Problems with Residual and Additive Elements and their Control through Specifications

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I. RECYCLING AND COMPOSITION

Problems with residual and additive elements and their control through specifications

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Circumstances responsible for a specification approach to the control of residual elements are reviewed. For deleterious elements, response varies from insistence on 100 % use of virgin materials to setting maximum limits on a large number of residual elements, to specifying the relative quantities of two or more interactive species. For beneficial elements, minima must be set and testing techniques must assure that the desired element is present not only in the proper amount but also in a state and location where its meliorating effects can be realized. Examples from both the alloy and ceramic fields are discussed.

Introduction

Concern about residual elements is not new. Ercker (1580) wrote 400 years ago, 'It often happens that silver is embrittled in remelting, owing either to a harmful smoke or to the unintentional presence of tin from tin-bearing bad groschen† among the billon‡. It can be rendered malleable in the following way....' We may also speculate that the basis for the complaint of one Nanni, almost 4000 years before our time, in a letter (Hawkes 1973) to his copper broker, Ea-nasir of Ur, may also be lack of residual element control: '...you said, "I will give good ingots to Gimil-Sin". That is what you said, but you have not done so; you offered bad ingots to my messenger, saying, "Take it or leave it". Who am I that you should treat me so? Are we not both gentlemen?' Clearly Nanni had need of a better specification!

Why, then, has there been an intensified interest in this subject in recent years? In the writer's view this stems from three current trends: the increasing degree to which many common base materials are recycled, our increasing sophistication in understanding of the degree to, and means by, which practical properties are affected by very tiny amounts of critical elements, and our increasing ability to control composition, often in the parts/10^6 or even parts/10^9 range.

The current U.S. status of recycling in a few base materials is summarized in table 1. Apart from actual materials shortages, real or anticipated, other incentives for increased recycling in the future, at or above the levels shown in table 1, include the energy shortage, the shortage of capital for new plant and equipment, and environmental problems. These factors, singly or in combination, will make it increasingly attractive to recycle material rather than to produce from virgin raw material.

Sophistication in our understanding of the role of trace quantities of elements has come about not only through the steady progress of materials science in general but also by the emerging

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† An old German silver coin.
‡ A coinage alloy consisting of gold or silver and base metal.

Table 1. Extent of recycling in the U.S. for selected base materials

material	percentage of U.S. consumption from recycling of: new and old scrap	old scrap	percentage of old scrap recycled
Pb	42	37	38
Cu	41	23	41
Fe	32†	24†	—
Sn	23	15	—
Zn	21	5	4
Ni	18	15	30
Al	17	7	13
Mg	14	6	—
Hg	—	15	—
W	—	4	—

Source: U.S. Bureau of Mines (1976, 1977).
† U.S. experience for Fe has not changed substantially over the past 25 years.

importance of new fields, highly demanding in materials performance, such as semiconductor technology, biochemistry and nuclear technology. In these new fields, entirely different effects of residuals are often encountered that must be controlled. For example, in nuclear applications stringent limits must be set, even in conventional alloys, on elements affecting neutron economy, e.g. B; on those giving rise to long lasting radioisotopes, e.g. Co and Ta; and on those strongly affecting radiation damage, e.g. Cu. The programme of this very symposium is replete with examples from many fields of both this understanding and its application, but we may also cite other review sources: Schumacher (1950), Strauss (1953), A.S.M. (1957), A.S.T.M. (1962, 1967) and Holt & Wallace (1976).

Enhanced compositional control has come about through the introduction of completely new processes such as vacuum melting, ion exchange purification, ion beam deposition and zone refining; through automation and computer control of even conventional processes; and

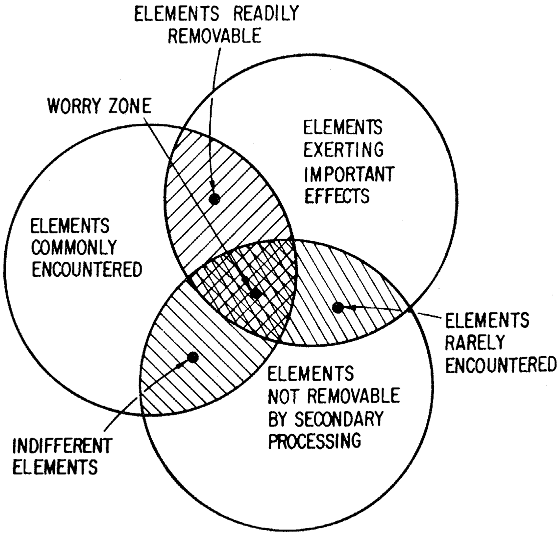

Figure 1. Preliminary identification of residual elements for consideration for specification control.

through adoption of ever more powerful analytical techniques such as emission spectroscopy, mass spectroscopy or atomic absorption methods.

The reflexion of such developments in specifications forms the subject of this article. Elements to be subjected to specification control are not necessarily defined by our processing and analytical capabilities. Considering only recycled materials, we may focus attention on a selected group of residual elements by examination of the Venn diagram of figure 1. Here we have represented: our knowledge of the physical metallurgy of residual element effects, that of the process metallurgy of secondary recovery, and of the origin of compositional alteration during recycling (i.e. accumulations of foreign elements in service, contamination in mixing of charged material, difference sources of ore or other raw material, or alterations due to the processing itself). Good specification practice will restrict requirements to those elements *only* that form that common set in the centre of the diagram pertinent to the particular alloy and application at hand.

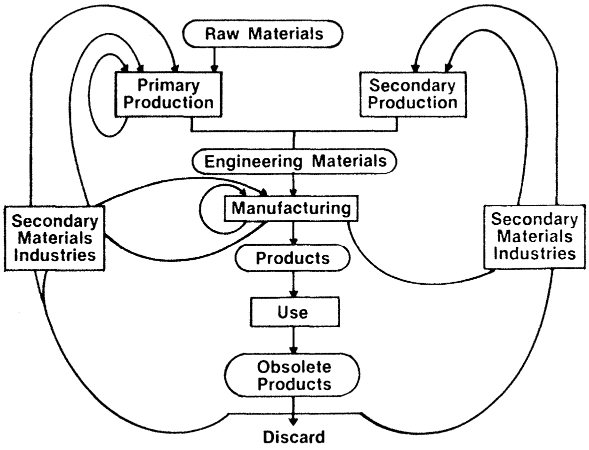

FIGURE 2. Flow in the materials cycle (after Bever 1977).

We must also recall that effective control of residuals or additives may be imposed at various places in the total materials cycle (see figure 2) other than on the end-use material, for example on raw materials, on process materials, on secondary materials (scrap and processed intermediates) and on the materials processing itself. In cases where analysis is difficult or where performance is affected by interaction between several elements or interaction between trace element composition and some other factor such as microstructure, it may be more effective to control residuals or trace additives other than through specification requirements on the compositional limits of the critical elements. We include here such approaches as specification of performance parameters, processing limitations, or of the microdisposition or chemical state of critical elements. In later sections of this article I give examples of many of these techniques of residual control. It must be emphasized, however, that all approaches are not generally applicable; each situation must be studied carefully to determine which approach will give the most effective and most economic control. A specification that excessively demonstrates the erudition of the writer, that includes too many or too severe restrictions, will usually be counterproductive. Problems in writing effective compositional specifications and the reasons for the surprisingly frequent absence of compositional specifications are discussed in later sections of this paper.

TIME TRENDS

The increased amount of recycling occurring and the changes in the mix of material being recycled have given rise to concern about residual build-up with time. These subjects cannot be examined in detail for all materials, but it may be instructive to review some recent reports on steel (Kaplan 1975; Duckett 1977; Stephenson 1974). In this instance attention centres on elements such as tin because, as in the scheme of figure 1, tin is not removed in steel processing, it is a significant component (0.1–0.4 %) in the ferrous content of municipal solid waste (m.s.w.) which is increasingly promoted for recycling, and it does have deleterious effects on critical properties such as hot shortness, ductility and toughness (Duckett 1977; Stephenson 1974). Figure 3 shows the results of several surveys of the American steel industry with regard to the metallic residual elements of most concern (D. J. Blickwede 1978, personal communication). Except for chromium, the other elements, Cu, Sn and Ni, do not exhibit levels greater than their historic maxima. However, at the time of the most recent survey shown in figure 3, no significant input of m.s.w. had yet entered the ferrous materials cycle. Kurakhtanov *et al.* (1965) and Laycock & Winfield (1976) indicate, however, more alarming trends in residual build-up in Russian and British steel respectively than in the American experience just cited. Whether this is due to differences in steel making practice or to differences in the charged material is difficult to say.

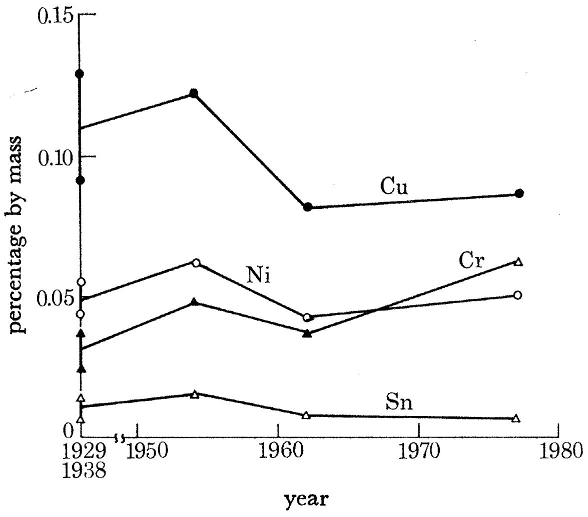

FIGURE 3. Time trends in residual elements in U.S. steel (AISI Survey).

Duckett (1977) has reported on the results of a geometric progression model which permits calculation of maximum residual tin concentration in steel given the average tin content of magnetics from m.s.w. (*ca.* 0.3 %) and the scrap charging rates in the steel-making furnace. Some typical results of the application of this model are shown in figure 4. It is concluded that with reasonable assumptions about recovery and charging rates the steady-state build-up of tin would, on average, be within specification limits for all but the most critical applications; heat-to-heat variations, however, might cause problems.

Although the average contents of Al and Zn in steel scrap are also building up with time (because of increasing substitution in the automotive industry of Al for steel for mass saving and of galvanized steel for untreated carbon steel for corrosion resistance), these pose no serious

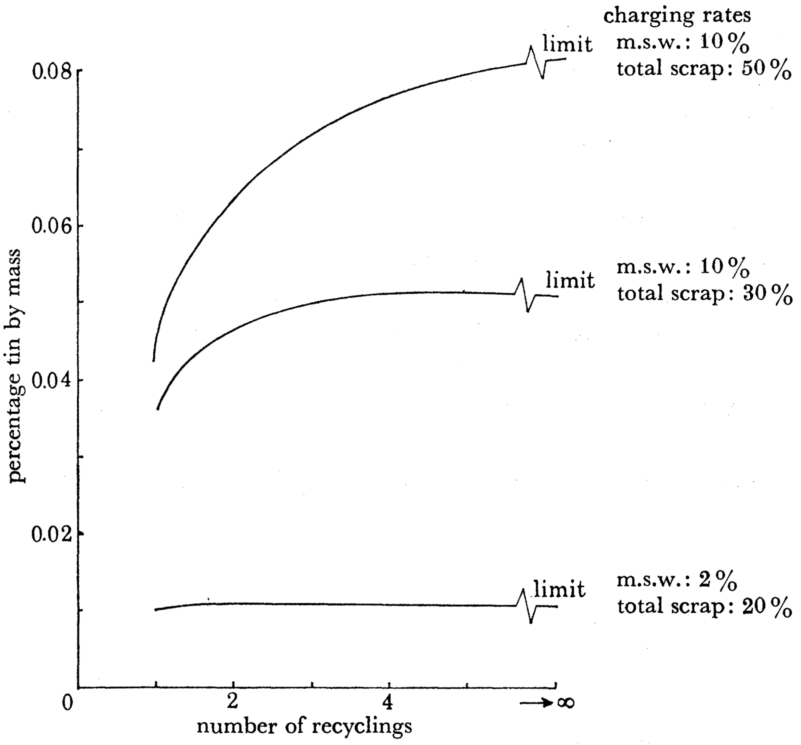

Figure 4. Results of modelling calculations for tin buildup in steel due to reuse of municipal solid wastes (m.s.w.) magnetics in combination with other purchased scrap (after Duckett 1976).

problem in carryover to the product steel. Aluminium and zinc, as well as lead, largely partition to fume, slag or an insoluble pool in the furnace and do not dissolve in the steel; hence they pose problems to the steel maker, though not the steel user.

Use of specifications at various points in the materials cycle

Before examining more esoteric instances of the use of specifications to control residuals and additives, and hence critical properties, it will be well to review some typical cases where specification of the residual content effectively defines the alloy type itself. We shall consider first the 356 aluminium alloy (UNS A03560) and its derivatives. These are 7 % Si, 0.3 % Mg compositions whose properties are affected by certain of the residual elements as shown in table 2. The lower level of impurities (particularly Fe) called for in A356 relative to 356 significantly improves the mechanical properties, especially elongation and impact strength, and as well conveys an improved corrosion resistance. Alloy 357 (UNS A03570), with slightly

Table 2. 7.0 Si, 0.3 Mg aluminium casting alloys

(Maximum percentage by mass unless range is stated.)

	UNS									others	
alloy	number	Si	Mg	Ti	Be	Fe	Cu	Zn	Mn	each	total
356	A03560	6.5–7.5	0.20–0.40	0.25	—	0.60	0.25	0.35	0.35	0.05	0.15
A356	A13560	6.5–7.5	0.20–0.40	0.20	—	0.20	0.20	0.10	0.10	0.05	0.15
357	A03570	6.5–7.5	0.45–0.60	0.20	—	0.15	0.05	0.05	0.03	0.05	0.15
A357	A13570	6.5–7.5	0.40–0.70	0.1–0.2	0.04–0.07	0.20	0.20	0.10	0.10	0.05	0.15

Source: the Aluminum Association.

higher Mg content and still greater reductions in iron as well as in other residual elements as shown in table 2, shows further improvement in properties, but naturally at higher cost. The related alloy, A357, utilizes a trace of Be for higher strength values without loss of toughness, but tolerates the same residual levels as 356. It is also to be noted that, since the iron content can only be lowered by dilution, any recycling has to be in the direction A356 → 356 → 356 (secondary). Such alloys are also frequently modified with trace additions of sodium or strontium to counteract high residual phosphorus, which tends to cause formation of a coarse acicular eutectic structure, and thus to ensure the desired fine fibrous structure (Scolliet & Gerat 1978).

Another very different example is afforded by the MgO powder insulation in the familiar metal-cased, nichrome, heating elements used in both domestic and industrial applications (M. Borom 1978, personal communication). Some typical specification chemistries are shown in table 3. While physical characteristics of the powder are also essential to adequate performance, long life and service temperature capability are primarily defined by the residuals and additives.

TABLE 3. MgO INSULATION FOR METAL-CLAD NICHROME HEATING ELEMENTS

GE grade ...	12708	12707	12702
application range ...	low temp.	medium temp.	high temp.
composition			
SiO_2 (max. % by mass)	no	3.8	3.0
CaO (max. % by mass)	compo-	1.9	1.2
Fe_2O_3 (max. % by mass)	sitional	0.2	0.08
R_2O_3 (max. % by mass)	limi-	0.3	0.2
B (typical, parts/10^6)	tation	300	20
specific impedance/MΩ m			
at 750 °C	0.025	—	—
at 875 °C	—	—	5.08
at 975 °C	—	0.011	1.52

Source: Product Data Specifications of General Electric Chemical Materials Department.

Raw material sources are limited to a few natural deposits. Calcia, and especially boron, must be kept low to avoid formation of a glassy phase which leads to sintering and hence cracking of the oxide during element formation, and eventual 'hot spots' and premature failure. High residual iron degrades the resistivity and must be kept low; Fe^{2+} is more damaging than Fe^{3+} so a final oxidizing heat treatment is a standard part of the processing regimen. Although there is no effective means of eliminating boron, small additions of silica bind calcia and reduce its deleterious effects. What a world of complex chemistry in a homely, utilitarian device!

Figure 5 shows the pronounced effects of certain additives and their interaction with residual sulphur at very low concentration levels on the high temperature stress–rupture properties of nickel. In the late 1950s this effect was discovered almost accidentally when the markedly improved behaviour of certain superalloy melts was associated with pickup of boron and zirconium from the ceramic crucibles used. Today these elements, usually in combination, are *specified* constituents of most nickel-based superalloys (B in the range 0.005–0.05 %, Zr from 0.03 to 0.1 %). The mechanism of the effect is still not fully understood, but clearly a grain boundary phenomenon is involved which operates to counteract the embrittling effect imparted by sulphur impurity present. Boron and zirconium can give similar effects if added individually, but they behave somewhat in a complementary fashion so that the best results are achieved when they are employed in combination. Both, however, must be controlled within rather narrow limits as excess amounts of either additive quickly degrade properties.

Other instances where specified amounts of trace additions have substantial effects on practical properties may also be cited. Grain size stabilization in platinum is achieved by additions at parts/10^6 level of zirconium in the powder metallurgical processing of the material (Selman *et al.* 1974). The desired 'non-sag' grain structure of tungsten lamp filaments is achieved by minute additions of K, Si and Na (Snow & Dunham 1975). In the welding field, freedom from cold cracking of 960 MPa weld metal deposited from gas metal–arc bare wire electrodes can be assured if the hydrogen content is kept below 3 parts/10^6 (Gross 1968). The toughness of an HY-130 (T) weld metal is optimized when it contains about 0.012 % Ti (Dorschu & Lesnewich 1964).

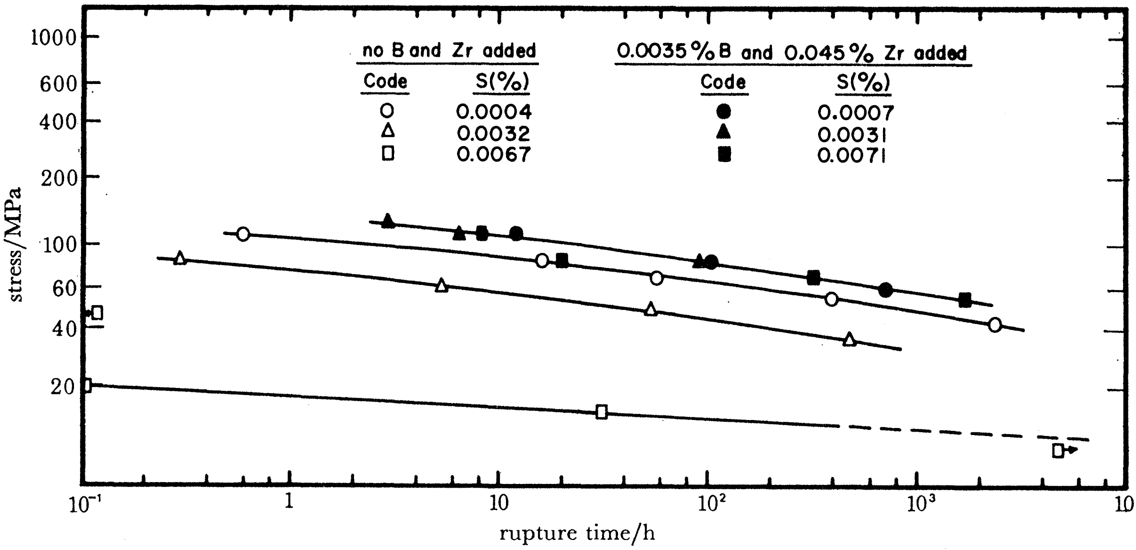

FIGURE 5. Effects of residual sulphur and its interaction with boron and zirconium additions on the 650 °C stress–rupture behaviour of nickel (after Schultz 1965).

In the instances so far discussed the intent of the specification is to control the properties desired in the product material to optimize its application. We may, however, look forward to a day, with recycling even more prominent than it is now, when specifications may be written solely to improve the recyclability of the material even when there is not benefit to application properties. It has already been suggested that it may be useful to make certain parts from a nickel-based alloy rather than a nickel plated steel. The alloy part would be separable and recyclable, the nickel plate cannot be economically recovered and may even be detrimental if allowed to enter the recycle materials flow.

Curiously we even encounter instances of specifications for additives, written not because they are essential to performance but because the markets served by the products in question have come to expect them. Varnishes used as a substitute for tin plate for food canning now are being made with a small content of tin powder to restore the familiar 'tin taste' (Robins 1978). The Prime Western grade of zinc normally contains of the order of 1 % Pb. Secondary zinc recovered by the electrolytic process must therefore be adulterated with Pb to serve markets accustomed to Prime Western grade (A. W. Blackwood III 1978, personal communication).

Inference has already been made in the previous section that the secondary smelter may take a different approach to specifications. He may use 'origin' type specifications. He may write compositional specifications for the scrap he purchases for remelt and he may be working to produce a secondary product to meet the specification demands of his market. Take for example the secondary aluminium industry. Ginsburg (1972) has stated that its products were then consumed 60% by die casters, 25% by permanent mould and sand casters, 10% by steel mills for deoxidation and 5% by zinc alloy producers for hardening purposes. Not only do each of these consumers of secondary aluminium have different requirements as far as residuals are concerned, but the secondary smelter is also constrained by the nature of his incoming material.

Table 4. Tentative chemical composition limits (percentages by mass) for recovered aluminium compared withselected alloys and typical Al fraction from incinerated refuse

	grade						3004	380	384	incin.
element†	1	2	3	4	5	6	A93004	A03800	A03840	refuse
Si	0.30	0.30	0.50	1.00	9.00	9.00	0.30	9.5	11.5	1.05
Fe	0.60	0.70	1.00	1.00	0.80	1.00	0.70	2.0	1.3	0.65
Cu	0.25	0.40	1.00	2.00	3.00	4.00	0.25	4.0	4.0	0.25
Mn	1.25	1.50	1.50	1.50	0.60	0.80	1.50	0.50	0.50	0.45
Mg	2.00	2.00	2.00	2.00	2.00	2.00	1.30	0.10	0.10	0.05
Cr	0.05	0.10	0.30	0.30	0.30	0.30	—	—	—	—
Ni	0.04	0.04	0.30	0.30	0.30	0.30	—	0.50	0.50	—
Zn	0.25	0.25	1.00	2.00	1.00	3.00	0.25	3.00	3.00	0.20
Pb	0.02	0.04	0.30	0.50	0.10	0.25	—	—	—	0.10
Sn	0.02	0.04	0.30	0.30	0.10	0.25	—	0.35	0.35	—
Bi	0.02	0.04	0.30	0.30	0.10	0.25	—	—	—	—
Ti	0.05	0.05	0.05	0.08	0.10	0.10	—	—	—	—
others, each	0.04	0.05	0.05	0.08	0.10	0.10	0.05	—	—	—
others, total	0.12	0.15	0.15	0.20	0.30	0.30	0.15	0.50	0.50	—
Al	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.

Source: A.S.T.M. Subcommittee E-38.03, November 1977, and EPA Report no. 670/2-75-034, 1975.

† By agreement between purchaser and producer, analysis may be required and limits established for elements or compounds not specified above.

Although some secondary smelters have been dedicated to processing a certain type of scrap, e.g. containers, the more usual secondary aluminium smelter must do his best by sorting and blending various types of scrap to produce the highest grade of product at the least cost. He can fairly readily produce casting grades such as 380, which are relatively high in Si, Cu and Zn, but he has considerable difficulty in meeting the specification requirements of a wrought grade such as 3004 (UNS A93004) for beverage can stock. As a consequence of this situation and reflecting the increased interest in recycling, it has been reported (Alter 1978) that A.S.T.M. Committee E38.03 has recently proposed specification limits for six grades of recovered aluminium as shown in table 4, where they are compared with the limits for typical wrought and cast alloys and a typical analysis of aluminium recovered from incinerated municipal waste. Grades 1–4 are a hierarchical categorization of specifications (with increasing limits on both

Table 5. Proposed maximum allowable concentrations (percentages by mass) of residuals for various ferrous secondary markets

element	iron and steel†	foundry	ferroalloy
C	—	—	0.06
P	0.03	0.03	0.03
S	0.04	0.04	—
Si	0.10	—	—
Mn	—	—	0.35
Ni	0.08	0.12	—
Cr	0.10	0.15	0.15
Mo	0.025	0.04	—
Cu	0.10	0.20	0.20
Al	0.15	0.15	0.15
Sn	0.30	0.30‡	0.30
Pb	0.15	0.03	—
Zn	0.06	0.06	—
Ti	—	—	0.025

† Incinerated scrap will probably not meet these requirements, particularly with regard to Cr, Cu and Al.
‡ 0.10% maximum for steel castings.

alloying elements and residuals) mostly intended for recycling into wrought grades, whereas grades 5 and 6 are suited for casting compositions of the Si–Cu and Si–Cu–Zn types respectively.

Let us turn now to consideration of secondary ferrous materials. Again, A.S.T.M. Committee E38 (Alter 1978) has proposed some tentative specifications, as shown in table 5. Against these may be set some recent experience in recycling such materials. Daellenbach *et al.* (1976) reported on the production of cupola grey iron from mixtures of automotive and refuse scrap. Residuals of Ni (0.11%), Mo (0.019%) and Cr (0.08%) in automotive scrap were decreased

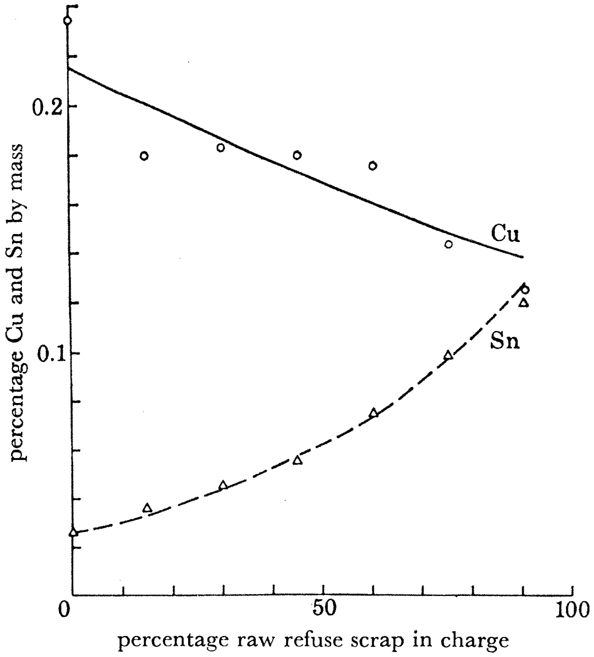

Figure 6. Residual levels of Cu and Sn achieved in cupola grey iron with the use of refuse and automotive scrap (after Daellenbach *et al.* 1976).

by admixtures of refuse scrap. Al in refuse scrap of the order of 1 % was reduced to levels of 0.033–0.059 % by oxidation and loss to slag. Pb and Zn in the recycled product were nil as a result of oxidation and vaporization. The trade-off between high residual tin in refuse scrap and high residual copper in automotive scrap can be exploited by using a mixed charge to the cupola as shown in figure 6. Under these circumstances there seems to be no difficulty in meeting most grey iron specifications with regard to residuals.

TABLE 6. COMPOSITION (PERCENTAGES BY MASS) OF STEEL INGOTS AS PRODUCED FROM VARIOUS SOURCES†

	C	Mn	Si	Cu	Sn	Cr	V	Ni	Pb	Al‖
starting material for Corten B										
purchased‡	0.14	1.13	0.23	0.31	< 0.01	0.40	0.04	0.03	< 0.02	0.05
prime scrap	0.14	0.83	0.08	0.38	< 0.01	0.97	0.09	0.04	< 0.02	0.19
incinerated scrap	0.18	0.75	0.08	0.23	0.15	0.43	0.02	0.07	< 0.02	0.24
starting material for 1030 carbon steel										
purchased§	0.31	0.70	0.20	0.03	< 0.01	0.02	< 0.01	0.02	0.02	0.01
prime scrap	0.36	0.88	0.08	0.06	0.01	0.07	¶	0.03	0.02	0.21
various scrap mixtures	0.19–0.48	0.31–0.79	0.04–0.12	0.06–0.21	0.04–0.37	0.06–0.12	< 0.01	0.04–0.21	0.02–0.11	0.20–0.25

† P < 0.02 %, S < 0.05 %. ‡ U.S. Steel. § National Steel. ‖ Al is high because of deoxidation practice used in experimental melts. ¶ Not detected.

Similarly, investigators at the U.S. Bureau of Mines (Cramer & Makar 1976) have produced both carbon steel for reinforcing bar and a typical high strength low alloy steel (Corten-B) from ferrous can scrap and mixtures of prime scrap with incinerated, non-incinerated and detinned, and non-incinerated and non-detinned scrap. The analysis of the products obtained showed the values listed in table 6 for the principal residual metals where the range represents the extremes encountered for all combinations of charge investigated. While these values are in excess of the standard specifications for 1030 carbon steel (UNS G10300) and Corten-B, properties were not

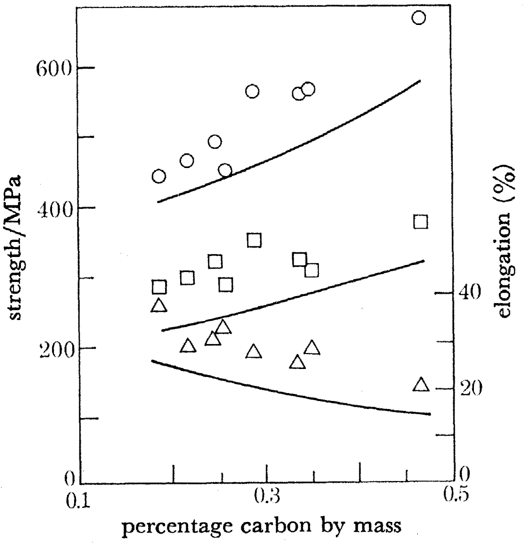

FIGURE 7. Properties of $\frac{1}{2}$ inch (1.3 cm) 1030 carbon steel made from can scrap (points) and typical specification values (curves): ○, tensile strength; □, yield strength; △, elongation. (After Cramer & Makar (1976).)

degraded, as shown in figure 7. The Cu, Sn, Cr and Ni residuals have somewhat improved tensile values by solid solution hardening, impact properties were found to be unimpaired, and atmospheric corrosion values actually improved slightly by the residual tin. On the other hand, other investigators have encountered high temperature embrittlement induced by tin and which is aggravated at high copper levels. British experience (Melford 1966; Menter 1972) suggests that in mild steels of this type, residuals specification should call for $Cu + 8\ Sn < 0.4\,\%$ and $Cu/Sn > 4.0$.

We have thus far spoken of specification control of residuals in terms of its application to end-use material or in the secondary materials industry. Specifications may also be effective in residual control when applied in primary processing. That is, the specification is written to bear upon raw materials such as ores, slag additions and inoculants or upon processing materials such as fuels, atmospheres or refractory brick. Thus, although it has to date been unnecessary to set limits to the arsenic content of U.S. and Western European steels because the content of ores is well within the usual tolerance level of 0.1 %, this is not so in the U.S.S.R. The Russians have found it necessary to limit As to 0.08 % in many of their carbon steels because, with their ores, contents as high as 0.15 % may be encountered, as seen in table 7. Other instances of specifications in primary processing may also be cited. The detrimental effects of high S and high V in certain fuels may proscribe them from use in metal processing. One source of fluorspar is preferred over another in steel melting because of a lower Sb content. Fire-clay brick for aluminium remelting furnaces must be free of significant amounts of iron oxide, otherwise the reducing action of the molten aluminium will cause iron to be incorporated in the metal. In general where compositional control of refractories is inadequate, resort may have to be made to specifying melting of 'wash' heats in a furnace, ladle or crucible before introducing production material.

TABLE 7. ARSENIC IN STEEL (PERCENTAGES BY MASS)

country of origin	range of arsenic
U.S. and Canada	0.018–0.028
Britain	0.020–0.054
Japan	0.026–0.093
Germany	0.05–0.06
Russia	0.03–0.15

SPECIFICATION APPROACHES OTHER THAN BY DIRECT LISTING OF THE COMPOSITIONAL LIMITS OF THE CRITICAL ELEMENT

Frequently it will be more effective, or at least more economic, to control the effects of residuals and additives other than by compositional specification directly. A few examples may make this clearer.

Adverse effects of residual elements are often exacerbated at high strength levels. Mulford *et al.* (1976*a*) show such an effect of phosphorus in a NiCr steel in figure 8. In this instance, a specification limiting the maximum hardness to about 250 diamond pyramid hardness would effectively ensure that the transition temperature was below room temperature regardless of phosphorus content.

Because of the pronounced interactive effects between elements even at the very low levels typical of residual and additive elements, compositions are often specified in terms of ratios rather than absolute levels. Thus in Nb-stabilized stainless steels the Nb level may be specified as '8 × C content minimum, 1.0 % maximum.' Such a procedure ensures that essentially all the carbon is tied up as NbC, leaving none to precipitate as $Cr_{23}C_6$, degrading the intergranular corrosion resistance. Again the surface hot shortness of copper-bearing mild steel, aggravated by residual contents of Sn and Sb, according to the findings of Melford (1966), can be controlled by holding $Cu + 6\,(Sn + Sb) < 9/E$ where E is an enrichment factor defined as the ratio of the average concentration of the residual in the oxide subscale to the bulk residual concentration.

Many of the adverse effects of residual elements manifest themselves through some type of embrittlement. It is therefore common for specifications to include some performance test of deformability in addition to a compositional requirement. Seamless steel tubing forms a case in point where we find, 'Tubing shall be capable of being flared without formation of cracks or other visible defects... The specimen shall, at room temperature,... produce a flare having the permanent expanded outside diameter specified in the following table.'

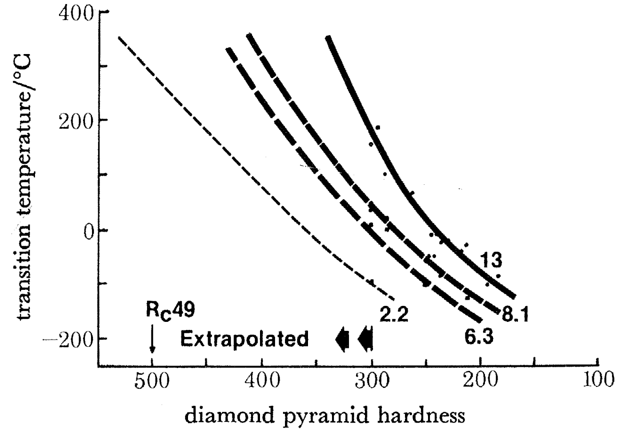

FIGURE 8. Effect of strength level on the embrittling effect of phosphorus in a NiCr steel at various grain boundary concentrations of phosphorus (given in atomic percentages) (after Mulford *et al.* 1976*a*).

In cases where the nature or source of the deleterious contaminant is ill-defined but where the material purchaser has been able reliably to distinguish good material from bad by association with the material vendor or one of his suppliers, the purchaser may restrict in his specification the approved vendors and/or their sources of raw materials.

A type of specification extensively used by the secondary materials industry is the 'origin specification'. Such specifications both describe the material and frequently its prior application form, and thus define its source and limits of principal contaminants. Origin specifications are essential for 'prompt' and 'home' scrap and are especially applicable where hand sorting is feasible. The U.S. National Association of Recycling Industries, Inc., has, for example, some 47 different origin specifications for copper-based alloys (N.A.R.I. 1977). Two of these are:

'*New yellow brass rod ends*

Shall consist of new, clean rod ends from free turning brass rods or forging rods, not to contain more than 0.30 % tin and not more than 0.15 % alloyed iron. To be free of Muntz metal and naval brass or any other alloys. To be in pieces not larger than 12 inches [30.5 cm] and free of foreign matter.

Mixed unsweated auto radiators

Shall consist of mixed automobile radiators, to be free of aluminium radiators, and iron finned radiators. All radiators to be subject to deduction of actual iron. The tonnage specification should cover the gross weight of the radiators unless otherwise specified.'

Processing limitations may be specified because of their association with improved control of composition (with respect to both residuals and additives), homogeneity, or other factors. Thus specifications for premium quality steels, ball bearing or aircraft grade, may require, over and above a compositional requirement, that 'the material shall be made by a vacuum melt process' or 'the steel shall be made by the consumable electrode melt process'. In another instance a customer may specify electrolytically refined rather than chemically refined or fire-refined copper because of his empirical experience even when he cannot identify a compositional correlation with service behaviour; or process specifications may be required as well as compositional specification with respect to a trace additive in order to ensure its retention in an effective state.

Sometimes control of residuals in the end product is assured by control of the composition of processing materials with which the material for application may have come in contact at some stage of its synthesis, processing, fabrication or testing. Thus we find specifications written on residual control of such substances as furnace linings, slags, deoxidants and inoculants, furnace atmospheres, welding fluxes, lubricants, cleaning agents and hydrostatic test fluids. For example, lubricants containing significant amounts of sulphur, lead, bismuth and selenium may be banned because of the ease with which such elements penetrate grain boundaries of stainless steels and nickel-based alloys and cause loss of ductility or corrosion resistance. In another instance in fuels used during the heat treatment of nickel-based alloys, the sulphur content 'shall be limited to 0.5 % sulphur maximum for oils, and 30 grains of sulphur maximum per 100 cubic feet [2.8 m^3] for gaseous fuels'. Again the presence of sulphur in the alloy impairs both toughness and corrosion resistance. As another instance of specification control for processing materials, drawing lubricants used for producing arc welding electrodes must be free of calcium so as not to degrade the stability of the arc during welding.

The effects of some contaminant species are so severe that the only effective control may be an absolute ban on the presence of any materials containing them from the plant in question. Such is frequently the case for Sn, Pb and Cd in zinc-based die casting plants.

PROBLEMS WITH COMPOSITIONAL SPECIFICATION CONTROLS

It is not as straightforward as it might seem to impose a cost-effective control of residuals and additives by setting maxima or minima or both for selected elements. If the limits set are too stringent, not only will the material be more expensive but the available sources for the material may be unduly restricted. An illustration of this is afforded by figures cited by Goller (1967) on the cost of restriction of cobalt in steels for nuclear application, as shown in table 8. Apart from costs, blindly setting restrictive limits on all elements other than major alloying additions may inadvertently exclude the beneficial effects (possibly unrealized) of certain elements. Finally reducing the margin between the specification and the production target increases the risk that an acceptable product will be unjustly rejected because the test procedure gives results that vary from laboratory to laboratory.

The latter point underlines the need for good standard samples and for well documented, reliable test methods. This matter has been of considerable concern in the U.S. superalloy industry and resulted in the formation of an A.S.T.M.–A.S.M.E. Task Force on Trace Elements. This body enlisted the cooperation of some 28 laboratories in the synthesis and analysis of 'Tracealloy', a superalloy standard. The results of this effort have been described by Cremisio *et al.* (1977). The base composition chosen was essentially IN 738 + Hf and was doped with Pb, Bi, Tl, Te, and Se in the range 0.5–10 parts/10^6. Analytical results obtained by the 28 laboratories on the remelted doped material indicated good homogeneity of the samples and remarkably good reproducibility and modest coefficients of variation in view of the low levels of the elements analysed and differences in analysis technique and equipment among participating laboratories. Effort is now underway to obtain NBS certification as a standard reference material.

TABLE 8. INFLUENCE OF COBALT RESTRICTION ON RELATIVE PRICE OF STEEL

max. percentage Co by mass	1958	1966
0.20	1.0	1.0
0.10	1.1	—
0.05	2.0	1.1
0.01	—	3–5
0.005	5–7	—

Concern for this problem is also reflected in the generation of an SAE Specification AMS 2280. This document is intended to be invoked for selected high stress applications as a supplement to the normal materials specification. It is composed of four subclasses according to whether limits are specified for Pb and Bi alone, in combination with Se, Te, and Tl, in combination with certain other elements, or in combination with Se, Te, Tl and the same group of other elements. The maximum limits (in parts/10^6) in all cases are: Bi, Te, 0.5; Se, 3; Pb, Tl, 5; the elements Sb, As, Cd, Ga, Ge, Au, In, Hg, K, Ag, Na, Th, Sn, U and Zn all to be under 50 each and less than 400 in total. The tellurium value in particular is near the limit of reliable analysis as found in the Tracealloy study (0.68 ± 0.52 part/10^6).

Other problems with specification control of residuals relate to the distribution of the element, which cannot be ascertained from a bulk analysis. Not only can interdendritic, grain boundary, or surface segregation of residuals give enormous concentration ratios (hundreds or thousands), but, depending on the property in question, some of these sites may pose far more hazard than the same concentration isolated in bulk material. With the recent development of Auger electron spectroscopy it is now possible, in principle, to specify compositional limits on grain boundary surfaces rather than averaged over the whole polycrystalline material. To the best of the author's knowledge, however, this type of requirement has not yet been written into a commercial specification. The Auger technique has, however, shown the enormous enhancement of the concentration of residuals at grain boundaries and demonstrated that segregation of a given residual is affected by alloying elements present, as seen in figure 9. Thus, even in the absence of direct specification control on grain boundary composition, benefit may be derived indirectly by lowering the upper levels allowed in bulk materials for those elements demonstrated to segregate strongly.

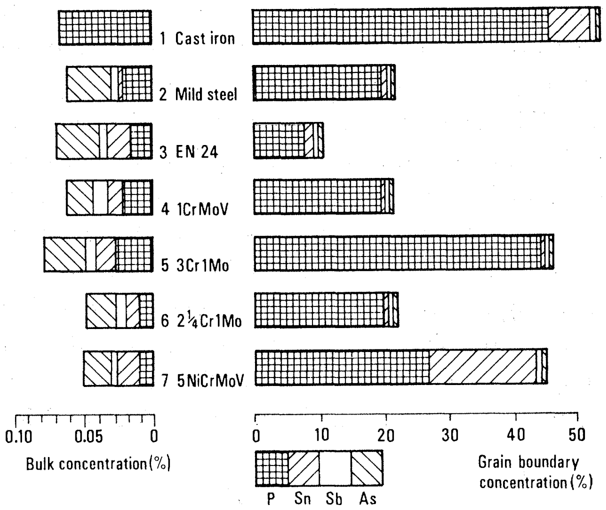

Figure 9. Comparison of the concentration of four principal residual elements in common commercial steels at the grain boundaries and in the bulk material (after Hondros *et al.* 1976).

Some analytical techniques do not adequately identify the state of the element in question and this may make all the difference. Iron impurity in tough pitch copper is usually present as an oxide, in which form it is relatively innocuous. That same concentration in OFHC copper, however, will be in solid solution where it could impair the electrical conductivity substantially. Nor will bulk chemical analysis reveal the morphology of a second phase with which a trace element may be associated. Sulphur in the form of a grain boundary film or long thin stringers of sulphide may be disastrous to the performance of an alloy; but coalesced into isolated spheroids it may be quite harmless. Many beneficial effects of trace additives in counteracting the deleterious effects of residuals such as sulphur are realized through just such a mechanism of morphological change.

The temper embrittlement problem (Mulford *et al.* 1976*a*, *b*; Capus 1962; Newhouse & Holtz 1968) will illustrate the fact that fixing a maximum level of residual may not be an effective control in all situations. Figure 10 (Capus 1962) shows the variation of ductile–brittle transition

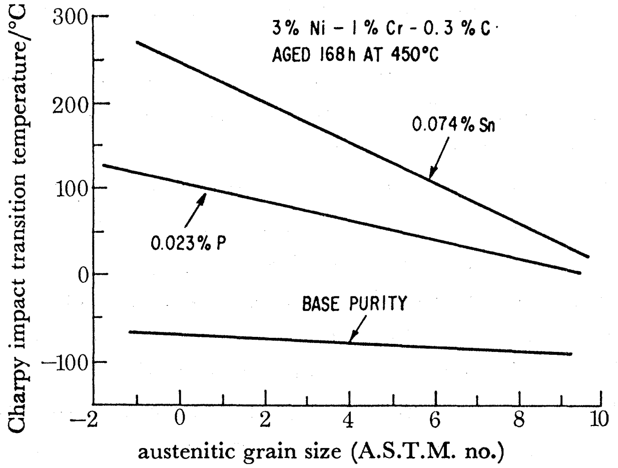

Figure 10. Effect of austentic grain size on temper embrittlement of a NiCr steel at three purity levels (percentages by mass) (after Capus 1962).

temperature with austenitic grain size at a fixed hardness level and different contents of the embrittling species P and Sn. It is clear that concentrations that might be tolerable at fine grain sizes are extremely embrittling at coarse grain sizes, presumably owing to a concentrating effect on these boundary segregants. The presence of certain alloying elements can also affect the level at which a residual element becomes seriously embrittling. Work on turbine rotor steels (Newhouse & Holtz 1968) has shown that Ni and Cr *in combination* considerably exacerbate the embrittling effect of phosphorus as shown in figure 11, even at comparable grain size and strength level.

There are also interaction effects between the residuals or additives themselves to be considered. Ortner & Lassner (1977) have shown with Auger analyses that the grain growth reduction in tungsten imparted by phosphorus segregation to grain boundaries is profoundly affected by co-segregant species such as Ca, Ba, Si, N and O. Schelling (1967) has demonstrated the interaction effects of residuals and additives with the Mg inoculant on graphite spherulite formation in nodular iron as seen in figure 12. It is to be remarked that nodular iron specifications generally are in terms of mechanical property or microstructural requirements rather than on details of chemical composition.

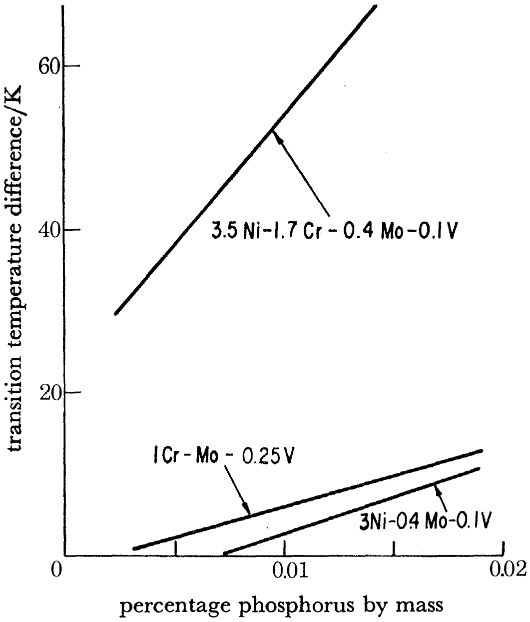

FIGURE 11. Effect of major alloying elements on phosphorus induced step-cooled temper embrittlement of forging steel, relative to the water quenched condition (after Newhouse & Holtz 1968).

Interaction effects between residuals can obtain even at startlingly low concentrations. An example is afforded by observations of grain boundary hardening in high purity alloys doped with selected additives (Aust *et al.* 1968). Such hardening phenomena have been shown to correlate with embrittlement, grain growth inhibition, corrosion cracking and other macroscopic properties. Table 9, for zone-refined lead, shows the effects of additions of gold or calcium at 1 part/10^6, singly or in combination, on grain boundary hardening. The neutralizing effect of the calcium addition is astounding to say the least and both warns against too facile definition of active levels of residual elements and illustrates the possible opportunity for beneficial application of additives if the pertinent species can be properly identified.

Finally there are frequently strong interactions between processing method and trace elements that must be considered in writing specifications for control of residuals or additives. A few examples (A. W. Blackwood III 1978, personal communication) may make this clearer. The maximum allowable Pb content is lower for copper that is to be rolled and welded to form tubing than for copper to be processed to tubing by extrusion because of the need to avoid cracking during rolling. Environmental considerations forced a change from horizontal retorting to electrolytic processing of secondary zinc. The latter process fails to remove traces of residual chlorine from skimmings recovered from galvanizing baths and the electrolyte eventually becomes poisoned; hence the requirement for a new specification. Galvanizing steel was formerly made from rimmed or aluminium-killed steel. The continuous casting process now used for the production of such stock employs silicon-killed steel, and it has now become desirable to set a maximum silicon content in the steel in order to assure good reactivity in the subsequent hot-dip galvanizing process. Retention of critical volatile additives in welding rod may require the adoption of a hyperbaric welding process. Thus in all instances the critical level of the trace addition or residual is not uniquely associated with the base material, but is also tied to the particular processes involved, either in primary production, secondary recovery or application processing.

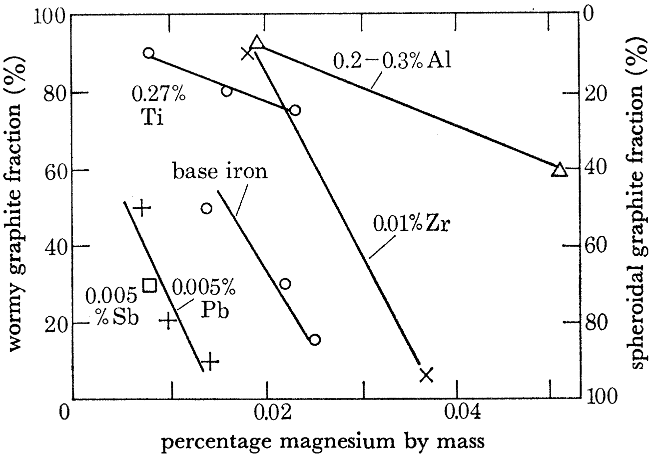

FIGURE 12. Effect of trace elements on graphite morphology in Mg/Ce treated ductile iron (after Schelling 1967).

TABLE 9. MICROHARDNESS (MEGAPASCALS) OF DOPED ZONE-REFINED Pb, 5 g LOAD, 5 s LOADING TIME

	grain boundary	grain	ΔH_B(%)
zone refined (z.r.) Pb	38	38	0
z.r. Pb+1 atom Au/10^6	53	38	+38.0
z.r. Pb+1 atom Ca/10^6	35	38	−7.7
z.r. Pb+1 atom Au/10^6 +1 atom Ca/10^6	38	38	0

ABSENCE OF SPECIFICATIONS

Paradoxically, there are fewer explicit instances of control of residuals and trace additives through specifications than might be expected, given the present state of metallurgical knowledge and our growing capabilities for analysis and control. There are a number of reasons why this is so. (*a*) Because of the complex interaction effects between elements at the trace level or between them and the major alloying elements, it is often difficult to write a meaningful specification. (*b*) When adequate controls can be achieved by means other than compositional definition in the specification, the former is frequently the preferred option because of a desire for proprietary advantage or a reduction in the costs that would otherwise affect both purchaser and vendor from a complex and restrictive compositional specification. (*c*) Certain advances become so much an accepted state of the art that it is almost unnecessary to write them into a specification. Thus virtually no superalloy could be sold if it were not vacuum melted. (*d*) Internal processing may be such an effective screen for certain residual-induced impairments that compositional specification for the culprit species is unnecessary. Elements that embrittle certain cast superalloy compositions need not be explicitly proscribed in their wrought counterparts because intermediate forging or extrusion operations separate out the embrittled material before it ever leaves the producer's shop. Traces of Pb can render stainless steel so hot short that it breaks up during blooming of the ingot; yet if the material passes this stage, it can be brought all the way to finished coil without further trouble. (*e*) Control of certain other elements or of the microstructure may obviate the need to control a known deleterious element. For example, phosphorus embrittles 310 stainless steel (UNS S31000) at the 0.010 % level if the material is purely austenitic; by varying the Cr and Ni contents to obtain about 5 % δ-ferrite, the phosphorus level required for the same degree of hot cracking embrittlement is raised to 0.1 % (Linnert 1967). In another instance, thallium is known to degrade the corrosion resistance of zinc-based die casting alloys but is not often listed in the specification because specifying a maximum cadmium content is sufficient: processing to remove cadmium takes the thallium along too.

CONCLUSION

This review has attempted to show the complexities of the control of residuals and additives through specifications. It has emphasized the intimate interrelationships between specification practice and material processing on the one hand and specification practice and material application on the other. Effective use of specifications for control of trace quantities demands attention to *all* parts of the materials cycle, not just the end product.

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