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The Influence of Residual and Trace Elements on Hot Shortness and High Temperature Embrittlement

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The influence of residual and trace elements on hot shortness and high temperature embrittlement

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[Plate 1]

The problems of hot shortness and overheating have beset the metallurgist, forgemaster and smith for a surprisingly long time. In recent years the increase in electric steelmaking has emphasized the difficulties arising from the steady build up of residual elements which is the inexorable consequence of scrap recirculation.

Although many of the early investigations considered the influence of individual trace elements on hot ductility, in practice such relatively simple situations seldom arise. More often than not it is the interaction between a combination of trace elements which has to be understood if their net influence on high temperature mechanical properties is to be evaluated.

This survey of the present state of knowledge in this field therefore places particular emphasis on the need for an understanding of the interactions between trace elements.

1. Introduction

Discussion of the effect of trace elements on hot shortness in iron and steel has been going on since ancient times. This paper continues it.

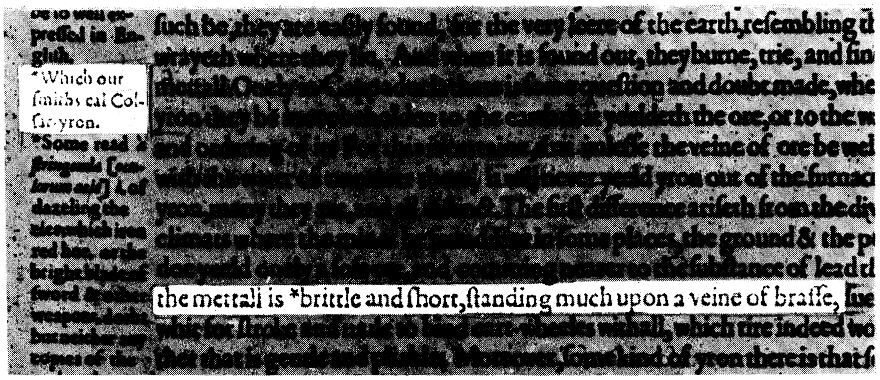
Pliny, in his *Natural history* published about 78 A.D., makes it abundantly clear that the metallurgists of his day were well aware of the effect of trace elements on the properties of iron. A modern translation by Rackham (1952) renders the passage as follows: 'There are numerous varieties of iron; the first difference depending on the kind of soil or of climate – some lands yield a soft iron closely allied to lead, others a brittle and coppery kind that is specially to be avoided for the requirements of wheels and for nails, for which purpose the former quality is suitable'.

When this passage was translated into English in 1601 by Holland, he used the words 'brittle and short' to translate the Latin word 'fragile' (figure 1). This is the first recorded use of the word 'short' in this context and it seems clear that it derives from a corruption of the Swedish abverb 'skört' meaning fragile. Substantive forms like rödskörhet (red shortness) have been common metallurgical usage in Sweden for hundreds of years and 'short' was clearly common parlance in England in 1600. The adjectival form in Swedish, however, is skör and in a marginal note relating to his 'brittle and short' iron, Holland adds 'which our smiths cal Colsar yron'. This too is probably a corruption of the Swedish adjective 'koldskör' (cold short). The existence of these various forms seems to have led to some confusion in the minds of the English metallurgists of the day. For example, by 1665, Dud Dudley was using the term 'redshare' (cf. rödskör, redshort) apparently under the mistaken impression it was associated with ploughshare performance.

Pliny qualified 'fragile' by adding 'et aerosum' which strictly means 'full of brass'. Rackham renders this as 'coppery' whereas Holland used the phrase 'standing much upon a veine of brasse, . . .'. This creates a distinct impression that both Pliny and Holland were all too familiar with the trying consequences of attempting to hot work iron containing appreciable quantities of copper. It would in fact be of some interest to enquire whether the sources of iron ore available to the Romans, such as those in Cappadoccia, were likely to have been contaminated with copper or other residuals.

With such a venerable ancestry it would be presumptuous to suggest any major change in what is meant by the term hot shortness. Nevertheless, there is room for improvement in the precision with which it is often applied. The following suggestions are advanced in the hope they will lead to a greater clarity of debate when this topic is discussed in the future.

Hot shortness: a lack of ductility in circumstances where incipient liquation has occurred and a molten phase is present. Modern metallographic techniques now enable such a situation to be recognized with some certainty.



*Which our ſmiths cal Colſhyron.

the mettall is *brittle and ſhort,ſtanding much upon a veine of braſſe,

FIGURE 1. The first recorded use in the English language of the term 'short' to describe brittleness in iron or steel (from Holland 1601).

Hot brittleness: a lack of ductility at high temperatures in circumstances where no molten phase is involved, for example that produced in steel by the precipitation of aluminium nitride. High temperatures in this context will be taken to mean $T > 0.5\, T_{\mathrm{m}}$, where T_{m} is the melting point temperature in kelvins.

The problem of what constitutes a trace element may be left to be debated in a wider context. There are, however, two further terms relevant to any discussion of hot shortness which would benefit from some clarification in their usage. 'Residual' and 'tramp' are usually applied in a derogatory sense to adventitious constituents to which some harmful effect is ascribed. Frequently, however, one man's residual element is another's alloying addition. This confusion could be mitigated if the term residual were applied only to those elements that are *intrinsically* residual in that they are not removed to any significant extent in the steelmaking process because, for thermodynamic reasons, they do not oxidize in the presence of iron. This will include nickel, copper, tin, antimony, lead, arsenic and also sulphur and phosphorus.

Any undesirable constituent may reasonably be termed a tramp but only a few are true residuals.

2. THE PROVENANCE OF RESIDUAL ELEMENTS

Trace elements and residual elements that can give rise to hot shortness enter the steel through four main routes:

(*a*) From the iron ore or pig iron. The early references to observations of hot shortness relate mainly to the effects of three elements: sulphur, phosphorus and arsenic. Depending mainly on the source of the iron ore these are the only three that can be present in sufficient quantity in virgin iron to render it hot short. Neither sulphur nor phosphorus represents a major problem in modern steelmaking practice since economic means exist for their removal into the slag. They will thus not be considered in as much detail as the more intractable residuals.

(*b*) From impurities in ferro alloy additions. Deliberate alloying additions can result in the adventitious arrival of unexpected elements. Bismuth, for example, has been reported as an impurity in the ferro-molybdenum added to austenitic stainless steel, with dramatic effects on its hot ductility. Molybdenum oxide, another form of molybdenum addition, can contain copper.

(*c*) From refractories. Some trace elements such as boron can be picked up from, or transferred via the furnace lining.

(*d*) From the recycling of scrap steel. Compared with this source of residuals, the other three are relatively trivial and do not constitute a major problem of current and future importance.

It is possible to distinguish several categories of contaminant whereby residual elements enter the scrap. Some examples are shown in table 1.

TABLE 1

bearings: white metal → Sn, Pb, Sb
bearings: bronze → Cu, Sn
plated material: cans → Sn, Pb
plated material → Ni
electric wiring → Cu
brass → Cu
alloy steels → Ni

Although such contamination occurs as an ongoing characteristic of the scrap recycling process, it is not the sole cause of the inexorable increase in residual element levels with which steelmakers have to contend. The increase in electric arc steelmaking capacity, particularly in the last two decades, has accelerated scrap recycling, many plants relying on a 100 % scrap charge. It is the recycling process itself which is at the heart of the problem.

It is common practice for a steel works to draw some of its scrap supplies – where it can – from any major customers, particularly if they happen to be local. This is intrinsically likely to be material of consistent quality. In addition, there is scrap arising within the steel works itself. It is not unusual therefore for the same steel to pass through the furnace every 2 or 3 months, if not more frequently.

Each time the metal is recycled, melting losses due to oxidation of the iron take place which can amount to 3–4 %. Modern, rapid steelmaking techniques exacerbate this effect still further. Residual elements (as defined at the beginning of the paper) do not oxidize in the presence of iron and hence they come to constitute a steadily increasing proportion of the melt. Were this process to continue unchecked, a simple calculation suggests that the steel would have to be recycled about 25 times for the residual content to double. Under these hypothetical circumstances this process would take no more than 3 or 4 years.

To combat this trend, the steelmaker pursues a policy of residual element control by diluting the charge to the furnace with material low in residuals: scrap, pig iron or, more recently, pre-reduced iron pellets. These control techniques are enlarged upon in another paper at this conference. When such diluents are not readily available the problem is a very real one. In West Berlin, for example, during the 'Cold War' period in which it was virtually cut off from the outside world, the level of residual elements increased at three times the rate elsewhere.

The steelmaker has already to tailor residual contents by careful scrap selection where steel specifications require it. His capacity for doing this at an economic cost varies with the price and availability of high quality, low residual scrap. Not only is this problem unlikely to go away, it will get worse.

3. Interactive effects between residual elements

The detrimental effect of residual elements on the hot ductility of steel is exhibited in three forms. First, some can give rise to hot shortness in the bulk of the steel. Secondly, they can have a particularly adverse influence on the surface properties after reheating for hot working. Thirdly, to a greater or lesser extent, they cause bulk hot brittleness.

There are undoubtedly situations where such effects can be ascribed to the presence of a single residual element. In most practical situations, however, several such elements are simultaneously present and their net effect is a product of the interactions between them.

In the discussion that follows therefore, it is these interactive effects that are emphasized wherever information is available.

Unless otherwise stated, typical residual element levels (percentages by mass) will be taken as: Ni, Cu $\leqslant 0.3$; P, S, Pb, As, Sb, Sn $\leqslant 0.05$.

4. Bulk hot shortness

Almost certainly the earliest observations of hot shortness relate to the sense in which it is defined at the start of this paper: that of liquation cracking. Sulphur, which as FeS forms a eutectic with iron melting at 985 °C, is likely to have been the cause, and Dud Dudley (1665) must have been one of the first to comment on this effect. It is worth quoting in full the passage from his *Metallum martis* referred to in the introduction. '...; fourthly, the Cannock or Cannot-stone, which last may wel be so caled, yet this Stone is so Sulphurous and Terrestrial, not fit to make Iron, because the Iron thereof made is very Redshare, which is that if a workman should Draw or Forge out a Share mould fit for a Plough in that red heat, it would crack and not be fit for the Use of the Husbandman's Plough or Share.'

Later, in an uncharacteristically modest reference to previous authors, he remarks, 'I must confesse, there is given unto some Phylosophers some few terms how the Sulphurious, Arsenical, Bituminos, Antimoniall, Venerial and other poysonous qualities...may be in part at the Furnace separated, and not permitted to incorporate in the Iron,....' The term 'Bituminos' refers probably to excessive carbon. The remaining 'poysonous qualities', however, are residual elements within the definition of this paper, since 'Venerial' in this alchemical sense means 'coppery'. Their removal in the furnace, a matter of some interest, is alas, apparently a lost art. It is unfortunate that no references are quoted.

For the next one or two centuries the problem of hot shortness due to sulphur had to be evaded by the careful selection of raw materials: both the iron ore and also the coal or coke used for reduction, since the latter often contained pyrites. The two Mushets, father and son, solved this problem. In 1801, David Mushet evolved the practice of adding manganese oxide to the melt and in 1857 Robert Mushet obtained a patent for the addition of 'spiegeleisen' to Bessemer

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steel, which revealed that the manganese was playing a dual role. First it acted as a deoxidant and secondly it combined with sulphur to form compounds which, because of their relatively high melting point, were harmless if they remained in the steel.

An understanding of a problem in scientific terms can be set back many years by the early discovery of an empirical solution. Examples of this fact litter the history of technology. There is seldom a lack of enthusiasm for discovering why something went wrong but only the discerning few pursue the problem of why it went right.

Thus it was not until 1931 that Benedicks & Löfquist described the FeS–MnS system for the first time with estimated subsolidus curves. Vogel & Hotop (1937) gave a eutectic temperature of 1180 °C. This was later modified by Mann (1974) to 1110 °C.

More recently still, in an important contribution to this topic, Mann & Van Vlack (1976) have established the FeS–MnS equilibrium system in the presence of excess iron, a situation corresponding closely to that of most practical interest. They suggest that the FeS–MnS system in fact forms a peritectic under these conditions with a ternary invariant point at 997 °C, and not a simple eutectic as had been previously believed. Their proposed version of the pseudo-binary FeS–MnS system in the region of the peritectic point is illustrated in figure 2.

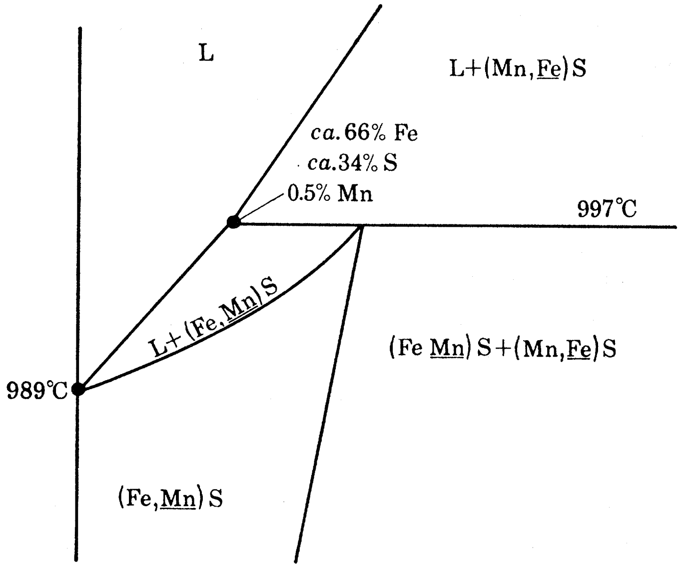

FIGURE 2. The FeS–MnS system in the presence of excess iron. Mann & Van Vlack's proposed version in the region of the peritectic point (from Mann & Van Vlack 1976).

They further quantify what has been known for some time (but often insufficiently appreciated) that to avoid FeS formation, and hence hot shortness, the Mn:S ratio must increase as the sulphur content diminishes. They suggest in fact the relation $M_{\mathrm{Mn}} \geqslant 0.4 + 2M_{\mathrm{S}}$, where M represents percentage by mass. Thus 1.0 % Mn may be sufficient for a free cutting steel with 0.25 % S giving a Mn:S ratio of 4, whereas for a steel containing 0.005 % S a Mn:S ratio of at least 50 is required. The advent of continuous casting in the past two decades has underlined the importance of adhering to such rules if stresses in the partly solidified strand are not to lead to internal hot tears in the steel.

Much of the hot shortness problem arising with sulphur is due to the fact that it is relatively insoluble in iron: less than 0.03 % by mass at 1200 °C in the absence of manganese.

Lead is also almost completely insoluble in austenite. As well as arriving accidentally in the steel generally through the remelting of solder-seamed tin cans or white metal bearings, it is deliberately added in amounts up to 0.25 % by mass to improve machinability. The lead is present in the steel as globules of elemental lead – liquid above 327 °C – often associated with MnS particles and showing no tendency to form grain boundary films. Under these circumstances it has little effect in promoting hot shortness in plain carbon and ferritic stainless steels although Bergh (1949) and Ervall *et al.* (1951) have shown that as little as 0.002 % can drastically affect the hot workability of austenitic stainless grades. This well illustrates the crucial importance of interfacial energy in determining the extent to which the presence of a molten phase is detrimental to hot ductility.

Similarly, bismuth has been added to leaded plain carbon steels in amounts up to 0.1 % to improve machinability still further without incurring severe rolling problems. The bismuth alloys with the lead globules in the microstructure. Jensfelt & Norrman, however, reported (1962) that as little as 0.0005 % Bi by mass produced cracking during hot forging of type 316 austenitic stainless steel (figure 3, plate 1). In this case the bismuth was proved to have been an adventitious impurity in the ferro molybdenum used. Its effect was ascribed, without any direct evidence, to its capacity for wetting the austenite boundaries and for forming low melting eutectics with other impurities, thereby increasing the volume fraction of the liquid present.

Phosphorus, although forming a low melting eutectic between Fe_3P and iron at 1050 °C, is in fact a ferrite stabilizer and up to 2.8 % by mass is soluble in α-iron at the eutectic temperature. The ternary iron–carbon–phosphorous eutectic, steadite, containing 6.9 % P and 1.9 % C (both by mass) has a somewhat lower melting point still. Nevertheless, except where severe segregation is present it appears to give less of a problem with hot working than it does with cold deformation.

Similar arguments can be advanced for the other ferrite forming residuals, arsenic, antimony and tin. Cameron & Waterhouse (1926) did attribute hot shortness in 0.5 % C (by mass) steel to arsenic present in amounts up to 0.45 %. A later investigation (Portevin 1962), using more advanced techniques, suggests, however, that it has a negligible influence. At hot working temperatures these elements do not form liquid phases on their own unless very severely segregated. At the levels at which they are normally present in steels (less than 0.1 %) this is very unlikely to happen. They do not thus contribute to bulk hot shortness but some, as will be seen later, exacerbate surface hot shortness and give rise to hot brittleness.

Copper, on the other hand, does form a liquid phase once its solubility in austenite is exceeded. It is the only true residual other than lead and sulphur to do so. The solubility in austenite, however, extends to *ca.* 9 % and varies little in the temperature range 1050–1250 °C. Once again, therefore, it is not likely by itself to give rise to bulk hot shortness without severe segregation or enrichment. A common cause of such enrichment arises at the surface of the steel as a consequence of oxidation during reheating before hot working.

5. SURFACE HOT SHORTNESS

For the same reason that they are not removed in the steelmaking process – their inability to oxidize in the presence of iron – residual elements become enriched in the subscale region whenever the iron is subsequently reheated in an oxidizing environment.

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FIGURE 3. Bulk hot shortness in type 316 stainless steel attributed to the presence of 0.0005 % bismuth (by mass) (reproduced from Jensfelt & Norrman 1962).

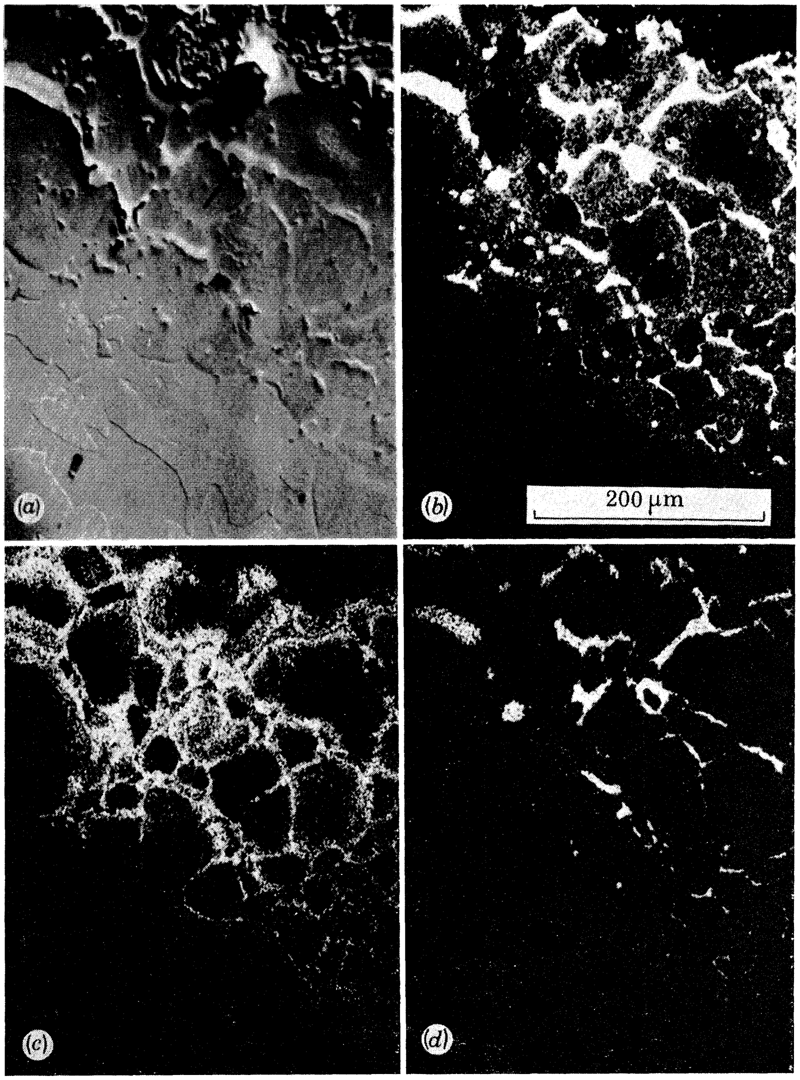

FIGURE 4. Surface enrichment of residual elements in mild steel. The arrow in the electron image (*a*) indicates a manganese sulphide inclusion that has become converted to copper sulphide. (*b*) Copper; (*c*) nickel; (*d*) tin. All micrographs are at the same magnification.

Sulphur behaves somewhat differently from other residuals under these circumstances. Oxygen ions diffusing into the metal react with MnS inclusions and also produce internal oxidation of Mn in solution, giving rise to subcutaneous MnO particles. Iron sulphide is produced which can then form a low melting eutectic with FeO. In free machining steels, containing up to 0.3% S by mass, the presence of this liquid phase can lead to practical difficulties such as roll skidding when the ingot is being cogged.

The other residual elements, nickel, copper, tin, antimony and arsenic, steadily become enriched in solid solution in the austenite at the scale–metal interface as oxidation proceeds. This has been confirmed experimentally by Melford (1962, 1966), Salter (1966, 1969) and others using the electron probe microanalyser. The hot shortness problem due to residual elements in fact played a major role in motivating the further development of the scanning electron probe microanalyser and provided one of its first applications.

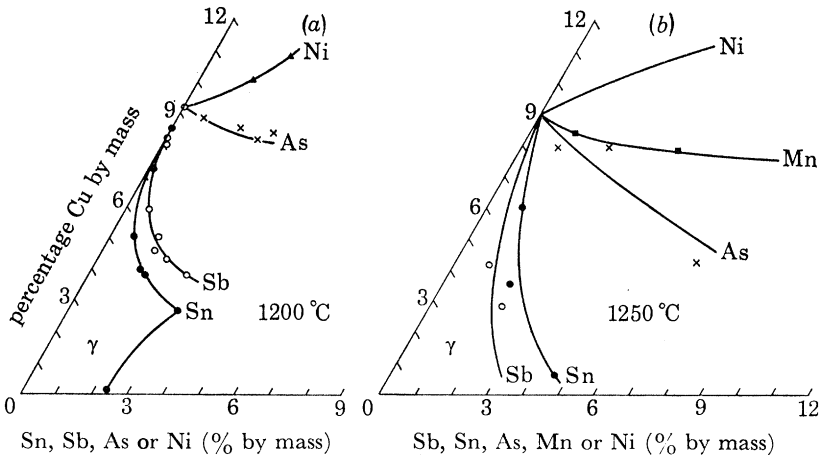

FIGURE 5. Ternary isotherms illustrating the influence of various elements on the solubility of copper in austenite ((*a*) after Melford 1966; (*b*) after Salter 1966).

At temperatures around 900 °C these enrichments tend to be distributed around the austenite boundaries near the surface, while at 1050–1150 °C a more planar enriched layer is formed. Above 1200 °C, internal oxidation leads to engulfment of the subscale into the oxide before enrichment proceeds very far.

As enrichment increases, the key to what happens next lies in the behaviour of copper. This element alone among the others forms a liquid phase when its solubility in austenite is exceeded. When only copper is present, enrichment to levels of over 9 % Cu is perfectly possible under conditions of severe oxidation in the temperature range 1100–1200 °C. At these temperatures the copper-rich phase that precipitates is molten and tends to penetrate the austenite grain boundaries leading to surface fissuring when any tensile stress is applied.

Tin and antimony greatly reduce the solubility of copper in austenite and hence lead to the precipitation of a molten phase and grain boundary penetration under conditions of much less severe enrichment (figure 4, plate 1). Furthermore this phase remains molten to a significantly lower temperature, *ca.* 820 °C.

Arsenic has only a mildly detrimental effect in that it reduces the solubility of copper in austenite slightly. Nickel, on the other hand, if present on its own together with copper, will have a beneficial effect in that it stabilizes the austenite (Kisfaludy & Tardy 1970). When tin or antimony are present as well, however, nickel has no such beneficial effect (figure 4). These interactions are conveniently displayed on the iron rich corner of the Fe–Cu–X ternary system, where X is any one of the other residuals. The 1200 °C isotherm as determined by Melford (1966) is illustrated in figure 5 together with the 1250 °C isotherm determined by Salter (1966).

On the question of solubilities, Salter reports very similar effects to those already described. He includes manganese as well in his determination which turns out to have a neutral effect. Both electron probe microanalysis and metallographic point counting techniques were used to determine solubilities, and good agreement was reported between the two. The latter in particular yielded unexpected evidence of a sudden increase in the amount of copper-rich phase at about 1100 °C. This implies a decrease in the solubility of copper in austenite (mild steel) at this temperature, which could not have been anticipated from the binary phase diagram in its currently accepted form.

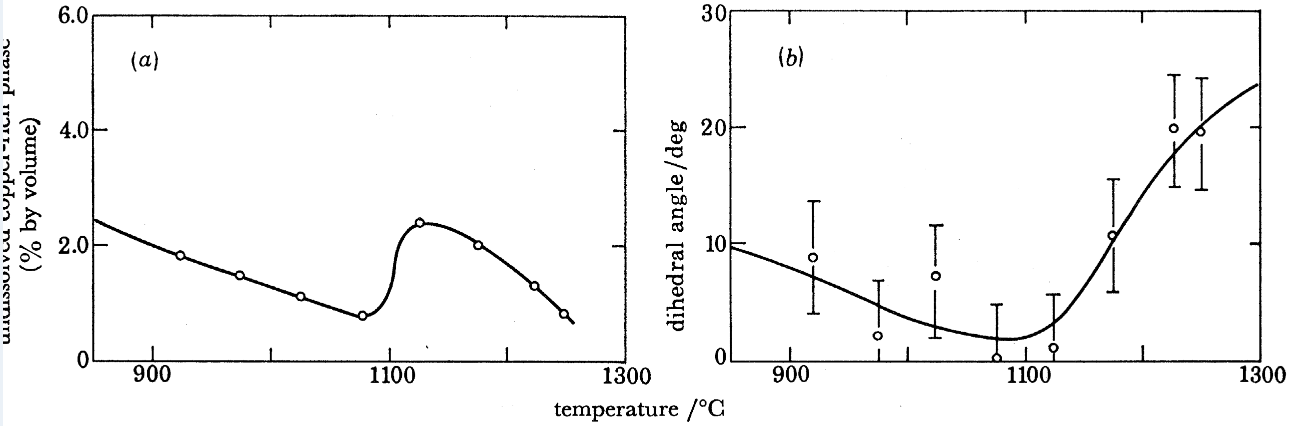

Figure 6. Variations in the amount of copper-rich phase present (*a*) and the dihedral angle it forms with austenite (*b*), both as a function of temperature (from Salter 1966).

The influence of molten phases on the development of hot short behaviour depends markedly on the extent to which they wet and penetrate the austenite grain boundaries. Salter (1966) made careful measurements of dihedral angles in his experimental alloys and found, in copper, a minimum dihedral angle approaching zero at a temperature close to 1100 °C. His results, illustrated in figure 6, thus suggest that a maximum hot shortness effect would be observed at this temperature owing to the combination of two hitherto unexpected effects: a maximum in the amount of molten copper-rich phase present and a maximum in its tendency to penetrate grain boundaries.

In a later paper Salter (1969) considered the simultaneous presence of nickel and tin as well as copper. This work indicated that the temperature of maximum susceptibility to hot shortness dropped to the range 1000–1050 °C and confirmed that very little tin was required to remove any beneficial effect that nickel may exert on its own.

This constitutional approach to the interaction between the various residual elements and their net effect on surface hot shortness also sheds some light on the physical meaning of empirically developed limitations such as $\mathrm{Cu} + 8\,\mathrm{Sn} \leqslant k$, where k is often 0.4 and the residual element levels are expressed in percentages by mass. Such equations can be thought of as crude approximations to the limit of stability of the austenite phase in the ternary system at the reheating temperature. The constant k depends on the degree of enrichment which is a function of furnace atmosphere, temperature and time in furnace. For any given reheating régime, however, it is usually sufficiently consistent to make such an equation a useful guide.

Since it has become apparent, however, that antimony has as severe a detrimental influence as tin, an improved version of such an equation might be $\mathrm{Cu} + 6\,(\mathrm{Sn} + \mathrm{Sb}) \leqslant k$.

The influence of various oxidizing atmospheres on the enrichment process has been studied by Hough and Rolls (1969). One particular set of conditions that had escaped any laboratory study is, however, worth mentioning because of its considerable practical importance. In the secondary cooling chamber of a continuous casting plant, water sprays cool the surface of the strand which, if it is sufficiently massive, will reheat between sprayings and continue to oxidize. This situation can be simulated with difficulty in the laboratory by dropping water onto a sample while it is being heated in an induction coil. Burden *et al.* (1979) have shown that vigorous spraying, by a combination of enhanced oxidation coupled with intermittent descaling, can produce very severe enrichments of residual elements in a very short time. It is likely that some of the surface cracking effects on continuously cast material, which have in the past been attributed to copper pickup from the mould, have in fact been the result of this rapid enrichment process.

Copeland and coworkers (Copeland & Kelley 1972; Copeland 1974; Copeland & Howe 1975) have studied methods of avoiding surface hot shortness by preventing the precipitation of copper-rich phases. The approach has been to add silicon to the steel and encourage the formation of molten fayalite ($2\mathrm{FeO}\ \mathrm{SiO_2}$) at the surface. They report that 0.3 % Si (by mass) and 2 % excess oxygen (by volume) in the furnace atmosphere will prevent molten copper-rich phases from forming on heating above 1205 °C in steels containing up to 0.8 % C by mass. Further enrichment during hot rolling cannot, however, be prevented. An extension of this work to steels containing antimony, tin and arsenic suggested that provided sufficient amounts of nickel and silicon were added, precipitation of molten copper rich phases could be suppressed.

Fisher (1969) also has studied the effect of nickel additions on the prevention of molten, copper-rich phase formation. He points out that while a Ni:Cu ratio of 1.5 or 2.0:1 is required for nickel to increase the solubility of copper in austenite sufficiently to prevent liquid phase formation, ratios of 1:1 or less can be effective by promoting internal oxidation and subscale occlusion at temperatures as low as 1150 °C.

It would be reassuring if these studies of preventive measures were supported by evidence of hot cracking tests to demonstrate that the cure is not likely to be worse than the disease.

The influence of residual elements on surface hot shortness has been outlined in some detail because it is a topical and practical problem of continuing importance. There is still much that is imperfectly understood, particularly the effect of thermal cycling when this extends to the region of ferrite–austenite stability. Nickel enrichment will tend to stabilize austenite locally, for example at grain boundaries near the surface. Cooling to the duplex temperature range will encourage further nickel migration into the areas of residual austenite, possibly exacerbating the segregation. Wynne (1966) has reported that such localized nickel enrichment can stabilize austenite at room temperature to the extent that any subsequent rapid heating and cooling cycle, such as electric resistance welding, for example, will produce martensitic grain boundaries at the surface. These give rise to cracking during subsequent cold manipulation.

Similarly the surface cracks, often shallow in themselves, resulting from the enrichment processes that have been discussed, can act as notches for more serious bulk cracking if the steel is hot brittle. This is discussed further in the next section.

6. Bulk hot brittleness

There seems clear evidence that, even in the absence of surface enrichments or the presence of liquid phases, many residual elements nevertheless have a detrimental influence on the bulk hot ductility of steel. It is important to note that the mechanism of this embrittlement subscribed to by most authors is different from that described earlier in this paper. Bulk hot shortness and surface hot shortness involve grain boundary decohesion due to the presence of liquid phases. In hot brittleness the effect is attributed to the precipitation of second phases which inhibit recrystallization and the mobility of austenite boundaries during deformation. Reynolds & Tegart (1962) make a particularly clear distinction between the two mechanisms when they suggest that this is so.

At temperatures above 1100 °C in heavily segregated, copper-containing steels it is likely that a liquid phase is in fact present and the phenomenon is better described as hot shortness. Below this temperature, in the range 800–1100 °C, a different explanation appears necessary. Unhappily, ternary isotherms such as those illustrated earlier do not appear to have been determined in this temperature range and interpretation of interactive effects is thus more difficult.

Rossard & Blain (1959) used the hot torsion test in an inert atmosphere to study the individual influences of copper, antimony and arsenic and also the combined effect of copper and arsenic. Their samples were carefully homogenized and in general the detrimental effects were more marked at 1 rev/min than at the higher strain rate of 1000 rev/min used in their study. They report that 0.1% Sb (by mass) or an increase of copper from 0.11 to 0.28 % (by mass) reduced the hot workability of their steel by 50 %. They stress the point that in the case of the antimony-containing steel, they could find no traces of segregation.

Arsenic had a somewhat less detrimental effect in these tests and actually appeared to improve the ductility of the copper-containing steel above 1100 °C.

Their evidence for suggesting that the presence of residual elements impeded recrystallization is based on the observation that the deformation torque increased in each case when the residual element was added.

Portevin (1962) used both tensile and torsion tests to study the behaviour of as-cast material cut from a large ingot containing both copper and tin. He also studied the influence of Al and As. He observed deteriorations in ductility in residual-containing material which in all cases below 1100 °C he ascribes to the presence of second phases, either ferrite or the copper-rich solid ε phase.

This exposes the major problem in understanding the behaviour of residual elements in this context. What is the enrichment mechanism necessary to produce these second phases? In hot shortness due to sulphur, the typical sulphur content of the steel exceeds its solubility in austenite. In surface hot shortness, selective oxidation of the iron provides the enrichment mechanism. In hot brittleness, however, there is a problem. The typical residual element contents of steel lie well within their solubility limits in austenite. Why, then, should ferrite or any other phase precipitate during hot working?

Portevin answers this question in a number of different ways:

(*a*) *Tin.* This segregates during solidification, and as-cast material is embrittled as a consequence of the formation of ferrite in tin-rich regions. Annealing at 1200 °, however, readily homogenizes the tin content and Portevin (1962) quotes both Philibert and Kohn as having been unable to demonstrate any tin segregation in homogenized material. He further reports that, once homogenized, tin at these levels (*ca.* 0.1 % by mass) has *no* adverse effect on hot ductility.

(*b*) *Copper*. Even after annealing at 1200 °C and slow cooling to room temperature, small particles of almost pure copper are visible in the microstructure. Hornbogen & Glenn (1960) have shown a very rapidly decreasing solubility of copper in ferrite from about 2.1 % by mass at 850 °C to as little as 0.02 % at room temperature. As a result, the ε phase containing about 98 % copper (by mass) precipitates and Portevin suggests that this redissolves only slowly if the steel is reheated at temperatures up to 1084 °C. Thus, although not in equilibrium with the austenite, the ε particles are able to impede the mobility of the γ grain boundaries during deformation and embrittle the steel. Above 1084 °C, the ε phase decomposes through a peritectic reaction and the resultant liquid, it is suggested, rapidly homogenizes into the austenite since the ductility then improves considerably. The precipitation of ε and hence this form of embrittlement can be suppressed by rapid cooling from the annealing temperature. At about 1200 °C in as-cast material, a different form of embrittlement was observed, accompanied by the observation of 'dark veins' at grain boundaries, which proved to contain both sulphur and copper. Portevin emphasizes that this was only found in samples containing segregation effects and the mechanism was one of the intergranular decohesion due probably to the presence of liquid film (i.e. hot shortness rather than hot brittleness). This observation will be further discussed later.

(*c*) *Aluminium*. Portevin's most controversial suggestion concerns the behaviour of aluminium, which is not a true residual but a trace element having an important influence on hot ductility. Ductility troughs in the region of 800–1000 °C are normally associated with the precipitation of aluminium nitride. Direct experimental observations of nitride precipitates at grain boundaries are, however, rare and Portevin makes the further point that the maximum drop in ductility occurs at a temperature when the aluminium nitride has almost redissolved. He suggests therefore that this resolution produces local aluminium enrichments which have a powerful ferrite stabilizing influence thereby giving rise to a duplex structure at temperatures well into the γ range. In other words, the role of aluminium nitride precipitation is simply as a mechanism for producing local aluminium enrichment. This ferrite-forming tendency of aluminium, he suggests, is further accentuated by the presence of arsenic.

Other workers have found difficulty in confirming Portevin's view of the role of aluminium nitride, and recently, Funnell & Davies (1978) have obtained evidence that suggests that the size of the aluminium nitride particles has an important influence on whether or not bulk hot ductility is impaired.

Their results for two steels containing similar amounts of nitrogen precipitated as AlN are shown in figure 7. In one case, however, the mean particle size is more than twice that in the other. The larger AlN particles have a negligible effect on hot ductility whereas the smaller reduce it dramatically. If the mean particle sizes are reversed in these two steels by suitable heat treatment, their hot ductility behaviour is also reversed.

Burden *et al.* (1979) suggest an important link between surface hot shortness effects due to residual element enrichment and bulk hot brittleness due to aluminium nitride. They report that the surface cracking can initiate deeper cracks in the substrate if that is in an embrittled condition and thus one effect exacerbates the other. The conditions in the secondary cooling

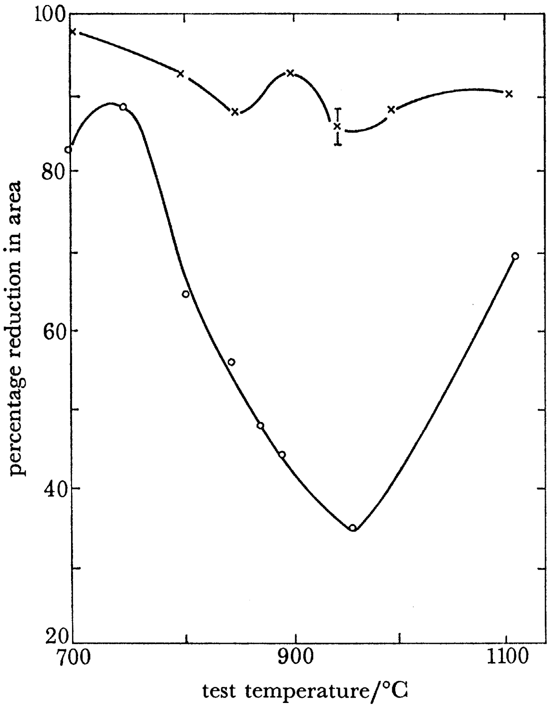

FIGURE 7. Hot brittleness due to AlN precipitation: ×, 80 μg/g N as AlN (mean particle size 0.21 μm); o, 72 μg/g N as AlN (mean particle size 0.09 μm). The cast exhibiting the sharp ductility trough contains the finer dispersion of AlN particles. Suitable heat treatments which reversed the precipitate size distribution in these two casts also reversed their hot ductility at 950 °C (after Funnell & Davies 1978).

chamber of a continuous casting plant, referred to earlier, which give rise to severe residual enrichment, can also lead to precipitation of aluminium nitride below the surface.

If the steel is subjected to a hot cracking test at *ca.* 1000 °C while in this condition it will be seen from figure 8 that the crack depth continues to increase with the intensity of water spraying. If the same material is tested at 1200 °C when the AlN is in solution, no such continuous increase

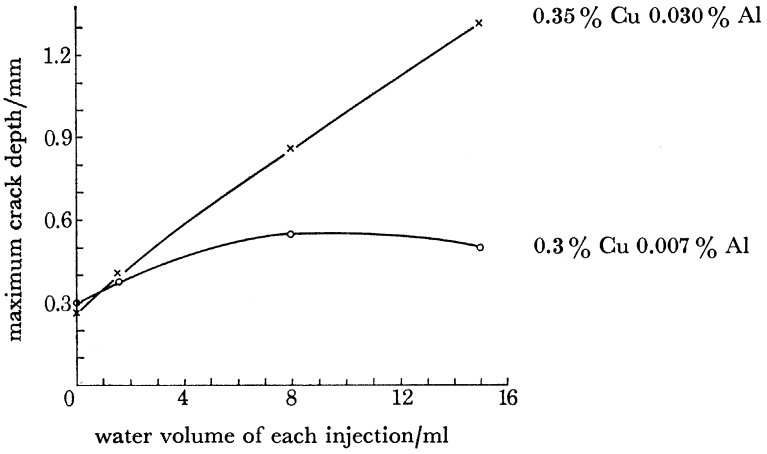

FIGURE 8. Interaction between surface hot shortness and hot brittleness illustrated by hot bend test results at 1000 °C. Increasing the copper content above 0.3 % by mass does not lead to increased depth of cracking under these conditions unless the substrate is embrittled by AlN precipitation (after Burden *et al.* 1979).

in crack depth occurs, neither does it occur even at 1000 °C if insufficient aluminium is present to lead to such precipitation.

This is another example of the need for an understanding of the interactions between residual and trace elements if a proper degree of quality control is to be exercised.

Under somewhat similar working conditions, i.e. tube manipulation to form elbows in the temperature range 750–950 °C, Cooper & Burns (1974) describe hot cracking which they attribute to an interaction between copper and sulphur, but at a much lower temperature than that found by Portevin. Reference is made in their paper to the presence of an unidentified phase at the ferrite boundaries. It is difficult to accept this interaction on the basis of the evidence presented. No analyses for antimony, tin, arsenic, aluminium or nitrogen are given so that other possibilities cannot be excluded.

Nevertheless, sulphur undoubtedly does interact with the other residual elements as Portevin suspected and can play a part in producing highly localized enrichments. Copper sulphide, for example, is often present (Melford 1962) at the surface of residual containing steel, since in the presence of oxygen at reheating temperatures it is more stable than the sulphides of either manganese or iron. A good example of this effect is indicated by the arrow in the electron image of figure 4.

More importantly, perhaps, sulphides in 'A' segregate regions of ingots seem able to 'getter' significant quantities of nickel, copper, tin and antimony. The fluid flow through the 'A' segregate channel in the final stages of solidification – a mechanism first postulated by McDonald & Hunt (1969) – affords an opportunity for mixed sulphides to precipitate from a liquid highly enriched in residual elements. On cooling, reversion to a normal manganese sulphide takes place with an associated precipitation of a phase so enriched in residuals as to be virtually non-ferrous. Such phases have been observed in association with manganese sulphides by several authors, notably Salmon-Cox & Charles (1965). Here, then, is apparently a further mechanism for the production of localized enrichments in residual elements.

For completeness it should be added that sulphur present as manganese sulphides has a somewhat adverse effect on hot ductility, although free machining grades with up to 0.3 % S (by mass) are rolled successfully. Void formation occurs during deformation at the inclusion–matrix interface and internal necking between voids leads to crack propagation and fracture at low values of reductions in area.

Nicholson (1964) has published a brief but useful review summarizing the effects of many trace elements on the bulk hot ductility of iron. Phosphorus up to 0.38 % by mass is credited with having little effect on the ductility of plain carbon steels, and nickel up to 5 % by mass – present on its own – actually improves it.

7. SUMMARY

This paper has described the influence of residual elements on the hot ductility of steels and has identified three categories of behaviour:

1. Bulk hot shortness in which intergranular cohesion is lost due to the presence of liquid films. Among the true residuals – apart from lead – only sulphur, which has minimal solubility in austenite, is normally present in steels in sufficient quantities to give rise to a separate liquid phase. This is now known to persist down to temperatures close to 1000 °C if the manganese content is less than 0.35 % by mass. Manganese is, of course, normally added to prevent this

form of embrittlement. With the other residuals, nickel, copper, tin, antimony, arsenic and phosphorus, unusually high levels coupled with exceptional segregation during solidification (as in very large ingots) would be required to produce bulk hot shortness. In austenitic stainless steels, however, very small quantities of lead and bismuth have been shown to give rise to this effect. The fact that lead does not cause problems with plain carbon steels is indicative of the crucial importance of the extent to which the molten phase wets the grain boundaries.

2. Surface hot shortness in which the embrittling effect is once more due to grain boundary liquation. Selective removal of the iron by oxidation provides the enrichment mechanism necessary for such liquation to occur at the relatively low residual concentrations typical of most steels. In this case, some interpretation of the interactive effects is possible as a consequence of the availability of limited information on ternary constitution. Nevertheless the influence of thermal cycling, particularly into the temperature range where ferrite can precipitate, is little understood at present and may have considerable practical importance.

3. Bulk hot brittleness in which residual elements, by giving rise to the formation of second phases, impede the grain boundary mobility and recrystallization of austenite during deformation and initiate fracture without the formation of any liquid intergranular films. Here there is much less uniformity of view on the nature of the enrichment processes that must precede or accompany the formation of such second phases. Furthermore, the lack of constitutional data in the temperature range 800–1200 °C makes prediction and interpretation of interactive effects a matter for speculation.

Thus in spite of the great antiquity of this subject, there is still much to do before the gaps in our present understanding are filled and it becomes possible to provide a wholly adequate explanation of the behaviour of residual elements in modern steels.

I am indebted to Professor R. Kiessling for advice on Swedish metallurgical terminology, ancient and modern, to Mr G. D. Funnell for many helpful discussions and to the Chairman of Tube Investments for permission to publish this paper.

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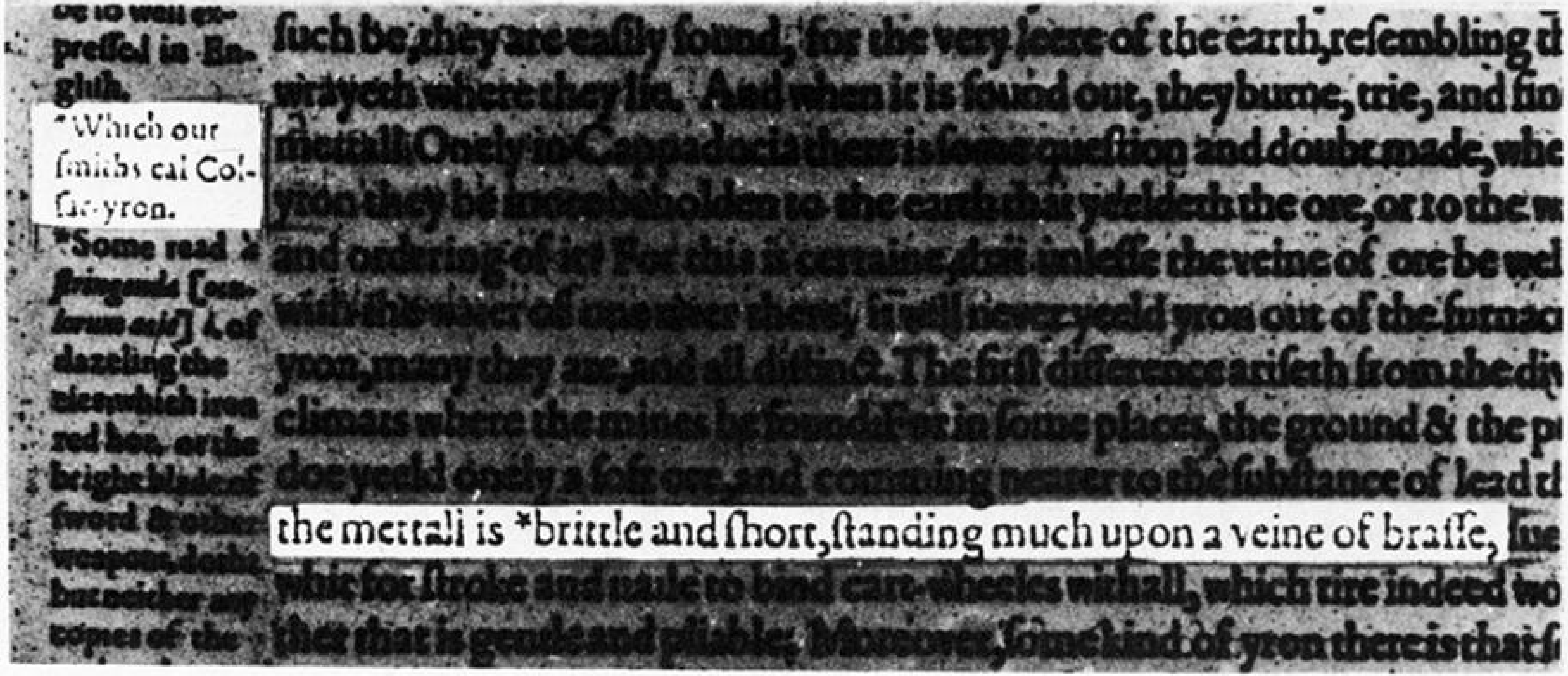

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FIGURE 1. The first recorded use in the English language of the term 'short' to describe brittleness in iron or steel (from Holland 1601).

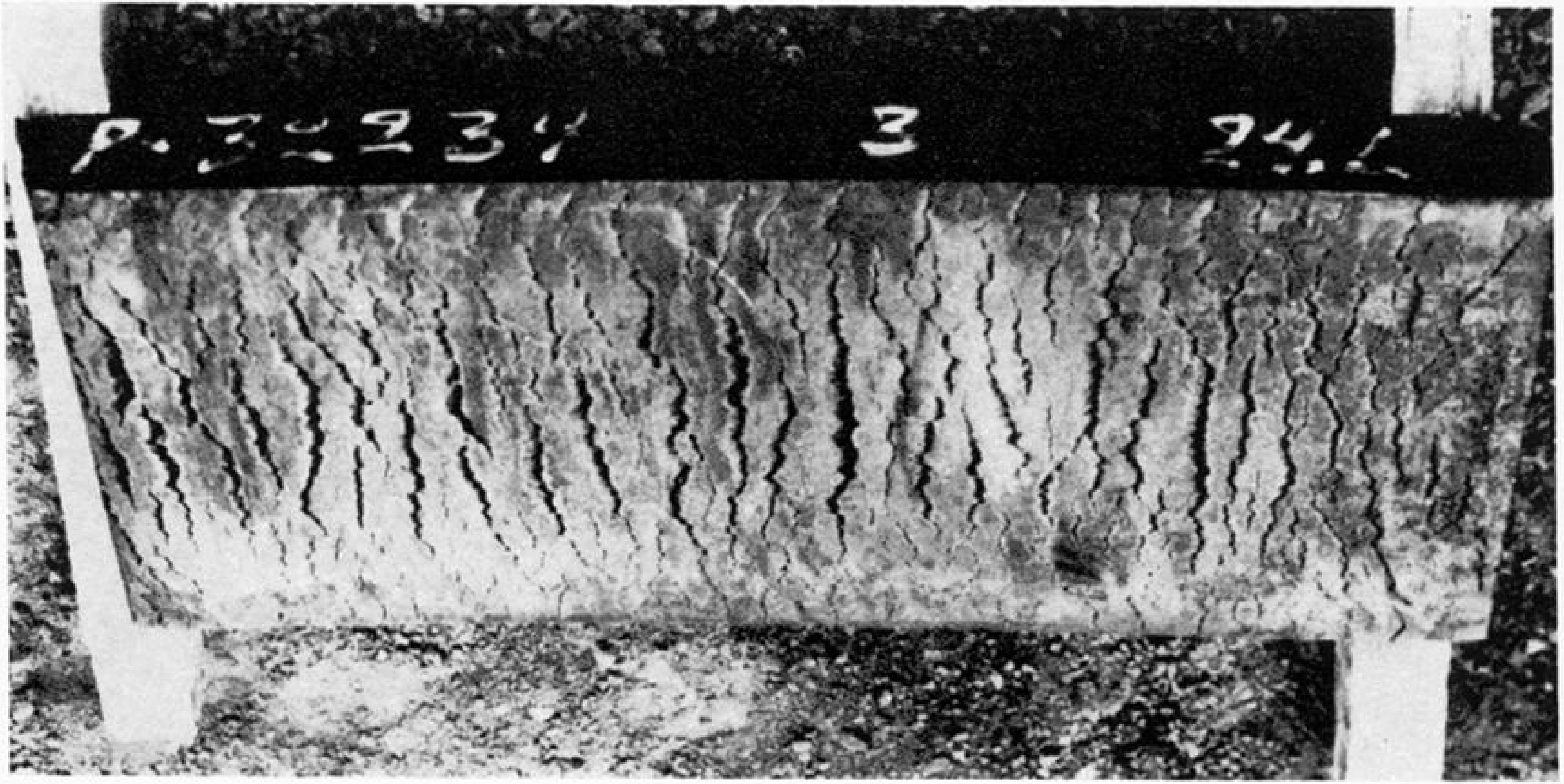

FIGURE 3. Bulk hot shortness in type 316 stainless steel attributed to the presence of 0.0005 % bismuth (by mass) (reproduced from Jensfelt & Norrman 1962).

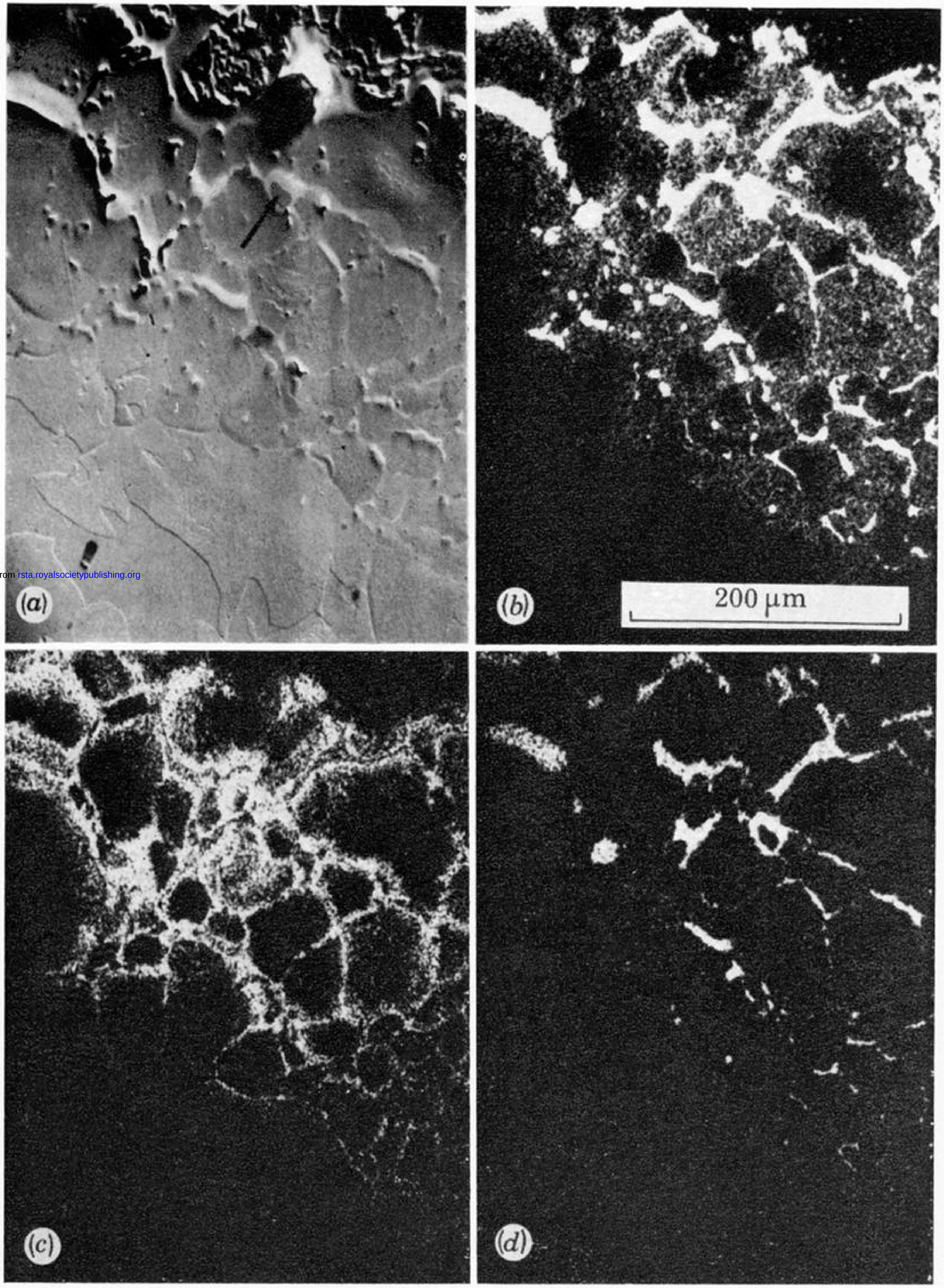

FIGURE 4. Surface enrichment of residual elements in mild steel. The arrow in the electron image (*a*) indicates a manganese sulphide inclusion that has become converted to copper sulphide. (*b*) Copper; (*c*) nickel; (*d*) tin. All micrographs are at the same magnification.