

# The influence of quenching rates on the microstructure and properties of plasma-dissociated zircon

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The physical nature of what is usually described as "plasma-dissociated" zircon is very much dependent on the rate of quenching of the molten material after it has passed through or around the plasma. A product composed of small particles is rapidly cooled and the dominant microstructure is that of tiny crystallites of monoclinic zirconia intimately intergrown with a matrix of amorphous silica. If, as a consequence of the layout of the device itself, the product is in a more massive form, then the cooling rates in the interior are slower and considerable grain growth occurs. The zirconia forms segregations of comparatively large grains which, though still surrounded by silica, lack the intimate intergrowth we now find to be necessary to impart certain unique properties recently shown to be of interest to the ceramic colour, refractory and metallurgical industries. There is a continuous relationship between microstructure and quenching rate, whether the samples come from the same or different plasma furnaces.

## 1. Introduction

Two types of material can be derived from plasma-dissociated zircon ( $ZrSiO_4$ ) (DZ), both of which have useful commercial properties. One is made by milling DZ to produce a homogeneous powder. The other is a form of zirconium oxide made by leaching the silica constituent from the DZ. Milled DZ ("Dizirc"\*) has now proved itself to have unique properties which promise possible applications in the fields of ceramic colour making [1], the fabrication of ceramic nozzles for pouring steel [2], the manufacture of tableware kiln furniture and perhaps others. Experiments have shown that not all plasma DZ types are equally suitable for all these applications.

We have previously described DZ [3] whose microstructure and composition is such as to render it suitable for all the above uses. This DZ was produced in the AMA<sup>†</sup> (formerly Ionarc)

furnace which is a large scale plasma device that has been in commercial operation for some years. The DZ leaving the plasma zone is mainly molten and it is very rapidly quenched in extremely turbulent conditions as it is spheroidized by free fall through a controlled atmosphere tank [4, 5]. This rapid quenching is aided by the fact that the vast majority of the particles are less than 400  $\mu\text{m}$  diameter.

If the DZ is not spheroidized and rapidly quenched, then the microstructure can be considerably different, with consequent modification of its properties. We have recently examined DZ from two furnaces in which this is the case. The first is a furnace developed by Swiss Aluminium Ltd which is d.c.-driven, water-stabilized and operates at 200 kW. The second is operated by Plasma Materials Inc, it has a d.c. arc-heater modified for particulate heating at high enthalpy.

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Three distinct products can be made, depending on the residence time in the hot zone and the intensity of the adjacent gas flow. One of these products is very similar indeed to that of the AMA furnace which we have previously described, the other two are essentially identical with DZ produced in the Swiss Aluminium furnace. In all the furnaces the cooling rate is simply a function of particle size. Thus, for example, the Plasma Materials furnace can produce both rapidly and slowly quenched DZ.

## 2. Nature of the furnace products

### 2.1. Rapidly quenched DZ

As typified by the AMA DZ, this consists of three types of grains which we have designated types I, II and III. Under normal operating conditions ( $180 \text{ kg h}^{-1}$  feed rate) type III grains form 90% or more of the product and represent spheroidized DZ. Type II grains are zircon grains which have undergone various degrees of dissociation in the solid state and thus have retained the detrital outlines of the original feedstock and type I grains are non-dissociated zircon. This nomenclature will be used as appropriate in our descriptions of the products of the other furnaces. It is the composition and microstructure of the types II and III grains, particularly type III, which gives AMA DZ its commercially useful properties. We have already described the microstructures of these grains in detail [3] and will only briefly recapitulate our descriptions here.

In the type II grains all degrees of dissociation are present from incipient zirconia and silica development to complete replacement of the zircon grains. The dissociation products are tiny elongated monoclinic zirconia grains in a matrix of amorphous silica. The zirconia grains have commonly been nucleated by the grain boundaries of the parent zircon and have grown inwards (Fig. 1).

The type III grains are mainly spheroids, most of which have diameters of 25 to  $250 \mu\text{m}$ . There are two main types of spheroid. The common one (type IIIa, forming about 90%) consists of such fine-grained material that even when ground down to thicknesses of about  $10 \mu\text{m}$  it is only barely translucent. The surface has a well-developed polygonal pattern (Fig. 2) with  $120^\circ$  triple junctions, a normal characteristic of fully equilibrated systems [6]. Microscopic examination of thin sections and polished sections stained with methylene blue

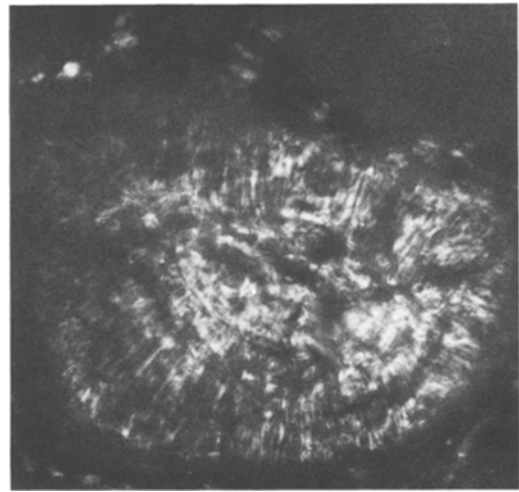


Figure 1 A type II grain showing subparallel growth of zirconia fibres. AMA DZ thin section, crossed polars ( $\times 206$ ).

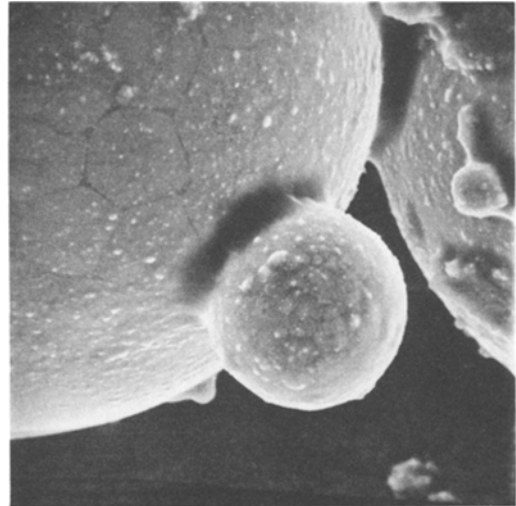
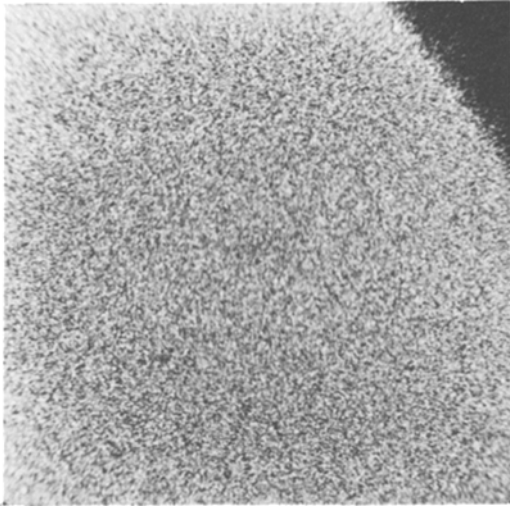
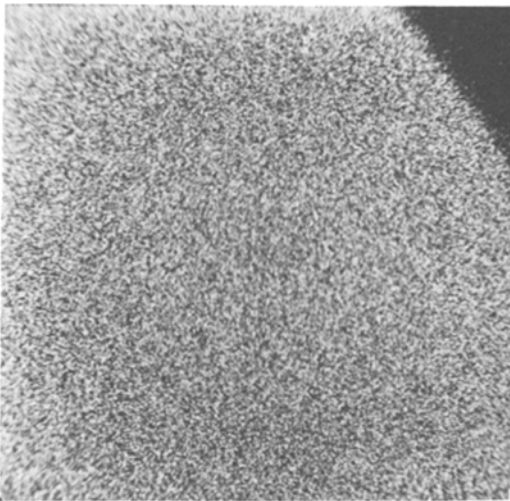


Figure 2 Scanning electron micrograph of type III spheroids from AMA DZ showing the polygonal microstructure and the radial development of zirconia crystallites within the polygons. The dark interstitial phase is silica ( $\times 322$ ). (No etch reagents were used on any of the specimens and only normal coating techniques have been employed.)

reveals that this polygonal grain structure is present throughout the interior of the spheroids. The polygonal grains now consist of tiny arborescent crystallites of monoclinic zirconia with a radiate texture embedded in amorphous silica. The minor phase between the polygons is amorphous silica probably strained and microcracked. In general terms this material exhibits the characteristics of the foam texture described by Smith [6].



*Figure 3* Photomicrograph (EPMA) of distribution of silicon in an AMA DZ type IIIa grain. Width of field about 70  $\mu\text{m}$ .



*Figure 4* The same as Fig. 3 but showing zirconium distribution.

The spheroids were studied on an electron probe microanalyser in an attempt to outline the microstructure by photographing the elemental distributions. This proved to be impossible as shown by Figs. 3 and 4. Clearly the microstructure is too fine-grained to be resolved by this method. As the resolution of the microanalyser is about 2000  $\text{\AA}$  this confirms the very intimate intergrowth of the zirconia and silica, an intergrowth so fine that it could not be achieved by any form of mechanical mixing of the two materials.

The spheroids are commonly porous and the pores represent bubbles of included gases, probably silicon monoxide [3]. The second type of spheroid (IIIb) consists of intergrown bladed or tabular crystals of monoclinic zirconia up to 60  $\mu\text{m}$  long set in a matrix of silica. Tiny zircon inclusions are common in this type.

Silica is vaporized during the dissociation process [4]. Some of it passes out with the exhaust gases, the rest forms thin envelopes of various thicknesses on all the particle types and also a few rounded grains of discrete silica. Analyses of this silica have shown a zirconia content of 12% [7], an unexpectedly high figure which merits further investigation. The silica envelopes and the internal silica are highly reactive and all the silica can be leached from the type III grains by 50% NaOH solution at about 80°C in under 2 h. We suspect that the silica may be oxygen-deficient [3] and this may provide a partial reason for its reactivity. Other reasons may include its high zirconia content or its formation by hyperquenching. But it is more likely that the microstructure may play the dominant role in promoting an "osmotic surge" resulting in a rapid wetting of the individual zirconia particles once any solution of the silica phase occurred. This expression has been used by Moilliet and Plant [8] to refer to cases of wetting in which the required free energy comes from the process of solution of a soluble substance (silica here) surrounding the particle to be wetted (zirconia). This, rather than the interfacial tension, is the important factor in many technical wetting processes. A similar mechanism may explain the easy solubility in hot concentrated sulphuric acid of the fully leached oxide derived from DZ [9], since it appears to us that from its very nature osmotic surge will be more effective on very small particles than on larger ones.

It is difficult to distinguish the true plasma effects from those which are purely thermal in the operation of the AMA furnace. Any plasma effects which must, by definition, involve the transfer of energy by electrically conducting particles will necessarily arise in the actual plasma zone which itself is only of relatively small volume. However, the oxygen deficiency already referred to may be an indication that such processes do occur. On the other hand, the fact that increases above the normal feed rate give rise to a rapid decrease in the degree of dissociation, may be evidence that the

phenomena are mainly the results of energy transferred radiatively or by the recombination of nitrogen ions on a surface and hence are thermal in origin.

Rapidly quenched DZ from the Plasma Materials furnace is identical in most respects with that from the AMA furnace but contains a higher percentage of type IIIb grains.

## 2.2. Slowly quenched DZ

### 2.2.1. General macroscopic nature of the product

Owing to their differing geometries, both the Swiss Aluminium and Plasma Materials furnaces can produce more slowly cooled DZ. This takes the form of large masses of white fasciculate cylindrical bodies of various diameters which may branch, rejoin and swell out in places to become quite bulbous (Fig. 5).

### 2.2.2. Microstructure

Optical examination of thin sections (15 to 25  $\mu\text{m}$  thick) revealed that the outer parts of the cylindrical bodies are optically so dense that virtually no light penetrated them. They must, therefore, represent a very fine-grained chilled margin with a microstructure comparable with that of the AMA type IIIa grains. This was confirmed by scanning electron microscopy which revealed the presence of a similar polygonal pattern (Fig. 6) again composed of grains of zirconia-silica intergrowths with interstitial silica.

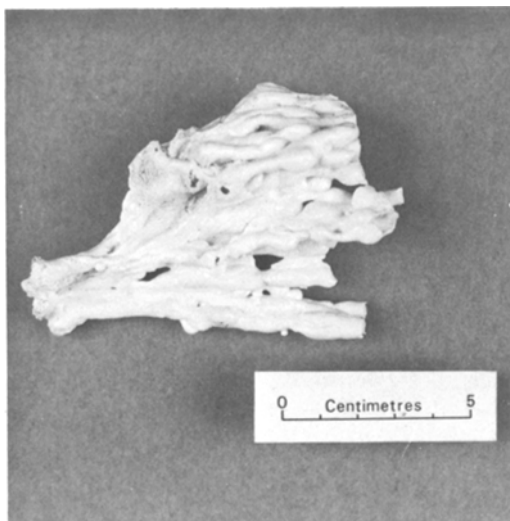


Figure 5 Sample of dissociated zircon from the Swiss Aluminium Furnace.

Like the AMA DZ spheroids, these grains now consist of a growth of tiny elongated zirconia crystallites having a radiate texture and set in a matrix of silica (Fig. 7).

Traced from the chilled margin inwards, the granularity showed a gradual but irregular increase and various microstructures became optically resolvable, grew in size and changed in form. The first noticeable effect was the appearance of the polygonal texture originally revealed in the chilled

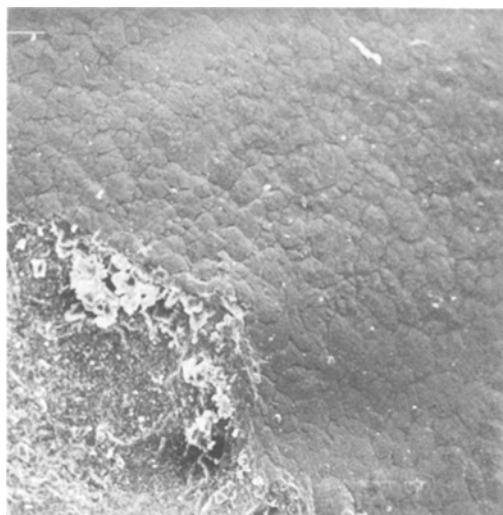


Figure 6 Scanning electron micrograph of part of the surface of a DZ specimen from the Swiss Aluminium Furnace ( $\times 40$ ).

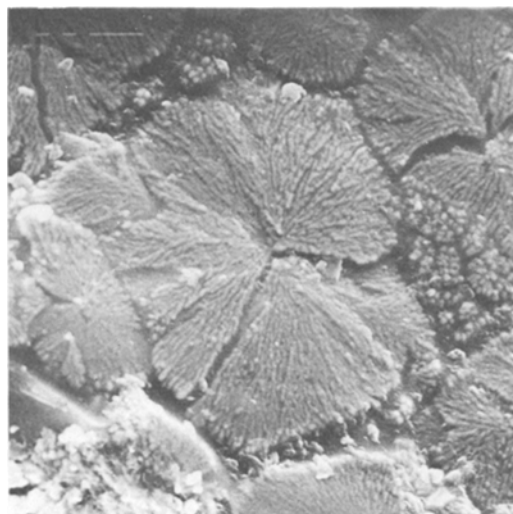
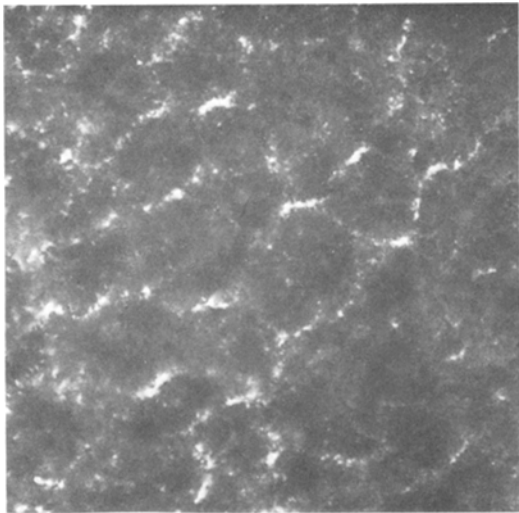
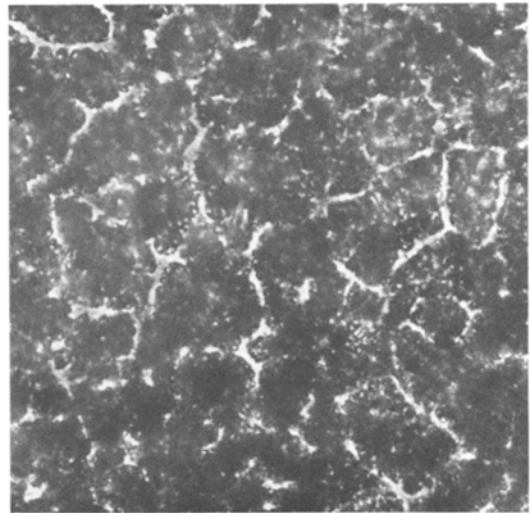


Figure 7 Enlargement of the polygons seen in Fig. 6 to show the detailed texture of the radiating zirconia crystallites. Note their arborescent nature. Swiss Aluminium DZ, ( $\times 413$ ).



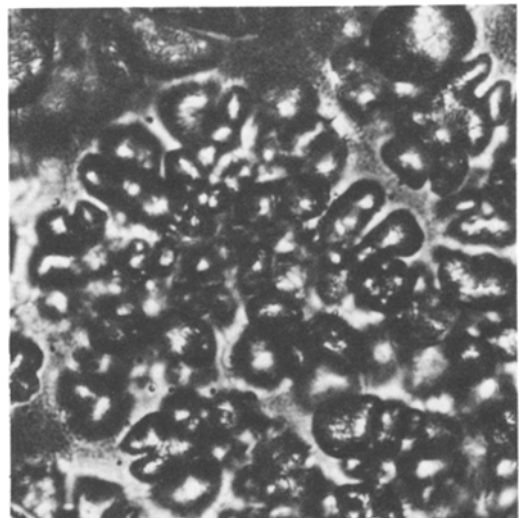
*Figure 8* Photomicrograph of an area near the chilled margin of a cylindroidal DZ body. The patches of bright light outline the silica segregations between the polygonal grains. Thin section, Swiss Aluminium DZ, plane polarized light ( $\times 24$ ).



*Figure 9* Photomicrograph of an area nearer the centre of a cylindroidal DZ body showing a coarser granularity and larger silica segregations. Thin section, Swiss Aluminium DZ, plane polarized light ( $\times 35$ ).

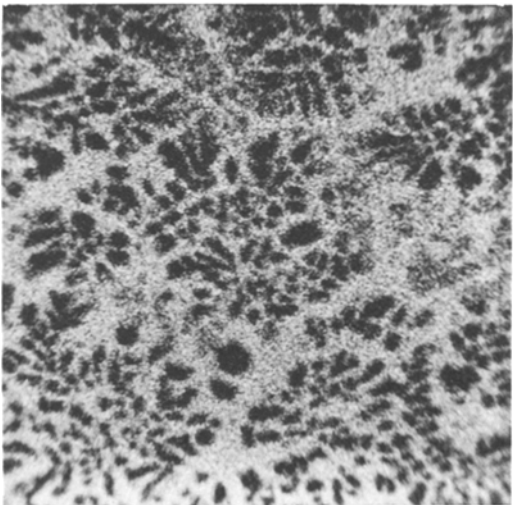
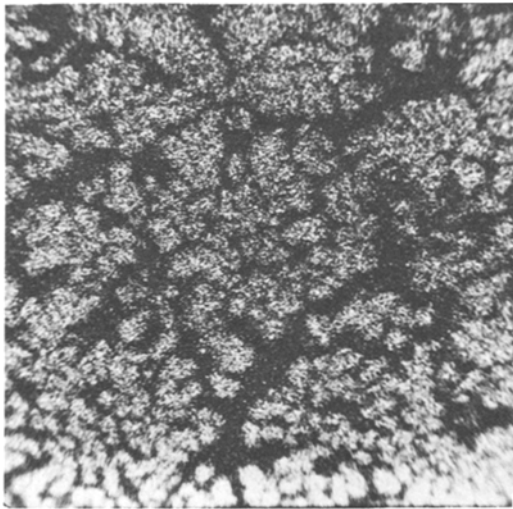
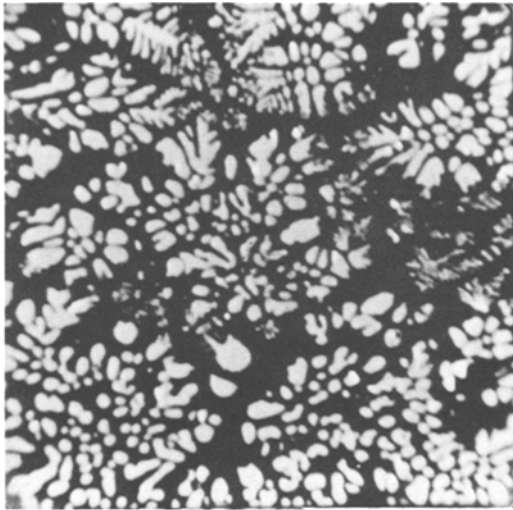
margin by the scanning electron microscope. It was now on a much coarser scale, but the grains were still optically rather dense and most of the light was transmitted through the silica segregations between the grains (Fig. 8). Moving inwards the texture became better defined (Figs. 9 and 10), the areas of interstitial silica were larger and the detailed texture within the polygons became well defined.

In the coarsest grained areas the polygons became less clearly defined as the two oxides separated more completely and discrete grains of zirconia were clearly seen. Some of these still retained the radial texture seen in the chilled margin. In others it had totally disappeared and the grain size was sufficiently large for fine grinding to liberate the two oxides from each other to an appreciable degree [7]. Finely ground DZ of this type would then only possess in small part the intimate intergrowth present in the rapidly quenched DZ and this could affect its technological properties. The clear separation of the two phases is particularly well shown by photomicrographs taken on a microanalyser (Figs. 11 to 13). The coarsest zirconia grains averaged 10 to 12  $\mu\text{m}$  in length, the largest of them being about 22  $\mu\text{m}$  long and about 10  $\mu\text{m}$  in intermediate diameter. The zirconia from the Swiss Aluminium furnace was colourless whilst that



*Figure 10* Coarse-grained zirconia showing relict radiate texture. The polygonal texture is now largely destroyed and the silica segregations are larger. Thin section, Plasma Materials DZ, plane polarized light, ( $\times 580$ ).

from the Plasma Materials furnace was the typical yellow–brown colour of monoclinic zirconia. X-ray diffraction studies showed that the zirconia from both furnaces was almost entirely monoclinic with just a trace of cubic zirconia. It has not so far been possible to locate this cubic zirconia precisely within the structure as a whole. The amount of zircon in both furnace products of the slower quenched type was below the detectable level



showing that this DZ, taken as a whole, has a higher degree of dissociation than the more rapidly quenched type. This was confirmed by optical examinations, using the immersion method, of large samples of crushed DZ, when only a few type I and II grains were found.

Both yellow-brown and colourless silica was present in the DZ from both furnaces. All the silica was optically isotropic and X-ray diffraction analysis did not suggest the presence of any crystalline phases. It was all presumed to be amorphous.

### 3. Conclusions

Both the macro- and microstructural characteristics of plasma dissociated zircon have been shown to be critically dependent on the maximum quenching rates inherent in the mechanical and geometrical arrangements of the plasma furnaces concerned. All forms of DZ examined so far possess in part or in whole certain common features: a substantially complete separation, disruption and reaggregation of the original zircon grains into masses, large or small, of discrete grains of monoclinic zirconia fully wetted by an amorphous silica matrix; and a foam texture wherein plane-surfaced domains of intergrown zirconia and silica are bounded by thin, volumetrically insignificant, strained amorphous silica films. In its outer chilled margins, slowly quenched DZ, usually in relatively massive form, was found to have a similar composition and microstructure to rapidly quenched DZ, and all such materials would probably have identical technological ceramic colour and refractory properties. The major part, however, of the slowly quenched DZ was much coarser grained. By comparison with the chilled margin, considerable grain growth and segregation of the zirconia from the silica has occurred. The fine grinding of such material would result in a powder which possessed the properties of a mechanical mixture of the two oxides and which would not retain the intimate ultra fine-grained intergrowth of rapidly quenched DZ which imparts special properties to the powder possessing it. The difference in microstructure of the two types of DZ has been shown to be related in a logically continuous manner to their different rates of cooling.

*Figure 11* Electron image (above), zirconium distribution (centre) and silicon distribution (below) in coarse-grained Swiss Aluminium DZ. The width of the scanned area is about 150  $\mu\text{m}$ .

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