanism involving SiO, $FeCl_3$ and other vapour species.
3. The variation of composition, which originates from the changing deposition rate of various vapour components into the catalyst droplet surface during the reaction period, results in a change in whisker morphology.

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