Effect of interfacial energies on heterogeneous nucleation

From experimental evidence it has previously been shown that heterogeneous nucleation is non-reciprocal and therefore that the balance of interfacial energies is a controlling factor. If $\sigma_{NL} > \sigma_{NS}+\sigma_{SL}$, the nucleus S can grow from the liquid L on the substrate N. When nucleation takes place the contact angle θ is small and there is epitaxy between the nucleant and the nucleus that reduces the σ_{NS} to very low values so that, as a first approximation, heterogeneous nucleation can be expected when $\sigma_{NL} > \sigma_{SL}$. Interfacial energies σ_{SL} are roughly proportional to the melting point, and high melting point phases usually nucleate lower melting phases. The contrary may happen if the low melting phase has a low symmetry crystal. Nucleation can take place on high index faces of this crystal because, although its average σ_{NL} is lower than the σ_{SL} of a higher melting point, high symmetry crystal, the σ_{NL} of its high index faces may be higher than the σ_{SL}.
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Introduction

In the freezing of bulk metals and alloys the undercooling for nucleation is usually low and indicative of heterogeneous nucleation. There is still much controversy as to the factors that control heterogeneous nucleation, but there is mounting evidence[1-17] that nucleation is non-reciprocal in the sense that if α-phase nucleates β-phase at low undercooling, the β-phase does not nucleate the α-phase at low undercooling, if at all. From this non-reciprocity, the balance of interfacial energies (Fig. 1) emerges as a controlling factor in heterogeneous nucleation: if $\sigma_{NL} > \sigma_{NS}+\sigma_{SL}$, the nucleus S tends to spread on the nucleant N to reduce the total energy of the system and growth of the nucleus can proceed.

Information on solid/liquid interfacial energies is scarce and not very reliable. As shown in a previous paper,[18] the values in the literature for some of the low melting point metals may vary up to one order of magnitude. For higher melting point metals, the variation is somewhat less, but more owing to the fact that fewer values have been published than because of increased accuracy of the determinations. Thus, a quantitative test of the above inequality is not possible. However some discussion and speculation on the values involved may clarify the situation.

Energy levels

It has been shown by measurement of the contact angles between nucleus and nucleant[18-23] that when nucleation takes place the contact angle θ is usually very small and does not exceed 20°. Thus, the values of $\cos\theta$ are very close to unity ($>0{\cdot}93$) and, as first approximation, the term $\cos\theta$ can be taken as unity and neglected.

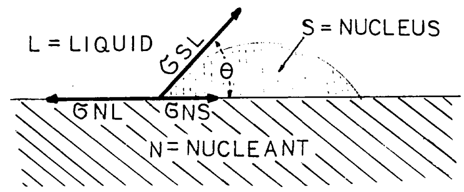
In low melting point metals,[18] the value of σ_{NS} is generally lower than σ_{SL} or σ_{NL}. From the few data published on $\sigma_{\alpha\beta}$ (where α and β are two different solid phases) for high melting point metals,[19, 24, 25] it can also be inferred that for high melting point metals the values of $\sigma_{\alpha\beta}$ are lower than either $\sigma_{\alpha\alpha}$ or $\sigma_{\beta\beta}$.

The energy σ_{NS} is greatly reduced if there is epitaxy between N and S, which results in low disregistry between the two phases. When crystallisation on substrates was investigated, it was always found that when nucleation took place at low undercooling, there was a fit between the lattices of the nucleant and the nucleus so that the disregistry between them was small. There are data in the literature[24-28] on interfacial energies between phases of coupled eutectics where the crystallographic fit reduces the energies. However, coupling of eutectics is seldom (if ever) perfect so that the values reported (e.g. the data in Table 5 of Ref. 18) are too high, because they are for a mixture of epitaxial and random boundaries. Moreover, in coupled eutectics, the fit has to be three dimensional, whereas in nucleation only a planar fit is necessary. More representative are the data on interfacial energies of precipitates that form from supersaturated solid solutions, because the precipitate usually has a very good fit in at least one direction and the disregistry is concentrated in the other directions. From the few data available,[29-31] it can be concluded that the interfacial energies between precipitate and matrix is of the order of 10% of the corresponding energy without crystallographic fit. This is in agreement with the energy of twin boundaries, the structure of which is very similar to the boundary between nucleus and nucleant.

From the considerations above, it can be safely concluded that the level of σ_{NS} in the inequality is very low and within the ±20% error on solid/liquid energies.[32] Thus, as first approximation, the terms $\cos\theta$ and σ_{NS} can be neglected and heterogeneous nucleation can be expected if $\sigma_{NL} > \sigma_{SL}$. Of course, this requires that there be a couple of planes, one from the nucleant and one from the nucleus, that have a good crystallographic fit.

The values of the interfacial energies found in the literature are usually for pure metals, whereas alloys are involved in heterogeneous nucleation. Although the addition of an element of low interfacial energy to a phase of higher energy decreases the energy of the phase, even when the decrease is substantial, the interfacial energy of the phase will always be higher than that of the addition. If $\sigma_{NL} > \sigma_{SL}$ for pure metals, the difference between σ_{NL} and σ_{SL} may be reduced by the alloying of the nucleus metal into the nucleant, but it will never reach $\sigma_{NL} \leqslant \sigma_{SL}$. Thus, the actual values may be changed, but the basic conditions remain the same.

Interfacial energies are roughly proportional to the melting point, as shown in Fig. 2, in which are plotted the values of σ_{SL} obtained by Miedema and Van Den Broeder.[33] Similar plots can be produced for the other interfacial energies and from other published data. On this basis, it can be expected that the higher melting point phases will have higher values of σ_{NL} and will be nucleants for the lower melting phases. This is often the case, but there are instances in which a lower melting phase nucleates a higher melting point phase.



σ_{NL} nucleant/liquid interfacial energy; σ_{NS} nucleant/nucleus interfacial energy; σ_{SL} nucleus/liquid interfacial energy; θ contact angle

1 Balance of interfacial energies in heterogeneous nucleation

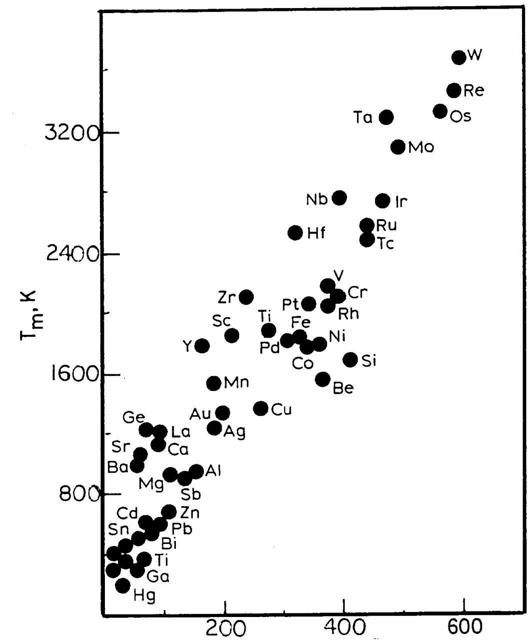
Energies of various crystal faces

The interfacial energies that have been discussed so far are average energies. This means that their values tend to be low, since crystals tend to be delimited by the faces of highest atomic density and therefore lowest energy, whereas nucleation would be expected to take place on the faces of the nucleant with the highest energy.

Nucleation on high order planes can explain why the less symmetrical crystals can be good nucleants.[2] In highly symmetrical crystals (fcc, bcc, and hcp), the difference in energy between low and high index planes is relatively small, whereas it is much larger for less symmetrical crystals (tetragonal, orthorhombic, etc.). Thus, if the nucleant has a low symmetry crystal structure and the nucleus has a higher symmetry crystal structure, even if the fit is between two high energy planes, the nucleant plane will have a higher energy than the nucleus plane and growth of the nucleus on the nucleant will reduce the total energy of the system.

Data from the literature on the solid/solid interfacial energies of several planes of fcc,[34,35] bcc,[36] diamond cubic,[37] and tetragonal[38] $CuAl_2$ crystals are plotted in Fig. 3. Many more data of this type can be found in the literature and, although most are only for a few low index planes and different values are reported, the same trends are shown. The data in Fig. 3 are for solid/solid energy values, but the same behaviour has been reported for other types of energy. Heyraud and Métois[39] found that the increase of the solid/vapour energy with increasing area/atom for indium (tetragonal) was twice that for lead (fcc); Naidich *et al.*[40] found that in the wetting of germanium by its melt, the angle θ increases in the order (111), (110), (100).

From Fig. 3, it is evident that in fcc and bcc crystals the increase of energy with increasing area/atom is relatively small and probably the energy of a high index plane is not more than 25–30% higher than the energy of the lowest energy plane. On the other hand, in crystals of low symmetry, the energies of the high index planes may be as much as 100% higher than that of the lowest energy plane. The decided difference between high and low symmetry crystals is indicated also by the data of Miller and Chadwick[41] and Nelson *et al.*[42] It also corresponds with the fact that high symmetry crystals tend to have rounded dendrites, whereas low symmetry crystals exhibit faceted dendrites.



2 Values of solid/liquid interfacial energy (σ_{SL}) of various metals as function of their melting points (After Ref. 33)

Nucleation by low melting point phases

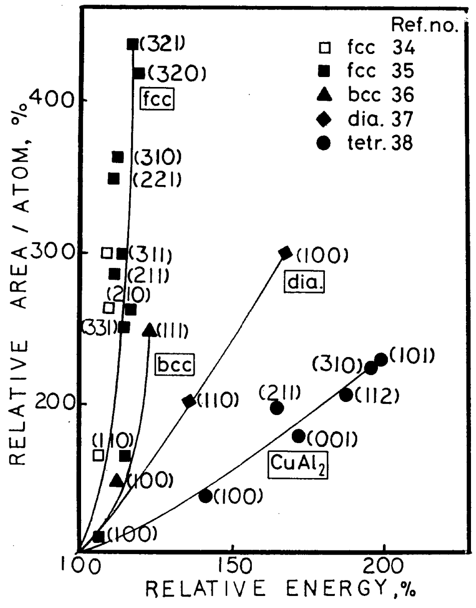
The more pronounced increase in energy with increase of area/atom of the low symmetry crystals can be used to explain how nucleation of one phase by another having a lower melting point can take place. Data[2,18] concerning the known cases in which a lower melting point phase nucleates a higher melting point phase are given in Table 1. In every example the nucleant has a less symmetrical lattice, so that its high index faces can have an energy higher than that in the high symmetry nucleus, in spite of the fact that the average energy of the nucleant is lower than that of the nucleus.

Calculations of the values of the energies involved in the nucleation of aluminium by $CuAl_2$ are a good example of this effect. If the average energies of aluminium and $CuAl_2$ are proportional to their melting points, the average energy

Table 1 Melting points and crystal structures of some phases that nucleate higher melting point phases[2,18] (detailed description of technique is given in Ref. 2)

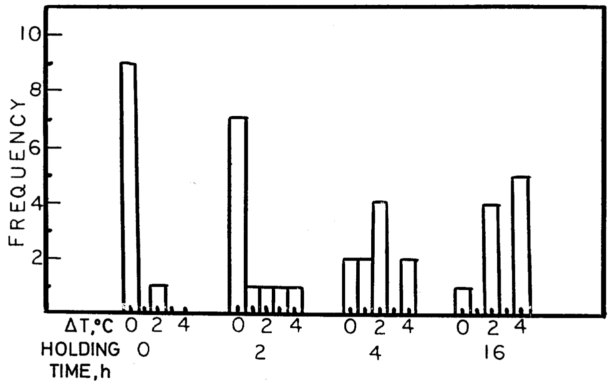
Nucleant	Melting point, °C	Crystal structure	Nucleus	Melting point, °C	Crystal structure
Bi	271	Rhomb.	Cd	321	hcp
Bi	271	Rhomb.	Zn	419	hcp
Bi	271	Rhomb.	Ag	960	fcc
Sn	232	Tetr.	Pb	327	fcc
Sn	232	Tetr.	Tl	303	hcp
Sn	232	Tetr.	Ag_3Sn	480	hcp
Ge	937	Dia.	Ag	960	fcc
Cd	321	hcp (c/a = 1·88)	Pb	327	fcc
$CuAl_2$	591	Tetr.	Al	661	fcc
$AuPb_2$	254	Tetr.	Pb	327	fcc
$AuSb_2$	460	Cub. Compl.	Au	1063	fcc
Pb_2Bi	184	hcp	Pb	327	fcc

Rhomb. = rhombohedral; tetr. = tetragonal; dia. = diamond; cub. compl. = complex cubic.



3 Interfacial energies of various planes in fcc, bcc, diamond (dia.), and $CuAl_2$ tetragonal (tetr.) crystals as function of area/atom (both energies and area/atom are plotted as percentages of values for lowest energy plane, i.e. (111) for fcc and dia., (110) for bcc and $CuAl_2$)

for $CuAl_2$ should be 80–90% of that of aluminium. However, the (112), (310), (101) planes of $CuAl_2$ have an energy some 80–90% higher than the lowest plane,[38] whereas the energy of the high index planes of aluminium does not exceed 25–30% of the value for the lowest plane. Taking a value of $\sigma_{SL} = 160\ \mathrm{mJ\ m^{-2}}$ for aluminium,[33] the average σ_{SL} for $CuAl_2$ should be in the range 130–140 mJ m^{-2}. This range is very close to the value that can be obtained from the work of Hamar *et al.*[43] who calculated a value of $\sigma_{SS} = 273\ \mathrm{mJ\ m^{-2}}$ for the (110) plane of $CuAl_2$. Assuming $\sigma_{SL} = \frac{1}{2}\sigma_{SS}$ and considering that the (110) face of $CuAl_2$ has the lowest energy, a value of $\sigma_{SL} = 140\ \mathrm{mJ\ m^{-2}}$ for the average energy of $CuAl_2$ is very conservative. On this basis, the energy of a high order plane of $CuAl_2$ should be in the range 245–260 mJ m^{-2}, whereas a high index plane of aluminium should not exceed 200 mJ m^{-2}. Thus, even allowing for a value of $\sigma_{NS} = 30\text{–}40\ \mathrm{mJ\ m^{-2}}$, the inequality $\sigma_{NL} > \sigma_{SL} + \sigma_{NS}$ is satisfied.



4 Undercooling for nucleation of primary phase in Al–1Mn alloy held at 1040°C for increasing times (replotted from data of Ref. 44)

From the orientation relationships for nucleation reported in the literature, matching of low index planes is usually indicated. However, it cannot necessarily be concluded that nucleation is on the low index plane given: a low index match may result from nucleation on a high index plane of the nucleant. For example, the orientation relationship for the nucleation of aluminium by $TiAl_3$ often found is $(001)_{TiAl_3}||(001)_{Al}$ $[100]_{TiAl_3}||[100]_{Al}$. In Table 2, 34 couples of planes of $TiAl_3$ and aluminium, with indices 5 or less, that fit that orientation relationship are presented. For some of these couples, the disregistry is too high to produce low values of σ_{NS} and other couples involve high index planes the appearance of which in crystals is improbable. However, there still remains a large number of couples, several with disregistry values lower than the (001)||(001) couple, and the $TiAl_3$ planes on them have greater probability of being the nucleation sites than the (001) plane. Thus, a fit between low index planes does not exclude nucleation on high index planes.

Experimental evidence

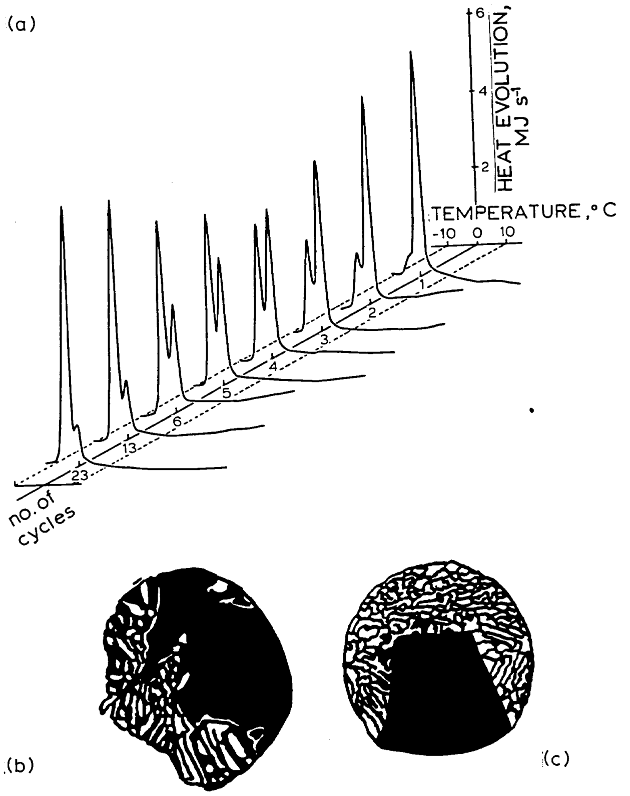
There are data in the literature that indicate nucleation preferentially on high index, high energy faces. In a study of the effect of superheating on aluminium alloys,[44] it was found that, as the time that a melt was held at high

Table 2 Matching planes of $TiAl_3$ and Al with (001)||(001) and [100]||[100] orientation

Matching planes $TiAl_3$ Al	Disregistry* δ, %	Area/atom of $TiAl_3$, nm²	Change of area,† %	Matching planes $TiAl_3$ Al	Disregistry* δ, %	Area/atom of $TiAl_3$, nm²	Change of area,† %
(001)||(001)	7·1	0·0741	+10·1	(111)||(221)	6·4	0·2451	+0·05
(100)||(100)	7·8	0·0828	+0·91	(121)||(241)	7·3	0·3750	−0·66
(110)||(110)	7·7	0·1169	−1·10	(113)||(334)	4·1	0·3228	−1·25
(210)||(210)	8·0	0·1852	−0·78	(115)||(445)	29·5	0·4382	+34·1
(310)||(310)	7·8	0·2616	−0·94	(223)||(233)	21·9	0·2303	+10·6
(320)||(320)	7·7	0·2984	−1·06	(223)||(321)	7·3	0·3075	−0·46
(410)||(410)	7·8	0·3412	−1·02	(312)||(311)	0·9	0·1362	−0·39
(430)||(430)	7·9	0·4136	−0·87	(322)||(321)	7·3	0·3075	−0·46
(510)||(510)	7·9	0·4220	−0·93	(332)||(331)	4·9	0·1713	+4·38
(520)||(520)	7·8	0·4452	−1·00	(325)||(322)	25·2	0·7025	−26·0
(530)||(530)	7·9	0·4826	−0·95	(334)||(553)	33·0	0·3100	−24·3
(540)||(540)	7·8	0·5300	−0·95	(335)||(443)	35·4	0·3800	+49·3
(201)||(401)	7·4	0·3392	−0·43	(412)||(411)	0·8	0·3489	−0·57
(203)||(203)	35·2	0·3938	−29·5	(512)||(511)	4·7	0·2063	+3·00
(103)||(304)	34·0	0·2773	+19·4	(514)||(512)	6·4	0·4500	−0·25
(302)||(301)	7·1	0·2591	+0·04	(522)||(521)	33·0	0·4517	+23·6
(304)||(530)	26·4	0·2950	−9·54	(532)||(531)	7·6	0·2440	−0·63

* The values of disregistry δ are given by $\left\{\left[\frac{a_{Ti}-a_{Al}}{\frac{1}{2}(a_{Ti}+a_{Al})}\right]^2+\left[\frac{b_{Ti}-b_{Al}}{\frac{1}{2}(b_{Ti}+b_{Al})}\right]^2\right\}^{1/2}$, where *a* and *b* are two dimensions of the plane lattice at 90° to each other.

† The sign + or − on the area changes corresponds to a shrinkage (−) or an expansion (+) in the transition from the $TiAl_3$ to the Al lattice.

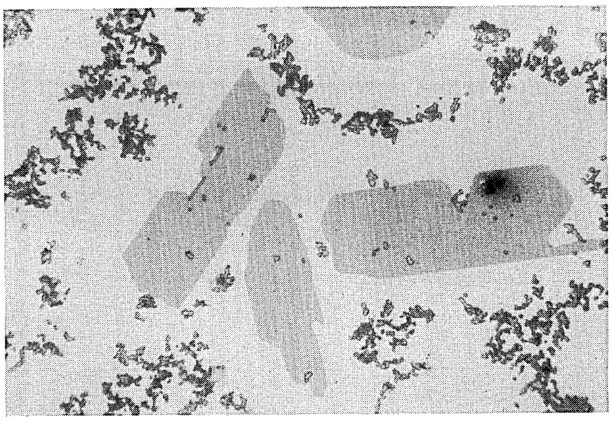


a cooling curves of droplets of bismuth rich Cd–Bi alloy repeatedly melted and frozen; *b* structure of droplet after first cycle; *c* structure of droplet after 23 cycles (*b, c* ×1000)

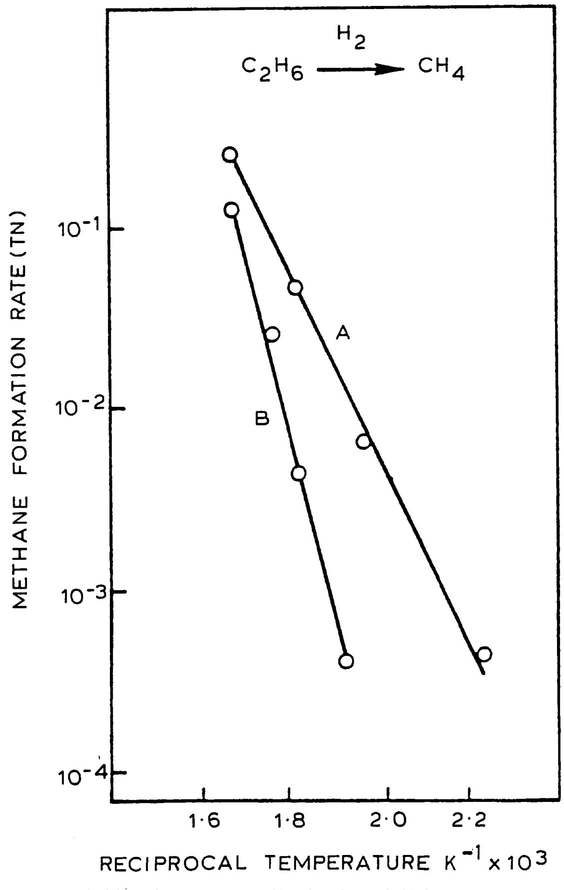
5 Cooling curves and structure of droplets of bismuth rich Cd–Bi alloy after melting and freezing: note shift of nucleation peak to lower temperature and faceting of bismuth primary crystals after cycling (Courtesy of Professor Perepezko)

temperature was increased, the undercooling for nucleation increased (Fig. 4), most probably because the high energy faces of the nucleant were replaced by lower energy faces. This phenomenon has been demonstrated very clearly in work performed by Osaka.[45] Working with droplets of a bismuth rich Cd–Bi alloy dispersed in an inert matrix he found that, as the droplets were melted and frozen repeatedly, nucleation, which at the beginning was at low undercooling (Fig. 5*a*) shifted to higher undercooling. The change of structure is the most obvious demonstration of the phenomenon: at the beginning of cycling, the primary crystal of bismuth that nucleated the eutectic was ragged (Fig. 5*b*), so that faces of high index were present, but after many cycles the primary crystal was well faceted (Fig. 5*c*) from which the presence of only low index, low energy planes can be inferred.

A similar effect is found in aluminium when grain refined by the addition of titanium and boron. The master alloys used for the refining are produced by reacting aluminium with boron and titanium halides. As prepared, they contain crystals of TiAl$_3$ and an aluminium rich boride (AlB$_2$ or (AlTi)B$_2$) in a matrix of aluminium. The TiAl$_3$ crystals produce the nucleation which causes the grain refinement through the peritectic reaction: Liq. + TiAl$_3$ → Al (solid solution). This reaction produces crystals having the structure of aluminium, above the freezing point of the melt. The TiAl$_3$ crystals tend to be well faceted and it has been reported[46] that of the thousands of TiAl$_3$ crystals in the melt, only a few actually act as nucleant. The nucleating crystals are probably those in which, through some accident, high energy faces are present; the majority of the crystals, delimited by low energy faces, remain inert. In equilibrium conditions, the structure of the grain refiner alloys should consist of TiB$_2$ (with only a small amount of aluminium in solution) and TiAl$_3$ in an aluminium matrix. Thus, there is a reaction by which the aluminium rich boride dissolves and its boron content reacts with the TiAl$_3$ to form a titanium rich boride.[47] This reaction requires that the TiAl$_3$ crystals dissolve, at least partially. As this dissolution takes place, high energy faces become uncovered and many more TiAl$_3$ crystals can act as nucleants. Hence, the enhanced grain refinement due to boron. In Fig. 6, from the work of



6 Al–Ti–B alloy after heating to 1000°C: note small boride crystals forming on and inside large TiAl$_3$ crystals and irregularly sided cavities in them, where high order planes become exposed (From Ref. 48, courtesy of Professor Bäckerud) ×580



A over (100)$_{Ni}$ face; B over (111)$_{Ni}$ face (TN is turnover no., i.e. product molecules/substrate surface atoms/second)

7 Methane production from ethane over nickel catalyst (Courtesy of Dr Goodman[50])

Kiusalaas,[48] some crystals of $TiAl_3$ undergoing the reaction are shown. Note the irregular sides of the cavities in the $TiAl_3$ crystals in which TiB_2 crystals are forming and in which high order planes are being revealed. Formation of TiB_2 crystals on $TiAl_3$ has also been reported by Guzowski *et al.*[49]

A similar effect has been found in catalysis. Goodman[50,51] has shown (*see* Fig. 7) that the catalytic efficiency of the (111) face of nickel is much larger than that of the (100) face, although the difference of energy between the two faces is only a few per cent.[36,52,53]

Conclusions

1. The balance of interfacial energies is a controlling factor in heterogeneous nucleation.

2. When nucleation takes place both the contact angle and the nucleant/nucleus interfacial energy are small, so that, as a first approximation, nucleation can be expected if $\sigma_{NL} > \sigma_{SL}$.

3. The interfacial energies involved are not the average energies of the crystals, i.e. those which are usually measured, but the energies of the actual face of the nucleant on which nucleation takes place and the face of the nucleus that matches it.

4. Nucleation takes place preferentially on high index, high energy faces, although these faces are unstable and tend to be replaced by lower energy faces.

5. Low symmetry crystals can nucleate higher symmetry crystals even if their average energy is lower, because, in low symmetry crystals, the energy of high energy faces is much higher than that of the more stable low energy faces.

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