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SEGREGATION IN TITANIUM ALLOYS

1 - INTRODUCTION

As in all alloy systems, the mechanical behaviour of titanium alloys is strongly influenced by the way in which the constituent elements segregate on solidification. During the early stages of development in titanium alloys there was a strong tendency to restrict compositions to extremely simple combinations of elements in solid-solution alloys. This trend, coupled with the fact that all titanium alloys initially solidify as single-phase solid-solution β-phase crystals means that segregation problems in titanium alloys are very different from those existing in, say, superalloys or alloy steels. Segregation leading to the precipitation of, for example, congruent melting second phases is essentially absent in this alloy system. On the other hand, segregation cannot easily be dismissed as a problem in titanium alloys because homogenization times and temperatures are excessive. In principle, one might eliminate the segregation of a β-stabilizer in an α/β alloy by long time/high temperature homogenization, but this approach is not feasible on economic grounds. It would require inert atmosphere processing at temperatures approaching 1600°C for many hundreds of hours. We must therefore address the question of reducing ingot

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segregation to an acceptable level by suitably adjusting melting practices.

The concentration gradients represented by segregation are divided by dimension into macrosegregation and microsegregation; the wavelength of the former being ingot radius, that of the latter being the primary dendrite spacing.

2 - MACROSEGREGATION

The constitutional rejection of solute during alloy freezing results in macrosegregation when there is a net bulk displacement between the precipitated solid and remaining liquid, e.g. by fluid flow, or by density separation. The resulting concentration gradients depend on the applicable phase diagram. Although the latter are not available for the complex titanium alloys, we can generalize in some simple cases from the binary diagrams (1) (Fig. 1). Elements which cause a rising liquidus in increasing concentration will segregate negatively (e.g. oxygen) and vice versa (e.g. iron). As a result, the base and edges of a large CP titanium ingot are enriched in oxygen whilst the central core, particularly at the head of the ingot, is enriched in iron.

In what would be normally considered as a remelting process (VAR, ESR, EB etc.), the ingot temperature gradients are sufficiently steep that solidification takes in a columnar dendritic mode, due to a combination of low process temperatures, low melting rates and a predominance of relatively small ingot diameters. The titanium case differs from the above situation (2). The titanium alloys are melted at very high rates (relative to, for example, steels) in order to preserve the surface quality for economic reasons; the consequent process temperatures are high; also the ingot diameter, with few exceptions, are as large as is technically feasible. The result is that the ingot pool is very large and in a typical industrial case only the outer third of the radius solidifies in the columnar dendritic mode. These two features are illustrated in Figures 2 and 3. The central core of the ingot has temperature gradients of less than 18°C/cm which represents the boundary between columnar and equiax solidification for Ti6Al4V under this particular set of flow conditions. The result of this transition is twofold.

First, in the equiax region there exists the possibility of large displacements of solid and liquid by bouyancy forces. Such displacements are responsible for the aluminium variations seen in Ti6Al4V in large ingot sections and are also responsible for the majority of "β-fleck" defects seen in the high-alloy systems. where the β-stabilizing elements segregate positively (e.g. Fe in Ti6Al4V or in Ti-17). The liquidus/solidus gap required to create this situation is not large (Figure 4). In comparison to superalloys, the titanium alloy systems have very small solidification ranges. However, when coupled with the high enthalpy input and low thermal diffusivity of titanium alloys, the result is a ready transition to the equiax mode of solidification.

The second aspect is contained in the flow conditions at the beginning and end of the melting process. The formation of a rapidly-chilled skin of metal at the ingot base (and at the ingot surfaces) takes place in these alloys as a planar solidification front with strong liquid flow over its surface. The solid is therefore in equilibrium with the bulk liquid and we observe a "zone-refining" effect in which the solid is enriched in oxygen, and depleted in alloy elements such as Fe or Cr. As the metal shell thickens the temperature gradients decrease and the planar front degrades to a dendritic one, leading to the familiar columnar dendritic solidification structure, with very little macrosegregation.

At the end of the melting sequence, the liquid metal pool is very large, and as can be seen from Figure 5 the terminating melt-rate sequence is very important in eliminating the resulting shrinkage cavity. During this hot-top process, the temperature gradients are very low and the solidification structure is primarily equiax. The density differences between solid and liquid can lead to a bouyancy-driven macrosegregation although in most titanium alloys this is small.

The solidification of Ti6Al4V, for example produces a primary solid in which the aluminium content is higher than that of the bulk liquid by approximately 0.5 wt%. This segregation is probably not the cause of α-2 defects, but can create problems in precision heat-treatment through its influence on the transus temperature (3) (Figure 6). The segregation caused by the bulk liquid/solid flows in α/β alloys is largely manifest in β-stabilized regions, which although not strongly segregated are sufficiently so to depress the transus below the precise range required for heat treatment. The ranges permitted are small enough that even in Ti6Al4V there can be segregation of iron and copper which is large enough to produce β-fleck. In this alloy also, there is significant dependence of aluminium macrosegregation on melting parameters which has lead to difficulties on occasion in obtaining precise composition control in large diameter ingots.

3 - MICROSEGREGATION

The solidification structure of titanium alloys has not been studied but we may assume that as single-phase solid-solution β-phase precipitates, it will be accompanied by segregation as indicated in the appropriate phase relationships. The dendritic structure is not visible in α or α/β alloys due to the transformation at lower temperature, but the wavelength of segregation within a given primary grain corresponds to that which might result from dendrites with primary spacings of 200-800 μm. The strongly-segregation elements in the interdendritic regions are all β-stabilizers notably Cu, Fe, Ni and Cr. Other β-stabilizers such as Mo do not segregate strongly and do so into the primary solid, not the interdendritic liquid. The normal level of microsegregation has not proved to be a problem in any commercial alloy, but when it is coupled with additional effects it has generated difficulties. The two principal effects are described below.

The high heat input necessitated by the titanium VAR process is concentrated in the region of the active arc. The melting conditions are normally arranged so that this arc is a constricted one, and is quite long (30-40 mm) by the standards of practice in superalloys or steels. The constricted arc is very stable and must be caused to move across the electrode/ingot surfaces by means of an externally-applied magnetic field. The field also causes the liquid metal pool to rotate. Both of these effects are used to re-distribute the incoming heat flows to the pool so that the ingot axial surface temperature is maximized and the surface quality maintained. The thermal disturbances which accompany the above effects, however, also cause irregular growth of the solidification front, with accompanying variations in the local microsegregation. The result is a pattern of concentric paraboloids of segregation changes which when intersected by a radial cut appear as "tree rings" on the radial surface (Figure 7). The etching effect is highly visible, but as yet it has not been established that the segregation is sufficient to cause any mechanical property changes. Similar effects in steels have been shown to cause a decrease in LCF life of approximately 10%, but at much higher relative strength levels than are used in titanium alloys.

The second major effect is that of "freckles" (3). The bulk liquid pool movement interacts with interdendritic liquid to form channels in the dendrite network. This defect is well-known in other, lower melting-point systems and represents a very serious mechanical property problem in the product. The channel flow is density-driven and since it requires relatively large changes in density as the interdendritic liquid is formed, the mechanism is very seldom found in the present range of commercial alloys. However, it can, and does, exist in these materials (Figure 8).

4 - DISCUSSION

The specific kinds of segregation found in titanium alloys must be eliminated by suitable changes in the melting practice and cannot be rectified by homogenization and /or mechanical working. Since the VAR process requires a high heat input to maintain surface quality, it is also clear that the options for solidification control are severely limited. Indeed, it is already probable that the practical limits have been reached in respect of melting rates and ingot diameter for the present range of commercial alloys.

The limiting feature of VAR is the direct linkage between melting rate and power input. For solidification control we must un-link these two parameters, as is achieved in either EB or plasma melting. Once this aim has been satisfied, we can increase the ingot temperature gradients to the point at which the condition of 100% columnar-dendritic structure is obtained and macro-segregation is absent. At the same time, by removing the need for strong external electromagnetic stirring, the fundamental cause of the microsegregation defects will have also been removed. The result will be a more uniform ingot composition and also the possibility of making the segregation-sensitive grades in larger ingot diameter should this prove necessary in the future.

5 - REFERENCES

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(4) S.M. Copley, A.F. Gamei, A.F. Johnson, M.G. Hornbecker, Met. Trans. , l, 2193, (1970).

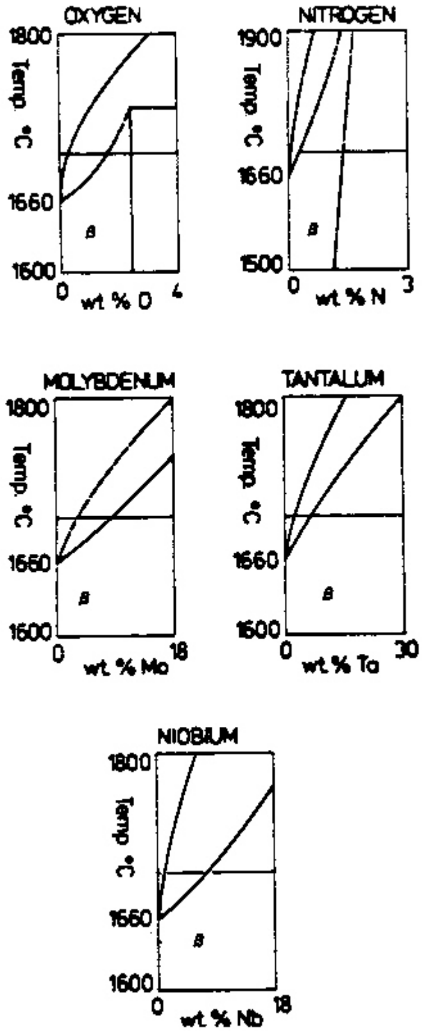

Fig. 1A - Phase diagrams for solid stabilizing elements in titanium in the titanium rich region.

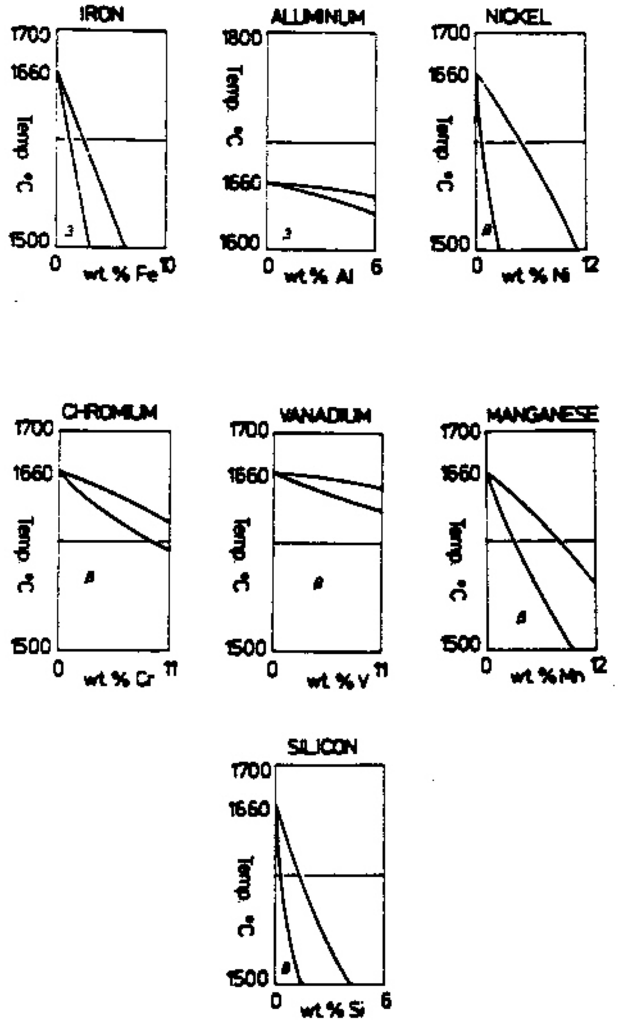

Fig. 1B - Phase diagrams for solid stabilizing elements in titanium in the titanium rich region.

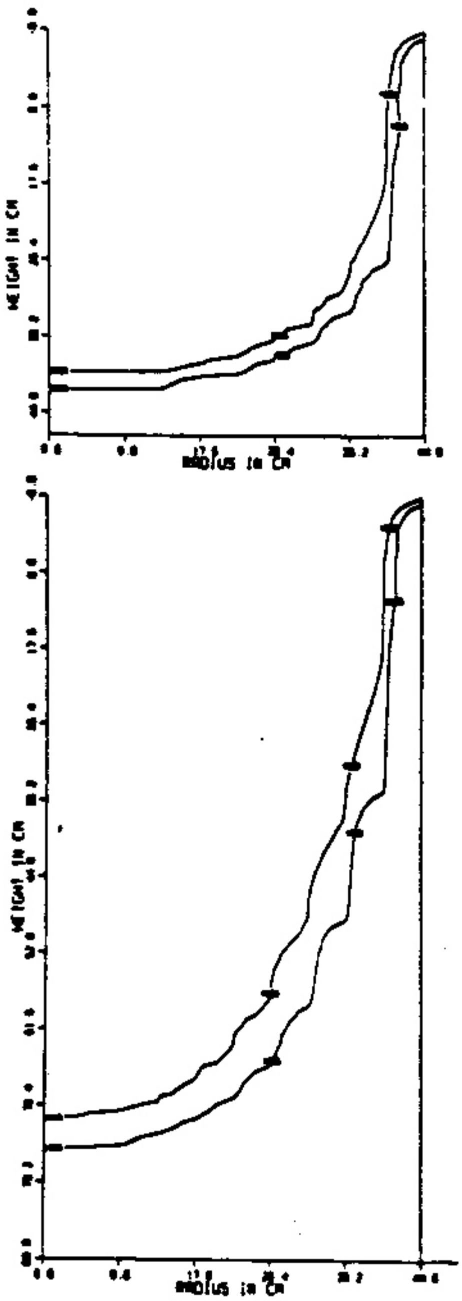

Fig. 2A - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) at a melting rate of 700 kg/hr during the initialstages of melting.

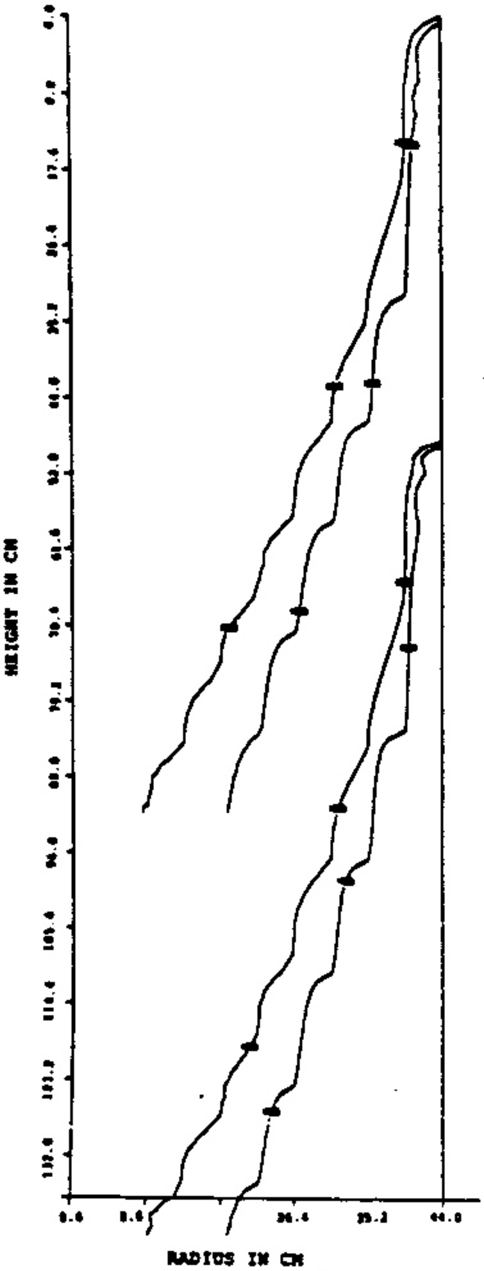

Fig. 2B - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) at a melting rate of 700 kg/hr during the final stages of steady state melting.

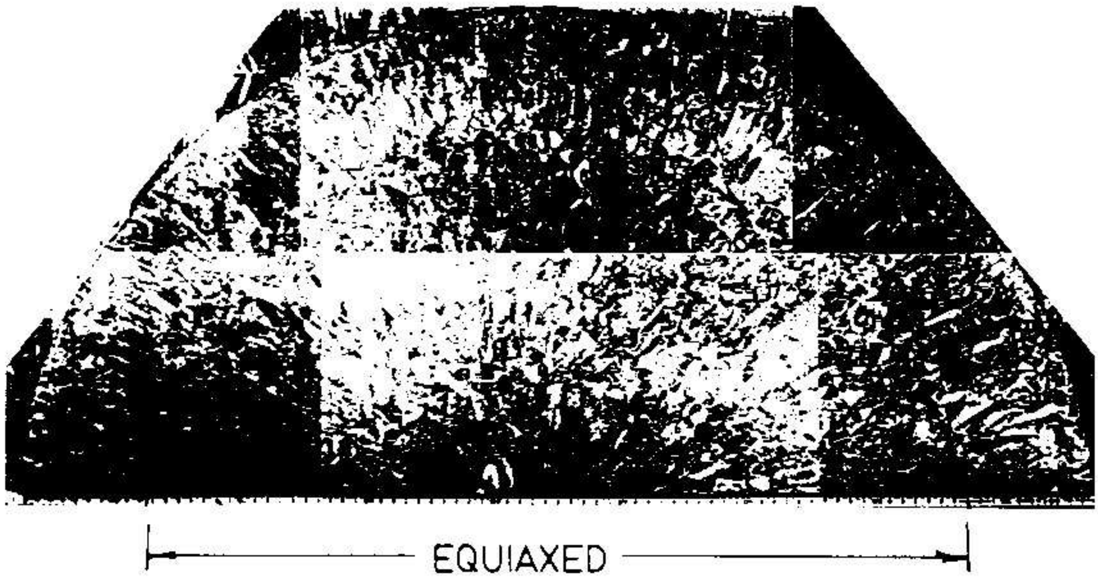

Fig. 3 - Ingot structure in a VAR ingot of Ti6Al4V showing the transition from columnar dendritic to equiaxial grain growth at the mid section of the ingot shown in fig. 2

		Element Wt pct	SE of Coefficient
β Transus, °C = 872	-7.7	Mo	1.0
	+23.4	Al	1.8
	-4.3	Zr	1.4
	-12.4	V	0.9
	-14.3	Cr	1.5
	-8.4	Fe	6.8
	+32.1	Si	25.5
Significance Level : 0.7			
Multiple Correlation Coefficient (r^2) : 0.89			

Fig. 4 - Liquidus and solidus temperatures for various commercial titanium alloys.

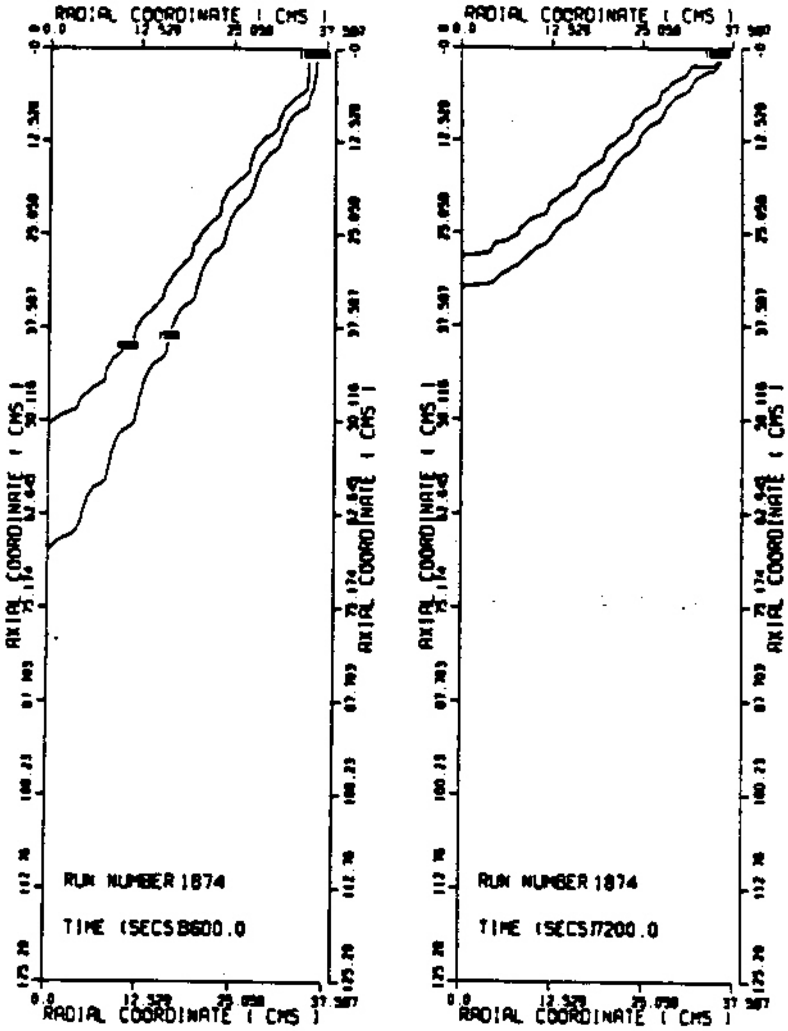

Fig. 5A - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) during the hottop sequence.

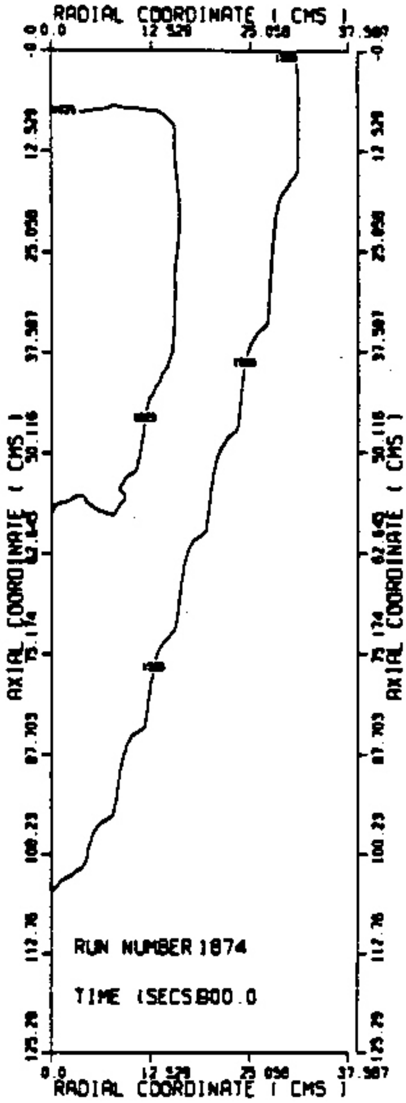

Fig. 5B - Liquidus-solidus profiles in an ingot of Ti6Al4V (VAR) after steady-state melting using no hottop sequence.

Alloy	$T_L(°C)$	$T_S(°C)$
6Al 4V	1625	1595
8Al 1Mo 1V	1610	1580
5Al 2.5Sn	1590	1545
6Al 6V 2Sn	1630	1615
6Al 2Sn 4Zr 6Mo	1625	1550
5Al 2Sn 2Zr 4Mo 6Cr	1615	1520

Fig. 6 - The variation of Beta transus temperature with composition for various alloying elements in titanium.

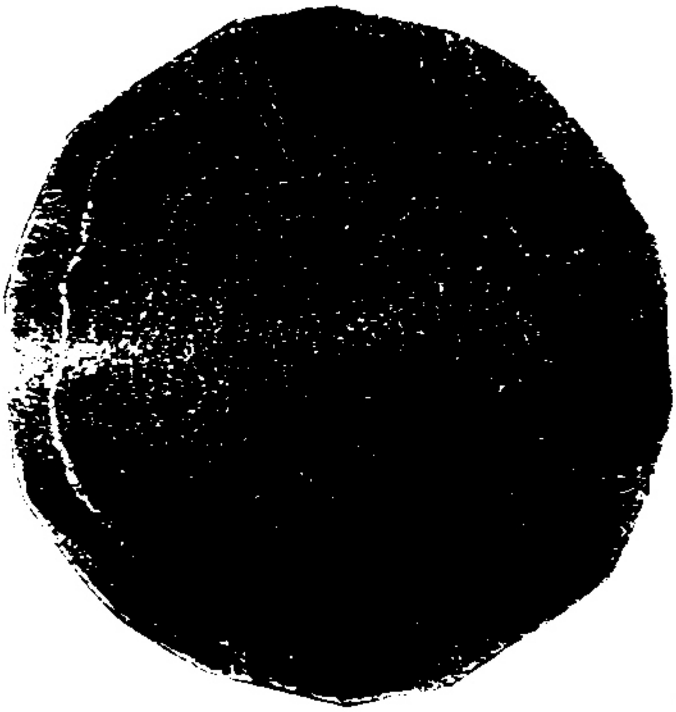

Fig. 7A - Tree-rings in Ti-17 alloy

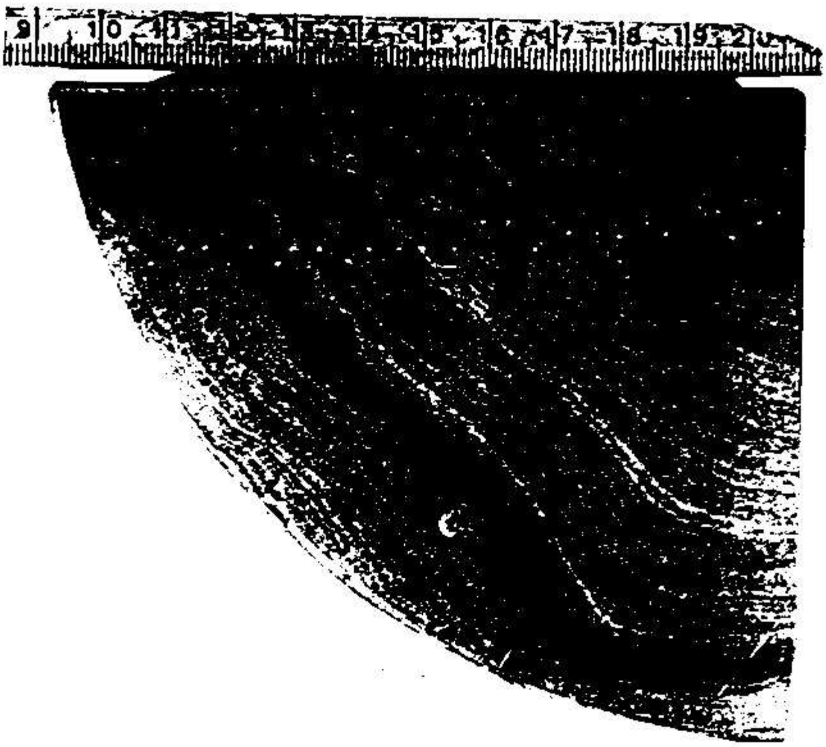

Fig. 7 - Tree-rings in Ti6Al2Sn4Zr6Mo alloy

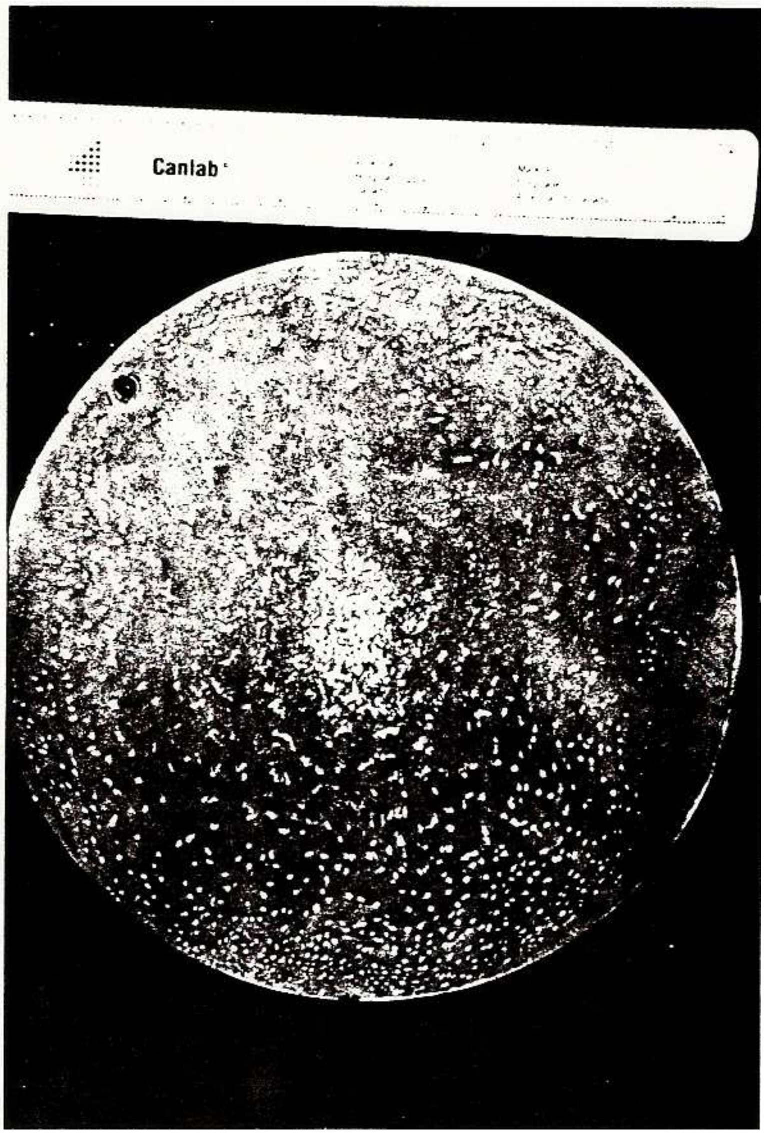

Fig. 8 - Freckles in a near-beta alloy