

The texture of diffusion-grown HfAl₃ layers

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THE TEXTURE OF DIFFUSION-GROWN HfAl_3 LAYERS

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Summary

HfAl_3 layers were grown on hafnium and aluminium substrates. A [001] fan texture was observed in HfAl_3 grown by solid state diffusion on textureless hafnium substrates. If layers were grown on a hafnium substrate with a pronounced single-component sheet texture, the texture in the HfAl_3 layer was not rotationally symmetric around the direction of diffusion, but a related sheet texture developed. An orientation relation is proposed. Layers grown from the vapour phase on aluminium substrates show an $\langle 841 \rangle$ fibre texture.

1. Introduction

Little is known about the causes of the development of a texture in diffusion-grown layers of intermetallic compounds. In our laboratory many studies have been performed of both phase diagrams and diffusion kinetics. In a number of systems textures have been observed. This has led to investigations into the relation between the structure of the intermetallic layer and its texture. Further, we have examined the dependence of the texture produced on the substrate and diffusion conditions.

We have previously presented results obtained for diffusion-grown disilicide layers on molybdenum and tungsten [1]; in this paper results will be presented for HfAl_3 layers. HfAl_3 has a tetragonal unit cell with $a = 0.3989$ nm and $c = 1.7155$ nm.

The experimental procedures which were used for the preparation of the reaction layers and for the subsequent texture investigations are described in Section 2. The experimental results are presented in Section 3, and a discussion of these results is given in Section 4.

2. Experimental details

Three different techniques were used to produce the HfAl_3 layers.

Firstly, use was made of the diffusion couple technique. Al–Hf–Al sandwich couples were heated in a vacuum furnace under a load. Although a number of intermetallic compounds exist in the Hf–Al system [2, 3], only HfAl_3 and HfAl_2 layers were observed in the solid–solid couples. The HfAl_2 layers were very thin even after prolonged annealing. Optical microscopy showed that the contact between the HfAl_2 layer and the hafnium substrate was lost, probably owing to differences in thermal expansion.

Secondly, HfAl_3 layers were produced by vapour transport in an iodine atmosphere. HfAl_2 , produced by argon arc melting and subsequent grinding, was heated together with iodine and an aluminium substrate in an evacuated silica capsule at a suitable temperature.

Thirdly, we attempted to produce HfAl_3 layers above the melting point of aluminium by using the pack cementation process. A hafnium substrate was heated at 700 or 800 °C in a closed alumina container. The generator used consisted of a mixture of Al_2O_3 , aluminium and CrF_2 in a mass ratio of 90:20:10. Under these conditions, however, only HfAl_2 layers were formed.

The aluminium substrates (purity, 99.99%) were obtained from Drijfhout, The Netherlands. Two types of hafnium substrates were used, namely hafnium platelets (Koch-Light, Gt. Britain; purity, 99.9% including 3.0% Zr) showing a pronounced sheet texture and fine-grained polycrystalline substrates without texture which were produced by argon arc melting.

For the examination of the texture in the reaction layers sections were prepared parallel to the substrate–layer interface.

Pole density measurements were performed using a Philips PW1078 texture goniometer. The measured intensities were corrected for the intensity loss due to defocusing [4, 5]. Correction curves were obtained by measuring intensities on texture-free powder samples of HfAl_3 . These samples were made from HfAl_3 produced by argon arc melting. After grinding, the sieve fraction below 37 μm was pelletized by cold isostatic pressing.

Pole figures were measured using a Siemens texture goniometer with an automatic pole figure plotter [6]. Lücke's method was adopted.

3. Results

To investigate the kinetics of the layer formation Hf–Al diffusion couples were heated for various times at temperatures of 550, 595 and 640 °C. The results are shown in Fig. 1 where it can be seen that the parabolic growth law is not obeyed.

When the iodine transport reaction was used an HfAl_3 layer 72 μm thick was formed after 28 h at 640 °C and a layer 22 μm thick was formed after 47 h at 595 °C.

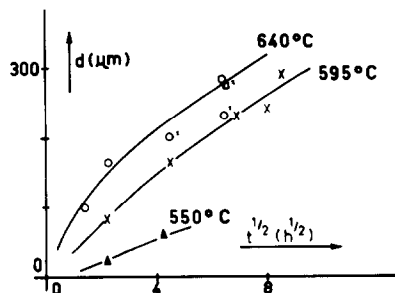


Fig. 1. Layer thickness vs. $t^{1/2}$, where t is the time, for HfAl_3 layers in Hf-Al diffusion couples: \circ , \times , \blacktriangle , layers grown on hafnium with a sheet texture; \square , layers grown on textureless hafnium substrates.

3.1. Texture measurements on the hafnium substrates

Our first investigation showed the presence of an unusual non-rotationally symmetric texture in the HfAl_3 layers grown on the Koch-Light hafnium platelets. Further experiments showed that this texture was related to a texture in the substrate. Therefore we shall first describe the texture observed in these substrates. Before use, the hafnium plate was heated for 24 h at 640°C . A pronounced sheet texture was found. The $[11\bar{2}0]$ direction was situated approximately in the rolling direction and the normal to the (0001) planes was tilted about 30° – 35° with respect to the substrate normal in the transverse direction. Figures 2(a) and 2(b) show the pole figures of the 101 and 0002 reflections respectively. These figures correspond well to those described for hafnium by Wassermann and Grewen [7]. The texture remained unaltered during the formation of the diffusion layers in the temperature region 550 – 640°C .

We also used polycrystalline textureless hafnium to investigate the influence of the substrate texture on the texture of the diffusion layers. For

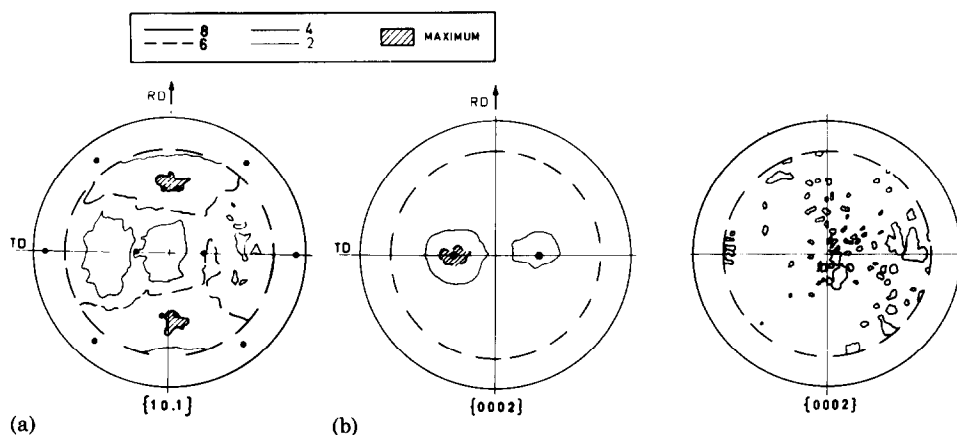


Fig. 2. Pole figures of hafnium substrates with sheet texture: (a) 101 reflection; (b) 0002 reflection.

Fig. 3. $\{0002\}$ pole figure of the textureless hafnium substrates.

comparison Fig. 3 shows a pole figure of the 0002 reflection of these substrates.

3.2. Texture measurements on HfAl_3 layers

HfAl_3 grown on textureless hafnium substrates showed a rotationally symmetric texture with respect to the direction of diffusion. From the texture measurements for various reflections the presence of a [001] fan texture could be established. Table 1 gives the measured angles of the maxima with respect to the direction of diffusion. For comparison we also give the positions calculated for a [001] fan texture parallel to the direction of diffusion. The texture sharpness was maximum at the Hf– HfAl_3 interface and gradually diminishes towards the HfAl_3 –Al interface.

TABLE 1
Results of X-ray measurements on HfAl_3

hkl	d (nm)	I/I_0^a	χ_{calc}^b (deg)	χ_{meas}^b (deg)
004	0.429	32	90.0	> 80
101	0.3885	50	13.1	12
103	0.3272	24	34.9	39
110	0.2821	24	0.0	0
105	0.2601	26	49.3	50
114	0.2356	100	33.3	38
008	0.2143	21	90.0	> 80
200	0.1995	33	0.0	0
211	0.1774	15	5.9	0
215	0.1583	23	27.5	30
310	0.1261	—	0.0	0

χ is the tilt angle with respect to the direction of diffusion.

^a Mean relative intensities of textureless powder samples.

^b χ_{calc} and χ_{meas} are the calculated and measured values respectively for a [001] fan texture parallel to the diffusion direction. All reflections show a broad maximum, e.g. the width at half-maximum height for the 110 reflection was 40° (weak texture).

As mentioned earlier, a non-rotationally symmetric texture was observed in HfAl_3 layers grown on hafnium substrates with a sheet texture. Figure 4 shows pole figures of some important reflections. The texture of the layers grown in Hf–Al diffusion couples was always very weak near the Al– HfAl_3 interface. Nevertheless we found that the remaining texture near this interface always remained non-rotationally symmetric. The texture sharpness increased on going in the direction of the HfAl_3 –Hf interface. At a certain depth in the layer, which depended on the total thickness, the sharpness of the non-rotationally symmetric component reached a maximum. On proceeding to the HfAl_3 –Hf interface the texture became more rotationally symmetric. In fact the same texture component developed as was found in the HfAl_3 layers grown on textureless hafnium, i.e. a [001] fan texture. This transition of the non-rotationally symmetric to the rotationally symmetric component took place

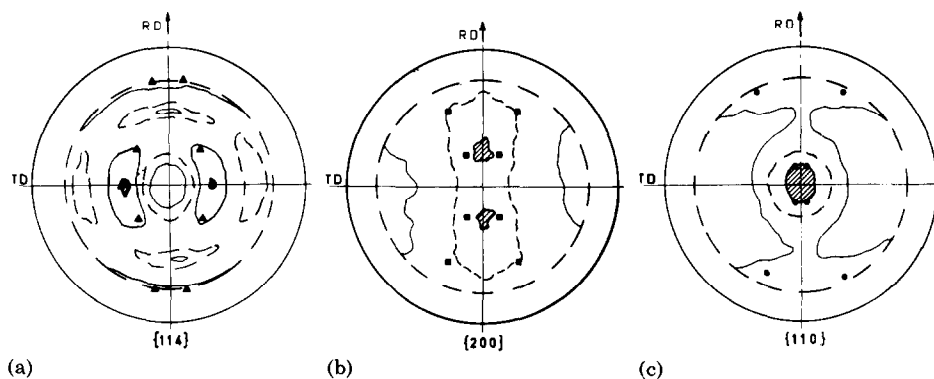


Fig. 4. Pole figures of HfAl_3 diffusion layers grown on hafnium with a sheet texture: (a) 114 reflection; (b) 200 reflection; (c) 110 reflection.

gradually. It is important to note that at the same time a considerable increase in grain size occurred in the diffusion layer (Fig. 5). Moreover, the transition occurred more slowly at 595°C than at 640°C .

HfAl_3 layers grown on aluminium substrates via the iodine process also showed a texture. At 640°C the crystal growth was so fast that hardly any texture could be seen in the coarse-grained layers. After growth at 595°C the layer consisted of fine grains near the HfAl_3 -Al interface, and the grain size increased towards the HfAl_3 -vapour interface. A moderate-to-sharp rotationally symmetric texture was observed in the layer, with maximum sharpness at the HfAl_3 -vapour interface.

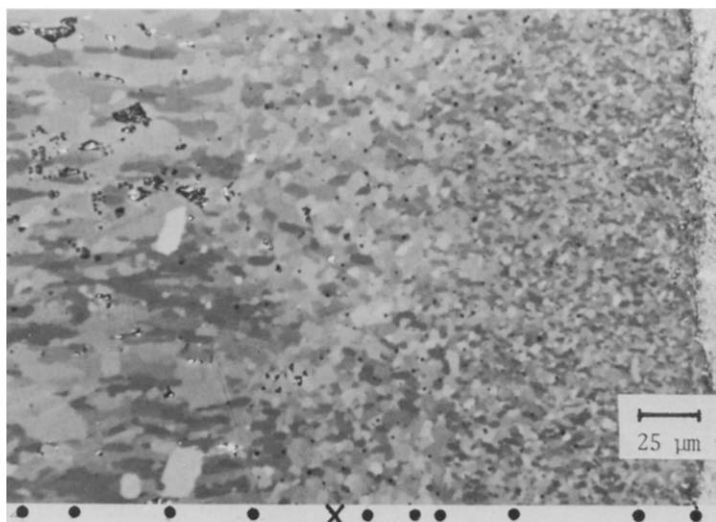


Fig. 5. Photomicrograph of an HfAl_3 layer grown on hafnium with sheet texture (41 h at 640°C) (left-hand side, HfAl_3 -Hf interface; right-hand side HfAl_3 -Al interface): ●, positions in the layer where the pole figures were measured; ×, position where the maximum texture sharpness of the non-rotationally symmetric component is observed.

TABLE 2

Measured and calculated tilt angles χ of the maxima of different reflections assuming an $\langle 841 \rangle$ fibre texture in the HfAl_3 layers

hkl	χ_{meas} (deg)	χ_{calc} (deg)	hkl	χ_{meas} (deg)	χ_{calc} (deg)
004	65	64	103	26, 55	25, 55, 66
101	30, 55	28, 47, 61	105	34, 52	31, 54, 79
110	26, >70	31, 73	204	25, 56	24, 57, 80
114	0*, 63	18, 62, 90	211	0*, 30*	18, 32, 55, 61
200	35, 63	36, 66	215	0, ...*	2, 33, 47, 53 64, 74, 79

* Maxima very broad or absent owing to strong overlap.

The results of texture measurements show that no low index crystallographic axis can be considered as a fibre axis. The best correspondence between the calculated and the measured angles of the maxima was found for an $\langle 841 \rangle$ direction parallel to the fibre axis (Table 2).

For completeness we mention that in the HfAl_2 diffusion layers a sharp $[0001]$ fan texture occurs. This compound has a hexagonal structure.

4. Discussion of the results

We first discuss the results obtained for HfAl_3 layers grown on hafnium with a sheet texture. If the pole figure of the 114 reflection of HfAl_3 (Fig. 4(a)) is compared with that of the 0002 reflection of hafnium (Fig. 2(b)), it can be seen that the positions of the maxima correspond. If the tetragonal cell of HfAl_3 is approximated by four cubic subcells, *i.e.* $a = b = 0.3989$ nm and $c = 1.7155$ nm = 4×0.4289 nm, the normal to the close-packed (114) plane can be considered as a $[111]$ direction in the cubic lattice. In that case we expect the relation

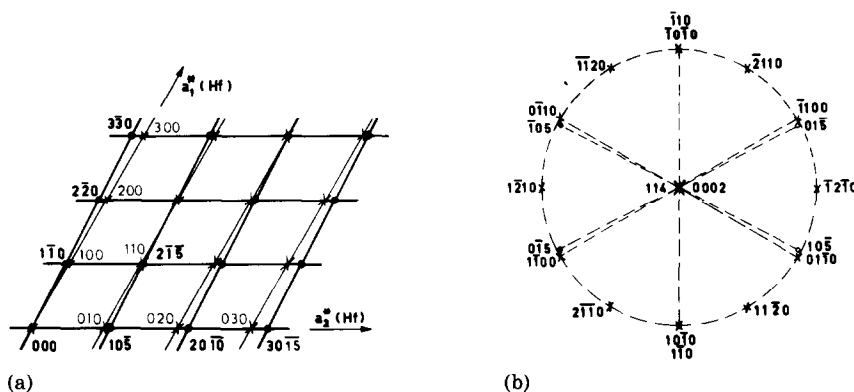
$$\text{Hf}(0002) // \text{HfAl}_3(114)$$

to exist. From the reciprocal lattices of hafnium and HfAl_3 it can also be seen that a reasonable fit between the two lattices is possible in this way (Fig. 6 and Table 3). Therefore we conclude that the following orientation relation exists between hafnium and HfAl_3 :

$$\text{Hf}(0002) // \text{HfAl}_3(114)$$

$$[11\bar{2}0]_{\text{Hf}} // [841]_{\text{HfAl}_3}$$

In the layers grown on aluminium substrates via the iodine process the $\langle 841 \rangle$ direction again plays an important role (in the cubic subcell this would be a $\langle 211 \rangle$ direction since $a = b \approx \frac{1}{4}c$). We therefore conclude that the first stage of the layer growth is epitaxial.



(a) Superposition of the zero layers of the reciprocal lattices of hafnium (x) and HfAl₃ (●) (hafnium zone axis [0001]; HfAl₃ zone axis [551]); (b) stereographic projection of hafnium (x) and HfAl₃ (●) with their respective [0001] and [551] zones.

TABLE 3

Quantitative data for the orientation relations Hf(0002) // HfAl₃(114) and [1120]_{Hf} // [841]_{HfAl₃}

Hf	HfAl ₃
Angle between:	Angle between:
(0002) and (0110) = 90.0°	(114) and (105) = 91.8°
(0002) and (1100) = 90.0°	(114) and (110) = 90.0°
(0002) and (1120) = 90.0°	(114) and (215) = 88.9°*
(0110) and (1100) = 60.0°	(105) and (110) = 62.5°

Misfits: $(d_{(110\ 0)} - d_{(105)})/d_{(105)} = +6.4\%$; $(d_{(110\ 0)} - d_{(110)})/d_{(110)} = -1.9\%$; $(d_{(110\ 0)} - d_{(215)})/d_{(215)} = +1.0\%$.

*The [841] direction is almost perpendicular to the (215) plane.

However, the non-rotational texture component caused by the substrate texture is not stable. After some time (*i.e.* going in the direction of the HfAl₃-Al interface) the texture sharpness decreases. On going to the HfAl₃-Hf interface the new texture component is the same as that formed in HfAl₃ layers on textureless hafnium substrates, *i.e.* the [001] fan texture. The transition from a sheet texture to a fan texture appears to be accompanied by a change in grain size and morphology (Fig. 5) and, at the same time, by a change in the growth kinetics of the layer (Fig. 1). If it is assumed that aluminium is the only diffusing species the reaction proceeds at the Hf-HfAl₃ interface. In this case the oldest part of the layer has apparently been formed in a very short time as indicated by the numerous small crystals present. The youngest part of the layer grows very slowly with the result that a few large crystals are formed.

Figure 6 shows that the early stages of growth are dominated by an epitaxial mechanism. A volume diffusion process appears to dominate in the later stages, resulting in a fan texture. This gradual transition of the texture proceeds much more slowly at 595 °C than at 640 °C, which again shows the importance of the large crystallites at the HfAl₃-Hf interface.

5. Summarizing remarks

HfAl₃ layers grown between 550 and 640°C on textureless hafnium substrates show a [001] fan texture. This means that the *c* axes of this tetragonal compound are preferentially orientated perpendicular to the direction of diffusion. A single-component sheet texture in the substrate can influence the texture in the diffusion-grown layer considerably, as shown for a hafnium substrate with a sheet texture. In this case a non-rotationally symmetric texture develops in the HfAl₃ layer. This texture can be related to the texture in the hafnium substrate. If HfAl₃ is grown from the vapour phase on aluminium substrates an $\langle 841 \rangle$ fibre texture is observed.

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References

- 1 J. H. Maas and G. D. Rieck, *High Temp. High Pressures*, 10 (1978) 297.
- 2 M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.
- 3 R. P. Elliott, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1st Suppl., 1965.
- 4 E. M. C. Huyser-Gerits and G. D. Rieck, *J. Appl. Crystallogr.*, 7 (1974) 286.
- 5 J. R. Holland, *Adv. X-Ray Anal.*, 7 (1964) 86.
- 6 U. Kobbe and H. Schuon, *Siemens-Z.*, 47 (1973) 119.
- 7 G. Wassermann and J. Grewen, *Texturen Metallischer Werkstoffe*, Springer, Berlin, 2nd edn., 1962.