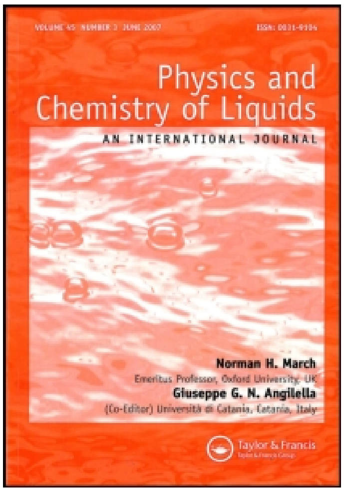

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Surface Segregation and Related Properties in Binary Liquid Transition Metal Alloys Containing Mn and Cr

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Letter

Surface Segregation and Related Properties in Binary Liquid Transition Metal Alloys Containing Mn and Cr

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In solid transition metals, the bulk modulus varies systematically with the filling of the d-band. Assuming this behaviour remains true just above the melting temperature, 21 binary liquid transition metal alloys with Mn as solute in dilute concentration are predicted to exhibit Mn surface segregation while the remaining 5 alloys may or may not. With Cr replacing Mn, the corresponding numbers are 9 and 17. Certain Cr rich alloys are also deemed worthy of further investigation.

Bhatia and the writer[1] have put forward a phenomenological theory of surface tension in liquid binary mixtures and have demonstrated that some of its major predictions are borne out in a variety of metallic alloys. Their theory relates the surface tension σ of the liquid mixture to bulk mixture properties and the "thickness" l of the liquid-vapor interface by

$$\frac{\sigma}{B} = l\left[1 + \frac{\delta^2\langle\Delta c^2\rangle}{\rho k_B T} B\right]^{-1} \tag{1}$$

where B is the bulk modulus of the alloy, ρ the number density, δ measures the size difference between the two component atoms while $\langle\Delta c^2\rangle$ describes the concentration fluctuations in the bulk alloy. In later work[2], the relation of the phenomenological theory[1] to the statistical mechanical theory of the surface of liquid mixtures based on low-order gradient expansions has been clarified.

The above liquid state studies have been complemented by a number of calculations of solid state surface segregation, recent contributions being those of Kumar *et al.*[3,4] who introduce short-range order parameters; these being closely related[5] to the concentration fluctuations in Eq. (1). The work of Lambin and Gaspard[6,7] treats solid alloys of transition metals by electronic structure theory, using a tight-binding approximation to the d-bands.

In the present work, attention is drawn specifically to the potential interest of an experimental study of surface segregation and some related properties in binary liquid transition metal alloys containing Mn and Cr.

It has been established for a long time[8] that the bulk moduli of the 3d, 4d and 5d transition series in the solid state exhibit a pronounced dependence on the filling of the d-band. In contrast to the 4d and 5d series, the 3d series shows a pronounced dip occurring at Mn. The formula (1), in the pure metal limit,[9–11] predicts a close correlation between σ and B and it therefore comes as no surprise that σ plotted against d-shell occupancy also shows a dip at Mn for the 3d series.[12]

Returning now to the alloy problem, Bhatia and the writer[1] emphasize that if a result from electron theory for the shift in the Fermi level in an alloy, with a valence difference between solute and solvent atoms, at small solute concentration c, is invoked, then a sufficient, though not a necessary, condition for surface segregation in very dilute binary alloys is

$$\left(\frac{dB}{dc}\right)_{c=0} < 0. \tag{2}$$

In the absence of evidence to the contrary, we shall now make the assumptions that (a) for pure transition metals, the bulk modulus variation with the filling of the d-shell retains the same characteristics just above the melting temperature as in the solid phase and (b) based on known specific examples, the sign of dB/dc can be predicted from the bulk moduli of the two pure metals involved. Then, given assumptions (a) and (b), the criterion (2) predicts that in binary liquid transition metal alloys with Mn as solute in dilute concentration c, Mn will segregate to the surface in 21 out of the theoretically possible 26 alloys. The remaining 5 are specifically Sc, Y, La, Tc and Re, and because condition (2) is sufficient but not necessary, surface segregation of Mn may or may not occur in these cases.

While, according to the criterion (2), 9 dilute Cr-liquid transition metal alloys should show Cr segregation to the surface, and the remaining 17: Sc, Y, La, Ti, Zr, Hf, Nb, V, Mo, W, Mn, Fe, Pd, Ni, Cu, Ag and Au may or may not, there is, we suggest, also interest here in the Cr rich transition metal alloys. The reason for also studying this latter regime for Cr is that in solid alloys like $Cr_{1-c}Co_c$ and $Cr_{1-c}Fe_c$, in the range $0 < c < 0.05$ say, rather dramatic changes in B with temperature can take place[13,14] for a given alloy, because of the existence of a magnetic transition temperature. In the most extreme case of those yet studied, namely CrFe with 3.8 at % Fe, the bulk modulus is decreased at the Néel temperature T_N to about 6% of its value well away from T_N. This "dip" in B is known to correlate with the anomaly in the magnetic contribution to the specific heat[13] at T_N. In addition to proposed liquid studies, it would be of considerable interest if the surface segregation properties of the above Cr rich alloys with Fe and also Co could be studied around the Néel temperature.

To summarize, it is proposed that a useful test of current theories of surface segregation in binary liquid mixtures should be afforded by studying systematically binary liquid transition metal alloys with dilute concentrations of Mn solute. We predict surface segregation of Mn in 21 out of the 26 alloys with 3d, 4d and 5d transition metals as solvents. The remaining 5 cases, which were listed specifically above, may or may not exhibit Mn surface segregation. Turning finally to Cr in place of Mn, the corresponding numbers are 9 alloys predicted to show Cr segregation to the surface, while 17 may or may not. For Cr, it should also be worthwhile to combine the above liquid studies with further solid state measurements on Cr rich alloys; specifically, near the Néel temperature of $Cr_{1-c}Fe_c$, with $c = 3.8$ at %. Here, a dramatic decrease of B is known to occur. Will this dip be reflected in marked changes in surface energy and surface segregation, though the latter study might well involve the complication of ternary alloy behaviour also. Will the vacancy formation energy, and therefore probably atomic diffusion, be appreciably affected in the vicinity of the magnetic phase transition in $Cr_{1-c}Fe_c$: $c = 3.8$ at %, since, at least under normal circumstances, vacancy energy correlates with elastic properties.[15,16]?

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