

# IN SITU INVESTIGATION OF OXIDATION MECHANISM OF $\beta$ - $\text{Si}_3\text{N}_4$ BASED CUTTING TOOL BY MEANS OF HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY COMBINED WITH TECHNICAL FOCUSED ION BEAM

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**Abstract:** *The oxidation mechanism of  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool, used in the machining of gray cast iron FC 250, was investigated by means of HRTEM analysis. The cross section samples, obtained in the edge and in the region where the chip separates from the tool, were prepared by focused ion beam and analyzed with a high resolution transmission electron microscopy. Complementary techniques, such as EFTEM, were employed in the mapping of chemical elements. It was demonstrated that  $\beta$ - $\text{Si}_3\text{N}_4$ , adjacent to the edge surface of the cutting tool, it oxidizes to form an  $\text{SiO}_2$  layer with 12 nm thick. The oxygen at the surface, diffuses through this layer going to react at the interface  $\text{SiO}_2/\text{Si}_3\text{N}_4$ , giving rise to 7 nm  $\text{Si}_2\text{N}_2\text{O}$ . Concomitantly, there was a diffusion of rare earth elements toward the surface of the oxide layer. The rare earth metal ions reacted with  $\text{SiO}_2$  to form a new material with a diameter of 2 nm. The oxidation wear mechanism developed at the  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool in the machining of gray cast iron FC 250 is mainly the result of internal tensions developed between the  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  as a result of these two different density materials. These internal tensions favor the separation of the  $\text{SiO}_2$  surface of the tool in the form of fragments that are transported from the bottom chip's surface to the position where it separates from the tool.*

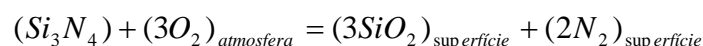
**Keyword:** *oxidation,  $\beta$ - $\text{Si}_3\text{N}_4$ , machine, transmission electron microscopy, focused ion beam.*

## 1. INTRODUCTION

The  $\beta$ - $\text{Si}_3\text{N}_4$  based ceramics have been studied since the early 1960s (Takatori et al. 1991). This material was first used in gas turbine as their properties at high temperatures (Bocanegra-Bernal et al. 2009). However, it was only in the late 1970s that the  $\beta$ - $\text{Si}_3\text{N}_4$  based ceramics started to be used as cutting tools.

The  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tools are often used in machining, particularly for cast iron at high cutting speed as it good resistance to wear, high hot hardness, high fracture toughness and good oxidation resistance.

The oxidation of pure  $\text{Si}_3\text{N}_4$  starts above 1000 °C resulting in the formation of a  $\text{SiO}_2$  layer on the surface of  $\text{Si}_3\text{N}_4$  (Deschaux-Beaume et al. 2009; Amin et al. 1989). Different other values are reported in the literature. According to Tokusou et al. (2001), the oxidation of  $\text{Si}_3\text{N}_4$  begins at 873 K. For the sintered silicon nitride, oxidation temperature may be lower due to the presence of sintering material (Deschaux-Beaume et al. 2009). The oxidation of  $\text{Si}_3\text{N}_4$  to  $\text{SiO}_2$  occurs according to reaction (Subramanian, 2000; Lewis, 1980, Oliveira et al. 2005; Ricoult et al. 2002):



According to Jacobson (1993), the oxidation of  $\beta$ - $\text{Si}_3\text{N}_4$  can be divided into the five steps described below, Fig. 1(a). First, under exposure to oxygen, the silicon nitride surface oxidizes to form silicon dioxide ( $\text{SiO}_2$ ). The oxygen diffuses across the surface of  $\text{SiO}_2$  layer in ionic or molecular form. This oxygen starts to react at the  $\text{SiO}_2/\text{Si}_3\text{N}_4$  interface, giving rise to  $\text{Si}_2\text{N}_2\text{O}$ . Finally, the  $\text{N}_2$  (g) diffuses through the oxide film toward the surface. In this model, the diffusion of oxygen through the layer is  $\text{Si}_2\text{N}_2\text{O}$  step slower process due to its structure is more compact than that of  $\text{SiO}_2$  (Du et al. 1989).

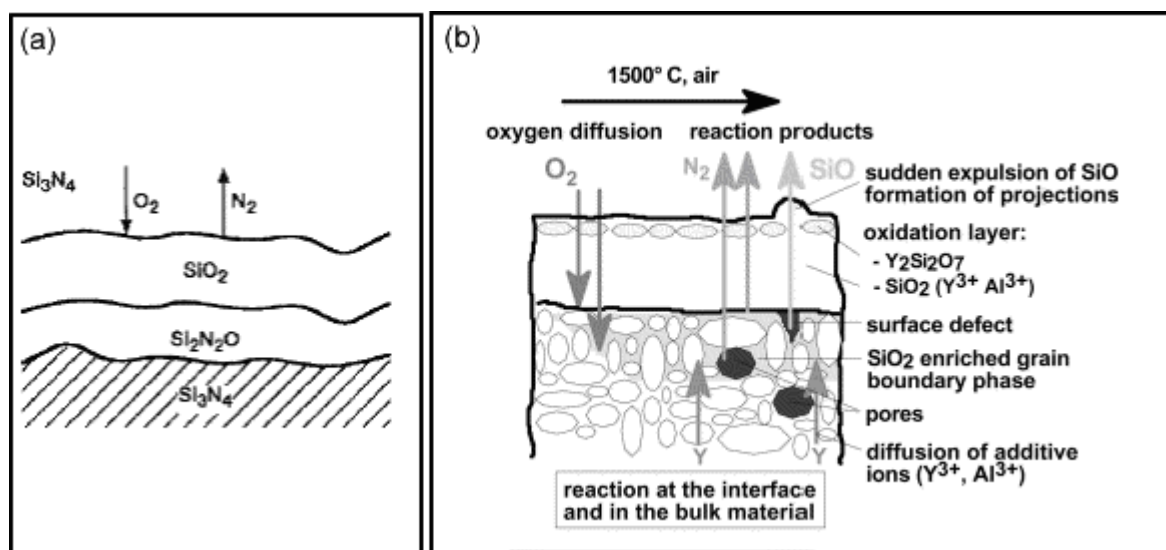


Figure 1 – Schematic diagram of the oxidation mechanism of (a)  $\text{Si}_3\text{N}_4$  pure (Jacobson, 1993).  
 (b)  $\text{Si}_3\text{N}_4$  materials with sintering additives (Klemm et al. 2003)

According to Ogbuji (1995), the intermediate layer of oxynitride has a composition that varies gradually between the  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$ , according to the equation  $\text{Si}_n\text{N}_m\text{O}_{4+n}$ , where  $n$  ranges from 0 in the oxide layer to 4 in the substrate.

Due to the covalent nature of  $\text{Si}_3\text{N}_4$ , sintering additives are used during manufacture of the tool. The model described above does not consider the presence of this material. The addition of sintering additives alters the oxidation mechanism of silicon nitride, as can be seen in the model shown schematically in Fig. 1(b). As oxygen penetrates the silicon nitride  $\text{SiO}_2$  is formed on the surface of  $\text{Si}_3\text{N}_4$  grains. After the initial formation of the  $\text{SiO}_2$  layer, a concentration gradient of ions of rare earth elements ( $\text{RE}^{3+}$ ) is formed between the  $\text{Si}_3\text{N}_4$  grains and the layer of oxidized material. The force resulting from the concentration gradient ions of  $\text{RE}^{3+}$ , promotes the diffusion of  $\text{RE}^{3+}$  ions toward the surface of the oxide layer. Ions of  $\text{RE}^{3+}$  react with oxygen and  $\text{SiO}_2$  to form  $\text{RE}_2\text{Si}_2\text{O}_7$  (Klemm et al. 2003). These reactions, which result in the formation of disilicate layer, depend on many factors, such as: distribution, composition and microstructure intergranular phase, the mobility of the cation and temperature. The consequence of the diffusion of  $\text{RE}^{3+}$  is a change in chemical composition and microstructure of the phase in the grain boundary, leading to degradation of  $\text{Si}_3\text{N}_4$  (Wong, 2004).

Study on oxidation mechanism of  $\text{Si}_3\text{N}_4$  with  $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$  ( $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$  combination is often used as sintering additives to form intergranular phases) developed by Backhaus-Ricoult and Gogosti (1995) suggests that oxidation occurs in follows:

1. formation of aluminosilicate of low viscosity;
2. aluminosilicate penetrates into grain boundaries of  $\text{Si}_3\text{N}_4$ ;
3. oxygen and aluminum are diffused into the grains of  $\text{Si}_3\text{N}_4$ ;
4. dissolution of the grains described in item 3 in aluminosilicate;
5.  $\text{Y}_2\text{Si}_2\text{O}_7$  and  $\text{SiO}_2$  are precipitated in aluminosilicate;
6. Nitrogen is diffused through to the surface of aluminosilicate.

The theoretical models presented were developed for a static condition where the surface is exposed only to an oxidizing atmosphere. Therefore, these models are very simplified compared to the conditions developed on the tool surface during the machining process. Thus, this paper aims to study *in situ* the oxidation mechanism of the  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool used in machining of gray cast iron FC 250 by means of high-resolution transmission electron microscopy combined with technical focused ion beam.

## 2. EXPERIMENTAL

The machining tests were developed by the process of longitudinal external turning with a  $\beta$ - $\text{Si}_3\text{N}_4$ -based tool, class CC6090, at cutting speeds of  $700 \text{ m}\cdot\text{min}^{-1}$ , keeping fixed  $f = 0.2 \text{ mm}$  and  $a_p = 2 \text{ mm}$ . It was used square tools, description snga 120408 T02520, in the form of reversible inserts mounted on a toolholder DSSNR 2525m12-2. Both cutting tools and the tool holder were supplied by Sandvik company. The experiments were carried out under dry cutting conditions to avoid thermal shock. The tool life criterion was a cutting length of 1600 mm.

The detailed characterization of the workpiece material and the cutting tool used in this research can be found in Pereira (2010). The characterization of the cross section of the tool edge and the material deposited at the end of the contact area chip tool, was performed in a transmission electron microscopy Jeol JEM 2100 HTP and Jeol JEM 2100F URP, both operating at 200 kV. The samples for analysis in TEM were prepared by focused ion beam as described by Pereira et al. (2010 a,b). High resolution transmission electron microscopy (HRTEM) images and mapping of chemical elements were obtained by EFTEM in the transmission electron microscope Jeol JEM 2100 HTP, with an resolution of 0.24 nm, and Jeol JEM 2100F URP equipped with Gatan Imaging Filter system (GIF) Tridiem®, respectively.

### 3. RESULTS

Details of the oxidation of cutting tool edge, used for machining gray cast iron at  $700 \text{ m}\cdot\text{min}^{-1}$ , are shown in the image of high-resolution transmission electron microscopy - HRTEM, Fig. 2. From the Fourier transform, attached to the HRTEM image, it is possible to identify spots related to the diffraction of  $\text{Si}_2\text{N}_2\text{O}$  oriented along the zone axis  $[0,1,1]$ . The diffuse ring in the Fourier transform suggests the presence of amorphous material. This observation is confirmed by the corresponding HRTEM image. Some spots in the Fourier transform were not identified.

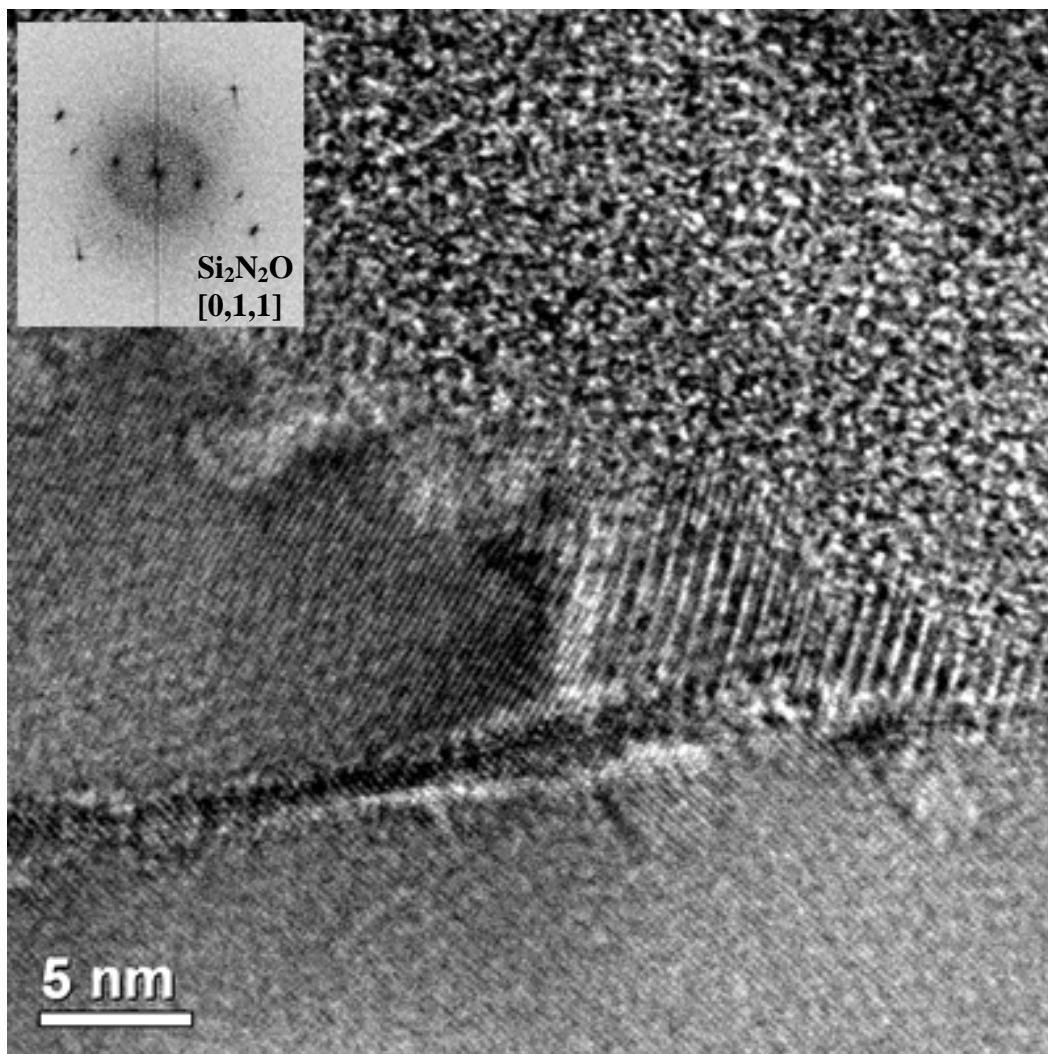


Figure 2 – HRTEM image of tool edge oxidized.

The HRTEM investigation revealed 12 nm depth of  $\text{SiO}_2$  near the cutting edge surface, Fig. 3. It is observed in the HRTEM image, Fig. 2, a reaction at the  $\text{SiO}_2 / \text{Si}_3\text{N}_4$  interface, giving rise to  $\text{Si}_2\text{N}_2\text{O}$ , oriented along the zone axis  $[0,1,1]$ . Oxidation is also displayed inside the edge, Fig. 3, in the form of circular islands with diameter of 4 nm. These areas are shown in Fig. 3 as isolated islands within the material without contact with the surface. However, by obtaining HRTEM images at different defocus values of the cross section of the tool, Fig. 4, shows that these islands are in contact with the surface through "paths". We mean by "paths" areas of material also changed but not circular.

These "paths" may indicate a loss of nitrogen or oxygen infiltration or both. Because the dimensions of these areas was not possible to perform chemical analysis and structural characterization.

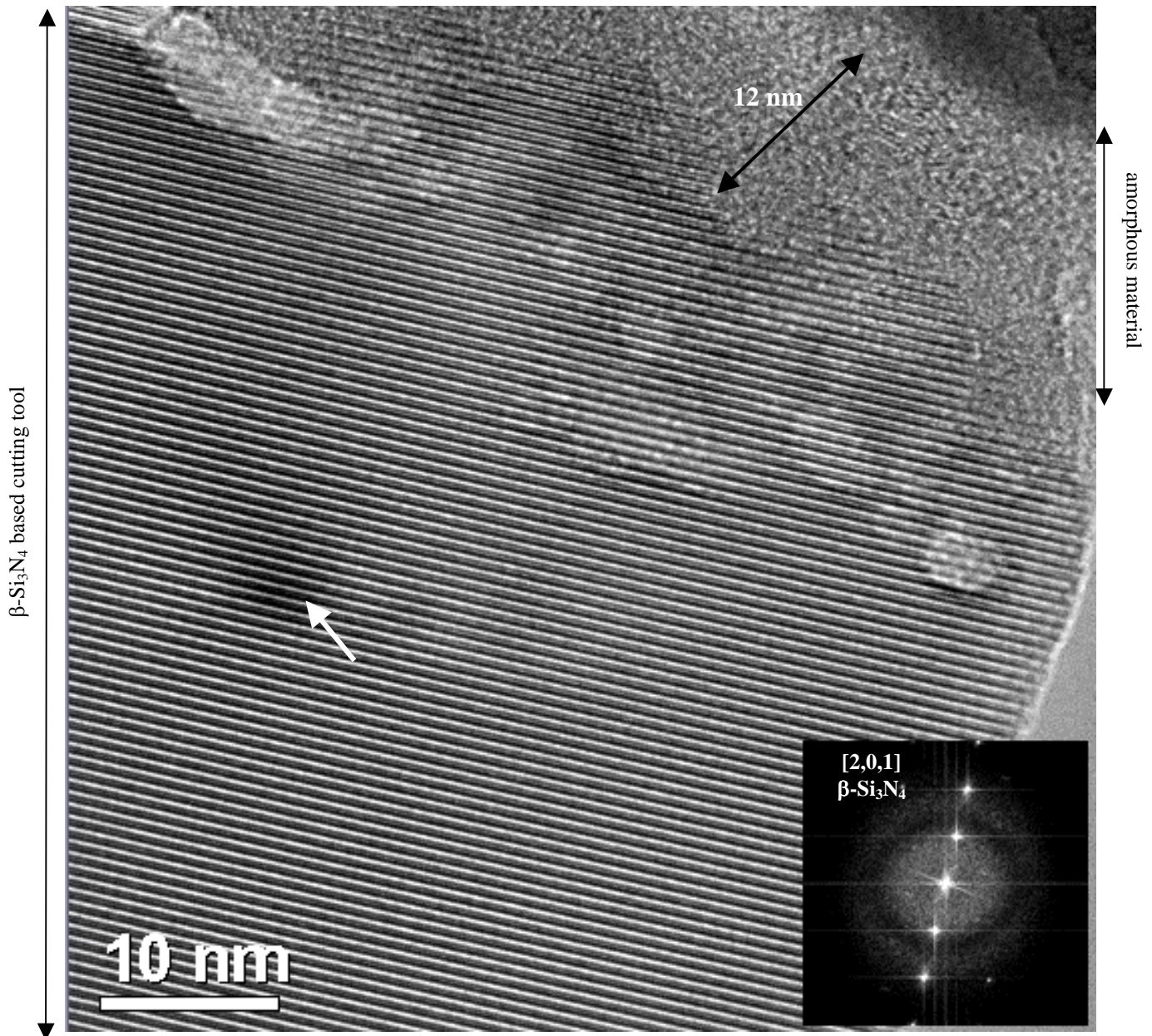


Figure 3 - HRTEM image of  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool showing the changes of the material inside and on the tool edge surface and its Fourier transform. The arrow indicates the region amorphized by the beam of gallium ions used in the preparation of the cross section samples.

Figure 5(a) shows details of the amorphous area that are in contact with the "island" of material changed within the tool material, previously shown separately in Fig. 3 and 4. From the Fourier transform, Fig. 5(b), it is only possible to identify the diffraction spots related to the  $\beta$ - $\text{Si}_3\text{N}_4$  oriented along the zone axis [0,0,1]. The diffuse ring in the Fourier transform suggests the presence of amorphous material. This observation is confirmed by the corresponding HRTEM image, Fig. 5(a). Further details of the identification and indexing of Fourier transform can be found in the work of Pereira (2010)

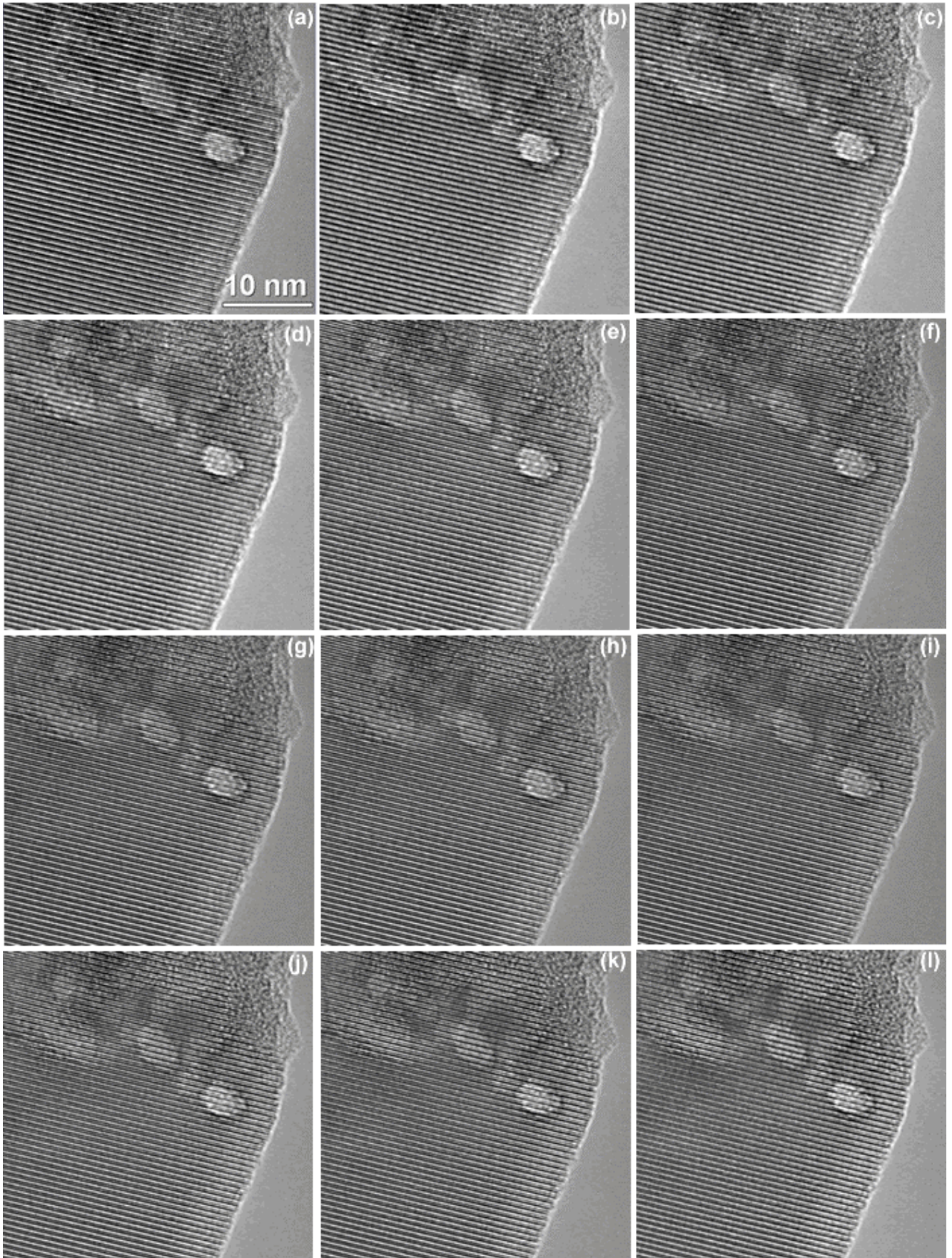
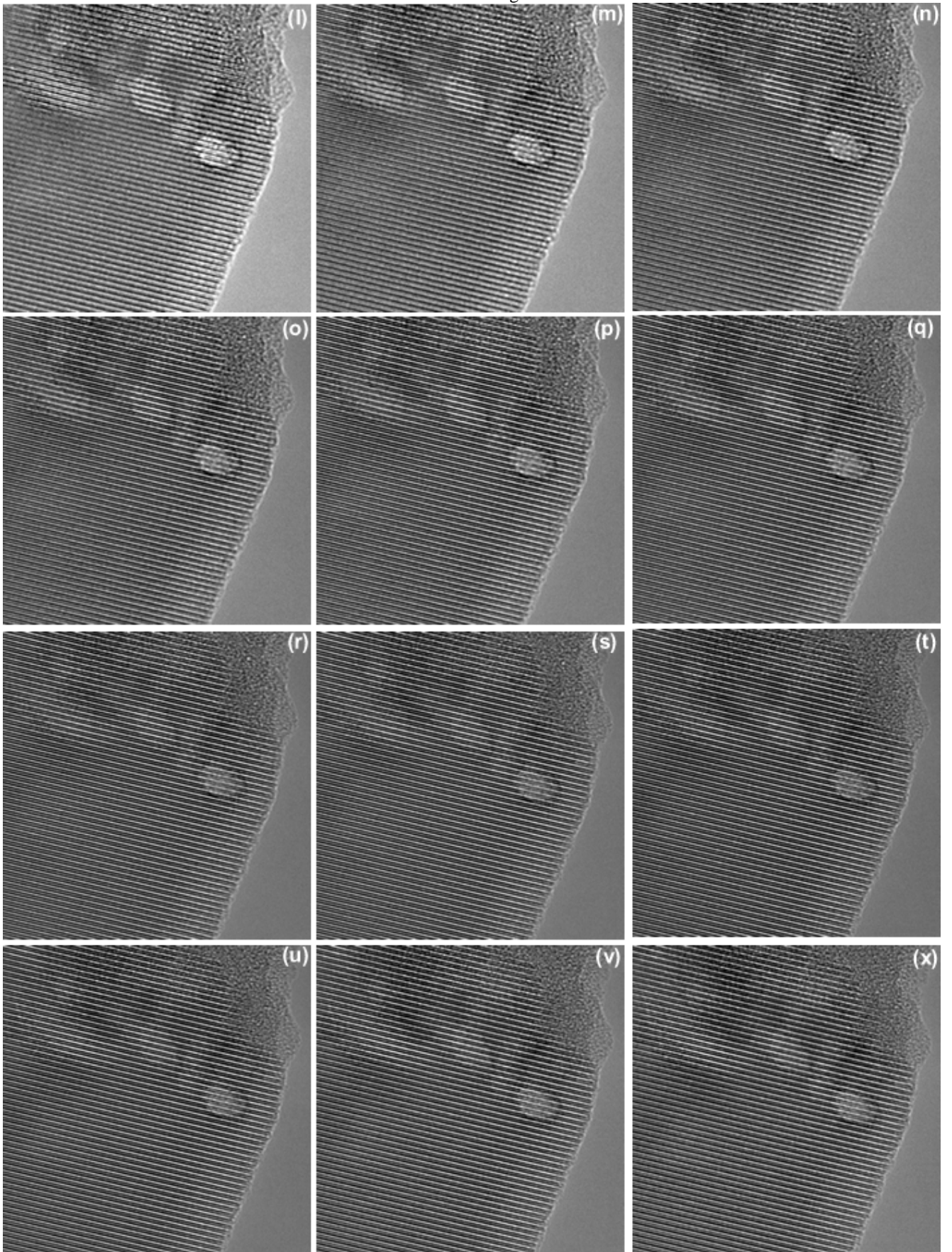


Figure 4 - HRTEM image at different *defocus* values of the cross section of the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> based cutting tool used in machining of grey cast iron FC 250. Continued on next sheet.

...continuation of Figure 4



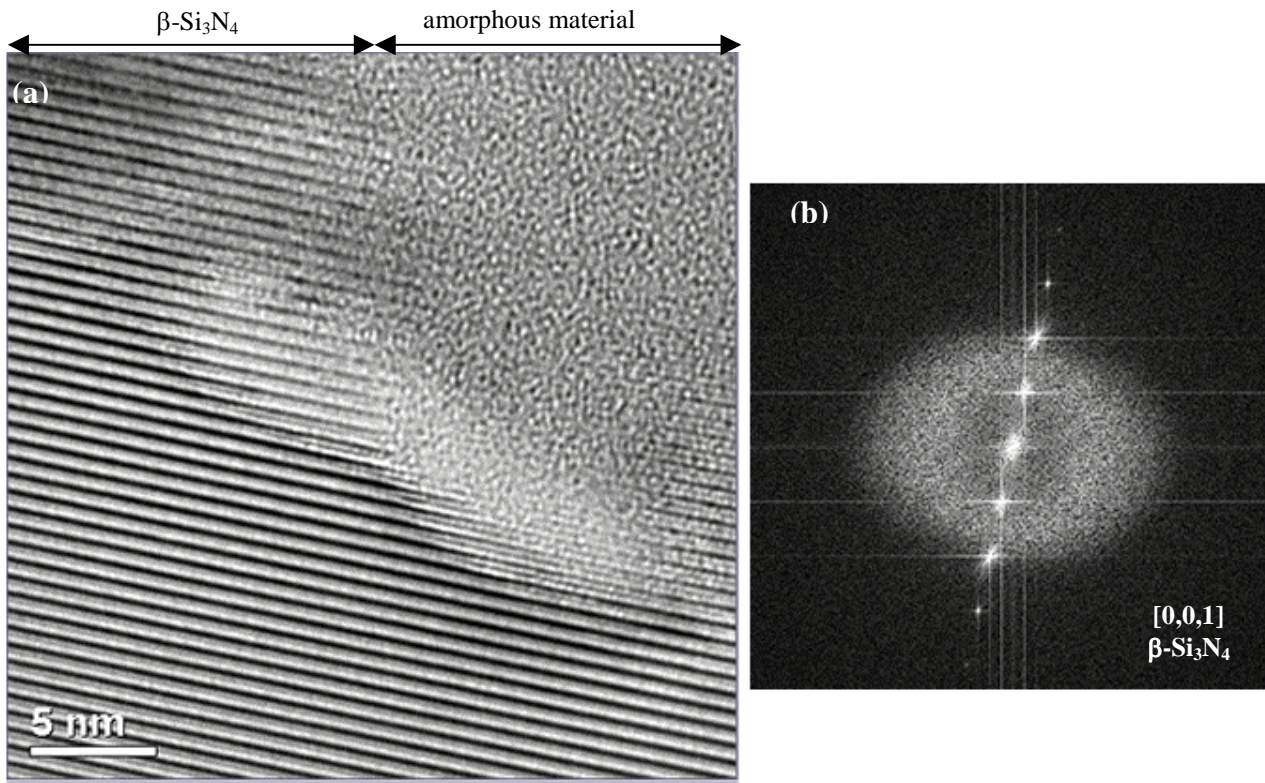


Figure 5 - (a) High resolution image - HRTEM of the changes on the surface of  $\beta\text{-Si}_3\text{N}_4$ .  
(b) Corresponding Fourier Transform.

The product of cutting tool - workpiece material interaction during the machining process is found at the end of the chip-tool contact area. For analysis of this material, cross sections were prepared by focused ion beam. The mapping of the chemical elements in the sample was performed by the use of EFTEM, as its better sensitivity compared to EDS. Fig. 6 shows the distribution of elements N and Si. The region was chosen for the mapping so that the cutting tool - workpiece deposited interface could be examined carefully. Both elements, probably from the  $\beta\text{-Si}_3\text{N}_4$ -based cutting tool, we present unevenly distributed. The images show that there are particles inside the material deposited, "rich" in silicon and "poor" or without nitrogen. Thus, it can be argued that silicon in the material deposited is not fully present in the form of  $\beta\text{-Si}_3\text{N}_4$ , suggesting that silicon is presented as  $\text{SiO}_2$ .

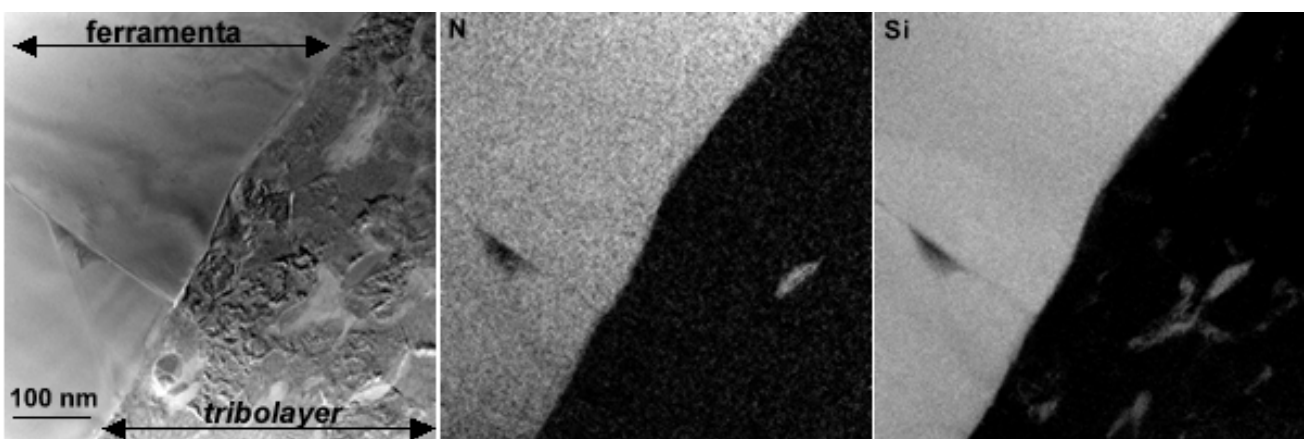


Figure 6 – Zero-loss EFTEM image and EFTEM maps.

Spherical areas, with a diameter of 2 nm, are visible on the oxide layer. They are indicated in Fig. 7 between two dotted lines. Based on the models previously presented, it is suggested that these areas are the result of the reaction of rare earth elements, diffused toward the surface of the oxide layer, with  $\text{SiO}_2$ .

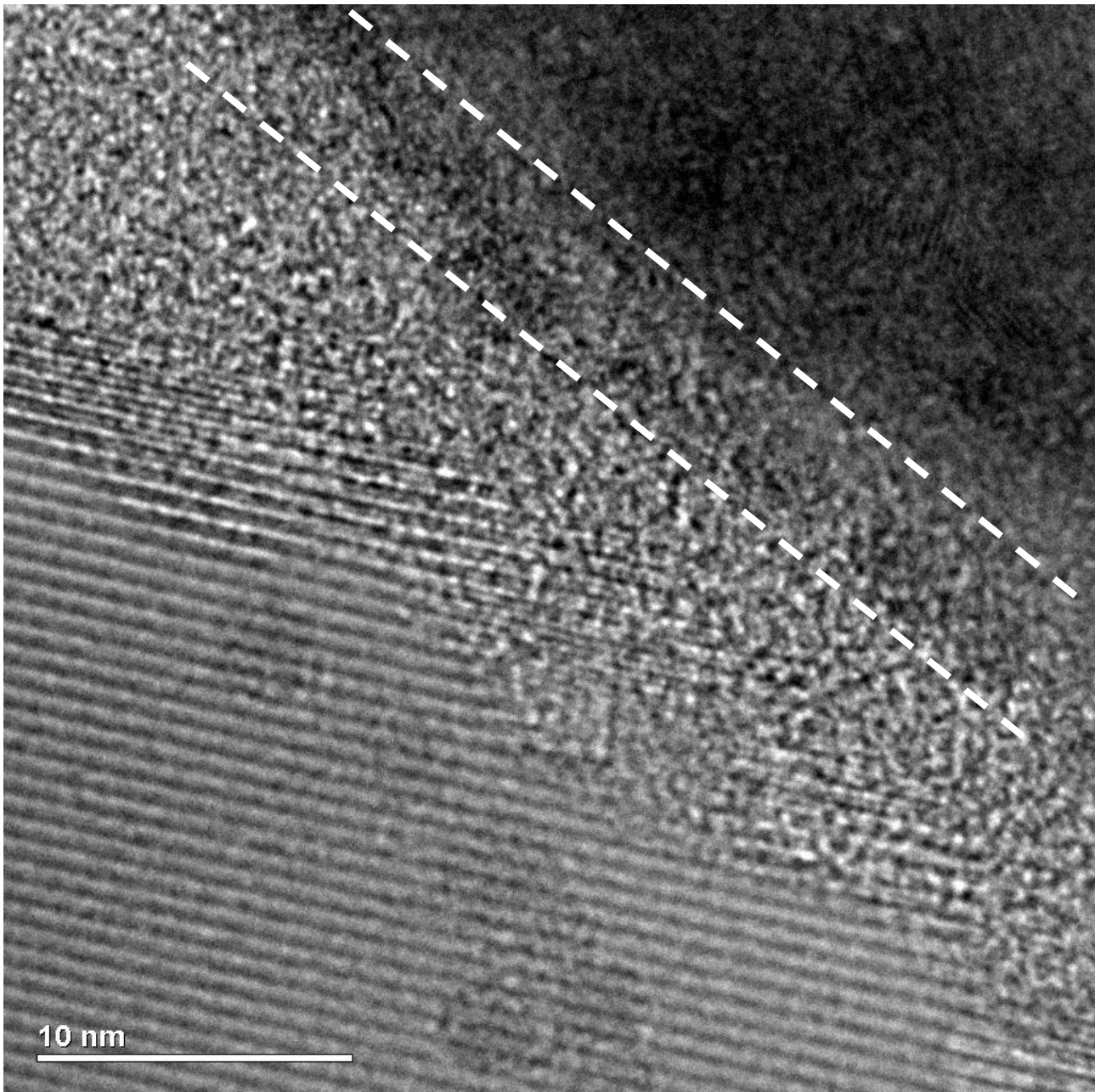


Figure 7 – Distribution of rare earth elements (indicated by dotted lines) on the surface of the oxide layer.

#### 4. DISCUSSION

As a result of high temperature at chip-tool interface,  $\beta$ - $\text{Si}_3\text{N}_4$  near the cutting edge surface oxidizes in the form of  $\text{SiO}_2$ . Although it is not possible to say what was the temperature on the tool surface during the machining process, based on the observation that the chip on the tool surface showed a incandescent color, it is possible to assume that the temperature in the chip-tool interface is sufficiently high to promote oxidation of  $\beta$ - $\text{Si}_3\text{N}_4$ .

It is suggested, based on models previously described and on the results presented, that the  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool oxidizes as follows: first, the surface oxidizes in the form of  $\text{SiO}_2$ . After the formation of this layer, rare earth ions diffuse toward the surface of the oxide. These ions begin to react with the  $\text{SiO}_2$  giving rise to a new compound. Simultaneously, oxygen diffuses through the surface layer of  $\text{SiO}_2$  going to react at the  $\text{SiO}_2/\text{Si}_3\text{N}_4$  interface, giving rise to  $\text{Si}_2\text{N}_2\text{O}$ .

As for the source of oxygen, for oxidation of  $\text{Si}_3\text{N}_4$ , it has been suggested that during the early stages of the machining process, when there is not still the formation of a protective layer on the tool surface, and considering the mechanism of chip formation at very short intervals, the oxygen comes in contact with the tool surface (at a high temperature), favoring the oxidation. It can also suggest the oxygen could come from the  $\text{Al}_2\text{O}_3$  used as sintering additives to fabricate  $\text{Si}_3\text{N}_4$  ceramic.



From the analysis of EFTEM images, it is suggested that oxidation is the dominant wear mechanism of  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool in machining of gray cast iron FC 250. The density of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  is  $2.2 \text{ g.cm}^{-3}$  and  $3.2 \text{ g.cm}^{-3}$ , respectively (Cai, 1989). According to Bin et al. (2007), this transformation of  $\beta$ - $\text{Si}_3\text{N}_4$  on  $\text{SiO}_2$  results in the expansion of 86% of the material, approximately. The internal tensions generated by oxidation of silicon nitride will be add the tension caused by the generation of nitrogen according to the reaction:  $(\text{Si}_3\text{N}_4) + (3\text{O}_2)_{\text{atmosphere}} = (3\text{SiO}_2)_{\text{surface}} + (2\text{N}_2)_{\text{surface}}$ . These internal tensions favor the separation of the  $\text{SiO}_2$  on the tool surface, in form of nanofragments, that are transported by the bottom chip's surface to the position where it separates from the tool.

## 5. CONCLUSIONS

By the means of high resolution transmission electron microscopy combined with the technique of focused ion beam has been shown that  $\beta$ - $\text{Si}_3\text{N}_4$ , adjacent to the tool edge surface, oxidizes into  $\text{SiO}_2$  with 12 nm thick. The oxygen at the surface diffuses through this layer going to react at the  $\text{SiO}_2/\text{Si}_3\text{N}_4$  interface, giving rise to 7 nm thick  $\text{Si}_2\text{N}_2\text{O}$ . At the same time, there was a diffusion of rare earth elements toward the surface of the oxide layer. The rare earth ions reacted with  $\text{SiO}_2$  to form a new material with an average diameter of 2 nm.

It is suggested that the oxidation wear mechanism developed at  $\beta$ - $\text{Si}_3\text{N}_4$  based cutting tool in machining of gray cast iron FC 250 is mainly the result of different density between  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$ .

The internal tension stress favors  $\text{SiO}_2$  removal from tool surface in the form of fragments that are transported for the bottom chip's surface to the position where it separates from the tool.

Although transmission electron microscopy is not commonly used in the study of wear mechanisms carried on cutting tools during the machining process, the results presented here show that this IS an indispensable tool in understanding the interaction between the workpiece material and the cutting tool.

## 6. ACKNOWLEDGEMENTS

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