Residuals and Properties

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Phil. Trans. R. Soc. Lond. A 1980 **295**, 9-23
doi: 10.1098/rsta.1980.0072

Phil. Trans. R. Soc. Lond. A **295**, 9–23 (1980)
Printed in Great Britain

Residuals and properties

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> 'But you must take special care that your Iron *burn* not in the fire, that is, that it do not *run* or melt, for then your Iron will be so brittle that it will not endure Forging, without breaking, and so hard, that a File would not touch it' (Joseph Moxon, *Mechanick exercises, or the doctrine of handiworks*, London, 1677).

The awareness of purity in materials in relation to properties is historically of long standing. Today, this awareness has been heightened both because of a better understanding and also because of the realization of the economic benefit in improved performance, especially in complex metallurgical structures. A further stimulus to the growing interest in this field has been a serious concern with an inevitable accumulation of unwanted impurities arising from increasing effort in materials recycling. By good fortune, the timely arrival of instrumental and other technical developments has opened up new opportunities for detailed investigations.

This introductory paper takes a synoptic view of the subject and in particular considers the common links underlying behaviour in a range of phenomena represented at the meeting. In terms of mechanisms, the main interconnecting thread lies in the capacity of dilute impurities to concentrate at various interfacial localities by equilibrium or kinetic processes. This may induce subsidiary effects, such as reduced cohesion or retarded surface reactivity. We are at a point when positive action can be taken to translate the new data into materials practice, both by tightening specifications in bulk impurity contents and also by introducing process remedies based on physicochemical treatments.

RESIDUALS, IMPURITIES AND METALS

The theme of this meeting is the awareness of purity in relation to materials behaviour. In metallurgical practice, this awareness of purity preceded any scientific understanding in the subject. Since, at least in terms of their civilizing influence, metals have a first place in any materials hierarchy, it is not unexpected that the earliest recognition of the importance of purity should have arisen historically in relation to metal culture.

The association of low ductility in steel with the presence of sulphur came early in the technological developments in steelmaking that ushered in the industrial revolution. Thus, in a work on assaying published in 1741, Cramer wrote 'our Sea-coals or Newcastle Coals, or in general all the fossil Coals which cake in burning and run into Cinders abound with Sulphur, and therefore are improper to be used about Iron, always making it brittle' (Ashton 1951). He then proceeds to recommend the careful choice of coals, such as those that burn to a white ash, as being the most suitable for making malleable iron. Observations and exhortations such as this formed the craft lore of successful steel making for many decades. By 1781, Bergman in Sweden demonstrated that the presence of carbon distinguished between pure iron, steel and cast iron (the minute amount of carbon needed having so mystified Bergman that he described this, the most important phenomenon in ferrous metallurgy, as the 'difficulty of difficulties'). It was not until about the beginning of this century that we see the first clear scientific measurements and exposition of the role of minor elements on metal properties. In his numerous investigations, Roberts-Austen took up a host of unrelated observations made during the growth of industrial metallurgy in the nineteenth century, and re-examined them with scientific insight. For instance, he quotes from an author writing in a civil engineering journal in 1883 that 'a submarine cable made of the copper of today will carry twice the number of messages that a similar cable of copper would in 1858', and commenting that it was the recognition of the need to remove foreign impurities that led to this important technological development (Roberts-Austen 1888). Using the limited investigational techniques available at the time, such as the optical microscope, etching reagents and dilatometers, Roberts-Austen attempted to correlate quantitatively the effectiveness of minute amounts of elements with their position in the periodic table.

One fascinating speculation slips out among the musings of this interesting writer: the suggestion that the very development of chemistry and metallurgy had been greatly influenced by this awareness of the strong effects procurable in metals by small quantities of added matter. This notion, he pointed out, sustained the belief among the early alchemists in the possibility of ennobling base metals or degrading precious ones. 'It is hardly strange,' wrote Roberts-Austen, 'that in the absence of a knowledge of analysis, they should have believed in the efficacy of a transmuting agent, when it is remembered that in the specimens submitted to the Society the presence of $\frac{1}{500}$ part of such metals as lead, bismuth, and potassium has entirely altered the appearance of the fractured surfaces of pure gold.' No doubt the catastrophic effects of traces of mercury on copper and copper alloys must have been known to the alchemists. In passing, it is interesting to conjecture that the main objective of alchemists, namely, to convert base metals into precious metals, is the earliest example of what we, in the modern jargon might describe as a large-scale mission-orientated technology! Furthermore, the outcome of this huge effort provides a salutary lesson on the need to carry out the basic science first.

Residuals are the elements that remain after the metal is produced, and which are difficult to extract economically. Thus, the presence of these residuals reflects the history of the alloy, from the ore, through the primary metallurgical route and to its prefabrication stage. Additives we define as elements which are deliberately introduced in order to obtain a specific property. The feature which distinguishes residuals and additives from alloying additions is essentially that of diluteness. This is indeed an artificial distinction; a second important consideration is that the residual produces an effect on properties out of all reasonable proportion to the amount of the element present. In the present usage of these terms, 0.05% nickel in iron would not be considered as a residual or an additive (from the point of view of effect on mechanical properties), in the sense that the same quantity of antimony in iron would be. Probably the most extensively investigated field from the point of view of effects of impurities is that of semiconductor materials. This important materials field will not be embraced in this meeting, which will deal principally with phenomena met with in the ferrous and non-ferrous metallurgical fields.

The central action of residuals and additives in polycrystalline materials, which runs as a common thread in the contributions to this meeting, lies in the elements' capacity to concentrate. This may take place at grain boundaries, free surfaces, phase interfaces, precipitate–matrix interfaces and other localities in the solid. One phenomenon that seems to be an exception to this is the role of interstitial impurities in increasing the low temperature yield strength of body-centred cubic metals, thereby inducing brittleness.

Recycling and compositional changes

The recent revival of interest and research activity among materials scientists on the effect of residuals on properties is due to a number of concurrent reasons: first, the realization, in a highly competitive materials world, of the economic benefits of improved and reliable performance; secondly, the stimulus and new understanding afforded by the timely arrival of surface techniques for examining the phenomena involved.

However, perhaps a more important motivation stems from the current social anxieties on the state of our environment, as well as fears of the depletion of non-renewable materials resources, which have led to strong pressures for the recycling of used materials. Clearly, this will exacerbate problems related to concentrations of various unwanted residuals: it is a general problem of looming importance and it is right at this time that we should try to anticipate any likely long-term effects and to have solutions available in time. This theme is a fitting starting point to this meeting, and specific contributions on this subject will form a canvas for the conference by providing a measure of the magnitude of the existing problem and how it is expected to grow in our lifetimes.

On this matter, the U.S. National Academy of Sciences, following a lengthy survey, recommended in its report on 'Materials and man's needs' that the 'sources of materials science and engineering be deliberately exploited and extended to upgrade the recyclability of materials through materials development and selection, meshed carefully with product design, and through the development of new recycling processes' (Cohen 1974). Uppermost in the thinking of the committee was the self-evident fact that after each recycling, the metal, plastic, glass or ceramic becomes degraded through compositional changes. Almost as a corollary, the committee added the notion of the inevitability of sacrificing performance: 'we must develop secondary and tertiary outlets for recycled materials whose properties no longer meet the requirement of primary functions'. There are indeed good examples of this approach having been used successfully: for example, the Tin Research Institute demonstrated that the addition of up to 2 % tin to iron powder accelerates markedly the sintering process and permits a reduced sintering temperature (Barua *et al.* 1969). Since sintered components, such as those used for automatic transmission in automobiles, have good dimensional tolerances and thus do not require post-fabrication machining, this processing route offers overall economic advantages. Furthermore, although 2 % tin in iron or steel would be considered disastrous for many applications, the specific strength requirement of these components was met.

This, however, cannot be the general answer to the problem of degradability resulting from recycling. High duty alloy steel components are generally made by electric arc melting of charges containing a high proportion of scrap. Performance cannot be sacrificed for these expensive components in exchange for a high build-up of copper and tin, for example. How to avoid loss of performance in the face of growing levels of residuals in fact forms one of the bases of this meeting.

Equilibrium and non-equilibrium adsorption to interfaces

Interfacial concentration of residual elements may occur by equilibrium and non-equilibrium processes through mechanisms that are now fairly well understood. Equilibrium enrichment of interfaces is the most ubiquitous mode of concentration. It is motivated by the reduction of the total free energy of the system by the expulsion of impurity species from the bulk to more accommodating sites at interfaces (Hondros & Seah 1977*a*).

Non-equilibrium segregation is an entirely different phenomenon, resulting from sharp temperature changes experienced by an alloy. It has been explained by the solute drag mechanism, namely that during rapid cooling from high temperature, vacancies flow to grain boundaries to preserve the instantaneous thermal equilibrium value. Because of a high binding energy between certain solutes and vacancies, there is an associated transport of vacancy–solute pairs towards the vacancy sink (the grain boundary). This mechanism can set up solute concentration gradients over distances much greater than the grain boundary width, i.e. distances of the order of micrometres (Seybolt *et al.* 1964). A number of phenomena encountered in ceramics, intermetallics and metals probably owe their origin to this mechanism, which will be reviewed at this meeting. It is certainly worthy of closer attention and in particular there is need for further research to correlate measured concentration profiles (by using perhaps transmission electron microscopy with electron energy loss analysis) with those expected from this mechanism.

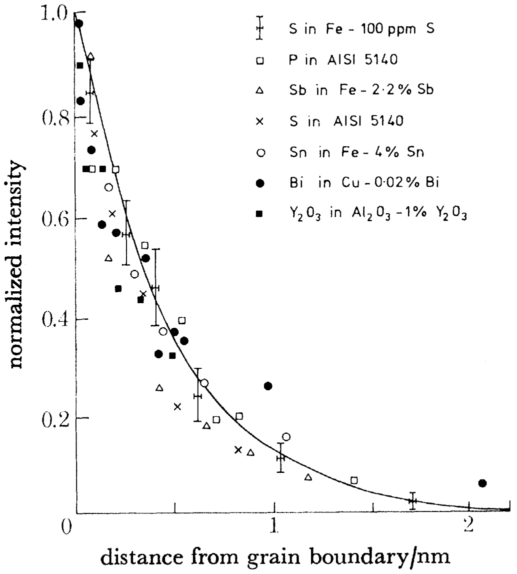

FIGURE 1. Concentration of solute and its variation with distance in depth from the grain boundary, for a number of systems. The zero point represents the plane of the boundary. Composite plot; data taken from: ○, Seah & Hondros (1973); □, △, ×, Marcus *et al.* (1972); ●, Powell & Mykura (1973); ■, Nanni *et al.* (1976).

Equilibrium or Gibbsian segregation mechanisms have now been studied fruitfully over a number of years, both by use of surface energy measurements, and more recently, by the newly arrived surface analysis techniques, in particular Auger electron spectroscopy. The most important experimental advance from these studies is the confirmation that surface active species segregate at equilibrium to localities very close to the grain boundary, typically within the first couple of atom layers on either side. This finding is illustrated in figure 1 for a number of segregant systems. It has been compiled from data obtained in several laboratories. The in-depth composition profile was obtained by sputter-stripping the fracture surface, followed by Auger electron analysis. The steep decrease in concentration defines a narrow width for the segregation zone. This confirms that the segregation phenomenon is essentially that of interfacial adsorption.

Again there is experimental proof that Gibbs-type adsorption occurs: the amount of enrichment resulting from equilibrium redistribution is given by the Gibbs adsorption theorem applied to an internal interface:

$$\Gamma_b = -\frac{1}{RT}\left(\frac{\partial \gamma_b}{\partial \ln X}\right)_T, \tag{1}$$

where Γ_b is the interfacial excess, γ_b the grain boundary energy and X the atom fraction of solute in the bulk. Figure 2 shows for tin in iron that, within experimental scatter, the value obtained by the Gibbs method (that is, measuring the grain boundary energy isotherm) falls on the curve extrapolated from values obtained at lower temperatures directly by Auger spectroscopy (Seah & Hondros 1973). The use of these advanced surface analysis techniques is now permitting the evaluation of changes in quantity of segregation with grain boundary type, multicomponent segregation to interfaces, and residual–alloying element interactions which are most important in temper embrittlement (Guttmann 1975).

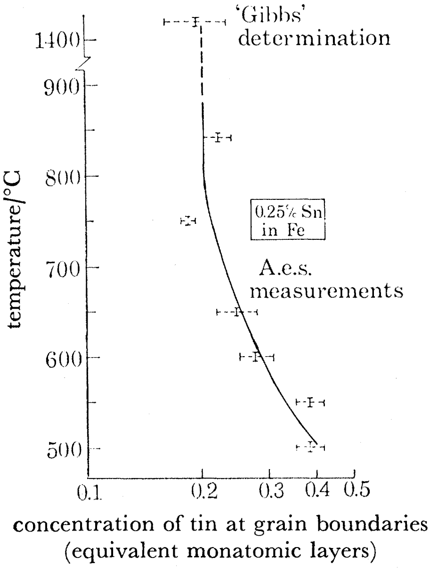

FIGURE 2. Temperature dependence of tin segregation at iron grain boundaries, measured by the Gibbs adsorption approach and by Auger electron spectroscopy in the same system.

Theoretical developments in grain boundary adsorptive systems show that a rapid route to characterizing behaviour is by adopting analogue procedures and translating the concepts and analytical treatments established in classical surface chemistry to internal interfaces in solids. Thus, the independently derived McLean (1957) equation for segregation is the grain boundary analogue of the well known Langmuir (1918) adsorption isotherm for free surfaces, i.e.

$$X_b/(X_{b_0}-X_b) = X_c \exp(\Delta G^s/RT), \tag{2}$$

in which the level of segregation X_b approaches saturation given by X_{b_0}, the number of adsorption sites, equivalent to between 0.5 and 1 monatomic layer. X_c is the bulk molar content and ΔG^s is the free energy of segregation.

By using the newly developed surface microanalytical techniques, a number of metallic and ceramic alloy systems have been examined and the Langmuir–McLean isotherm has been shown to apply, for example, in the segregation of sulphur in iron. However, it is clear that this is by no means the general adsorption behaviour and many deviations from the above ideal behaviour have already been recorded.

With the use of the analogue procedures, there are no intrinsic difficulties in analysing for departures from ideality. Thus, for example, the Langmuir isotherm presupposes that the occupation of one grain boundary site does not affect the occupation of the neighbouring site; that is, there are no adsorbate interactions. As in surface adsorption systems, this assumption may be quite crude, and to allow for the possibility of a chemical affinity between adsorbate atoms, we may extend a well known analysis, the Fowler–Guggenheim (1939) isotherm, to grain boundary behaviour. Essentially this involves subtracting from the energy of segregation term Q in the McLean analysis a smaller energy term which expresses the energy for mutual attraction or repulsion between atoms at the grain boundary. On testing data on selenium in iron with the use of classical analytical procedures, there are indications of such intense segregate interactions that it would correspond to condensation or phase formation, presumably in this case a two-dimensional phase (Hondros & Seah 1977*b*).

An even more striking illustration of the use of surface adsorption analogues to describe interface segregation behaviour was the use of multilayer adsorption theory to explain the observation of very high tin segregation build-ups at the grain boundaries of iron. At high bulk concentration of tin, but still within the solubility limit, Seah & Hondros (1973) measured tin concentrations as high as several equivalent monatomic layers. The results were analysed in terms of standard multilayer gas adsorption isotherms and it was shown that the well known BET theory (named after the founders Brunauer, Emmett and Teller (1938)) described the observations convincingly. The physical conception of multilayer grain boundary segregation involves a system of segregate atoms mingled with solvent atoms in a layer about the grain boundary.

Real engineering alloys are multicomponent systems and one might expect interactions between several solutes and between solutes and alloying elements. For a ternary system, a formal analytical expression for the Langmuir–McLean grain boundary isotherm can be obtained but with a greater complexity in terms. Since it has been known for a long time that in the temper embrittlement of steel, alloying elements such as manganese and nickel may exert an important influence on the role of segregate elements such as phosphorus, it is important to be able to describe bulk impurity – alloying element interactions in terms of the grain boundary adsorption isotherm. In his approach to this analysis, Guttmann (1975) followed closely the Langmuir–McLean treatment, but modified the segregation free energy by a term related to the interaction between the solute and the alloying element. This was in turn assessed approximately from the standard free energy of formation of the stable compound between the solute and the alloying element in question. This approach, albeit approximative, allowed one to rationalize long-established metallurgical observations on the effects of alloying elements in temper embrittlement.

Thus in brief, we know today that a variety of adsorptive behaviour is possible for impurities at grain boundaries, depending on the nature of the species involved, and, in general, a theoretical framework is available for describing the encountered behaviour. Furthermore, we now understand something of the nature of interfacial activity between solids, that is, the intrinsic tendency of solute species to enrich interfaces, and in principle we can predict the likely surface active species in a given system. This interfacial activity is classically defined as $(\mathrm{d}\gamma_{\mathrm{b}}/\mathrm{d}X_{\mathrm{c}})_T$, that is, the rate of depression of interfacial energy with changing bulk concentration in isothermal conditions. This may be expressed as a parameter β_b, termed the enrichment ratio. This is the ratio between the interfacial concentration, X_B, in fraction of a monolayer, and the bulk solute fraction, X_c. Thus,

$$\beta_b = \frac{X_b}{X_c} = -\frac{1}{RT\Gamma_b^0}\,\frac{d\gamma_b}{dX_c}, \tag{3}$$

where Γ_b^0 is the quantity of solute constituting one monatomic layer, in moles per square metre. Using this parameter, we may plot data obtained in the course of grain boundary energy measurements as well as direct spectroscopy analyses, and, as shown in figure 3, this yields a generalized plot between β_b and the inverse of the atomic solid solubility at the temperature of segregation (Seah & Hondros 1973). From such a plot, which was first noted empirically, but which has also been explained theoretically, we may make use of equilibrium phase diagram data to determine the enrichment factor, and furthermore to pinpoint the residual elements which are interfacially active in any given multicomponent system. This has already proved a useful predictive relation for evaluating systems which are impracticable to study experimentally by existing techniques.

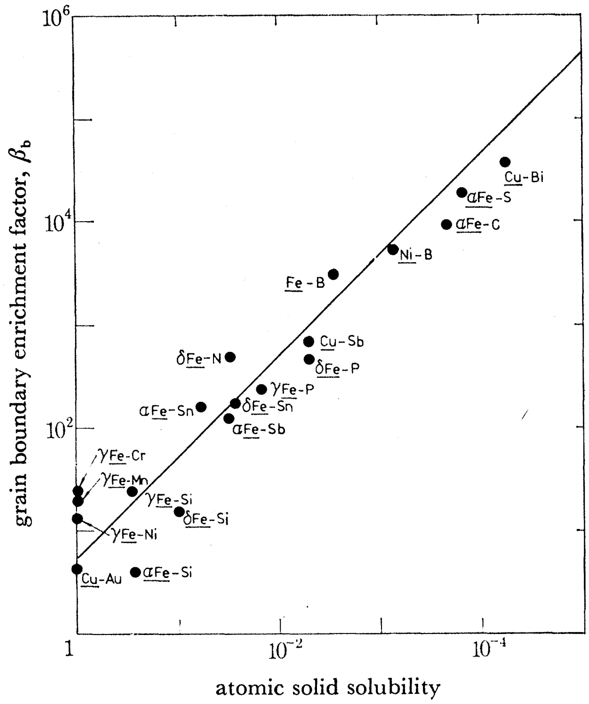

Figure 3. Dependence of the grain boundary enrichment ratio on the inverse of the solid solubility. In each binary alloy, the matrix element is underlined.

Emergence of new investigative techniques

It has already been mentioned that an important stimulus to more active investigations on the role of residuals on properties has been the recent emergence of suitable techniques. Phenomena related to residuals require information on the adsorption of species at internal and external interfaces. The ideal technique should have the following capabilities: (i) a high spatial and depth resolution, approaching the atomic scale; (ii) ability to detect unambiguously any element; (iii) ability to measure quantitatively all species present at the interface; (iv) provision of information on the state of chemical bonding of the species at the interface; and (v) ideally it should be able to operate on intact internal interfaces, without the need for exposure of the grain boundary surface by fracture.

Earlier techniques for investigating the present phenomena contained a serious disadvantage, namely the requirement of *a priori* knowledge of the nature of surface active species. Today the situation has been greatly altered by the advent of laboratory and commercial models of analytical techniques for direct surface analysis. These are based on a variety of physical processes, for example, secondary electron emission, sputtered ion mass spectrometry, ion beam backscattering, field ion microscopy with atom probe, scanning transmission electron microscopy with energy loss analysis or with dispersive X-ray analysis. Currently there is considerable activity among materials scientists and chemists eager to exploit these new techniques in relation to a broad spectrum of materials problems. The most appropriate surface analysis technique depends on the materials problem in hand: thus, in a study of lubrication and tribology, s.i.m.s. (secondary ion mass spectroscopy) and X.p.s. (X-ray photoelectron spectroscopy) appear to be the most appropriate. For the study of residuals–properties interactions in materials it seems that no single technique can satisfy all the requirements listed above; however, a number of techniques used conjointly and exploiting their capabilities in a complementary manner can be used to derive most of the information that is normally required. Thus Auger electron spectroscopy (A.e.s.) has proved a very powerful technique in segregation studies because of its ability to detect all surface active species on a grain boundary fracture surface and to provide a measure of the amount present. For many metallurgical situations, the identification role is of primary importance. However, the technique has a number of shortcomings: for example, it is not fully quantitative and, so far, chemical binding information cannot be easily derived. In particular, a feature that is general to a number of surface analysis techniques is the requirement to expose the grain boundary surface by fracture before Auger spectroscopy analysis. This limits the use of these techniques to systems displaying significant grain boundary weakness. There are many material situations in which effects other than reduced interfacial cohesion are important, for example retarded grain growth, and here, techniques such as f.i.m. or s.t.e.m. with energy loss analysis, which do not require the exposure of the grain boundary surface, may prove of increasing usefulness.

We are fortunate to have most of these techniques represented at this Conference. Together, these should provide the most up-to-date summary on the usefulness and promise of surface analysis in residuals-related work. One very valuable technical feature that is being increasingly appreciated is the ability to produce a near-surface compositional profile in depth, as illustrated in figure 1. This is generally carried out by combining the surface analysis with ion beam erosion of the surface, and from a knowledge or estimate of the sputter yield, the depth of material removed can be evaluated. This new experimental capability cannot be overestimated; for the surface scientist and the materials scientist it is providing a new dimension in understanding the role of interface chemical state on materials properties. This is being increasingly recognized in many fields, such as in semiconductor interfaces, in corrosion studies, catalysis and tribology.

The new understanding and the opportunities that have thus been created for improving materials behaviour and performance is so significant that one may discern the birth of a distinctive new stream in the physical sciences, that of *interfacial microchemistry*.

Range of materials phenomena

Through their ability to concentrate at interfaces, residual elements exert an influence, often at a controlling level, on a wide variety of materials properties and processes. In some situations, the effect is primary; in others, the residuals effect may be just one of a number of contending factors. In both instances, it is required to isolate and characterize the importance of the residuals factor. Phenomenologically, the action of residuals in materials behaviour is via two routes: one concerns phenomena which relate to altered *cohesion* and the other to phenomena related to altered *kinetics*. Within the framework of the present meeting, the subject matter which will be covered can be subdivided according to these two behaviour categories. This is shown schematically in table 1.

Table 1

residuals role

phenomena related to altered cohesion

phenomena related to altered kinetics

fabrication

hot shortness —
liquation cracking —
weld reheat cracking —
metal–precipitate adhesion —
reduced creep rupture life —
intergranular stress corrosion —
temper embrittlement —
intergranular fatigue strength —

—surface hardening reactions (carburizing, nitriding, etc.)
—inhibition of diffusion creep
—reduced grain boundary diffusion
—inhibition of grain growth
—controlled precipitate growth
—creep cavity nucleation
—grain boundary corrosion
—surface oxidation

performance in service

The various phenomena such as those under ‘altered cohesion’ have been classified further in terms of the position of the phenomenon in the materials cycle: for example, hot shortness and weld reheat cracking apply in general to the fabrication stage of the metallurgical cycle. On the other hand, phenomena such as temper brittleness and reduced creep rupture life refer more so to behaviour in service. Generally, the higher the location of the phenomenon in this presentation, the more important it is in the fabrication part of the cycle; conversely, the lower the placing, the more important it is in the performance part: in the middle range, it may refer to both. In the same way, phenomena under ‘altered kinetics’ may be classified according to whether they participate during fabrication or during use, but the division is clearly not so obvious. Thus, surface hardening reactions fall clearly in the fabrication stage whereas diffusion creep should be important also in performance.

In the structuring of this Conference, we have attempted to introduce another aspect in addition to the phenomenological one. This is the nature of the scientific or technological activity involved. In its broadest aspect, scientific methodology involves both the analysis and the synthesis functions. The most thorough and satisfying type of investigation combines both of these functions. However, one suspects that the general effort in materials during the past couple of decades has involved a disproportionate amount of analysis to the detriment of

Table 2

activity

analysis	**synthesis**
characterization of residual concentration phenomenon	assigning tolerance levels in relation to properties
metallurgical description of behaviour	procedures for control and remedy, e.g. gettering reactions
interfacial cohesion (thermodynamic and micromechanics description of fracture)	revision of specifications in residuals
detection of concentrating residuals	optimizing beneficial additives
evaluating potent residuals	

synthesis. The types of activity that fall in these categories are shown schematically in table 2. Thus, studies involving the detection of residuals, the characterization of adsorptive patterns, and analysis of grain boundary fracture modes fall in the category of analytical activities. Indeed, it is correct that these should precede the synthesis stage. Since the strategic aim of all this work is a control of residuals, as part of a materials design philosophy, it is *synthesis* that should now be emphasized. Where a residual impairs a particular property, the objective is to find a remedy; where a residual or a deliberate additive improves a particular property, the goal is to optimize its effect.

Two illustrative investigations

In spite of a growing interest in dilute additives for oxidation resistance, kinetics-based phenomena involving residuals have been rather neglected in comparison with phenomena involving cohesion or mechanical properties. In the following we consider one such example, which illustrates the action of residual impurities on an important metallurgical process. In addition, it typifies a research activity in the analysis category.

Effect of adsorbed impurities on surface reaction rates

The chemical composition of the free surface of a component may be rate-determining in a number of properties: this is well recognized in connection with, for example, the activity of supported catalysts. In relation to engineering properties, the chemical condition of the free surface of a component has not in general been closely studied, perhaps because such phenomena involve a subtle interplay between several disciplines.

There is now firm evidence that the rate of gas uptake of a metal depends sensitively on the chemical state of the surface: this is particularly well documented in the study of rates of surface-hardening reactions, such as carburizing. We recall that to improve the fatigue life and wear resistance of certain alloy steel components used as shafts, gears and rolls, the use of surface hardening treatments is quite common. The traditional practice is by carburizing or nitriding, while the more recent treatments involve the introduction of boron or chromium into the surface layers by gas phase reactions.

The factors that control the rates of carburizing or nitriding are important in production output, where time and temperature are commercially the significant steps. To what extent do adsorbed surface impurities affect the rate of acceptance of carbon or nitrogen into the surface layers? Some years ago Turkdogan & Grieveson (1967) demonstrated that in the nitriding of steel, the nitrogen transfer was controlled by the surface adsorption step, according to a first order reaction, due in this case to the preferential adsorption of oxygen impurity from the environment. In fact, the rate of nitriding is inversely proportional to the oxygen potential in the gas phase, from which it follows that simply cleaning the environment or using high purity nitrogen or ammonia should increase the rate of nitriding. This is an important piece of information in practices where nitriding times can be up to 100 h, depending on the depth of the hardened layer required.

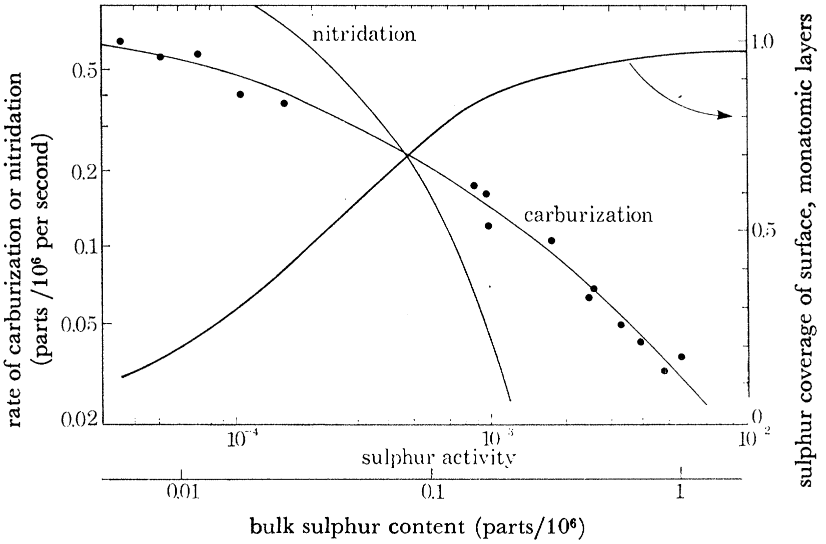

FIGURE 4. Dependence of the initial rate of carburizing or nitriding on the bulk sulphur impurity content and on the surface coverage of sulphur.

In recent work, Grabke *et al.* (1977) followed in detail the effect of the sulphur content of iron on the rate of nitriding or carburizing. The samples were first subjected to a treatment in a known gas mixture of H_2S and H_2 at a given temperature, from which the bulk sulphur activity was determined. The samples were next treated in appropriate N_2–H_2 and CH_4–H_2 mixtures, and the rate of nitriding or carburizing was measured with a sensitive resistivity technique that detects the concentration of atoms dissolved in the thin metal foils. The results, plotted together in figure 4 show that at 850 °C the nitrogen uptake decreases rapidly at a very low bulk sulphur activity of 0.01 μg/g and then continues to decrease rapidly with increasing sulphur content. In the same way, the rate of carburizing depends, but somewhat less strongly, on the sulphur content. By assuming that the rate-controlling step in the pick-up of nitrogen or carbon is the dissociation of the primary molecule, which in turn depends on the area of clean surface exposed, the authors determined the level of sulphur coverage on the surface as a function of bulk sulphur activity: this is also indicated in figure 4. Here we have a remarkable demonstration of how an important industrial process is sensitive to the chemical state of the surface which results from the presence of a bulk impurity.

ADHESION AT METAL–COMPOUND INTERFACES

The next example illustrates the wider understanding brought about by interfacial microchemistry and how this leads to ideas on the synthesis of interfaces of predetermined adhesive strength.

In preparing multiphase materials with particular properties and end uses, it would be valuable to have a theoretical framework that allows the design of interfaces having a particular work of adhesion. There are situations in which a low adhesion would be required, for example, to allow for energy absorption during fracture; on the other hand, good particle–matrix adhesion might be required in a dispersion alloy to prevent particle separation during deformation or to prevent spalling of an oxide from metal surfaces.

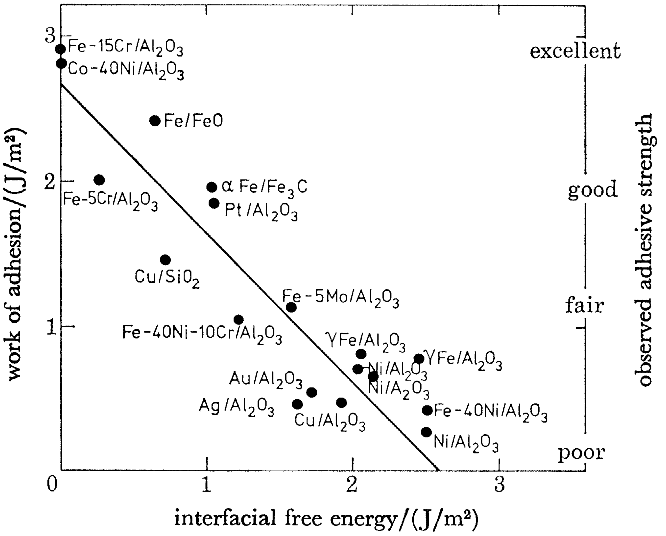

FIGURE 5. The thermodynamic work of adhesion and the practical adhesive strength as a function of interfacial free energy for metal–compound couples.

Basic data from various sources on the interfacial energy between a metal and another phase (generally a metal oxide) have been systematized and presented in figure 5 in terms of the thermodynamic work of adhesion (Hondros 1976). The data have been compiled in a number of ways, for example through measurements on the equilibrium contact angle between a decohered particle and the surrounding matrix. The classical formulation of the Young–Dupré equation, in terms of the algebraic sum of the two surface free energies and the interfacial free energy, was developed strictly for fluid systems. The extension of these adhesion notions to solid phases presupposes ideal adhesion across a planar interface, with atom to atom matching across it. The thermodynamic work of adhesion thus derived may or may not express the practical mechanical strength of the interface.

For the metal–compound pairs for which data are available, assuming a planar interface, the thermodynamic work of adhesion is plotted in figure 5 as a function of the interfacial energy. Within the scatter of the data points, there is a reasonable inverse correlation between the work of adhesion and the interfacial energy. The fact that experimental data from different sources and different systems can be plotted in this fashion suggests that, in general, adhesion does occur across a narrow interface and not at a diffuse chemical zone. The right ordinate shows various ancillary observations on the practical strength of bonding among the various systems. While it is not possible at this stage to quantify these measurements, there does seem to be a fair qualitative correlation between observed adhesive strength and the thermodynamic work of adhesion. Thus, consistent with practice, iron or nickel do not adhere very well to alumina and these have also a low measured work of adhesion. Figure 5 shows that the introduction of chromium in iron lowers the interfacial energy and increases the work of adhesion. Additions of nickel appear to counteract this behaviour.

Such observations can be rationalized in terms of the microchemistry of the metal–alumina interface. Simulated specimens were prepared on flat sapphire substrates, and then debonded on a fracture stage for analysis by Auger electron spectroscopy. Figure 6 shows the concentration profile for chromium in the metal component with distance from the interface. Clearly, chromium is highly enriched at the metal–ceramic interface and the observed strong adhesion is related to chemical bonding of chromium with species on either side. The interface has rearranged into a more relaxed structure as reflected in the lower interfacial energy. Nickel counteracts the effects of chromium presumably by lowering the bulk chromium activity.

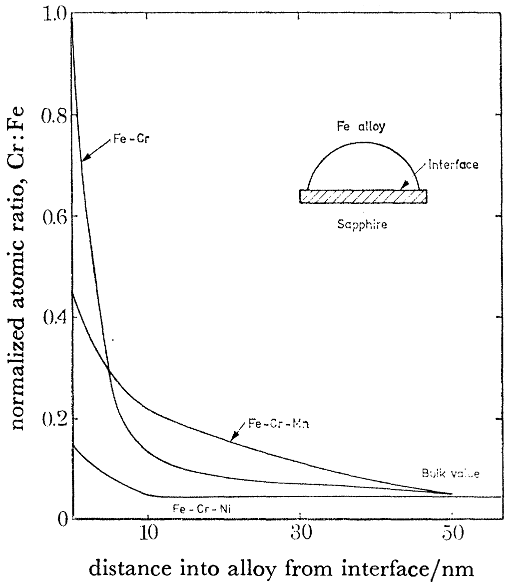

FIGURE 6. Concentration of Cr at the iron alloy–alumina interface and its variation with distance into the alloy. Zero point is at the plane of interface.

In principle it should be possible to introduce surface active species into the system to modify the adhesion. There are several observations in the literature on precipitate coarsening that suggest that surface active species adsorb at precipitate–matrix interfaces, reducing the energy and hence the coarsening rate. The above relation suggests that residuals or additives that adsorb at such an interface should produce strong adhesion since the interfacial energy will be reduced. This should be theoretically possible if the reduction in interfacial energy brought about by the adsorbing species is much greater than the reduction in surface free energies on the two separated components. This approach has not yet been systematically investigated.

The approach of optimizing properties

From what has already been stated, it is evident that the underlying methodology in the research work represented at this Conference is not essentially one of innovating new exotic materials, nor of revolutionizing materials processes: emotive expressions such as 'winner' and 'breakthrough' are not frequently heard in this type of activity. No one should expect sharp, discontinuous changes in the materials sphere arising from these activities, changes of the type that attended the development of stainless steels. The implicit long-term approach here is rather one of an understanding, leading to a better control and improved service performance – in short, a technology which aims to *optimize the properties of existing materials.*

The type of industrial activity and the long-term economic benefits of this approach are illustrated in figure 7 (McLean 1976) which shows the development in efficiency of electricity generating stations since the last war. The overall improvement in efficiency is from 21 to 30 %, most of which derives from improved engineering and plant design. The Carnot contribution is also shown. This relates to the temperature of the point of steam entry to the turbines and represents the efficiency of converting heat energy to mechanical energy. This Carnot contribution is about one-third of the overall efficiency. It is argued that the Carnot contribution is substantially due to improved materials design which allows higher operating temperatures. Research aimed at controlling the detrimental effects of residuals during creep will contribute to further improvements in the performance of such engineering materials.

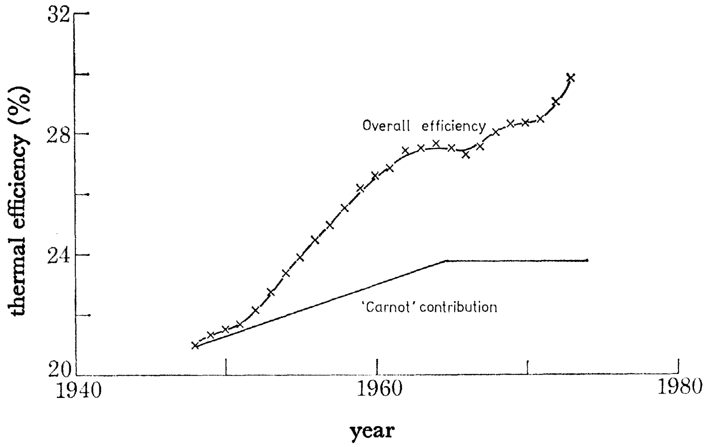

FIGURE 7. Growth in overall efficiency of electricity generating stations. The Carnot contribution is shown.

TABLE 3. AN ASSESSMENT OF INNOVATION ORIGINALITY

	U.S.A.	U.K.	Germany	Japan	France
improvement of existing technology	41	4	36	38	12
major technological advance	31	40	50	54	65
radical breakthrough	27	56	14	8	24

In a recent lecture, Nicholson (1977) stressed his belief that the regeneration of U.K. industry lay not so much in the continuous emphasis on 'big science', but on the benefits of research and development aimed at limited improvements in existing techniques. This view was backed by statistics drawn from a Hudson Institute survey from which table 3 is drawn: this shows that the U.K., while outstanding in 'radical breakthrough' developments in technology, is very weak in the field of innovations related to improvements in existing technology. The scientific and technological activities represented in this Conference are clearly in this field. Positive action to translate the new data into materials practice, both by tightening specifications in bulk impurity tolerance levels and by introducing additive remedial processes, should contribute to restoring the imbalance so lucidly noted by Nicholson.

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