

Segregation and Solidification in Titanium Alloys

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This work presents a study of the solidification modes of CPTi and alloys 10-2-3, 6-2-4-2 and Ti17, together with measurements of the segregation coefficients of elements in these alloys. The solidification modes observed in conditions found in VAR ingots suggest that whilst the alloys solidify as structures which closely resemble those of lower melting-point alloys, CPTi probably adopts a cellular mode until sufficient undercooling is present to convert the system to the equiaxial mode. The measured segregation coefficients indicate that theoretical values obtained from binary phase diagrams do not represent the actual values in multicomponent systems.

Keyword: solidification, titanium alloy, segregation, remelting

1. Introduction

Several workers ^{1-4,9)} have commented on the importance of solidification segregation in titanium alloys, relating the effect to observable defect structures in the final product, such as "soft alpha" and "beta fleck", both of which impart adverse mechanical properties to the product. Investigations on the formation of the segregation during solidification are hampered by the subsequent phase transformation which obscures the primary beta structure and hence renders an accurate definition of the original solidification structure impossible by conventional techniques such as chemical etching. Indirect methods have been used to outline the primary structure. Hayakawa et al ¹³⁾ used the ingenious technique of identifying the microporosity associated with solidification in CP titanium VAR ingots by ultrasonic examination: Nastac et al ⁵⁾ used the technique of rastered composition scanning on a scanning electron microscope to indicate compositional regularities in an alloy as-cast structure which were held to indicate the original dendritic structure in the material. Direct observation of the solidification structure by techniques used on lower melting-point alloys cannot be used on titanium alloys because of the metal's reactivity toward refractory containers. Attempts to produce, for example, directionally-cast samples in titanium alloys have been defeated in practice by reaction of the container leading to unacceptable contamination of the casting. For this reason, observations of the primary structure have been indirect, or limited to isolated examples of structures found in shrinkage cavities etc.

Segregation is best defined in terms of the segregation coefficient, k , which in equilibrium solidification conditions can be derived directly from the liquidus and solidus lines in the appropriate phase diagram ^{6 10)}. In most cases, the phase diagram is not well defined and the best available estimates for k are derived from binary phase

diagrams. Even in this latter case, for a number of alloy elements (for example nitrogen) the diagrams are tentative and the value of k so derived is likely to contain significant inaccuracies.

The purpose of the work contained in this report was twofold. First, to investigate the solidification modes in vacuum arc remelted ingots of CPTi and of typical titanium alloys and to compare these modes with the data available on steels and nickel-base alloys solidified under similar conditions. Second, to experimentally determine the segregation coefficients of elements in these materials in order to assess the accuracy of the phase diagram derivations and also to provide an accurate database for future work on computer modelling of segregation patterns in remelted alloy ingots.

2. Experimental Techniques

2.1 Segregation Measurements

The alloys chosen were 10-2-3, Ti-17 and 6-2-4-2.

Samples were obtained as full cross-section slabs cut from as-cast 3rd melt industrial VAR ingots. The samples were etched to outline the columnar directional macrostructure, which was identified by photography and hardness fiducial markers. The samples were then re-polished and the micro-compositional variation was measured by SEM-EDAX in a direction perpendicular to the columnar axis. Details of the techniques used are given in the literature ¹⁾.

Samples of the alloys were melted in a "zone refined" mode, by either laser floating-zone or by induction floating-zone furnaces. In this mode, under a steep temperature gradient and a slow solidification rate, the alloy is forced to adopt a planar solidification interface under which condition alloy elements segregate following the Pfann equation ¹¹⁾. Subsequent chemical analysis of the elemental distribution in the axial direction of the sample ¹⁾ shows that all elements follow a distribution described by

the Scheil relationship ¹¹⁾, from which we may derive the effective segregation coefficient. Values of this parameter obtained from both of the above techniques are listed in Table 1, together with the values previously derived from binary phase diagrams.

2.2 Solidification Measurements

Also available to the investigation was a macro-slice of a CPTi VAR ingot which showed the position of the columnar/equiaxial transition (CET) in the solidification structure, shown in Figure 1. Temperature gradients and solidification rates were also computed for this transition in a parallel investigation using a CFD model of VAR ingot solidification to derive the temperature gradients and solidification rates in the ingots in question. In Figure 2, the CET positions analysed in a large CPTi VAR ingot are superimposed on the accepted diagram for the lower melting-point alloys. Observations were also made of structures found in minor solidification cavities in the ingots. It is clear from the observations shown in Figure 3 that the alloys 10-2-3, Ti 17 and 6-4 solidify to form a columnar dendritic solid/liquid interface under the particular conditions prevailing at the time of formation of the solid. However, as shown in Figure 3, examination of a similar shrinkage cavity in CPTi showed formations which are more indicative of a cellular structure.

3. Discussion

3.1 Solidification Structures

Following the reports of investigations on the solidification of CPTi ¹²⁾ it appears probable that the solidification of this material differs from that of the alloys, even though CPTi contains a small quantity of O and Fe and might be considered also to be an alloy. Previous work ¹²⁻¹⁵⁾ (particularly ¹²⁾) suggests that CPTi solidifies as a cellular structure under high solidification rates (as are present in the outer and basal regions of a VAR ingot) and transitions directly to an equiaxial structure as the solidification rate decreases without an intervening dendritic region. In the case of alloy structures, the cellular region is essentially absent under industrial VAR conditions and we observe the equiaxial structure only when the solidification rate is very low. (It is notable that reports of the ingot structures found in 6-4 ingots made by EBCHM show no equiaxial region, which might be expected from the higher solidification rates present in this process.). When the computed solidification conditions are superimposed on the conventionally-accepted solidification diagram for lower melting-point alloys, we see that there is

a clear shift in the CET conditions, indicating that the Ti alloys and CPTi require enhanced nucleation conditions before the dendritic solidification mode breaks down into equiaxial nucleation.

3.2 Segregation Parameters

The measured segregation parameters show a significant deviation from those calculated on the basis of accepted phase diagrams. The inference to be drawn from this finding is not that the phase diagrams are in error, but rather that there exists a significant inter-element interaction in the multi-component alloys. On the basis of the thermochemical nature of the element-Ti interactions which might be anticipated, this finding is reasonable and highlights the need to input actual experimental data into computational databases rather than to rely on interpolated values. When this latter step is taken, the present CFD models of the VAR process for Ti alloys produce results which are well aligned with actual industrial data as to the element distributions in large VAR ingots. It is notable, however, as indicated in the literature ¹⁵⁾ that the level of segregation required to cause the "beta fleck" defect in these alloys can only be reached (as indicated by the Scheil relationship) inter-dendritically when more than 80% solidification has taken place. At this point in the solidification process it is difficult to envisage a mechanism permitting the substantial amount of liquid movement required to assemble the volume of remaining segregated liquid required to form a typical beta fleck.

4. Conclusions

- (1) The use of segregation coefficients derived from binary phase diagrams is not appropriate for complex alloys. Experimentally-derived values should be used for modelling purposes.
- (2) Nucleation of equiaxial solidification requires higher undercooling in titanium alloys than in lower melting-point alloys.
- (3) Titanium alloys solidify in the conventional manner with a transition from columnar dendritic to equiaxial mode as the solidification rate decreases. CPTi solidifies in a cellular mode until sufficiently low solidification rates are reached to cause the transition to an equiaxial mode.
- (4) It is difficult to account for the formation of beta fleck on the basis of conventional solute segregation since there does not appear to be a reasonable explanation of the liquid movement required to form the defect using the experimental value of segregation coefficients.

Table 1. Distribution coefficients of alloying elements in titanium alloys

Al	Sn	Zr	Mo	V	Cr	Fe	O	N	C	Note
1.05	0.92	0.90	1.50	0.90	0.70	0.60	1.60	1.58	0.50	Binary phase diagram, Binary alloy analysis ⁶⁾
1.13				0.95		0.38	1.33	1.45		Experimental, 10-2-3
1.06	1.15	0.77	1.15		0.74					Experimental, Ti 17
1.02	1.08	0.72	1.09							Experimental, 6-2-4-2

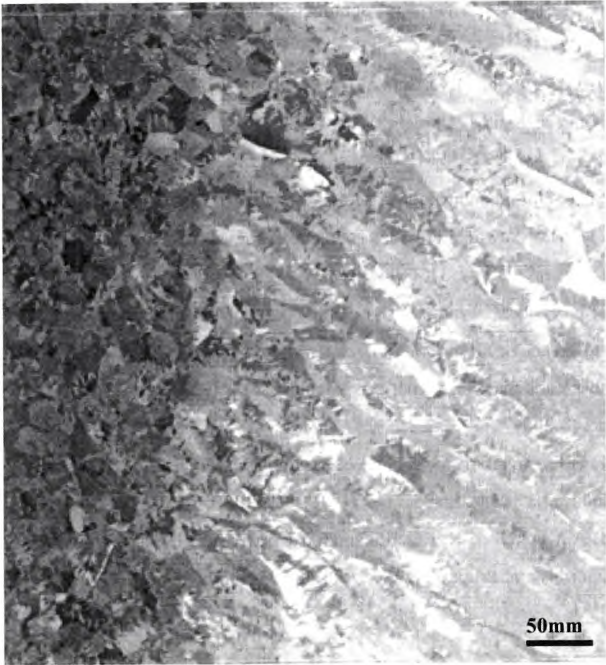


Figure 1. Columnar to equiax transition in CP-Ti. Axial section, as-cast VAR ingot 950mm dia

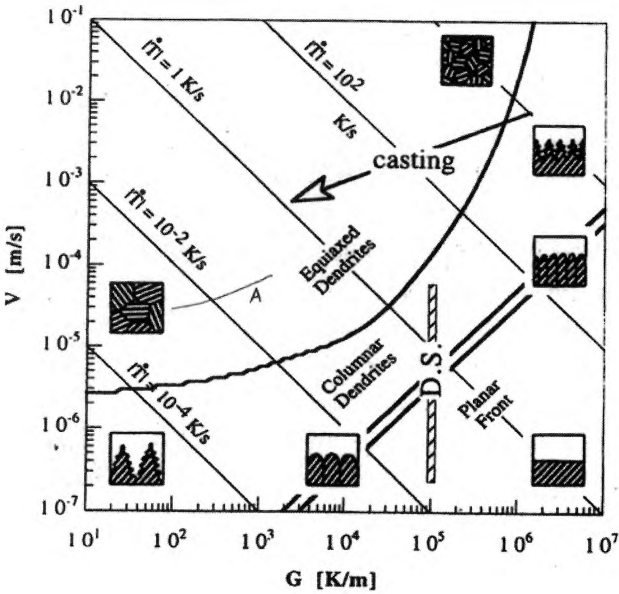
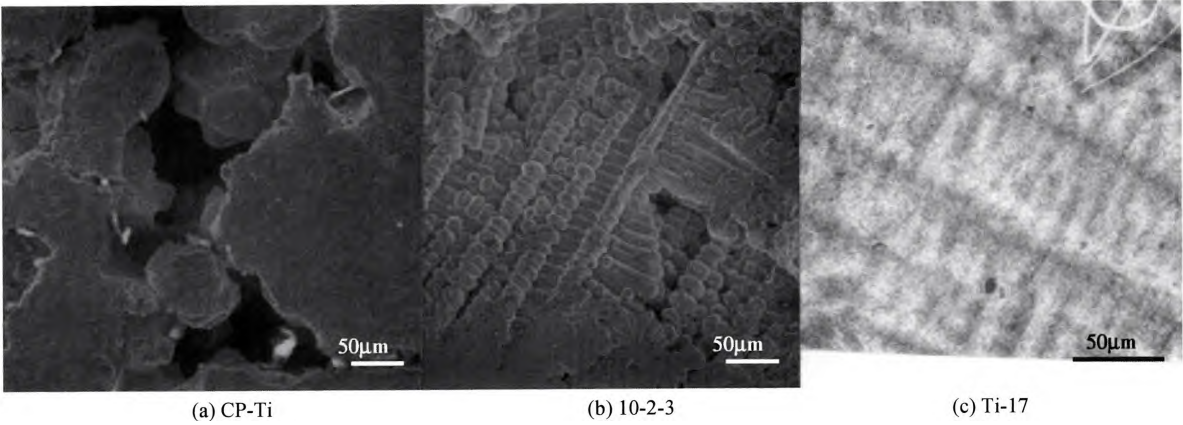


Figure 2. Solidification Map. Line "A" represents CET for CP-Ti as computed from VAR solidification.



(a) CP-Ti

(b) 10-2-3

(c) Ti-17

Figure 3. Solidification in CP-Ti and alloys, VAR ingot cavities ((a)CP-Ti , (b)10-2-3, (c)Ti 17).

Acknowledgement

The authors are grateful to TIMET Inc and to the Reactive Metals Corp for the provision of the VAR ingot sections used in this work.

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