JOURNAL OF CATALYSIS 27, 374-378 (1972)

Phase Stability of Alloy Catalyst Particles

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Received March 30, 1972

It is shown, in contradiction to a recently published analysis, that the effect of capillarity in stabilizing small alloy particles against phase separation is marginal. As an alternative, evidence is cited suggesting that small particle size may suppress the nucleation and growth mode of phase transformation. The maximum undercooling thereby obtainable is limited by the onset of spinodal decomposition. This mechanism leads to the prediction that the enhancement of phase stability by small particles should be largest in alloys where there is a significant difference in atomic size. Conceivably, single-phase alloy catalysts in fine particle form could be undercooled by more than 50%.

INTRODUCTION

The effect of small size in stabilizing binary alloy particles against phase separation was studied in a recent article by Ollis (*1*). The familiar concept that the surface to volume ratio increases with decreasing size served as a basis for analysis. In particular it was reported that "drastic" reductions in the critical temperature for phase separation should occur in particles as large as 200 Å in diameter. It was pointed out that an equilibrium effect of this magnitude would be of major importance with respect to alloy catalysis by enabling the investigation and utilization of single-phase materials over broad ranges of composition where the corresponding bulk phase is not stable.

The prediction of such a marked effect of particle size on phase stability is indeed a surprise and runs counter to the general trend for phenomena of this nature. Surface energies are usually so small relative to volume energies that capillarity effects only become significant at rather small sizes. For instance, the influence of size on the solubility of precipitates in a bulk phase, as given by the Thompson-Freundlich equation, is generally negligible above a diameter of 100 Å (*2*).

The purpose of this report is first to show that Ollis' findings are erroneous. The difficulty lies in an improper choice of energy for the internal phase boundary between the separating regions of unlike composition within a single particle. The correct analysis finds the particle size effect to be in line with other capillarity phenomena, and of marginal utility, if any, in stabilizing alloy catalysts. An alternative mechanism is proposed by means of which the stability of alloys could be significantly enhanced in fine particles.

CAPILLARITY EFFECT

The model system considered by Ollis is that of a spherical crystallite (radius r) containing atoms of two species whose behavior in the bulk is represented by a symmetric miscibility gap. Phase stability is tested by comparing the free energy for random mixing of solute throughout the crystallite with the free energy for segregation of solute into two randomly mixed regions of differing composition separated by a planar interface. While Ollis allows the overall composition of the crystallite to be arbitrary, the analysis is simplified and the point at issue clarified by limiting our attention to the equiatomic case with 50% of each component ($x = 0.5$). From the symmetry of the miscibility gap, we can then assume without loss of generality that the compositions of the unlike regions (after segregation of the solute) differ from 0.5 by equal magnitudes, one in the plus direction ($+\Delta x$) and the other in the minus ($-\Delta x$). The internal phase boundary bisects the particle and Eq. (5), given in Ref. (*1*) for the molar free energy change, becomes*

$$\Delta g = -\Omega(\Delta x)^2 + \frac{1}{2} RT[(1 + 2\Delta x) \ln(1 + 2\Delta x) + (1 - 2\Delta x) \ln(1 - 2\Delta x)] + \frac{3}{4}\frac{\sigma v}{r} \quad (1)$$

where Ω is the usual interaction parameter, R the gas constant, T the absolute temperature, v the molar volume and σ the excess free energy of the phase boundary per unit area. The critical temperature for phase separation in the crystallite (T_r) is found by setting Δg to zero and solving:

$$T_r = \frac{2\Omega(\Delta x)^2 - \dfrac{3v\sigma}{2r}}{R[(1 + 2\Delta x) \ln(1 + 2\Delta x) + (1 - 2\Delta x) \ln(1 - 2\Delta x)]}. \quad (2)$$

In the limit of large particles ($r \rightarrow \infty$) the interface term vanishes. The increment Δx becomes infinitesimally small near the center of a symmetric miscibility gap. Repeated application of L'hopital's rule yields

$$T_\infty = \frac{\Omega}{2R}, \quad (3)$$

the well known (*2*) regular solution approximation to the maximum critical temperature.

When r is small, the interface term becomes comparable in size to $2\Omega(\Delta x)^2$ and the critical temperature will be lowered. One has now to determine the magnitude of the excess surface free energy σ. The value of this quantity is strictly fixed by the model and is not a matter of choice, as assumed by Ollis (*1*). The interface separates the solute-rich region of the crystallite from the solute-poor region; the excess energy of the interface arises in this model only because the relative numbers of like and unlike atomic bonds across the interface differ from the corresponding numbers in either of the separated regions. Thus the excess free energy of the interface will be a sensitive function of the difference in composition ($2\Delta x$) between the solute-rich and solute-poor phases. The nature of this functionality has been considered by other workers (*3*) and the result, summarized in a recent review (*4*), has the form

$$\sigma = \Omega \frac{nz}{NZ} (2\Delta x)^2, \quad (4)$$

where n is the number of atoms per unit area in a plane parallel to the interface, and z is the number of nearest neighbor bonds per atom across the interface. The use of a constant surface tension σ independent of the compositions of the adjoining phases is inconsistent with the model, and is the cause of the unusual results cited in Ref. (*1*).

When Eq. (4) is substituted for σ in Eq. (3), $(\Delta x)^2$ appears in both terms of the numerator. Where the coefficient of $(\Delta x)^2$ was $(2\,\Omega)$ it now becomes $(2 - 3vnz/rNZ)\Omega$. Consequently one obtains for the critical temperature of a small particle:

$$T_r = \frac{(1 - 3vnz/2rNZ)\Omega}{2R}. \quad (5)$$

The fractional undercooling turns out to be:

$$\frac{T_\infty - T_r}{T_\infty} = \frac{3vnz}{2rNZ}. \quad (6)$$

For cubic crystals of lattice parameter a, with the internal interface parallel to a face of the unit cell, Table 1 lists values of (r/a) required to produce a 10% undercooling by this mechanism. As the lattice parameters of most disordered cubic metals

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* A factor of ($-R$), missing from Eqs. (5) and (12) of Ref. (*1*), does appear in that author's Eq. (2) and was presumably not neglected in the numerical computations.

TABLE 1
Crystal Radius for 10% Undercooling by Capillarity Effect

Crystal	Z	z	(nv/Na)	r/a
sc	6	1	1	2.50
bcc	8	4	1/2	3.75
fcc	12	4	1/2	2.50

and alloys lie below 4 Å, an effect of even this small magnitude should not occur in particles over 15 Å in linear dimension. Clearly the thermodynamic depression of the critical temperature to be expected in a 200 Å particle is negligible.

The difference between the present finding and that of Ref. (*1*) is illustrated more fully in Fig. 1. One sees that the results obtained using a constant surface tension [replotted from Fig. 5 of Ref. (*1*)] do not approach T_∞ in a very reasonable way. By comparison, Eq. (5) approaches T_∞ in a well-behaved manner as shown.

In support of his findings, Ollis cites the experimental results of other investigators. From the present considerations we conclude that any significant enhancement of phase stability observed in particles larger than 50 Å must arise from some cause other than capillarity.

Nucleation Effect

In the absence of a substantial capillarity effect one inquires whether there is any other basis by which particle size could influence phase separation behavior. The two mechanisms by which such phase separation can occur are nucleation and growth on the one hand and spinodal decomposition on the other. The existence and general nature of these competing mechanisms was first spelled out by Gibbs [see Ref. (*5*)]. The temperature–composition regime for spinodal decomposition is generally more restricted than for nucleation and growth. On cooling from high temperature, an alloy will usually enter a region where phase separation by nucleation can occur but the driving force is not yet sufficiently high for spinodal decomposition. Thus an effective lowering of the phase stability limit will result from any blockage or suppression of the nucleation mechanism.

An influence of small particle size on nucleation and growth has been observed in the study of other kinds of phase changes, for instance the formation of martensite in quenched steel (*6*). The effect of dividing an alloy into fine particles is to snuff out the growth stage in which the phase change spreads from a nucleation center into the

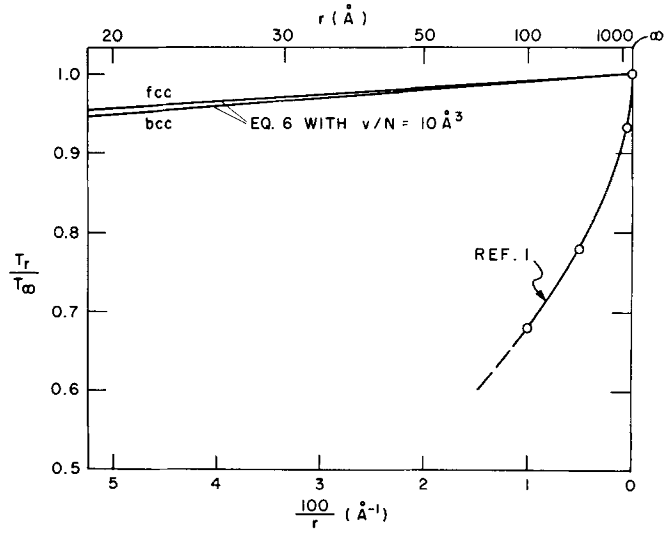

Fig. 1. Effect of size on the equilibrium critical temperature for phase separation in alloy particles, as predicted in Ref. (*1*) and by Eq. (6) of the present treatment on the basis of surface energy considerations.

surrounding material. Thus the phase change is restricted to those few particles in which nucleation happens to occur. Most of the material remains untransformed until the temperature passes below the limit for spinodal decomposition, whereupon the phase change occurs by another mechanism.

The maximum achievable undercooling depends on how far the spinodal temperature limit falls below the equilibrium phase boundary. This is, in turn, a function of the size difference between the component atoms. A certain minimum undercooling will be found when the atoms are of equal size, which is however zero in a 50–50 alloy. Using regular solution theory the depression of the "coherent spinodal" has been formulated (*7*) as a function of the lattice distortion coefficient η giving the rate of change $[(1/a)(da/dc)]$ in the crystal lattice parameter caused by the addition of solute:

$$\Delta T \cong 2v\eta^2 Ex(1 - x)/(1 - v)R.$$

Here E is Young's modulus and ν is the Poisson ratio. The influence of η on the phase boundary and spinodal boundary in an equiatomic alloy is plotted in Fig. 2 as computed by regular solution theory and also by the more accurate spherical model (*8*). One sees in this perspective that the elastic misfit of the atoms serves not so much to depress the spinodal boundary as to raise the equilibrium phase boundary by increasing the driving force for incoherent phase separation.

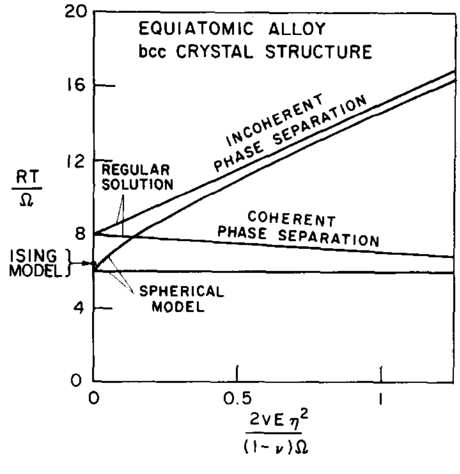

FIG. 2. Branching of critical temperature caused by mismatch in the atomic sizes of binary alloy constituents, as predicted by the regular solution approximation and by the more accurate spherical model.

While a more complete study of the computational models is presented elsewhere (*8*), one sees from Fig. 2 that the suppression of nucleation and growth in small particles could lead to undercoolings ($\Delta T/T$) of 50% or more.

CONCLUSIONS

We conclude that capillarity will contribute very little observable stability to alloy catalyst particles. Instead we propose an alternative effect based on suppression of the nucleation and growth mode of phase transformation. According to this proposal substantial undercooling effects are most likely to occur in alloys with large atomic misfit.

Many alloys systems that might be of interest as catalysts from an electronic standpoint do not follow a simple miscibility gap in their phase equilibrium behavior. Simple behavior of this kind is, of course, impossible when the pure components differ in crystal structure. Nevertheless, underlying the boundaries of the various equilibrium solid solutions that occur are corresponding spinodal boundaries. If phase separation by nucleation and growth is suppressed, then the spinodal mechanism will come into play. One should, in principle, be able to construct the spinodal phase diagram for any system of interest, finding much of the phase transformation behavior displaced to lower temperatures. This may be the diagram to be consulted with reference to the phase stability of small alloy particles. The largest depressions will be expected in those systems with large atomic misfit. If the particles are small enough, there may be a further depression of the spinodal boundary owing to the elimination of the long wave fluctuations.

ACKNOWLEDGMENT

The author expresses appreciation to Dr. N. A. Gjostein for bringing this matter to his attention, for valuable discussions, and for reviewing the manuscript.

REFERENCES

1. OLLIS, D. F., *J. Catal.* **28**, 131 (1971).
2. SWALIN, R. A., "Thermodynamics of Solids," p. 147. Wiley, New York, 1962.
3. SERVI, I. S., AND TURNBULL, D., *Acta Met.* **14**, 161 (1966).
4. RUSSELL, K. C., *in* "Phase Transformations," p. 229. Amer. Soc. Metals, Metals Park, OH, 1970.
5. CAHN, J. W., *Trans. AIME* **242**, 166 (1968).
6. MAGEE, C. L., *Met. Trans.* **2**, 2419 (1971).
7. HILLIARD, J. E., *in* "Phase Transformations," p. 61. Amer. Soc. Metals, Metals Park, OH, 1970.
8. HOFFMAN, D. W., unpublished data.