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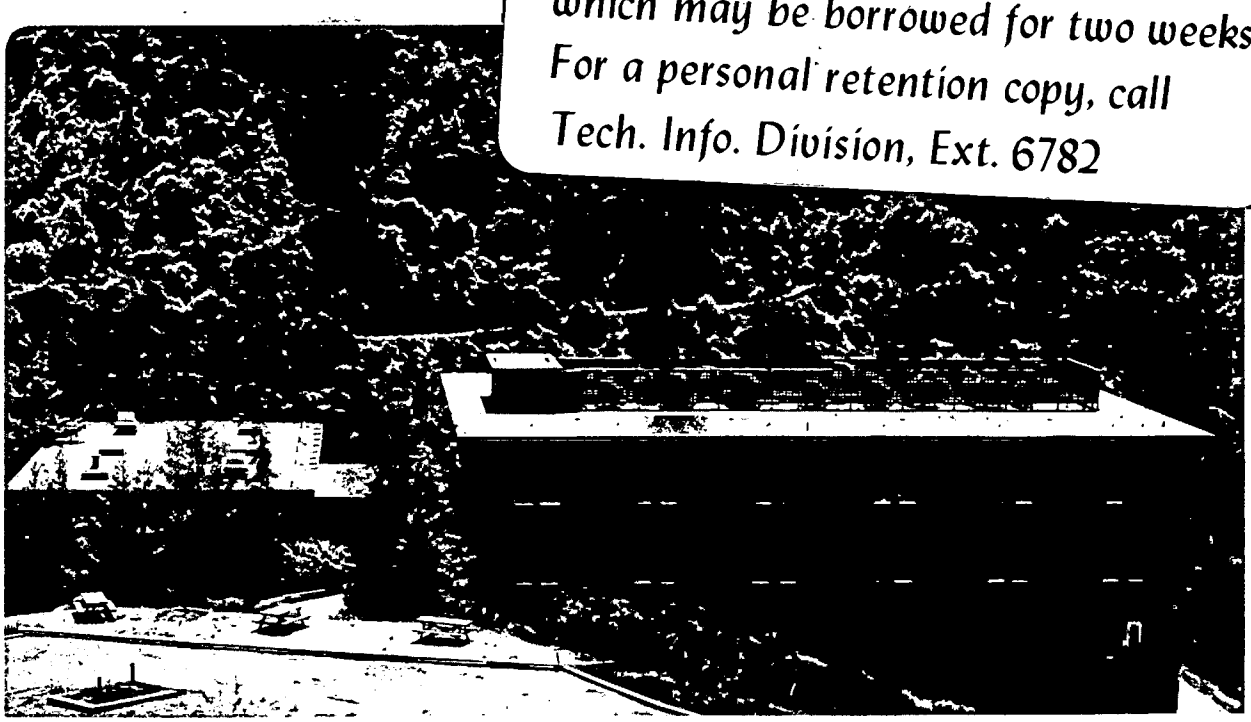

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Morphologies of Uniform, Adherent Scales on Binary Alloys

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Abstract The various scale morphologies arising from the oxidation and sulphidation of binary alloys are summarised. The relationships between simple, single phase morphologies and more complex, multi-phase, multi-layer cases are arranged diagrammatically by defining qualitatively the restrictions on the thermodynamic stabilities and transport properties of the oxidation products which result in increasing scale complexity. Factors which can cause the formation of non-uniform scales are considered briefly. Oxide and sulphide scales on binary alloys of Fe, Co, Ni, Cu, Mn, Cr and Al are discussed semi-quantitatively in an attempt to identify the important properties which cause changes in oxidation rates and morphologies.

Key Words: Oxidation, sulphidation, scale morphology.

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INTRODUCTION

The scale morphologies obtained by oxidizing or sulphidizing alloys were arranged schematically by Moreau and Benard[1] and their summary was subsequently adapted by Wood in his discussion of the high temperature oxidation behaviour of alloys[2]. More recent experimental work, especially on the sulphidation of alloys, has shown that scale morphologies can develop which are more complex than those considered by these authors and the present paper outlines the extension of the earlier scheme to include a more varied and comprehensive range of alloy behaviour. At the same time it is shown how the various morphologies can be related to one another, by considering the elemental distributions in the scales. The approach to scale morphologies presented here is complementary to that of Dalvi and Coates[3] in which diffusion paths corresponding to different morphologies are superimposed on the relevant ternary phase diagram.

It is noted that initially the discussion is limited to those cases in which the imposed oxidation conditions, controlling scale growth, remain fixed and that growth is essentially unidirectional and uniform. Factors which can lead to non-uniform growth are only considered briefly in the concluding section.

SCALE MORPHOLOGIES

Pure Metals

1. The simplest of all scales is the single, uniform layer of a compound B(X) on metal B, where X is the oxidant. A variety of examples can be given including oxides (Ni, Cr and under specific conditions Cu, Fe, Co), sulphides (Fe, Cu) and halides (Cu, Cd, Mg) and the growth rates and mechanisms have received extensive theoretical treatments, originating with the classical work of Wagner[4].

2. In a number of cases reference to the phase diagram B-X shows that more than one binary compound is stable at a given temperature and oxidant concentration.

Since, in principle, each of these phases can occur in the scale, it is implicit that a number of separate layers can form, each layer consisting of one of the compounds $B(X)_1 \ldots B(X)_n$. This morphology corresponds to an isothermal section across the phase diagram, superimposed on a gradient in the oxidant activity equivalent to the change in activity between the metal-scale interface and oxidizing atmosphere.

Examples of two layer scales are found on Fe under certain oxidation conditions while both oxide and sulphide scales on Co can also consist of two layer phases. Three layer scales are observed during the oxidation of Fe and the sulphidation of Ni and it appears possible, from an examination of relevant phase diagrams, that more layers could be anticipated on some metals (e.g. Co-S, Ni-S), although such scales have not been reported.

Once again the formation of these scales has received considerable theoretical attention, a general treatment being given by Shatynski et al[5]. Other relevant treatments were originally developed to interpret the formation of compounds during the interdiffusion of pure metals and a relationship has been derived for this case which defines conditions for the non-appearance of apparently stable compounds in the phase layers[6].

Binary Alloys - Single Phase Scales

A systematic arrangement of the scale morphologies which can be produced by the reaction between a binary alloy and a simple oxidant is given in Fig. 1. The alloys referred to are not necessarily single phase but it is obviously more probable that multiphase alloys will tend to form the more complex scales since each phase may oxidize independently to produce different products at different rates. Nevertheless it is still possible for a multiphase alloy to form a simple scale if both alloy components are oxidizable and there is only one possible oxidation product (e.g. Ag-Cu-S[7]).

1.* Probably the simplest scale which can be formed on a binary alloy A-B, where B is the base (i.e. thermodynamically more oxidizable or less noble) metal, is that produced when the noble metal, A, is thermodynamically inert and a B(X) scale is formed, as in the oxidation of pure B. In principle, multilayer scales consisting of compounds $B(X)_1 \ldots B(X)_n$ could be formed, as described above for pure B, but examples of this have not been recorded. The fundamental difference between the B(X) scale on a binary alloy and that on pure B metal is that scale formation in the former case must be associated with an enrichment of A in the underlying alloy. Scale growth can then be determined by the supply of B to the alloy-scale interface, as discussed theoretically by Wagner for the oxidation of Pt-Ni alloys[8]. Other examples are found in the sulphidation of Co-Cr alloys at low sulphur partial pressures (Table I) and Ni-Cr alloys at temperatures above ~1170K[9] when Cr is the base metal in both cases, Co and Ni remaining inert because their sulphides are unstable under the imposed conditions.

2. A particular case of the above type of oxidation occurs when the noble metal is completely inert and the alloy is relatively rich in B, the noble metal being incorporated into the scale as individual particles. The conditions leading to this morphology are those corresponding to the transition from a planar to an uneven alloy-scale interface, a situation which has been examined by Wagner[10], subject to certain approximations, and less restrictively by Whittle et al[11]. The general problem of interface stability has also received considerable attention in other studies of materials behaviour, including intermediate phase formation during intermetallic diffusion and solidification phenomenon[12]. However, the criteria deduced for the breakdown of interface stability are necessarily complex, in spite of their approximate nature. Systems studied in which interface stability is a relevant factor include the original treatment of Wagner, as referred to the sulphidation of Ag-Au alloys[10] (although this may be complicated further by the

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* Paragraph numbers in this and subsequent sections on binary alloys correspond to numbered items in Fig. 1.

miscibility of the sulphides, neither metal being totally inert) and, more recently, the sulphidation of Ni-Cr alloys[9].

3. When both components of the alloy are oxidized they both appear in the scale, where their relative proportions are determined by the oxidation potentials of A and B and their diffusion rates in the alloy and scale. In this case the simplest morphology is obtained when the oxidation products of A and B are completely miscible, producing a solid solution scale A(X) - B(X). A general treatment of scale growth for these conditions has been provided by Wagner[13] who pointed out that, unless the diffusivities of A and B cations are equal, their concentration will vary across the scale, the distribution of A and B depending on their relative diffusivities. The effect of these factors on the concentration and distribution of B in the scale has been examined by the present authors using Wagner's equations and quantitative calculations of growth rates have been made for Ni-Co and Fe-Mn alloys[14]. Similar scales are formed during the sulphidation of Fe-Ni and Fe-Co alloys and the oxidation of the same alloys when they contain low concentrations ($\lesssim$10 wt.%) Fe (Table I). The scales on some ternary oxidation resistant alloys containing both Cr and Al also fall into this group, since the scale formed is essentially the solid solution Cr_2O_3-Al_2O_3. However, the combination of the thermodynamic and the bulk and local transport properties of these oxides and the thinness of the scales formed makes it improbable that smooth concentration profiles can currently be detected within them.

A number of limiting cases of this type of scale are considered separately below, where it is also demonstrated that under certain conditions such scales could give rise to a layered morphology.

4. Even if A(X) and B(X) are miscible, virtually pure A(X) and B(X) scales can form on A-rich or B-rich alloys respectively, the essential purity of the scales depending on the relative oxidation potentials of A and B and the dilution of the

minor component in the A-B alloy. In the more restricted case, when the mutual solubility of the compounds is limited, the cation diffusion rates in the scale must be sufficient to prevent the solubility limit of the minor component in the scale being reached; otherwise precipitation of a second phase will occur. Concentration distributions similar to those occurring in case (3) above are to be expected, the theoretical treatment being identical, but the dilution of the minor component is often so low that such distributions are difficult to detect. Clearly examples can be drawn from very dilute alloys of the systems mentioned in case (3) and, in addition, Cr-doped oxide scales on Fe-Cr, Ni-Cr and Co-Cr alloys very dilute in Cr, when the solubility limit of Cr in the relevant cubic oxide (FeO,NiO or CoO) is not reached, and the essentially pure Cr_2O_3 or Al_2O_3 scales on Fe- Co- and Ni-base alloys which contain small amounts of the relevant, more noble, metal .

5. A type of scale intermediate between those described in cases (3) and (4) is obtained when A(X) and B(X) are only partially miscible and, although concentration variations occur, they are insufficient to cause supersaturation of one of the components.

Strictly speaking, the distinction between case (3)-(5) is an artificial one, depending only on the relative amounts of A and B in the scale and the recognition of limited miscibility in (4) and (5). However, it is a convenient arrangement since it relates the alternative morphologies produced when the limit is exceeded to a common simpler example. Typical scales are produced during the oxidation of Co-Fe and Ni-Fe alloys (Table I).

A particularly interesting case arises for scales composed of, or containing, ternary compounds, such as those with the spinel type formula $(AB)_3X_4$ where A, B = Fe, Co, Ni, Al, Cr, Ti, etc. and X = S or O. In some cases these compounds exhibit

negligible deviations from stoichiometry, e.g. $NiCr_2O_4$, and consequently they cannot tolerate a concentration gradient within them, although one might be expected to develop due to differences between the diffusion rates of the two cations. Hence their formation as single, continuous layers, with appreciable width in the predominant diffusion direction, is not expected since any concentration variation is inconsistent with their stability. In other compounds the range of stoichiometry is sometimes considerable, e.g. $Fe_{2-n}Cr_nO_4 (o \leq n \leq 2)$ and concentration distributions could be produced, providing that the alloy composition was consistent with the continued stability of the phase.

6. Finally, mention should be made of the special case where a complex dependence of the cation diffusivities on the oxidant activity can cause a maximum in the concentration profile in the central region of the scale, as revealed by studies of Fe-Co alloy oxidation[16]. As in preceding cases, if miscibility in the A(X)-B(X) system is restricted, this type of distribution could result in a layered scale with, say, a B-rich phase sandwiched between A-rich layers at low and high oxidant activities. This possibility will be re-examined when multilayer scales are discussed.

Binary Alloys - Multiphase Scales

7. In the preceding section some specific morphologies have been described which all exhibit the common factor of complete miscibility between the products of oxidation. However, when there is only partial miscibility of A(X) and B(X) and the alloy composition and/or the cation diffusivities are such that the solid solubility limit is reached in some part of the scale, precipitation of a second phase occurs, e.g. Ni- and Co-rich alloys with Cr and Ni-Fe alloys (Table I). The scales can then apparently consist of two layers, although they are in fact the same matrix solid solution throughout, with two regions, one containing precipitates and the other precipitate-free. However, the apparent layered effect may be enhanced by a change in the matrix grain structure coincident with precipitation front.

The nature and distribution of the second phase are difficult to define from first principles although clearly the compound precipitated must be consistent with the relevant phase equilibria in the A-B-X system. In each case the compound available for the relief of supersaturation by precipitation must be in equilibrium with the (A,B)X matrix and this must, in turn, be in equilibrium with the alloy at the alloy-scale interface. This does not necessarily require that the precipitate and alloy are also in equilibrium, because potential precipitation sites may only occur at positions remote from the alloy-scale interface.

The problem of precipitate distribution is not amenable to interpretation in terms of general principles at present. The equivalent but more easily controlled case which arises in the interdiffusion of ternary metal solid solutions has received considerable experimental attention and, while results have not been completely conclusive, some general rules have emerged for defining the conditions causing the instability of planar interfaces and the appearance of alternative morphologies[17]. In the case of spinel precipitation in scales on Fe-, Co- and Ni-base alloys with Cr, the mode of precipitation appears to be related to the composition ranges over which the spinel phases are stable. These ranges possible determine the spatial limits to which an isolated particle can grow into the depleted zone around the initial precipitate nucleus. Thus, the stability range for $NiCr_2O_4$ is very narrow and this, together with the effect of the difference between the diffusivities of Ni and Cr mentioned in (5) above, results in a particulate dispersion being maintained. In contrast, the range for $FeFe_nCr_{2-n}O_4$ is very wide ($o \leq n \leq 2$), the growth of nuclei in any direction is not strongly dependent on the availability of Fe and Cr in particular stoichiometric proportions and a continuous spinel layer can be formed. The Co-Cr spinel occupies an intermediate position since it exists over a range of compositions from $CoCr_2O_4$ to $Co_{1.3}Cr_{1.8}O_4$ and can form extended precipitates which sometimes approximate to a continuous layer. There are insufficient data available at present to determine if these observations have any wider significance for other alloy systems.

Although precipitate morphology is not predictable, the region in which precipitation occurs in the scale can be determined from a knowledge of the relative cation diffusion rates in the scale. Particular examples of the alternative precipitate locations possible are provided by Ni-Cr and Ni-Fe alloys. In the Ni-Cr case, Cr diffuses slower than Ni in the NiO scale and thus Cr segregates in the inner region of the scale where spinel is precipitated. Conversely in the oxide scale on Ni-Fe alloys, Fe diffuses faster than Ni causing Fe segregation and spinel precipitation in the outer part of the NiO scale[18]. The latter example also emphasizes the importance of defining the relevant solubility limits in terms of both cation concentrations and oxidant activity since $NiFe_2O_4$ precipitation does not extend to the outermost parts of the scale, where this activity reaches a maximum. This observation would be consistent with a boundary between the (Ni,Fe)O and (Ni,Fe)O+$NiFe_2O_4$ phase fields which is strongly dependent on the oxygen activity as well as the Fe concentration. Alternatively, the solid solution scale described in case (6), where a maximum occurs in the concentration profile, might produce the same precipitate distribution if a solubility limit was reached. However, the cation profile indicates that this is not the case in the scales on the Ni-Fe alloys mentioned above.

8. A limiting example of the above morphology occurs when the precipitates are distributed evenly throughout the scale. This requires that the cation distribution reaches the solubility limit everywhere in the scale, although this limit and the precipitate composition may vary also, depending on the nature of the equilibrium relationships in the A-B-X system. Alternatively, a change in the scale composition might change the equilibrium from that between the matrix and a precipitate rich in B, say, to that of equilibrium with one richer in X. A further possibility occurs when the composition of each of the precipitating phases is variable. There are obviously a comparable set of morphologies when B diffuses faster than A in the scale matrix, rather than A faster than B, as considered here. The important point is that the conditions imposed by ternary phase equilibrium

could result in various alternatives to the simplest case where a phase of fixed composition is precipitated in a matrix in which A and B concentration gradients are essentially absent. Even this latter case is uncommon in single layer scales, occurring more often in multilayer scales, as discussed below, probably because there is only a relatively narrow range of conditions where general precipitation throughout the scale does not lead to the formation of a continuous layer. Thus, unless the cation diffusivities in the matrix are exactly equal there must be some segregation at the phase boundaries and consequently the maximum precipitation rate will occur at one of them, with a tendency for the precipitates to coalesce into a continuous layer.

9. True double layer scales are formed when the layers are different phases which are only partially miscible. This case is distinguished from the morphology in (7) above where the term 'double layer' is often applied but where the matrix is the same throughout the scale and only the degree of precipitation varies. Examples of this simple morphology occur in sulphide scales on some Ni-Co, Fe-Cr and Co-Cr alloys (Table I) but in other cases it is complicated by precipitation within the layers, as discussed later. Two necessary conditions must be satisfied if either morphology is to be stable:

i) The layer forming next to the alloy, say B(X), must be stable there and not subject to conversion to A(X) by the exchange reaction:

$$B(X) + A = A(X) + B \qquad \Delta G^0_{ex}$$

The sign of ΔG^0_{ex} thus defines the stable phase next to the alloy, although the possibility of extensive depletion of the baser metal, as shown schematically in Fig. 1, may influence the situation, permitting the formation of a phase adjacent to the alloy which is apparent thermodynamically unstable with respect to the bulk alloy composition. This appears to be the case for sulphide scales on Co-Ni and Cu-Ni alloys (Table I), although there remain certain factors associated with the relevant exchange reactions which cannot be explained satisfactorily at present.

ii) In the morphology shown in Fig. 1 it must be possible for A to diffuse through B(X) at a faster rate than the host cation B in order that A(X) can continue to grow as an outer layer. This requirement is obviously aided by the segregation of A towards the outer interface of B(X) in the example illustrated but it must also apply when the concentration of A in B(X) is very low, as noted in a later section. Some double layer scales, particularly those of oxides, do not appear to obey this requirement but in such cases the outer layer is probably formed in the transient, scale-nucleation, stage and it does not continue to grow measurably thereafter.

10. In those cases where the binary A-X and B-X systems contain more than one intermediate compound there is a possibility that some or all of these phases can each form separate layers in the scale, subject only to their continued stability in a layered morphology and the need for the relative rates of cation diffusion in adjacent phases to be consistent with continued growth. Examples are found in sulphide scales on various Cu-Ni, Ni-Cr and Co-Ni alloys (Table I).

Although the initial scale formed may contain a number of phases occurring as discrete layers, this morphology need not include all the phases which could form between the alloy components and the oxidant. It is possible that the phases present originally may react subsequently to produce an intermediate compound, where they meet at a common interface, forming an additional layer as the oxidation reaction proceeds. In principle, the belated formation of such a layer is more probable when the original layered morphology results from the overgrowth mechanism described in case (14) below. There, two oxidation products of the alloy components are formed in reactions which proceed essentially independently of each other and the phases are not necessarily stable when they are in contact. However, once the layered morphology develops it may be impossible for growth of the outer layer to continue and it then becomes possible for the phases to interact, providing that the rates of interdiffusion between the phases are sufficiently large. Alternatively,

if diffusion rates are not fast enough a thermodynamically unstable morphology may be maintained because of kinetic restrictions. The spinels are perhaps the most important class of intermediate compounds which can be formed and Armijo has dealt with this general case[19], as well as considering the specific example of spinel formation between NiO and Cr_2O_3[20].

In contrast, if the layered morphology arises from the coordinated growth of super-imposed phases, as discussed in (9) above, the presence or absence of phases is presumed to be controlled by the balance of ionic fluxes in adjacent layers. The differences between these fluxes are expected to remain constant as the layered scale grows and it is not clear why an intermediate phase should form as an additional layer at some later stage of the oxidation process when there is neither an obvious change in the rate controlling process nor a significant change in the ionic fluxes which might be thought necessary to promote the nucleation of another phase. Nevertheless, at least one apparent example of this type of behaviour has been recorded for sulphide scales on Ni-Cr alloys[9], where the scale formed initially consists of two layers only, Cr_2S_3 and Ni_3S_2, but subsequently a spinel, $NiCrS_4$, grows at the orginal place on contact, until the Cr_2S_3 finally disappears. However, it is perhaps pertinent to enquire whether the initiation of an intermediate layer is associated with some disturbance in the original scale growth conditions in such cases, possibly due to alloy-scale separation. This could effectively isolate the scale from the alloy and promote the interdiffusion of the phases, in order to re-establish a different equilibrium configuration in the scale, consistent with the changed supply of cations.

11. The possibility of a further layered morphology has already been referred to in (6) where a phase rich in B, say, could be sandwiched between two layers, both consisting of the same phase, relatively richer in A, but containing different concentrations of A and also at different activities of X. The case is thus a peculiar hybrid of (9) and (10) since the scale only contains two phases but each

phase can exist in a number of separate layers, the phases alternating with one another through the scale. The formation of such a scale would require an unusual combination of the effect of oxygen activity on the cation diffusivities, as in Fe-Co, and the form of the phase equilibria between A(X) and B(X), particularly its dependence on oxygen activity. Nevertheless, it seems possible that such scales could form and an example might be provided by stratified oxide scales on some Fe-Cr[21] and Co-Mn[22] alloys.

12. Precipitation in double layer scales is governed by the same considerations as those applicable to single layers. A common morphology, examples of which occur in sulphide scales on some Ni-Cr and Ni-Cu alloys (Table I), consists of precipitates in the inner layer only. This is comparable to the simpler double layer scale, except that the balance of fluxes in the alloy and A(X) phases adjoining the B(X) phase are such that, when combined with a relatively low solubility of A in B(X), the flux of A through the inner B(X) layer is insufficient to maintain the concentration of A in B(X) below the solubility limit. Clearly it is possible that the alternative concentration distributions described for a single layer scale could also be found in multi-layer scales.

Precipitation of B(X) in the outer A(X) layer is not general observed, probably because the diffusion rate of B in A(X) in the relevant cases is slow. Thus any penetration of B ahead of the B(X)/A(X) interface is insufficient to develop a supersaturation which could lead to the independent nucleation of B(X). Nevertheless there is no obvious restriction which always prohibits such precipitation. Under favourable conditions, precipitation in both phases could probably occur, possibly in cases analogous to that of precipitation in a central band in oxide scales on Fe-Ni alloys[18], which appears to be determined by an unusual dependence of the solubility limit on the oxidant activity.

The precipitating phase need not necessarily be restricted to the terminal

phases A(X) and B(X) but could be a ternary compound, depending on the equilibrium relationships in the relevant A-B-X system.

13. At the opposite extreme to the case of completely miscible oxidation products a system can be considered in which the compounds formed during oxidation are completely immiscible. A layered morphology in which each layer continues to grow is then clearly impossible and the simplest alternative is that where only the baser metal oxidizes, as in (1). A more probable alternative arises when both metals oxidize and the scale consists of a mixture of the two immiscible phases growing cooperatively, both phases maintaining a continuous link between the alloy and gas interfaces. Such scales arise during reactions with complex oxidants[23] when the exact conditions governing the scale morphology can be determined by the nature of the oxidizing atmosphere.

14. When the initial growth rates of the oxidation products differ considerably the 'overgrowth' mechanism described by Wagner[24] may be operative. In this case a layered scale can be formed if the phases A(X) and B(X) are nucleated simultaneously but the faster growing phase envelops the slower growing phase and finally forms an outer layer. However, unlike the other layered morphologies described earlier, the outer layer ceases to grow once it is isolated from the alloy, following linking up of the slower growing oxide. Oxide scales on some Cu-Ni alloys (Table I) appear to arise by this mechanism and it is thought that the appearance of a layer of cubic oxide (FeO, CoO, NiO) outside Cr_2O_3 scales on the appropriate binary alloys (Table I) can be explained in the same way. The latter case provides an example of systems where the oxides formed initially from the component metals can interact subsequently to give ternary compounds, i.e. spinels in this case. Further examples are provided by oxide scales on a variety of Cu-base alloys containing Be, Al and Si[25]. The development of such morphologies, prior to the appearance of more uniform scales associated with steady scale growth kinetics, has been examined in detail by Chattopadhyay and Wood[25].

15. If the overgrowth mechanism proceeds without undercutting ultimately occurring the base metal oxide is formed as before but remains as isolated precipitates in the faster growing noble metal oxide matrix. Although the resulting scale may superficially resemble that described in case (7) its origins differ since it is not associated with a concentration profile of the base metal in the noble metal oxide. Such a morphology can only form on alloys relatively rich in the noble metal, otherwise sufficient base metal oxidizes and undercuts the A(X) phase.

As in case (14) it is possible that the precipitate and oxide matrix could eventually interact to produce an intermediate phase.

Binary Alloys - Internal Oxidation

16. When the partial pressure of the oxidant is suitably low, the diffusion of oxidant into alloys which are dilute in the base metal B produces internal precipitation in scales discussed in (7), it is not possible to define the precipitate morphology from first principles, although the case of precipitation at grain boundaries, which can act as preferential paths for the transport of the oxidant, is one exceptional example for which sites could be defined in the alloy. An approximate analysis of the transition between internal precipitation and surface scale formation has been developed by Wagner[27] and extended by Smeltzer and Whittle[28].

17. Alloys containing higher concentrations of the base metal than those referred to in the preceding case can form a surface scale in addition to internal precipitates. The simplest case occurs when the scale and precipitate are the same phase and the precipitate is absorbed by the scale as the alloy-scale interface recedes. Wagner[27] has examined this case theoretically and defined the conditions for which it is likely to occur, with particular reference to Cu-Pt and Cu-Pd alloys.

18. If the base metal is a relatively minor component in the alloy the surface

scale and the internal precipitate may be composed of different phases which are immiscible. The precipitate is then enclosed by the scale as the alloy-scale interface recedes and the precipitation pattern can be reproduced in the scale. When the base metal is present in greater proportions it is more probable that the morphology described in (17) will be produced.

19. In some cases the internal precipitate may be unstable when in contact with the surface scale (which can contain AO if the oxygen potential is high enough) and the equilibrium relationships in the A-B-X system require that the precipitates in the alloy and scale are different phases. An example is provided in the oxidation of dilute Ni-Cr alloys, where Cr_2O_3 is precipitated in the alloy but $NiCr_2O_4$ is stable in the surface NiO scale, essentially retaining the morphological distribution of the Cr_2O_3 as produced in the alloy. The phase transformation in the precipitates at the alloy-scale interface is obviously dependent on a limited amount of diffusion of the participating cations being possible; otherwise there will be a kinetic restriction on thermodynamic equilibrium being achieved. In other cases a limited amount of diffusion could lead to the appearance of a metastable, duplex precipitate consisting of an outer shell of the transformation product with an inner core of the phase originally present in the alloy still preserved in the untransformed state, giving a morphology analogous to those observed in classical peritectic reactions.

20. It is also possible, in systems where the stable compound of B and X is strongly dependent on the local oxidant concentration in the alloy, that the phase precipitated internally can change at critical depths within the alloy, as observed during the oxidation of Co-Ti alloys[29]. In these alloys $CoTiO_3$ occurs immediately below the alloy surface, where the oxygen activity is highest, while TiO_2, with some TiO, precipitates further into the alloy where lower oxygen activities prevail.
The reaction and transformation rates of the internal phases as the scale encroaches on the substrate depend on various factors.

Clearly internal precipitation is not restricted to cases where the surface scale consists only of a single layer and the morphologies described in this section could also be found in association with multilayer scales, possibly containing other phases precipitated within them.

SOME FACTORS INTERRUPTING THE FORMATION OF UNIFORM SCALES

The arrangement presented in Fig. 1 and discussed in preceding sections attempts to show how the simpler scale morphologies can be related to more complex ones by the imposition of different limiting conditions on the transport and equilibrium properties of the phases involved. However, such scales are only likely to continue growing if they remain coherent and if fixed boundary conditions prevail, i.e. by maintaining contact with the same alloy phase(s) and the same oxidizing atmosphere throughout the period of scale growth. When these conditions are not met more complex morphologies can develop and some of the possible alternatives are summarized below.

(a) In compiling Fig. 1 emphasis was given to those cases where a common oxidation product is formed over the entire surface of the alloy. Nevertheless, in principle, it is possible that for a multicomponent, multiphase alloy each element or compound could react independently to give different oxidation products, as in the simple example of the overgrowth mechanism described earlier. In such cases the oxidation behaviour could be considered as an approximation, as a number of different, localized reactions occurring on adjoining regions across the alloy surface. However, each region will interact with its neighbours and although the initial scale on a particular area might nominally correspond with one of those described earlier, the overall morphology will eventually consist of a complex mixture of the initial oxidation products and the results of interactions between them. The final predominant morphology will depend on the relative growth rates of the various oxidation products as determined by the factors discussed previously. Hence scale morphologies on

more complex materials will tend to exhibit lateral variations, as determined by the local composition and microstructure of the underlying alloy. However, it is still possible to obtain relatively simple scales on quite complex alloys when one element or phase is much more readily oxidizable than any of the others which are present. Such is the case with a number of heat resistant alloys which develop a uniform, protective scale of either Cr_2O_3 or Al_2O_3.

(b) As oxidation proceeds the alloy is consumed and, if alloy-scale adhesion is poor, a gap can be formed between the alloy and scale, without scale fracture occurring, if the scale is sufficiently plastic. Alternatively, as seems to be the case with some Fe-Cr-Al alloys, a localised gap can be formed by a mechanism involving combination of the scale components within the scale, rather than at either the outer or inner surface, causing the scale to grow away from the alloy[30]. Isolation of the scale from the alloy, without suppression of the driving force for continued outward movement of cations, leads to the development of porosity in the inner regions of single layer scales and the disappearance of the inner, relatively cation-rich phases in multi-layer scales, with the continued growth of the outer, oxidant-rich, phases, as found, for example, during the sulphidation of Cu-Ni alloys (Table I). It is also possible that the original oxidation reaction can continue by the transport of the volatile, scale-forming, metal across a closed void but the importance of this mechanism is restricted to high temperatures where metals such as chromium or aluminium exhibit significant vapour pressures. Alternatively the scale closest to the alloy may dissociate, thus re-establishing scale-gas equilibrium in the alloy-scale gap, and the oxidizing atmosphere produced can cause re-oxidation of the alloy. This mechanism has been invoked to interpret the porous, inner layer in sulphide scales on nickel and Ni-Cr alloys (Table I) and discussed by Gibbs in his study of the oxidation of mild steel in CO_2[31]. In general, for a scale separated from the alloy but still exposed at its outer surface to an oxidizing atmosphere, there will be a redistribution of the scale components in accordance with the new boundary conditions and this might also change any precipitate distribution which is present before scale separation occurs.

(c) When scale fracture occurs the oxidizing atmosphere can gain access to the underlying alloy which has, very probably been denuded of the less noble metal. If the less noble metal content is insufficient to ensure the re-establishment of the original scale a completely new oxidation reaction can ensue at each fracture site, with the scale incorporating relatively much larger fractions of the more noble alloy components than those in the original scale, as is well known from extensive research on the breakaway oxidation of heat resistant alloys. Morphologies in such cases can become very complex since re-oxidation is not determined by uniform outward growth but includes a lateral contribution, drawing oxidizable cations from alloy regions beneath the existing adherent scale. In addition compressive stresses, caused by the formation of new oxidation products which are less dense than the original scale, might cause further fracture.

(d) Transport of either metal cations or oxidizing species along preferential paths through scales such as grain boundaries, cracks and pores must obviously lead to deviations from morphologies based on uniform one-dimensional transport. Depending on the species preferentially transported, the possibilities include the non-uniform precipitation of a second phase within the scale and scale growth at preferred sites, causing the build-up of stress, followed by scale fracture, with the consequences noted earlier. Non-uniform internal oxidation of the alloy can also occur for similar reasons[32].

(e) In some cases, particularly where oxidation is carried out in atmospheres which are only slightly oxidizing, scale growth can be controlled by interfacial reactions and a linear rate law is obeyed. In such cases transport within the scale is faster than that required for scale formation and a further set of morphologies can be obtained. Thus, if diffusion is rate controlling, depletion of the less noble metal can occur within the alloy, while when interfacial control prevails alloy interdiffusion may be sufficiently rapid to minimize such depletions. Consequently, the phase in the adjacent scale, which is in equilibrium with the

alloy, could be different in the two cases and this appears to be so when Cu-Ni alloys are sulphidized according to linear[33] and parabolic (Table I) rate laws. Alternatively one or more of the phases present in multilayer scales formed when diffusion is rate controlling may be absent if interfacial processes are rate-controlling. In the latter case the potential formation rate of a given phase at one boundary may be controlled by the slower interfacial process, while at its other boundary it may be capable of being consumed at a faster rate if the growth of the neighbouring layer is determined only by diffusion processes. Consequently the equilibrium state could result in either the elimination of the former phase from the scale, assuming that it appeared in the initial stages of scale growth, or even its complete exclusion from the scale throughout the whole of the growth process, if the imbalance between the diffusive transport and interfacial reaction rates are sufficiently great. The variable oxidation behaviour of dilute Fe-Si alloys in oxygen and CO_2 atmospheres[34,35] might be interpretable in this way. If the process controlling the overall linear rate takes place at the scale/oxidant interface (e.g. gas dissociation or transfer across a stable boundary layer from the bulk gas to the interface) then cation-rich phases would be expected to predominate in a multi-layered scale while if the controlling process operates at the alloy/scale interface (e.g. metal transfer across the interface) oxidant-rich phases would probably be dominant.

(f) The fact that porosity can occur in scales as a result of the growth process has also been ignored so far. However, vacancies can exhibit the properties of elemental components in may respects and their precipitation can cause the formation of voids, in a manner analogous to the precipitation of other phases. Pores originating from the non-conservation of mass, caused by unequal diffusion fluxes, could occur in many of the uniform scales mentioned, except where phases are totally immiscible, but it is impossible to define specific morphologies without more detailed information on relative diffusion rates in particular scales. Porosity may develop in association with second phase precipitation within a scale since the particles act as preferential void nucleation sites. Grain boundaries,

where vacancy concentrations are effectively higher than in the surrounding scale, may also act as preferred sites. However, this is not always the case and apparently homogeneous phases can contain large, randomly distributed pores, e.g. Cu_2S layers on Cu-Ni alloys. Porosity may also arise as a consequence of alloy-scale separation, scale dissociation or mechanical failure, as noted earlier. The role of vacancies and the generation of porosity during oxidation reactions has been discussed extensively in a recent series of papers[36] and mechanisms for void formation in the underlying alloy have been examined in detail by Harris[37].

(g) The morphologies included in Fig. 1 are produced by the predominant outward flow of cations, a mechanism which is most commonly applicable to the oxidation of metals with close-packed crystal structures, although chromium is an exceptional b.c.c. metal which is included in this category. In the more usual cases where the oxidation of b.c.c. metals is examined the reaction proceeds by the inward diffusion of oxygen and, furthermore, some important b.c.c. metals exhibit a considerable solubility for oxygen (the situation regarding reactions with sulphur has received little attention and is consequently less clear). Hence a major difference between the oxidation behaviour of close-packed and b.c.c. metals is that for the latter, scale formation at the alloy-scale interface, coupled with changes in the properties of the underlying alloy due to oxygen absorption, can lead to compressive stresses being developed which are sufficient to cause scale fracture. As a result of this a continuous scale does not persist and the morphologies produced are excluded from the general scheme considered earlier. Even when continuous scales remain stable the virtual immobility of cations within them precludes the formation of cation distributions and their associated morphologies. Although multi-layered scales might still be expected, with the layered phases being determined by the variation in oxidant activity through the scale, layers containing more than one phase can only arise by either the mutually dependent growth of immiscible phases or the absorption of internal oxide into the surface scale as the alloy-scale interface recedes. Moreover, the latter mechanism is unlikely to be common since high

oxygen solubilities will often minimise the occurrence of internal oxidation. However, although the variety of uniform scale morphologies is restricted because of these properties, the possibility of mechanical failure is high and this can cause considerable complexity in practice.

APPLICATION TO UNIFORM SCALES OBSERVED ON SOME BINARY ALLOYS

Two general cases will be considered, the first being the limited sequence of scales formed during the oxidation of Fe-, Co- and Ni-base alloys and the second the apparent predominance of multi-layer scales when these alloys are sulphidized.

Oxidation of Fe-, Co- and Ni-base alloys

This subject has received a vast amount of attention and it is only intended to examine specific points which are amenable to semi-quantitative discussion. Consequently statements are restricted to Cr - containing alloys since, although the variation of the oxidation rate of Al-containing alloys with composition can be interpreted in a similar manner, quantitative information on diffusion rates in the relevant phases is largely unavailable. The experimental variation of oxidation rate, k_p, can be divided into four stages[15]:

(i) Small additions (< 1% or so) of Cr to the basis metal, Me, cause an increase in k_p due to the increase in cation diffusivities in the appropriate cubic oxide MeO. This increase can be described quantitatively for dilute Ni-Cr alloys but insufficient data are available to carry out the relevant calculations for Fe-Cr or Co-Cr alloys. Moreover, because the concentration of native cation vacancies increases in the order NiO < CoO < FeO, there is a progressively decreasing probability of Cr-doping producing a sufficiently large increase in the total vacancy concentration to be totally consistent with the observed increase in k_p. Other factors, such as internal oxidation and dissociative transport, may be responsible for the observed increase in such cases.

(ii) When the solubility limit for Cr in the noble metal oxide is exceeded a new

spinel phase can be precipitated. This corresponds approximately to a maximum oxidation rate although other factors mentioned above and discussed in detail elsewhere[15] cause the maximum value to persist over different concentration range in various alloy systems. Thus, in Ni-Cr alloys k_p is virtually constant between 1 and 10 wt%Cr, probably because $NiCr_2O_4$ forms small, discrete precipitates which do not interfere markedly with cation diffusion in the NiO matrix. For Co-Cr alloys there is a gradual variation of k_p across the composition range containing the maximum value and this is probably caused, at least partly, by the wider stability range of the spinel, from $CoCr_2O_4$ to $Co_{1\cdot3}Cr_{1\cdot8}O_4$. This favours precipitation over a range of scale compositions and also permits precipitate growth sufficient to cause at least partial blocking of diffusion in the CoO matrix, thus preventing the maintenance of a constant maximum value of k_p as the Cr content increases. As for Ni-Cr alloys there are other factors which contribute to the form of the k_p vs. %Cr curve. The extreme case, where the spinel has a sufficiently wide stability range to permit the eventual formation of a continuous blocking layer occurs in the Fe-Cr system where the phase $FeFe_nCr_{2-n}O_4$ $(0 \leq n \leq 2)$ is formed. This occurs on alloys containing less than 1%Cr; the increase in k_p, caused by changes in the properties of FeO noted above, is terminated when spinel particles are precipitated in the FeO layer next to the alloy and a complete spinel layer is ultimately formed at this location, in agreement with the relative diffusion rates of Cr and Fe in Fe_3O_4[38]. While diffusivities have not been measured in the Cr-containing spinel, a comparison of the relative rates in FeO and Fe_3O_4 shows that cation diffusion in the latter is much slower. Consequently, the formation of a continuous spinel layer causes a sharp increase in the oxidation rate immediately after the maximum is reached, as observed experimentally.

(iii) The detailed relation of k_p to %Cr and the composition range over which the value of k_p exceeds that for the pure noble metal component varies between different alloy systems[15] but in each case the upper Cr limit of this range is marked by a sharp decrease in k_p. As noted above for Fe-Cr alloys, the initial decrease is associated with the formation of an inner layer of the spinel $FeFe_nCr_{2-n}O_4$. A

further increase in the alloy Cr content eliminates FeO from the scale completely. At higher Cr contents the spinel phase is rendered thermodynamically unstable and this layer disappears also while, for alloys still richer in Cr, the scale consists solely of the sesqui-oxide $(Cr,Fe)_2O_3$. Cation diffusivities, and consequently k_p values, decrease rapidly in these compounds in the same order as they replace each other as the major phase in the scale. However, the actual growth rates of the sesqui-oxide scales are much greater than those predicted from diffusivities measured in single crystals, presumably due to short circuit diffusion effects. The Fe contents of these scales are small, typically ~ 1%, because of the very strong selective oxidation of Cr and the relatively fast diffusion rates in the alloy ($D_{ferrite} \simeq 100\ D^{Cr}_{Cr_2O_3}$).

The analogous sudden decrease in k_p for Ni-Cr and Co-Cr alloys could also, in principle, be related to the eventual formation of a continuous spinel blocking layer in the matrix of the cubic oxide formed originally. This supposition is consistent with the fact that the ratio between k_p for the pure noble metal and the minimum value of k_p for the alloy displays considerable agreement with the ratio between the cation diffusivities in the cubic oxide and the spinel, as shown in Table II. Values of the two ratios for other significant scale compositions are also included in Table II to demonstrate the general order of magnitude agreement between the variations in cation diffusivities and k_p values. However, in spite of these numerical similarities, there are no experimental observations of a spinel layer in the Ni-Cr system and, while there is some evidence for a rate-controlling layer in the Co-Cr system, this is limited to a very narrow alloy composition range. There is, moreover, considerable alternative evidence for a doped Cr_2O_3 scale when k_p is a minimum, as for Fe-Cr alloys.

(iv) The value of k_p increases from the minimum towards the value for Cr_2O_3 formation on pure Cr. For Fe-Cr alloys this increase is qualitatively consistent with the measured increase in cation diffusivities as the Fe content of $(Cr,Fe)_2O_3$ decreases, e.g. at 1273K $D^{Fe}_{Fe_2O_3} \simeq 0.005\ D^{Cr}_{Cr_2O_3}$. In other alloys it has been associated with a comparable decrease in the doping effect as the concentration of Ni^{2+} or Co^{2+}

in Cr_2O_3 decreases. However, the diffusivity measurements required to confirm these speculations have not been made at present and the implications of short circuit diffusion in the scales must always be considered.

The formation of multilayer oxide and sulphide scales

The morphologies of scales observed on a number of important binary alloys are summarised in Table I. Although many of the oxide scales are multi-layered they do not fall within the restricted definition of multilayer scales given in (i) above. Thus:

1. As stated earlier, the identification of two layers is based on changes in precipitation patterns in some cases, e.g. on Co-rich, Co-Cr and Ni-rich, Ni-Cr alloys, rather than the formation of different phases as discrete layers.

2. In other cases, i.e. CoO or NiO layers outside Cr_2O_3 and copper oxide layers outside NiO, there is a true layered scale but the outer oxide layer essentially ceases to grow after it becomes isolated from the alloy by a continuous layer of the inner oxide. These scales are excluded from the restricted definition of multilayer scales considered here which includes only those cases where all the layers can continue to grow and where the relative proportion of each phase in the scale is independent of time.

3. Some layered scales are derived directly from those formed on one of the pure component metals, e.g. $Cu|Cu_2O|CuO$ and $Fe|FeO|Fe_3O_4|Fe_2O_3$, and the oxide of the other alloying element does not form a continous layer.

Hence the morphologies which predominate in uniform, continuous oxide scales can be understood in terms of either cation redistributions in solid solutions and the precipitation patterns arising from them, modifications of multilayer scales formed on one of the pure component metals o the formation of an outer layer by an

overgrowth mechanism.

Similar examples are found among the sulphide scales, e.g. complete solid solution scales on Fe-Ni alloys and layering caused by precipitate density variations on Fe-Al alloys. However, another multi-layered morphology is also commonly observed where the sulphides of both alloy components form separate, discrete layers, as found on Co-Cr, Co-Ni, Fe-Cr, Fe-Mn, Ni-Cr and Ni-Cu alloys (Table I). The possible reasons for this preferred morphology are fourfold:

1. Examination of the available data on the relative thermodynamic stabilities of oxides and sulphides in Table II shows that the probability of preferential oxidation is greater than that of preferential sulphidation in a given alloy system. This favours the formation of sulphide scales in which the relative proportions of the components are comparable with those in the alloy rather than one of the components predominating, as in many oxide scales. This requirement is readily achieved if separate phase layers can be formed.

2. The diffusion rates in sulphides are relatively much faster than those in oxides and, as noted elsewhere[14], this also favours the condition in which the relative proportions of the components in the alloy and scale are equal.

3. There is apparently a tendency in some sulphides for the host cation to diffuse slower than foreign cations, which is a necessary condition for the continued growth of superimposed layers. This occurs even in cases where the solubility of the foreign cation is small, e.g. Cu in NiS, Ni in Cr_2S_3 and Fe in Cr_3S_4. The same relative magnitude of diffusivities can occur in some oxides, e.g. Fe in NiO, when it again leads to a morphology which resembles that of a double layer, although the phases are not separated completely into discrete layers in this case.

4. The formation of ternary solid solutions, in which consideration variations in the ratio of the metal components can occur, is much more prevalent in the case of sulphides, in comparison with oxides, e.g. for Co-Cr, Co-Ni and Fe-Mn alloys. Where such compounds can remain stable as the inner layer in the scale, the transport of one of the alloy components outwards to form an outer layer will be facilitated. However, it is noted that significant concentrations of both cations in a sulphide phase is not a necessary condition for the growth of layered scales, as shown by the scales on Fe-Cr, Ni-Cr and Ni-Cu alloys.

In principle, it is possible to describe the growth of multilayer scales quantitatively, if precipitation of a second phase does not occur, by extending Wagner's analysis for solid solution scales. This is considered briefly in the Appendix where a condition for the continued growth of an outer layer is obtained. The general absence of the necessary data to evaluate this expression severely limits the application of this and other more extensive analyses to real systems.

CONCLUSIONS

Scales on binary alloys show varying degrees of complexity, even when they are formed uniformly over the whole of the alloy surface. The simplest scales occur either when only one component of the alloy is oxidized or when the oxidation product is a simple solid solution containing both alloy components. More complicated morphologies occur when additional stable compounds can be formed between the alloy components and the oxidant. In such cases the phases can appear either as discrete layers or as precipitates distributed within a matrix of a second, major phase, the particular morphology developed being determined by the complex inter-dependence of the diffusivities of cations in the scale and the relative stabilities of the phases involved. Internal oxidation of the alloy can occur either in the presence or the absence of a surface scale and the greatest degree of scale complexity is attained when it occurs, possibly with more than one

phase precipitating at different depths within the alloy, in combination with multilayer surface scales which also contain different precipitates. The relationships between the different morphologies are outlined schematically in Fig. 1.

The uniformity of scale formation rate and morphology over an alloy surface can be disturbed significantly by the accumulation of vacancies, preferential localised growth and stress generation and these phenomena may eventually lead to mechanical failure of the scale, followed by the onset of new oxidation reactions.

The growth rates and morphologies of oxide scales on alloys of Fe, Co and Ni with Cr can be understood to some extent in terms of changes in the stabilities of oxides with alloy composition and the different cation diffusion rates in each phase. However, further quantitative data are needed before certain features can be explained satisfactorily, particularly the nature of the scale corresponding to the minimum alloy oxidation rate and the magnitude of the increase in the oxidation rate in Cr-rich alloys.

A comparison of the oxide and sulphide scales on a number of binary alloys (Table I) suggests that multiple layers capable of continued growth occur predominantly during sulphidation. This appears to be related to the faster cation diffusion rates in sulphides, the lower probability of preferential attack of one alloy component during sulphidation and the wider range of stoichiometry in ternary sulphides.

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APPENDIX

Growth of the Outer Phase in a Double Layer Scale

It is assumed that two oxidation products are formed from the alloy A-B, one rich in A, the α-phase, and the other rich in B, the β phase. Moreover, although both phases are considered to be stable over definite composition ranges, there is a miscibility gap in the pseudo-binary α-β system. The processes occurring during the growth of the superimposed phases by the outward diffusion of cations is shown schematically in Fig. A1.

The nomenclature is the same as that used by Wagner[13] in his analysis of the growth of a single layer solid solution scale.

At the boundary between the α and β phases (quantities at this interface being denoted by the superfix i) the A-rich phases grows by the incorporation of m additional A atoms into each mole of the B-rich phase and which concurrently releases n atoms of B, followed by their diffusion outwards to the scale/gas interface. The reaction at the α|β boundary is:

$$(A,B)^{\beta}X + mA = (A,B)^{\alpha}X + nB$$

By analogy with Wagner's analysis[13] the growth rate of the α-phase at this boundary is:

$$\frac{dX^{i\alpha}}{dt} = \frac{J_A^{i\alpha}\, V^{\alpha}}{m(1-\xi)^{i\alpha}}$$

where $J_A^{i\alpha}$ is the flux of A atoms in the α-phase at the α-β boundary, V^{α} is the molar volume of the α-phase and ξ is the local equivalent fraction of pure B(X) in the scale.

Similarly, consumption of the β-phase at the α-β boundary is:

$$-\frac{dX^{i\beta}}{dt} = \frac{J_B^{i\beta}\, V^{\beta}}{n\xi^{i\beta}} \qquad (1)$$

The growth rate of the β-phase at the scale-gas interface (denoted by superscript g) is:

$$\frac{dx^{g\beta}}{dt} = \frac{J_B{}^{g\beta}\ V^{\beta}}{\xi^{g\beta}} \qquad (2)$$

and from Equs. (1) and (2) the net growth rate of the β-phase is:

$$\frac{dx^{\beta}}{dt} = \frac{dx^{g\beta}}{dt} + \frac{dx^{i\beta}}{dt} = \frac{J_B{}^{g\beta}\ V^{\beta}}{\xi^{g\beta}} - \frac{J_B{}^{i\beta}\ V^{\beta}}{n\xi^{i\beta}}$$

For the β-phase to grow outside a layer of the α-phase, $dx^{\beta}|dt > 0$ or:

$$n\xi^{i\beta}\ J_B{}^{g\beta} > \xi^{g\beta}\ J_B{}^{i\beta}$$

Referring to Fig. A1 the mass balances for A and B at the α-β interface are:

$$J_A^{i\alpha}\,dt - J_A^{i\beta}\,dt = \left[\xi^{i\beta} - \xi^{i\alpha}\right] dx^{i\alpha}/v^{\alpha}$$

$$J_B^{i\alpha}\,dt - J_B^{i\beta}\,dt = \left[\xi^{i\alpha} - \xi^{i\beta}\right] dx^{i\beta}/v^{\beta}$$

In principle the diffusion fluxes could be written in terms of activity gradients, as for the case of single layer scales[13]. However, whereas in the latter case further simplification is often possible, by assuming ideal thermodynamic behaviour, it is more probable for partially miscible solid solutions to deviate from ideality and since the requisite thermodynamic data are generally unavailable, the consequences of such substitutions and approximations are not examined further.

Table I Experimental Observations of Oxide and Sulphide Scale Morphologies on Fe-, Co- and Ni-base Alloys

	OXIDATION					SULPHIDATION					
ALLOY A-B	TEMP RANGE °C	wt%B	OXIDE SCALE MORPHOLOGY	$\lvert\Delta G^o_{A(o)} - \Delta G^o_{B(o)}\rvert$ kJ/mole O_2		TEMP RANGE °C	wt%B	SULPHIDE SCALE MORPHOLOGY	$\lvert\Delta G^o_{A(s)} - \Delta G^o_{B(s)}\rvert$ kJ/mole S_2		REFS.
Co-Cr	1000	0- 15	alloy/CoO+Spinel ppts/CoO(dsCr)	$CoO-Cr_2O_3$	247	800	1	alloy/$(Co,Cr)_yS/Co_9S_8/CoS_{1+x}$	Co_9S_8-CrS	131	Ox.15
		>30	alloy/Cr_2O_3/CoO				5-25	alloy/$(Co,Cr)_yS/CoS_{1+x}$	CoS-CrS	134	Su.39
Co-Fe	1200	0- 10	alloy/(Co,Fe)O	CoO-FeO	76	533 -700	39-100	alloy/(Co,Fe)S	CoS-FeS	7.6	Ox.16,40 41 Su.42
Co-Ni	1000- 1200	0-100	alloy/(Co,Ni)O	CoO-NiO	37.5	445	20-80	alloy/$(Co,Ni)_9S_8$/NiS	$Co_9S_8-Ni_3S_2$	2.4	Ox.43
							90	alloy/$(Co,Ni)_9S_8/Ni_7S_6$/NiS	Co_9S_8-NiS	22.6	Su.44
							95	alloy/$(Co,Ni)_9S_8/Ni_3S_2/Ni_7S_6$/NiS			
Fe-Al	500- 700	4.4	alloy/α-Fe_2O_3	Fe O-Al_2O_3	520	500- 700	5	alloy/FeS+Al_2S_3 ppts/FeS			Ox.45 Su.46
		12	alloy/γ-Al_2O_3	$Fe_2O_3-Al_2O_3$	543						
Fe-Cr	800- 1000	2-10	alloy/Fe_3O_4+Spinel ppts/Fe_2O_3	Fe O-Cr_2O_3	178	700- 900	3- 7	alloy/FeS+$FeCr_2S_4+Cr_3S_4$/FeS(dsCr)	FeS-CrS	94.5	Ox.47 Su.48
		>10	alloy/Cr_2O_3(dsFe)	$Fe_3O_4-Cr_2O_3$	184		10-30	alloy/$FeCr_2S_4+Cr_3S_4$/FeS (dsCr)			
				$Fe_2O_3-Cr_2O_3$	208		35-80	alloy/Cr_3S_4(dsFe)/FeS (dsCr)			
Fe-Mn	1000	0-59	alloy/(Fe,Mn)O	FeO-MnO	221	700- 1000	0-10	alloy/(Fe,Mn)S+MnS ppts	FeS-MnS	11.2	Ox.49 Su.50
							11-70	alloy/(Mn,Fe)S/FeS (dsFe)+MnS ppts			
							>75	alloy/(Mn,Fe)S			
Fe-Ni	600- 1000	0- 2	alloy/FeO (dsNi)/Fe_3O_4/Fe_2O_3	FeO-NiO	100	560- 900	0-15	alloy/(Fe,Ni)S	FeS-NiS	47.9	Ox.47 Su.51
		2-35	alloy/$Ni_xFe_{3-x}O/Fe_2O_3$	Fe_3O_4-NiO	96						
				Fe_2O_3-NiO	73.1						
Ni-Cr	800- 1200	0-10	alloy/NiO+Spinel ppts/NiO(dsCr)	NiO-Cr_2O_3	282	600- 900	0-20	alloy/NiS(dsCr)+Cr_2S_3 ppts	NiS-CrS	144	Ox.15 Su.52,5
		20-100	alloy/Cr_2O_3/NiO				20-50	alloy/Cr_2S_3(dsNi)+NiS ppts/NiS			
							50-100	alloy/Cr_2S_3(dsNi)			
Ni-Cu	800	20	alloy/NiO(dsCu/CuO(dsNi)	NiO-Cu_2O	104	380- 500	20-50	alloy/Ni_3S_2/Ni_7S_6/NiS(dsCu)/Cu_9S_5/CuS	NiS-Cu_2S	28.7	Ox.54 Su.55
		50	alloy/NiO+Cu_2Oppts/CuO(dsNi)				60-93	alloy/Nis(dsCu)+Cu_9S_5ppts/Cu_9S_5/CuS	Ni_7S_6-Cu_2S	17.3	
		90	alloy/Cu2O+NiO ppts/CuO						Ni_3S_2-Cu_2S	3.6	

Note: (dsM) dilute solution of metal M ions in the preceding oxide

Table II. Comparison of the Oxidation Rate Constants and Cation Diffusivities for Scales on Cr-containing Binary Alloys

Alloy	Scale	k_p^{Metal}/k_p^{Alloy}	$D^{MeO}/D^{Oxide\ Scale}$
Co-Cr	Spinel (assumed $\equiv k_p^{min}$)	1.1×10^{-4}	5.1×10^{-4} 5.7×10^{-4}
	Cr_2O_3	6.7×10^{-3}	1.3×10^{-3}
Ni-Cr	Cr-doped NiO	7.4	16
	Spinel (assumed $\equiv k_p^{min}$)	1.7×10^{-2}	3.1×10^{-2} 6.1×10^{-2}
	Cr_2O_3	0.82	2.25

FIGURE CAPTIONS

Fig. 1. A schematic presentation of the relationships between scale morphologies on binary alloys. Numbered items are discussed in the corresponding paragraph in the text.

Fig. 1A. Double layer scale composed of partially miscible solid solutions.

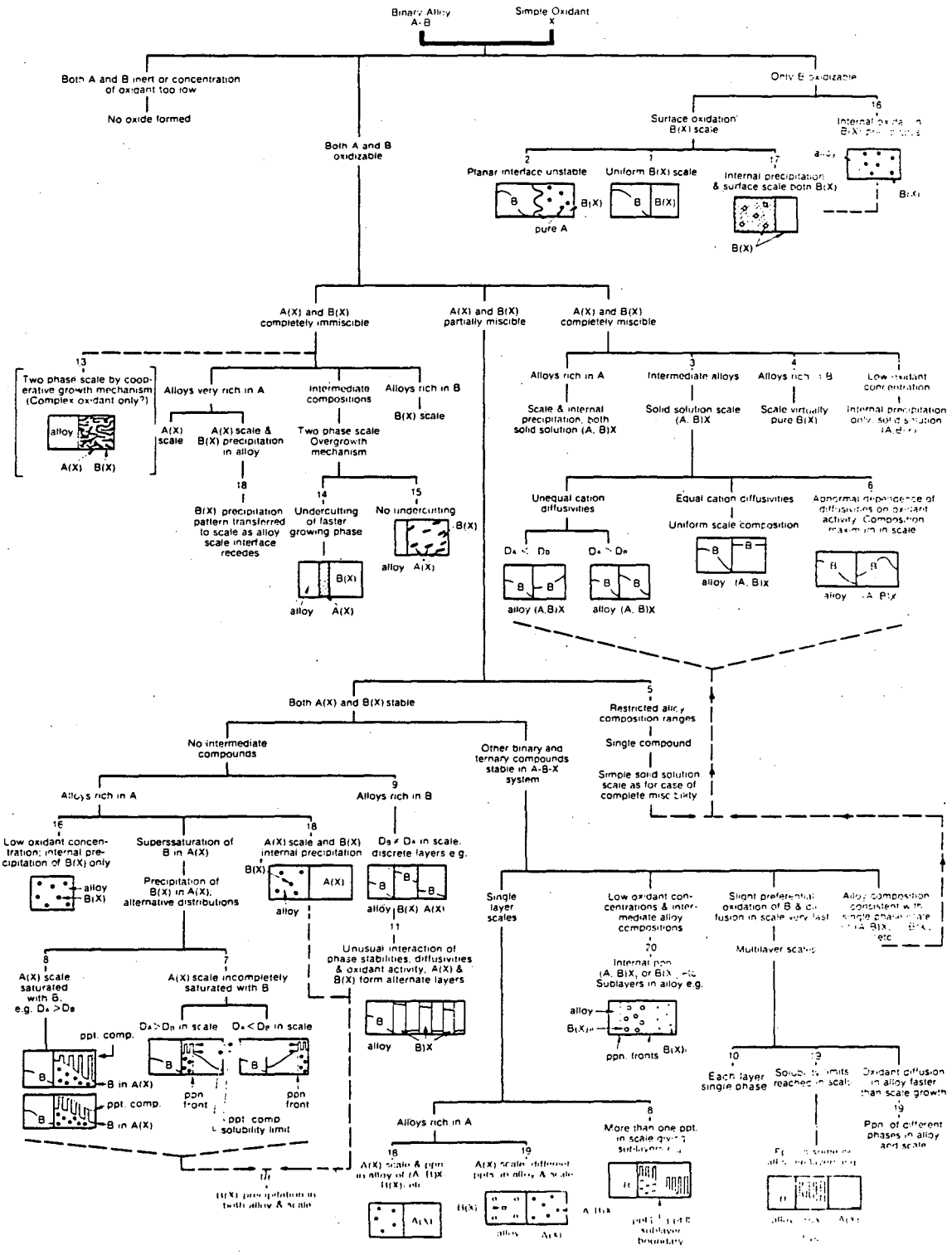
Binary Alloy A-B
Simple Oxidant X
Both A and B inert or concentration of oxidant too low
No oxide formed
Both A and B oxidizable
Only B oxidizable
Surface oxidation B(X) scale
Planar interface unstable
Uniform B(X) scale
Internal precipitation & surface scale both B(X)
pure A
A(X) and B(X) completely immiscible
A(X) and B(X) partially miscible
A(X) and B(X) completely miscible
Two phase scale by cooperative growth mechanism (Complex oxidant only?)
Alloys very rich in A
Intermediate compositions
Alloys rich in B
A(X) scale
A(X) scale & B(X) precipitation in alloy
B(X) scale
Two phase scale Overgrowth mechanism
B(X) precipitation pattern transferred to scale as alloy scale interface recedes
Undercutting of faster growing phase
No undercutting
Alloys rich in A
Intermediate alloys
Alloys rich in B
Scale & internal precipitation, both solid solution (A, B)X
Solid solution scale (A, B)X
Scale virtually pure B(X)
Unequal cation diffusivities
Equal cation diffusivities
Uniform scale composition
Both A(X) and B(X) stable
Restricted alloy composition ranges
Single compound
Simple solid solution scale as for case of complete miscibility
No intermediate compounds
Other binary and ternary compounds stable in A-B-X system
Alloys rich in A
Alloys rich in B
Low oxidant concentration; internal precipitation of B(X) only
Superssaturation of B in A(X)
A(X) scale and B(X) internal precipitation
Precipitation of B(X) in A(X), alternative distributions
Unusual interaction of phase stabilities, diffusivities & oxidant activity, A(X) & B(X) form alternate layers
A(X) scale saturated with B, e.g. $D_A > D_B$
A(X) scale incompletely saturated with B
ppt. comp.
B in A(X)
Single layer scales
Low oxidant concentrations & intermediate alloy compositions
Slight preferential oxidation of B & diffusion in scale very fast
Multilayer scales
Internal ppn (A, B)X, or B(X) Sublayers in alloy e.g.
ppn. fronts
Each layer single phase
Oxidant diffusion in alloy faster than scale growth
Ppn. of different phases in alloy and scale
Alloys rich in A
More than one ppt. in scale

Figure 1.

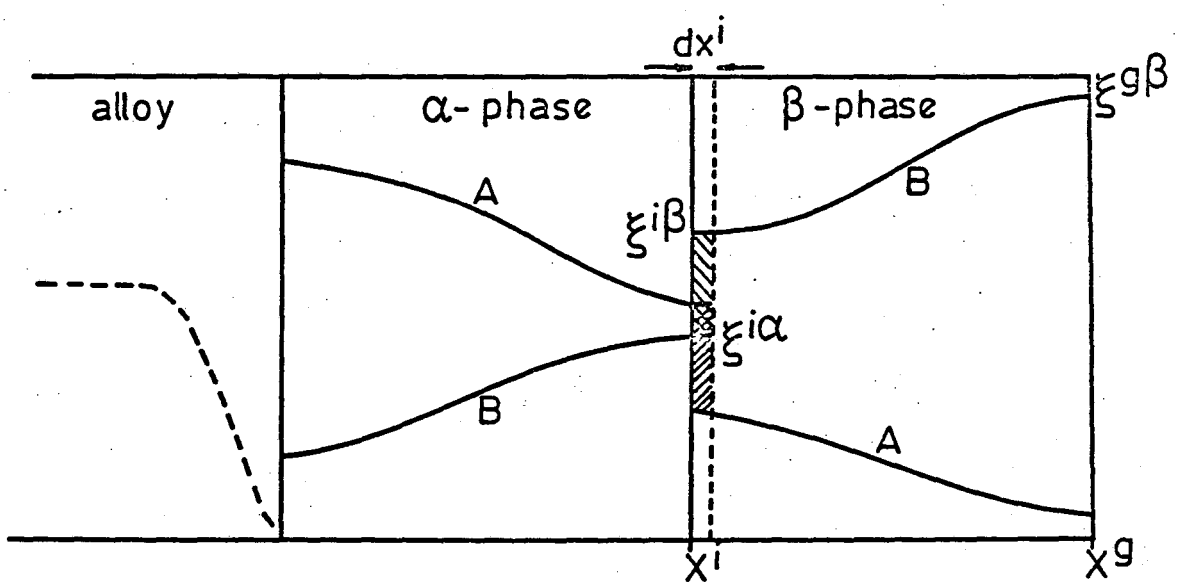

Figure A1.

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