

# A Review of the Mechanisms Regarding Duplex Layer Formation During Various Manufacturing Processes

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다양한 제조 공정하에서의 이중층 형성 기구에 관한 고찰

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**초 록** 다양한 제조 공정하에서 기판위에 형성되는 이중층은 공학적인 관점으로 볼때 매우 중요한 미세 조직들 중의 하나이다. 이중에서도 고온 산화시에 형성되는 이중층에 관하여는 많은 이론들이 있다. 이 논문에서는 이들 이론들에 대한 가정 및 이론 전개에 대한 고찰을 통해 이들 이론들을 검증하였다. 또 산화 이중층을 진공 박막 제조 및 응고시 형성되는 이중층들과 비교하였다.

**Abstract** Duplex layers are a very important class of film microstructures and form under a wide variety of conditions on a large number of substrates. In this paper, the available models for duplex layer formation during a high temperature oxidation are reviewed in detail. The basic assumptions which are based upon them are examined and pros and cons of these models are addressed. Then, these oxide duplex structures are compared with other double layer microstructures formed during thin film manufacturing processes and solidification process.

## 1. Introduction

The growth of an oxide film on a metal by thermal oxidation is usually discussed in terms of Wagner's theory in which the oxidation rate is controlled by the transport of ions across the oxide film under the combined effects of concentration gradients and electric fields<sup>1~4</sup>. This leads to parabolic growth kinetics with a single layer oxide growth. However, in many cases, the oxide scales grown on the substrates at high temperature consist of two distinctive layers which are an inner layer and outer layer respectively. This duplex layer has specific morphological characteristics. The inner layer consists of small equiaxed grains while large columnar layers overgrow them.

There is considerable technological interest in the mechanism for formation of the duplex layer since other important engineering systems, in addition to corrosion scales, such as deposited thin films by sputtering or physical/chemical vapor depositions and solidified ingot microstructure exhibit duplex layers. Therefore, it is worthwhile to review the available models for duplex layer formations, examine the basic assumptions which are based upon them and compare them with other important engineering systems, since there is the possibility

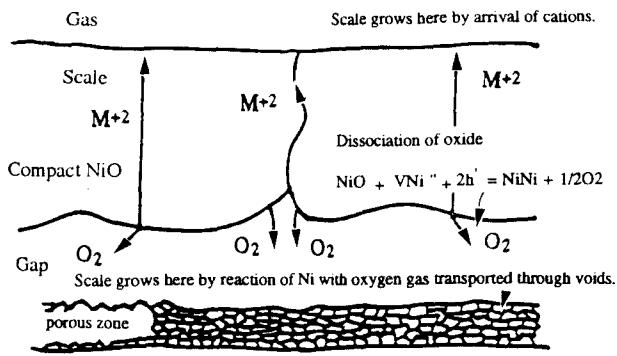
that the mechanism for formation of the duplex layer during high temperature oxidation and other duplex layers might share common working principles.

## 2. Controversial Issues Regarding the Models for the Duplex Growth

There are several models to explain the development of the oxide scale growth in a duplex fashion.

### (a) Dissociative Mechanism

A dissociative mechanism was proposed by Mrowec to explain a compact outer portion and a porous inner portion of scales which are frequently found during optical microscopy or scanning electron microscopy observation<sup>5</sup>. As the oxidation reaction proceeds, growth stresses are generated within the oxide. In systems where cations are mobile, growth stresses arise in the scale since the scale must relax to maintain contact with the metal. If the scale does not relax, voids will form at the scale/metal interface separating the scale from the metal. Frequently this loss of contact causes the formation of a porous zone of scale between the outer compact layer and the metal. When scale separation occurs, the metal activity at the inner surface of the scale is high and so cations still continue to migrate outwards. However, this causes the metal activity to



1. Oxide is separated from the metal due to insufficient oxide plasticity.
2. The oxygen activity at the inner surface rises.
3. Dissociation of scales occurs.
4. Oxygen migrates across the pore or gap.
5. Begins to form new oxide (inner layer) on the metal substrate.

Fig. 1. Illustration of Mrowec's dissociative mechanism

fall and the oxygen activity to rise correspondingly. As the oxygen activity rises, the oxygen partial pressure in local equilibrium with the scale inner surface rises and oxygen evaporates into the pore, diffuses across the pore, and forms oxide on the metal surface (inner layer). In this way, a porous inner layer can be formed next to the oxide/metal interface while maintaining outward diffusion. The schematic of the dissociative mechanism is presented in Fig. 1.

The particular problem with this model is that the dissociation vapor pressure of the oxide is much too low to provide sufficient oxidant flux to account for the observed oxidation rates. It is also questionable whether the dissociative mechanism can be applied to the growth protective chromia, alumina or silica scales which exhibit duplex scales<sup>6-9</sup>). The dissociative mechanism requires that scale growth occurs predominantly by cation diffusion and it appears that this criterion is not met for alumina and silica and perhaps for chromia under certain conditions. Furthermore, if a void formed, for example, at the interface between a chromia scale and its metallic substrate, the rate of transport of chromium vapor across the void could be greater than that of oxygen bearing gases, thereby precluding the onset of pore formation by a dissociative mechanism.

#### (b) Lattice Diffusion of Cations and Grain Boundary Diffusion of Anions

It is well established that the transport of cations and anions occurs along grain boundaries since grain boundaries provide short circuit diffusion paths<sup>10,11</sup>). If the short circuit paths along grain boundaries are blocked by foreign atoms or precipitates, then the transport of ions will occur by lattice diffusion. Lattice diffusion of cations and grain boundary diffusion of anions can

occur if the grain boundary segregants selectively occupy the cation sublattice sites along grain boundary, resulting in the blockage of the cation short circuit diffusion paths. As far as the author is aware, this model is most likely among the available theories.

This model can be quantified on the modified parabolic rate law with the assumption that grain boundaries are the only effective short circuit diffusion paths. It is, therefore, useful to examine this model as one of the limiting cases of the model suggested by Smeltzer<sup>12,13</sup>.

As a limiting case, it may be assumed that  $f_t$  (the fraction of the cross sectional area of the oxide along which grain boundary diffusion can occur) is not a function of  $P_{O_2}$  and  $D_o^b \gg D_{Me}^b$  and  $D_{Me}^l \gg D_o^l$  ( $b$ : boundary,  $l$ : lattice,  $Me$ : metal,  $O$ : oxygen and  $D$ : diffusivity), which is possibly achieved if the segregation of foreign atoms blocks the available cation diffusion paths along grain boundaries. In this case, parabolic rate constant ( $k_p$ ) becomes

$$k_p = k_p^l + \frac{1}{2} f_t \int_{P_{O_2}^i}^{P_{O_2}^a} D_{Me}^l \left( \frac{D_o^b}{D_{Me}^b} \right) d \ln P_{O_2} \quad (2.1)$$

It does not seem reasonable to assume that  $D_o^b/D_{Me}^l$  is independent of  $P_{O_2}$ . However, if  $D_o^b$  is independent of  $P_{O_2}$ , Eq. (2.1) becomes

$$k_p = k_p^l + \frac{f_t D_o^b}{2} \ln \frac{P_{O_2}^a}{P_{O_2}^i} \quad (2.2)$$

To examine the relative contributions of lattice diffusion of cations and grain boundary diffusion of anions to the value of  $k_p$ , it is useful to replace  $k_p^l$  ( $l$ : lattice) in Eq. (2.2) with

$$k_p^l = \frac{1+z}{\alpha} \frac{D_{Me}^l}{f_{Me}} \quad (2.3)$$

Eq. (2.3) is obtained when  $P_{O_2}^a \gg P_{O_2}^i$  ( $a$ : ambient,  $i$ : metal/oxide interface) and assuming that  $Me_xO$  is a  $p$ -type semiconducting compound ( $z$ : valence). Now we obtain

$$k_p = \frac{1+z}{\alpha} D_{Me}^l + \frac{f_t D_o^b}{2} \ln \frac{P_{O_2}^a}{P_{O_2}^i} \quad (2.4)$$

where  $D_{Me}^l/f_{Me}$  ( $D_{Me}^l$ : tracer diffusion coefficient,  $f_{Me}$ : correlation factor) has been replaced by the lattice self diffusion coefficient for cations ( $D_{Me}^l$ ). Typical values are  $z=2.0$ ,  $\alpha=1.0$ ,  $f_t=10^{-3}$  and  $D_o^b/D_{Me}^l=10^2$  to  $10^3$ . If, for example,  $D_{Me}^l=10^{-12}$  cm<sup>2</sup>/sec,  $D_o^b/D_{Me}^l=10^2$ ,  $P_{O_2}^a=1$  atm and  $P_{O_2}^i=10^{-20}$  atm (values of  $10^{-10}$  to  $10^{-30}$  atm would be typical), then

$$k_p^l(\text{lattice}) = f_k k_{pb}(\text{boundary}) \quad (2.5)$$

In this case, transport of both anions and cations contributes significantly to scale growth, and the possibility of the formation of new oxide within the existing layer may exist.

(c) Oxygen Inward Transport

Atkinson et al. performed tracer diffusion measurements on high purity nickel and Ni-dilute Cr and Al alloys by sequential oxidation in  $O_2^{16}$  and  $O_2^{18}$ <sup>14~20</sup>. In this experiment, the expected relationship between growth rate and diffusion constants is not confirmed and usually the oxidation rate is many orders of magnitude greater than expected. They argued that for Ni oxidation, the fast rates are a result of rapid diffusion along grain boundaries in the oxide and when this is taken into account the oxidation rates and diffusion data can be reconciled. However, in the case of Ni-Cr and Ni-Al oxidation even fast diffusion along grain boundaries is still apparently too slow to account for the measured oxide growth rates<sup>21~26</sup>. Short circuit diffusion of oxygen appears to occur to a greater or lesser extent in practically all oxide films. Consequently, they claimed that oxygen is transported as molecules along short circuit pathways. This inward oxygen gas transport is responsible for the growth of new oxide within the films and for the growth of the inner layer of the well developed duplex films which grow on the alloy. They proposed a mechanism whereby oxygen gas penetrates the films through fissures to form new oxide in the available space to explain the observations and the growth of duplex films. The actual pathways have not been identified, but it is assumed that they may be of a transient nature, i.e., they form, admit gas, then reseal during isothermal oxidation, as illustrated in Fig. 2.

Atkinson suggested that duplex film formation is de-

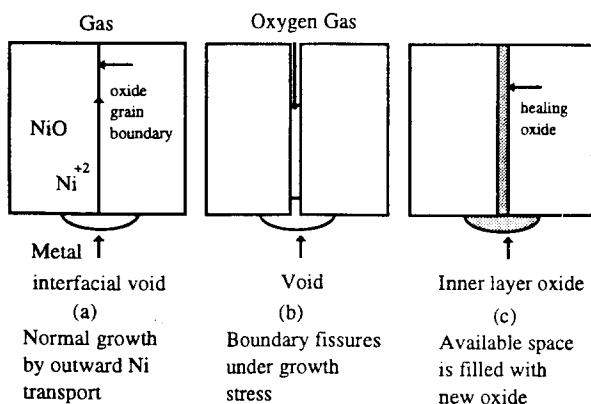


Fig. 2. Illustration of Atkinson's model for the inner layer

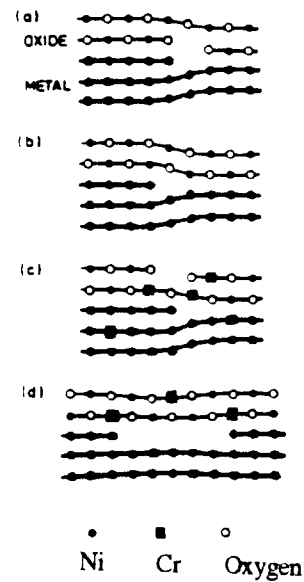


Fig. 3. Illustration of Manning's available space model (a) arrival of metal vacancy close to dislocation (b) climb of ledge by annihilation of vacancy (c) Cr atoms can surround dislocation and prevent its climb (d) further arriving vacancies nucleate vacancy-like dislocation loop

termined by the availability of space at the metal/oxide interface, i.e., the generation of interfacial porosity. The major questions which remain unanswered with this general explanation are how the fissures are generated in the growing film and how the porosity is generated at the metal/oxide interface.

(d) Available Space Model

Almost same idea was used in Manning's model<sup>27</sup> even though the oxygen pathways are different. The basis of this model is that single layers form when dislocation climb eliminates space created at this interface by outward metal diffusion. Factors which inhibit this volume collapse, such as sample corners or small quantities of certain impurities, lead to duplex scales. In these two models suggested by Atkinson and Manning, some porosity always exists in any growing scale, and a reaction at the oxide/metal interface directly initiates the inner duplex layer. These two models strongly depend on the movement of cation vacancies. According to them, vacancies will always arrive elsewhere at the oxide/metal interface and will pass into the highest metal plane. These vacancies will tend to condense into a series of vacancy-like dislocation loops (Fig. 3). It is less easy for the surrounding lattice to relax around these configurations, and their vacancy or microvoid character tends to be retained. Consequently, there is now space available for oxidation to occur at the interface if the oxidant has access to this interface as proposed. This process nucleates the inner layer. Oxidation

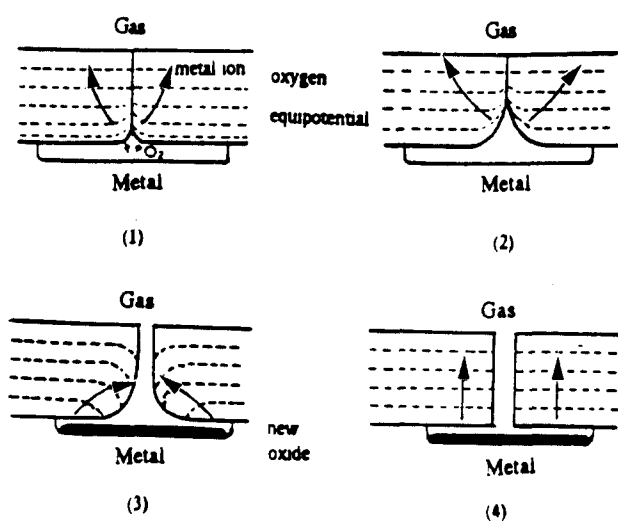


Fig. 4. Illustration of Gibbs and Hales mechanism (1) Pore opens below oxide layer by vacancy condensation and dissociation of oxide (2) Undersized pore grows by dissociation (3) Oversized pore fills in by the reaction with metal ion (4) Equilibrium size pore remains since the oxygen activity near the pore is equal to that in the adjacent oxide.

proceeds until the space is filled with new oxide which will form more inner layer oxide.

However, the fate of cation vacancies is still controversial<sup>28-30</sup>. Several possibilities appear to be available to accommodate this vacancy flux : 1) they accumulate at the interface as voids, 2) they are annihilated at the interface by the climb of interface dislocations, and 3) they diffuse into the metal where they either form voids in the metal, or are annihilated by the climb of metal dislocations.

(e) Gibbs' and Hale's Mechanism (Revised Model of Mrowec's Dissociative Mechanism)

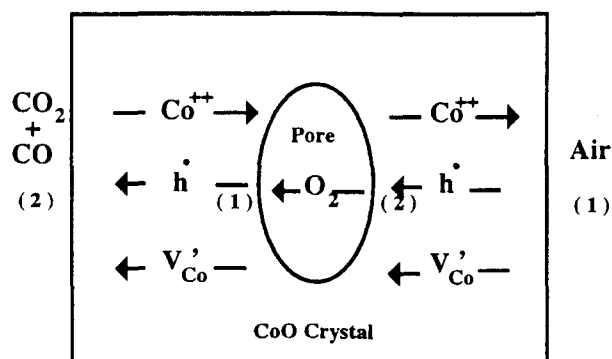
Mrowec's dissociative mechanism has been revised by Gibbs and Hales<sup>31</sup>. The Gibbs/Hales model has been considered as an important reference model for duplex scale growth. It is a quasi-equilibrium model of duplex scale growth, analogous to the Wagner's quasi equilibrium model of single layer growth. It was proposed that the oxidant can traverse the scale via pores which might form in the following manner. Metal diffusion along grain boundaries in the oxide creates an inward flux of vacancies. The vacancies could condense then they reach the oxide/metal interface and form cavities in the metal below the grain boundaries. A cavity would lower the oxidation rate locally and allow the oxide at the grain boundary to dissociate and open up into a pore (Fig. 4). Gas diffusion down the pore is rapid and one pore of diameter 1nm per outer layer grains is found to provide sufficient access to account for the observed oxidation rates.

A question frequently raised about such model is why do not the pores simply block up. There appears to be nothing to prevent the outward moving metal ions from meeting the inward moving oxidant molecules and reacting in the pores and filling them up. (This process was employed in the model of Rhines and Wolf<sup>32</sup>). Gibbs and Hales argued that this need not happen if the equilibrium diameter varied across the scale in such a manner that the oxygen activity at any position in the pore was equal to that in the adjacent oxide. Pores of smaller diameter would open up by dissociation, while pores of larger diameter would attract a metal flux which would tend to fill in the pore with new oxide forming inner layer.

However, it is questionable whether it is possible to apply concepts based on thermodynamics to the dynamic process such as the growth of scales. It is also pointed out that pores tend to block, because the supply of oxidant is too large and so the oxygen activity along pore surfaces is too high<sup>27</sup>.

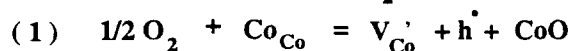
(f) Yurek and Schmalzried mechanism

This model is based on the same idea applied to the Mrowec and Gibbs-Hales model, i.e., the dissociation of the oxide. If an oxide single crystal is placed between two different oxygen potentials, the crystal begins to move towards the high potential side by diffusion of components<sup>33,34</sup>. Yurek and Schmalzried argued that in this way the total Gibbs energy of the overall system



— Pore Movement →

$$P_{O_2(1)} > P_{O_2(2)}$$



Model for pore movement in a cation deficient oxide which is exposed to an oxygen potential gradient

Fig. 5. Illustration of the pore movements under oxygen potential gradient suggested by Yurek and Schmalzried.

can be lowered. Experiments have shown that pores are formed in the originally nonporous single crystal at the lower oxygen potential interface and migrate to the higher oxygen potential interface (Fig. 5). Gas filled pores are short circuit paths for the migrating vacancies.

It is, therefore, argued that this is the reason why smaller pores have a higher migration rate when compared with bigger pores and eventually smaller pores coalesce to form bigger ones. Pore formation of this kind has been found in single crystalline solid solutions as well as in stoichiometric compounds such as CoO or NiO. This model would require porosity to initiate at the metal/oxide interface and migrate through the scale. Estimates of pore migration rates in NiO from the fastest moving pores in CoO (0.15cm/24hrs.)<sup>34)</sup> yield values of 0.06mm/hr for pore migration in NiO. The estimate is based on the ratio of cation vacancy diffusivities  $D_V(\text{NiO})/D_V(\text{CoO}) = 10^{-9}\text{cm}^2\text{sec}^{-1}/10^{-6}\text{cm}^2\text{sec}^{-1} = 10^{-3}$ , at 1200°C used in each experiment. Therefore the application of this model to the NiO system seems unlikely.

#### (g) Evans' model

Evans et al.<sup>35)</sup> suggested that the stresses produced by oxidation are a probable source of porosity which serve as available space for inner layer growth. This porosity would be created either by the plastic deformation or the creep of the oxide. They considered the plastic deformation of the rock salt structure oxide NiO growing on FCC Ni. In this system, the NiO grains are textured, being crystallographically oriented with respect to the substrate. According to the von Mises criterion, an arbitrary plastic deformation requires dislocation glide on five active, independent slip systems. In oxides, because of their ionic bonding, this is not likely to occur at typical oxidation temperatures, since only the primary slip systems such as  $\{110\} \langle 110 \rangle$  are likely to be active. Nevertheless, it was proposed that in the special case of NiO, because of texturing, the falling of the oxide towards the metal required for a single layer could be accommodated by slip using only the primary slip systems. Presumably, in this model, alloying restricts this slip and so porosity builds up leading to duplex growth. The problem with this mechanism is that it is specific to FCC metals, although the duplex layer formation is found generally in most oxidation systems.

#### (h) Kofstad's model

In any growing scale the increase in volume accompanying oxidation creates a natural tendency towards compressive lateral stresses and longitudinal strains. Such strains cannot in general be accommodated in a

polycrystalline oxide by dislocation glide, because too few slip systems are likely to be active at typical oxidation temperatures<sup>36)</sup>. This leaves creep as the remaining mechanism to relieve strain. Creep is the transport of matter in response to an applied stress and can involve intragranular diffusion, grain surface diffusion and dislocation climb. When creep occurs in a polycrystalline oxide, it is liable to introduce porosity as noted by Kofstad<sup>37)</sup>. Consider an array of hexagonal grains such as in Fig. 6. A vertical strain is produced by the flow of matter from the sides to the top and bottom of the grain. If this flow occurs without relative movement of the grains, voids are formed between the sides of the grains due to stresses (Fig. 7). This voiding can only be relieved by a grain boundary sliding. The problem with this mechanism is that stress relief by diffusional creep or grain boundary sliding in the oxide is more difficult for scales with columnar microstructures than for fine equiaxed grains because grain boundary sliding can hardly occur for a columnar microstructure.

#### (i) Recrystallization Model

In this model, the outer layer of the oxide is explained simply as the evolution of initially formed inner layers by means of recrystallization. The driving force for re-

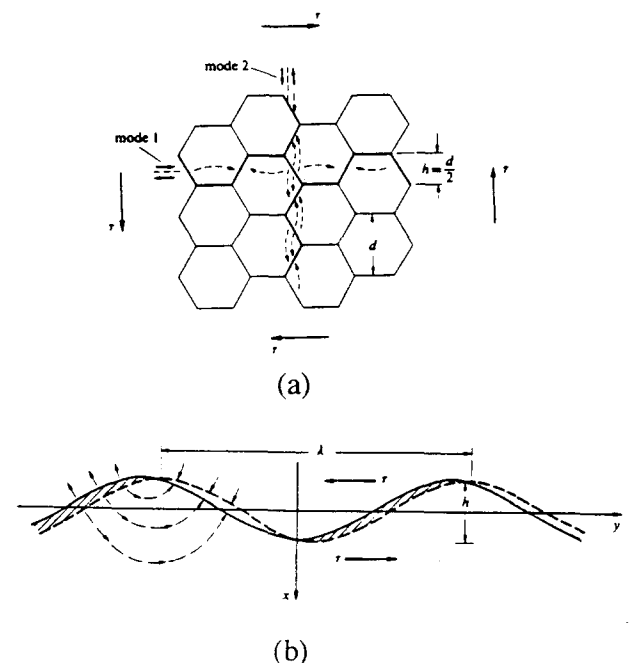


Fig. 6. Illustration of (a) the grain boundary sliding and (b) the formation of a cavity (From Raj, R and Ashby, M. F., Trans. AIME, 2, 1113, 1971) (a) Idealized model of a polycrystal as a hexagonal network of grain boundaries permitting grain boundary sliding according to two orthogonal modes. The accompanying vacancy flux is shown by the dotted arrows. (b) Sliding on a wavy grain boundary leads to the formation of a cavity (cross-hatched) which is transported as a vacancy flux into the overlap zones (dotted).

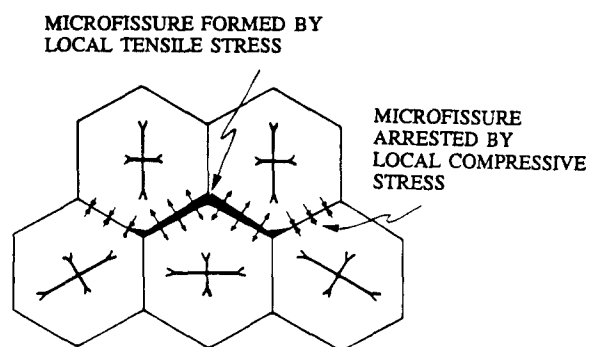


Fig. 7. Schematic drawing of the formation of microfissures due to the localized tensile and compressive stress

crystallization arises from the tendency to form larger oxide grains from grains which are either of smaller grain size or are more highly deformed than grains in the resultant recrystallized oxide. Since oxide scale morphologies generally manifest an increase in grain size with distance from the metal/oxide interface, this recrystallization model is a possibility.

#### (j) Duplex Layer Formation in Other Engineering Systems

##### 1) Duplex Layer Formation in Deposited Thin Films

The structure of as deposited thin films is often discussed in terms of structure zone models such as those proposed by Movchan and Thornton et al<sup>38, 39)</sup>. Thornton examined the microstructure of the thick sputter coated materials under the varieties of temperature and pressure conditions. He concluded that the microstructures found were generally consistent with the three zone model proposed by Movchan and Demchishin. Three different zones which were noted are : 1. At low argon pressures, a broad zone 1-zone 2 transition region consisting of densely packed fibrous grains was identified. 2. Zone 2 columnar grains tended to be faceted at elevated temperatures, although facets were often replaced by smooth flat surfaces at higher temperatures. 3. Zone 3 equiaxed grains were generally not observed at the deposition conditions investigated.

These modes all provide a general and highly qualitative picture of the expected film microstructure as a function of temperature. At low deposition temperatures, films generally exhibit an open columnar structure with extended voids along columnar grain boundaries. The columns themselves are not a single grains but are composed of smaller, more equiaxed grains (inner layer). Increasing the film growth temperature results in a filling in of the voids and a true columnar structure is obtained in which the columns are actually elongated grains. The boundary between these two

structural zones is often stated to be at  $T/T_m=0.3$  where  $T_m$  is the melting point of the film.

While this provides a general guideline, it should not be taken literally. The transition between structural zones does not occur abruptly at any given temperature, i.e., it is not a structural phase transition. Moreover, an attempt to define a universal reduced transition temperature  $T/T_m$  ignores the strong dependence of nucleation and growth kinetics on critical parameters such as substrate structure and orientation, film growth rate and the presence of impurities.

##### 2) Duplex Grain Structure in Solidified Cast Material

When metal is solidified, the morphology of the grain structure is usually not uniform, the extent of the non uniformity being dependent on the rate of cooling and other factors. When metal is poured into a metal mold, the metal in contact with the mold wall is cooled very rapidly. This high cooling rate at the surface influences the nucleation of crystals to a greater extent than their growth with the result that many fine grained equiaxed crystals are formed as shown in Fig. 8.

With increasing thickness of the chilled zone of crystals, the temperature gradient from the liquid to the mold wall becomes less steep and the rate of cooling decreases. Crystal growth rather than nucleation of new crystals is then favored and as a consequence the crystals at the liquid metal interface of the chilled zone begin to grow towards the center of the mold, so forming long columnar crystals. Some crystals have orientations such that their rapid growth direction, e.g.  $\langle 100 \rangle$  in cubic crystals, is along the direction of heat flow, and hence they grow more rapidly than their neighbors. During growth, these crystals widen and sti-

#### chill equiaxed columnar

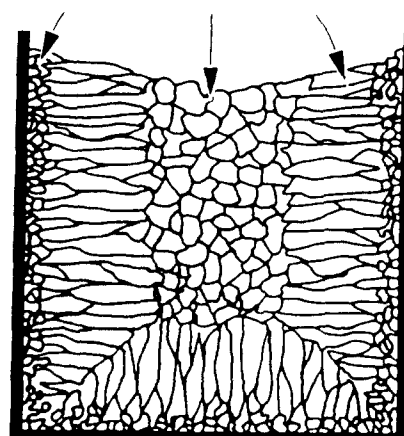


Fig. 8. Schematic drawing of a solidified cast structure showing the chill, columnar and equiaxed zones.

file the growth of slower growing crystals from the chilled zone, so that this selective growth process gives rise to a preferred orientation in columnar grains.

In pure metals the columnar zone may extend to the center of the ingot, but in alloys particularly, the liquid ahead of the growing columnar crystals is constitutionally undercooled and heterogeneous nucleation of new crystals takes place. These nuclei grow into coarse, randomly oriented, equiaxed crystals at the center of the ingot. A lowering of the temperature gradient increases the extent of the constitutional undercooling and hence the possibility of fresh nucleation. This is the just condition that exists in the final stages of solidification in an ingot when the temperature gradients have largely flattened out.

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