



# Cracking the pigment code

by Prof Johan de Villiers

During the production process of high-grade titania slag, the solidified tapped slag disintegrates. Prof Johan de Villiers and Alison Tuling investigated the problem to gain an understanding of the mechanism of the disintegration of the slag.

South Africa is a major producer and exporter of high-grade titania ( $\text{TiO}_2$ ) slag (>85%  $\text{TiO}_2$ ), currently supplying approximately one quarter of the world's titania requirements. This high-grade titania slag is used mainly in the production of white pigments for producing paint.

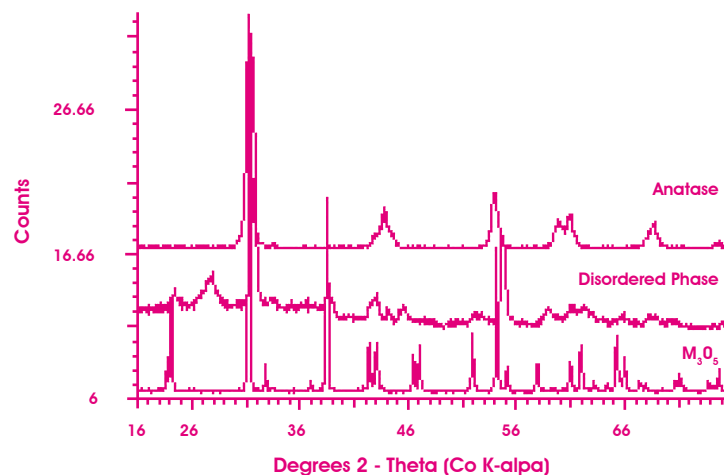
The production of titania slag involves the smelting of an ilmenite concentrate, derived from beach sands mined in the Richards Bay and Saldanha Bay areas. The liquid slag is tapped into ladles and cooled using water sprays until it has solidified. The ladles are then emptied and the slag is allowed to cool to ambient temperature. The solidified slag is milled and further refined to high-grade  $\text{TiO}_2$  pigment using one of two processes: the chloride process and the sulphate process.

All producers of high-grade slag encounter the problem of disintegration of the solidified tapped slag at relatively low temperatures as the slag blocks cool down. The disintegrated slag contains a large proportion of oxidised fine material (with a particle size of less than  $100\ \mu\text{m}$ ) that is considered unsuitable for further processing using the chloride process. The fine-grained fraction is normally sold to sulphate

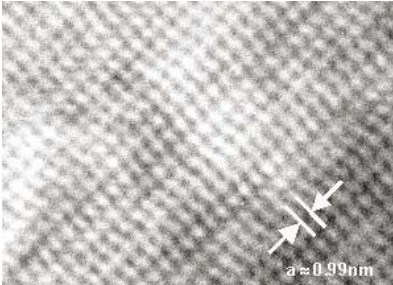
pigment producers, usually at a discount. Remedial action consists of rapid water-cooling of the solid slag blocks down to room temperature, but this is not always effective, and in some instances excessive amounts of fine material are still generated.

An investigation, aimed at gaining an understanding of the mechanism of decrepitation or disintegration of the slag on cooling in order to minimise the production of fine-grained material, was launched by Prof Johan de Villiers of the Department of Materials Science and Metallurgical Engineering at the University of Pretoria and Alison Tuling of the University's Industrial Metals and Minerals Research Institute. The main cause of decrepitation turned out to be an oxidation reaction that takes place at very low temperatures during cooling (around  $400^\circ\text{C}$ ).

The predominant phase in commercial high-grade solidified titania slags is a compound with the pseudobrookite or  $\text{M}_3\text{O}_5$  structure (M refers to a combination of metallic elements in this oxide phase). Cooling of the slag in air results in rapid oxidation of the pseudobrookite phase. High-resolution transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques were



→ 1. Comparison of the XRD patterns of the oxidation product of titania slags with those of  $\text{M}_3\text{O}_5$  and anatase.



→ 2. The selected area diffraction pattern of the disordered oxidation product.



→ 3. High-resolution TEM micrograph of the disordered product.

used to study the phase composition of the slag before and after oxidation. This investigation revealed that the precursor  $M_3O_5$  phase has an orthorhombic crystal structure, with a typical composition of  $(Fe_{0.27}Mg_{0.07}Al_{0.04}Ti^{3+}_{1.21}Ti^{4+}_{1.35})O_5$ . Oxidation of this slag during normal cooling appears to be associated with the formation of a new phase related to both  $M_3O_5$  and an anatase phase, as illustrated in Figure 1, where the strongest XRD peaks of all three phases are situated at similar angular positions. This oxidation product appears to be disordered in one crystallographic direction and has a composition corresponding to  $M_6O_{11}$ .

Prof De Villiers and Alison Tuling discovered that the disorder in the oxidation product of the slag



varies, but well-ordered crystals could not be found. It is postulated that, depending on the composition (mainly the iron content), the proportions of  $M_3O_5$  and anatase in the intergrowth will vary, giving rise to disorder in the structure of the oxidised product.

A comparison of the cell volumes of the precursor and product phases of similar composition shows that there is a volume expansion of approximately 5.5%, which could be the cause of the extensive cracking and decrepitation of the outside layers of the slag blocks, continually exposing fresh surfaces to the oxidising air. This reaction can only be avoided by preventing the oxidation of the pseudobrookite phase during cooling through the exclusion of air or rapid cooling. •

**Prof Johan de Villiers** is associated with the Department of Materials Science and Metallurgical Engineering at the University of Pretoria. ([johan.devilliers@up.ac.za](mailto:johan.devilliers@up.ac.za))

**Alison Tuling** is attached to the University's Industrial Metals and Minerals Research Institute. ([alison.tuling@up.ac.za](mailto:alison.tuling@up.ac.za))