

REVIEW OF HOT SHORTNESS PROBLEMS IN COPPER CONTAINING STEELS

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ABSTRACT

The problem of hot shortness is first briefly discussed in terms of the recycling of scraps and the occurrence of various residual elements in steel. The phenomenon is then defined and described as a function of the factors influencing its different stages : copper solubility in austenite, copper phase melting point, wettability of the liquid copper rich phase, oxidation, furnace atmosphere, occlusion and diffusion. The effect on these phenomena of other residual or alloying elements is discussed. The paper concludes with the different ways to minimize the hot shortness problems and with hints on the more efficient use of copper containing scraps.

INTRODUCTION

The presence of Cu in steel as a residual or as an intentional alloying element causes a major concern to metallurgists because of the problems encountered in hot rolling and, to a much lesser extent, in continuous casting.

Copper comes along with a series of other elements considered to be residual such as : Ni, Cr, Mo, Sn, As, Co, Sb and W. Other elements i.e. Al, Pb, Nb, Ti, V, Zn and Zr although affecting properties or causing problems in steelmaking are not considered as residuals since they partition during steelmaking away from the steel.

As an alloying element, Cu has a number of assets and it is the purpose of this conference to review the applications, actual and potential, of this element in steel. Because of the extended recycling of scraps and because also Cu partitions in the steel both aspects of the presence of copper, as a residual or as alloying element, are closely interrelated.

In this paper we shall attempt to review first briefly the present situation of recycling and its effects on residual levels and then to describe in more detail the hot-shortness problem and the ways to minimize it as a function of the mechanisms involved. The opportunities offered by the use of copper-containing scraps will be then discussed with, as a background, the papers and reviews presented at this conference.

RECYCLING

The evolution of residual levels in steel is related to the increasing use of scrap-intensive steelmaking processes.

As an example, fig. 1 (1) shows the continual increase in the production of electric furnace steel, using virtually 100 % scraps, awaiting the remote possibility of using iron from direct reduction processes which would tend, because of its purity, to decrease the residual levels in electric furnace steel. The evolution of the scrap to steel ratio, shown in fig. 2, indicates a fairly constant ratio over a long period of time although a definite trend for increasing ratios is visible over the last decade.

The evolution of the residual levels themselves for some elements is shown in fig. 3, based on U.S.A. data (1). The residual level for copper and the increase trend are more pronounced for engineering steels for which electric furnace melting is widely used. In UK for example, the upper boundary of the scatter band for such steels shifted from 0.2 % Cu in 1965 to 0.35 % Cu in 1975 (2).

There is a strong correlation between the residual level in steel and the element overall consumption. Table I reproduces some consumption data in USA and EEC showing that the levels of residuals, are approximately parallel to the consumption tonnages.

Considering the general trend and analyzing the sources of scrap, at least in the U.S.A., Stephenson (1) predicts that over the next decade residual levels of elements such as Cu, Ni, Cr and Mo will increase by 5-10 % whereas those of elements such as Sn and Sb will decrease by 10-20 %. The latter evolution is explained by the introduction of tin-free steel and Al for containers and of low Sb lead for batteries.

The reasons for controlling residual levels depend on the residual element considered and also on the steel specification. Residuals, depending on their nature, can affect behaviour during processing, the properties of both. As far as Cu is concerned it is fairly well established that its overall effects on product properties is favourable in contrast to other residual elements which are deleterious both to processing and to product properties. The recycling issue with the associated constraints on specifications is thus a raw materials management problem and it is in this context that the particular case of copper has to be situated. The various aspects of the role of residual elements in general have been recently reviewed in (3).

We shall now deal in more detail with the copper induced hot shortness of steel, which, as said before, is one of the major concerns of steelmakers.

THE MECHANISM OF HOT SHORTNESS

There are different mechanisms which can result in embrittlement and intergranular failure in steel. Briant and Banerji (4) classify the intergranular embrittling processes in eight categories of which a few apply to high temperature fracture and are therefore related to hot workability. The hot shortness corresponds in this classification to the "exposure to liquid metal". One can distinguish in this context (5) the "bulk hot shortness" which is due to the melting of low melting compounds, for example sulfides at the grain boundaries, and the "surface hot shortness" which, in the particular case of Cu consists in the in-situ formation, after oxidation, of a liquid phase followed by its penetration preferentially at the grain boundaries.

Cu, along with other elements Sn, Sb, Ni, Co, is less oxidizable than iron and will tend therefore to concentrate at the oxide-metal interface during oxidation of steel as it occurs inevitably on reheating ingots or slabs.

The extent of enrichment of Cu as well as that of other less oxidizable elements will thus be a function of the oxidation rate of steel.

When the Cu-content in the austenite exceeds the solubility limit, separation of a Cu-rich phase will occur. If the temperature is high enough the Cu-rich phase will melt and the liquid phase will be available for penetration.

The formation of the liquid phase at the interface metal-oxide is illustrated in fig. 4 concerning an experimental steel containing 3 % Cu and maintained for 3 hrs at 1100° C. The penetration phenomenon along austenite grain boundaries is shown in fig. 5 for the same steel maintained at 1100° C for 6 hrs. Under industrial additions, severe cracking can occur during hot rolling as shown in fig. 6. A parallel phenomenon is the possible occurrence of "slivers", shown in fig. 7, which form by a progressive bending of the cracks below and parallel to the surface. Such defects are of course unacceptable in high quality flat products.

We shall now examine in more detail the various stages in the hot shortness mechanism and by so doing we shall hint at the measures that can be taken in order to minimize the extent of the phenomenon.

FACTORS RELATED TO THE CU-ENRICHED METALLIC PHASE

We shall first consider some of the factors responsible for the formation of the Cu-rich phase and its penetration along the grain boundaries after Cu-enrichment has occurred due to the oxidation process.

The precipitation of the Cu-rich phase from the austenite will occur when the austenite reaches the saturation point for copper solubility which is of about 10 % at 1250° C. The solubility limit is dramatically affected, as shown in fig. 8, by the alpha-stabilizing elements Sb, Sn, As which are less oxidizable than Fe and will therefore also tend to enrich during the oxidation process. Ni, a gamma-stabilizer and an element less prone to oxidation than iron, increases the solubility of Cu in austenite. Elements such as Mn and Cr have only a small effect.

Once the Cu-rich phase has formed it will penetrate along the grain boundaries if it is liquid. Its melting point is therefore important. In this respect, examination of the ternary phase diagrams Fe-Cu-X show that Sn, Sb and As depress the melting point whereas Ni increases it, and Mn and Cr have only a small effect.

Figs. 9 and 10 illustrate the effect of, respectively, Sn and Ni by showing the isothermal diagram for the ternary system at 1250° C. In the Fe-Cu-Sn system a liquid phase can be stable at the steel corner even at very low Cu-contents, whereas nickel suppressed the occurrence of a liquid phase.

Once a liquid copper rich phase is formed, its penetration along the grain boundaries will be more pronounced, the more its wettability is high, i.e. the dihedral angle between the liquid phase and austenite will be small.

Fig. 11 shows that in the Cu-mild steel system the angle is minimum at around 1100° C.

The penetration is then the easiest at this temperature and indeed it is at this temperature that maximum cracking occurs, as shown in fig. 12 for various steels with increasing Cu-contents. At temperatures substantially below 1100° C the Cu-rich phase is solid while at much higher temperatures occlusion and diffusion reduce hot-shortness.

Wettability measurements in terms of dihedral angles, were made in order to assess the effect of ternary elements on the wettability of the copper rich phase (7). The results show a pattern similar to the one shown in fig. 11. The findings that elements such as Sn, Sb and As increase on dihedral angle is not predominant since the deleterious effect of Sn is well known whereas the beneficial effect of Ni is also well known.

OXIDATION RATE

TEMPERATURE

Oxidation rate increases with temperature, as illustrated in fig. 13, and the enrichment in copper would therefore follow the same pattern. At very high temperatures however the oxidation rate may be so high as to result in the occlusion of the Cu-rich phase in the oxide layer and in the diffusion of Cu away from the surface. Both effects prevent enrichment of Cu and therefore suppress hot shortness (fig. 12)

High soaking temperatures have been proposed as a possible way to prevent hot shortness but the modification of the process is not efficient due to unacceptable refractory wear and energy consumption (1).

FURNACE ATMOSPHERE

The effect of furnace atmosphere will be illustrated for the case of the constituents : H₂O, O₂ and SO₂.

Fig. 14 shows that at low temperatures i.e. 1000° C, increasing contents of oxygen and water vapour result in an increase in the severity of cracking of a Cu containing steel. At higher temperatures (1250° C), the severity of cracking is at maximum at about 5 % oxygen and then decreases as oxygen content increases.

Fig. 15 illustrates the favourable effect of SO₂ which is particularly pronounced at a temperature of 1100° C. The beneficial effect of SO₂ is attributed to the higher amount of Cu occluded in the scale as copper sulfide which forms preferentially to iron sulfide. At 1300° C the effect of SO₂ is marginal : at this temperature the severity of cracking is any way rather low due to the predominant effect of copper occlusion and diffusion.

ADDITION ELEMENTS

Elements more oxidizable than iron such as Cr, Al, Mn,... do not modify the oxidation pattern of Cu-containing steels at least at content levels encountered in unalloyed or low alloyed steels (9). They have therefore no effect on the hot shortness phenomenon (6).

A somewhat different behaviour is exhibited by Si. At temperatures below 1100° C, the presence of silicon (2 %) results in the occlusion of the Cu-rich phase and/or in a decrease of its fluidity due to a higher iron content caused by the formation of a "fayalite" layer at the interface steel-scale preventing the outward diffusion of iron (10).

The occlusion of the Cu-rich phase in a two phase layer formed at 900° C on a steel containing 2.7 % Cu and 2 % Si is shown in fig. 16. The overall effect was a decrease in the hot shortness tendency. It seems however that at higher temperatures encountered in hot rolling mills, Si gives rise to partly liquid oxide layers which enhance oxidation and restore copper enrichment and hot shortness (6). At the same time Si additions may result in severe surface defects on the hot rolled strips.

The beneficial effect of elements less oxidizable such as Ni is also, to a large extent, due to the modification of the oxidation mechanism associated with other effects which were discussed here-above. Contrary to what happens with Cu or Co, the presence of Ni gives rise at all temperatures to internal oxidation resulting in the occlusion of the Cu and Ni-rich phase in the oxide scale (6,11). The austenite grain boundaries are oxidized, while at the scale/metal interface a two-phase zone composed of oxide and solid metallic globules is formed. Fig. 17 illustrates this mechanism for an experimental steel containing 2.8 % Cu and 3 % Ni. This process is similar to what happens in a plain Cu-containing steel oxidized at 900° C i.e. at a temperature where the metallic phase formed is solid. Fig. 19 compares the mechanisms operating in a Cu and in a Cu-Ni steel oxidized at 1100° C. In the first case the Cu-rich phase is liquid and penetrates along the grain boundaries, whereas in the second case the Cu-Ni-rich phase is solid and is occluded in the scale by the internal oxidation process. It should be mentioned here that the same mechanism is operating when Cu is absent and explains the phenomenon of adherent scales encountered in steels with a high residual content in Ni (1).

Among the means to suppress the hot shortness no mention will be made here of the attempts to remove copper from steel melts. Such aspects are discussed in (13).

PROBLEMS AND OPPORTUNITIES

The review that has just been presented shows that Cu present as a residual element in steels, together with other impurities, does constitute a source of concern for the steelmaker. The latter does avail however of different means to manage the problem not only in a defensive and a passive approach but also in an offensive and positive way.

The factors involved in the hot shortness mechanism are summarized in Table II : they relate either to the scaling phase of the process or to the behaviour of the Cu-rich phase formed. Their understanding provides the means to minimize the problems as summarized in Table III.

As regards the residuals themselves adjustment of their levels can be done by the relations of the type : $Cu + 6(Sn + Sb) \leq K$, where K is often 0.4 or otherwise depends on the reheating regime (5).

The steelmaker can adjust the alloying elements, Ni and to a lesser extent Si, in order to prevent hot shortness in so far specification of steels produced allow to do so. Ni was shown to affect all stages in the mechanism of hot shortness : it increases solubility of Cu in the austenite, it increases the melting point of the Cu-rich phase and it promotes occlusion of the Cu-rich phase in the scale by internal oxidation. A Ni/Cu ratio of up to 1 was shown to suffice to suppress or to reduce substantially hot-shortness. Si, as mentioned here above, can also suppress hot shortness at least for temperatures not higher than 1100° C.

The control of process parameters involving such measures as hot charging and adjustment of the furnace atmosphere is still another means to minimize hot shortness problem. Because of the fact that control of furnace atmosphere is not always possible, at least in Pitts furnaces, the use of coatings has been suggested. Iron sulphide base coatings have been reportedly used (12) while Ni-Al coatings although technically feasible proved to be as expensive as incorporating a sufficient amount of Ni in the steel (9). On the other hand, the increasing use of continuous casting and the resultant use of slab reheating furnaces, which are far better instrumented, allow again a better control of the surface atmosphere and hence of the hot shortness phenomenon. Substantial tonnages of Cu alloyed steels have been produced with such installations without any hot shortness problems (14,15). Depending also on the types of steels produced and provided that the product mix is wide enough, careful scrap selection allows also their optimum use (1). Some steel grades are much more tolerant to high residual levels than others. For example, concrete reinforcing bars tolerate without problems high levels of residuals among which 0.5 % Cu, whereas in drawing quality sheets the limits are much more lower. The Cu limit for batch annealed steel sheets is quoted to be 0.06 % (1).

The potential for opportunities outlined in Table IV may be however most rewarding in the management of scraps as regards residuals in general, and especially Cu. Considering the range of beneficial effects of Cu scrap may be considered as a cheap source of alloying elements instead of being only a cheap source of iron (1). The use of high Cu scrap, could be diverted to corrosion resistant steels or to new grades such as Ni-Cu-Nb or of Cu-Si steels.

The wide range of types of scraps, the number of residuals and the constraints on steel specification and processing parameters require the use of computer assisted models in order to assist the steel maker in accommodating scrap in various steel mill processes (1,16). In this way it might be possible to use the available scraps more efficiently but also to achieve better properties of the steels produced at a lower cost.

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TABLE I - Consumption of various elements (tons)

	<u>USA (1977)</u>	<u>EEC (1975)</u>
Copper	2,243,000	1,974,000
Chromium	290,000	325,000
Nickel	155,000	150,000
Tin	60,700	68,400
Molybdenum	27,300	
Antimony	13,800	
Cobalt	8,300	5,936
Tungsten	8,500	7,870

TABLE II - Factors affecting hot shortness

- 1) Residual elements content
- 2) Alloying elements content
- 3) Oxidation rate
- 4) Oxidation potential of elements
- 5) Occlusion in the scale
- 6) Optimum oxidation-diffusion
- 7) Solubility limit of Cu in austenite
- 8) Melting point
- 9) Surface tension

TABLE III - Problem approach

- Alloying : Ni, Si

- Process parameters :
 - heating rate
 - soaking temperature
 - soaking time
 - furnace atmosphere

- Optimum scrap mix.

TABLE IV - Opportunities

- Improve product properties

- Scrap as a cheap source of alloying elements

- Computer assisted methods.

CAPTIONS FOR FIGURES

- Fig.1. Time trends in electric furnace production (AISI statistics)(1)
- Fig.2. Time trends in the ratio of scrap consumed to raw steel produced (AISI statistics)(1).
- Fig.3. Time trends in residual element concentrations in U.S. Steel (1).
- Fig.4. Lenses of Cu at steel-oxide interface. Steel containing 3%Cu held at 1100°C for 3h (6).
- Fig.5. Penetration of liquid Cu-enriched phase along austenite grain boundaries. Steel containing 3%Cu held at 1100°C for 6h (6).
- Fig.6. Cor-Ten steel without Ni addition : 1280°C for 3h hot rolled at 1100-1125°C (6).
- Fig.7. Slivers on Cor-Ten hot rolled strip (6).
- Fig.8. Effect of ternary additions on solubility of Cu in austenite at 1250°C (7).
- Fig.9. 1250°C isotherm for the mild steel Cu-Sn system (7).
- Fig.10. 1250°C isotherm for the mild steel Cu-Ni system (7).
- Fig.11. Dihedral angle as a function of temperature for the mild steel Cu system (7).
- Fig.12. Effect of Cu content and temperature on surface hot shortness (8).
- Fig.13. Effect of temperature on oxidation of a steel containing 3%Cu (6).
- Fig.14. Effect of furnace oxygen and water vapour on hot shortness in a 0.16% Cu-containing steel (8).
(a) oxidized 1h at 1000°C; (b) oxidized 1h à 1250°C.
- Fig.15. Effect of furnace SO₂ content on surface hot shortness (8).
- Fig.16. Scale on a 2.7%Cu-2%Ni after holding at 900°C for 24h (6).
- Fig.17. Scale formation on a 2.8%Cu-3%Ni steel after holding at 1200°C for 4h (6).
- Fig.18. Effect of Cu and Cu-Ni on the process of oxidation of steel at high temperature (1100°C)(6).

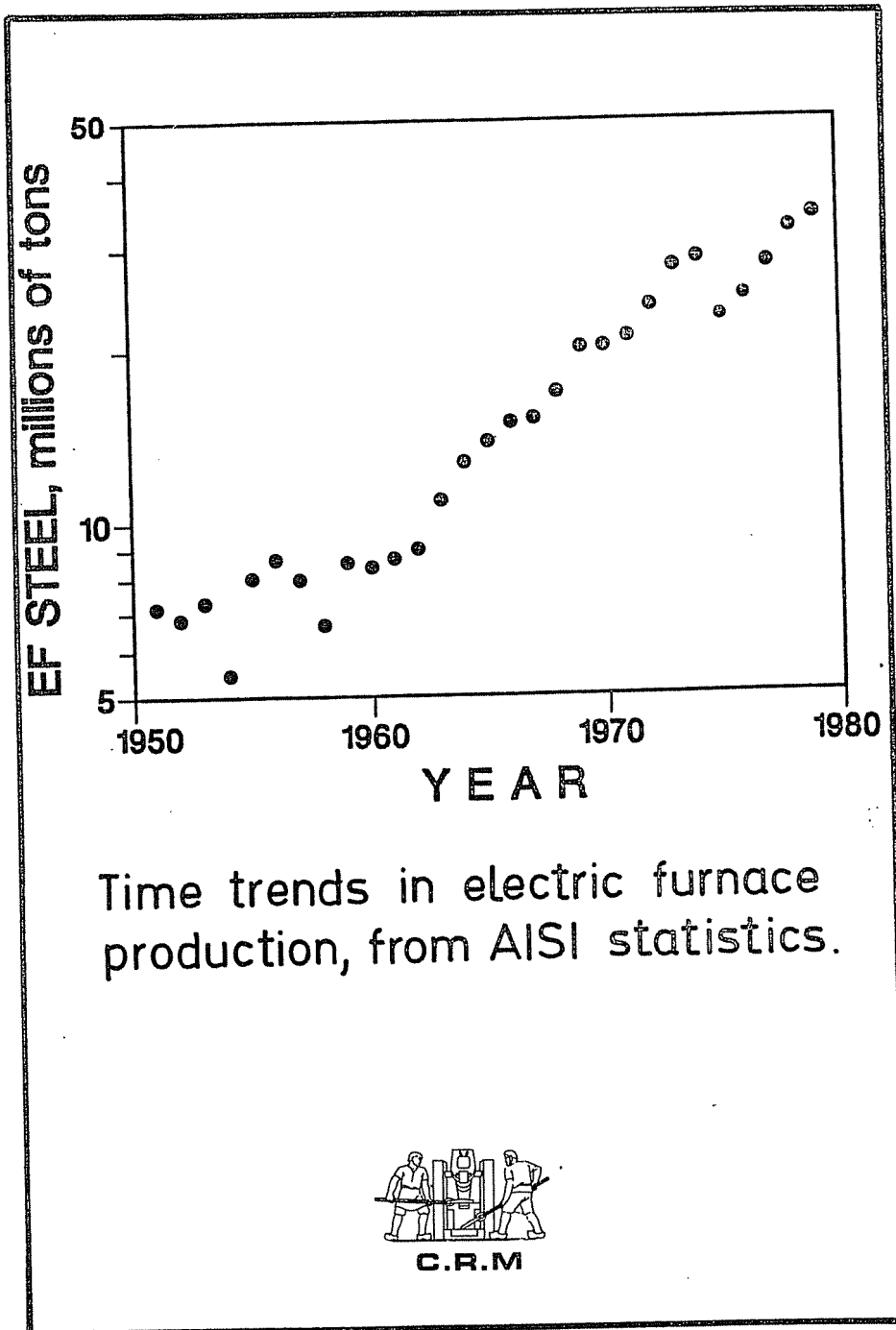


Fig.1.

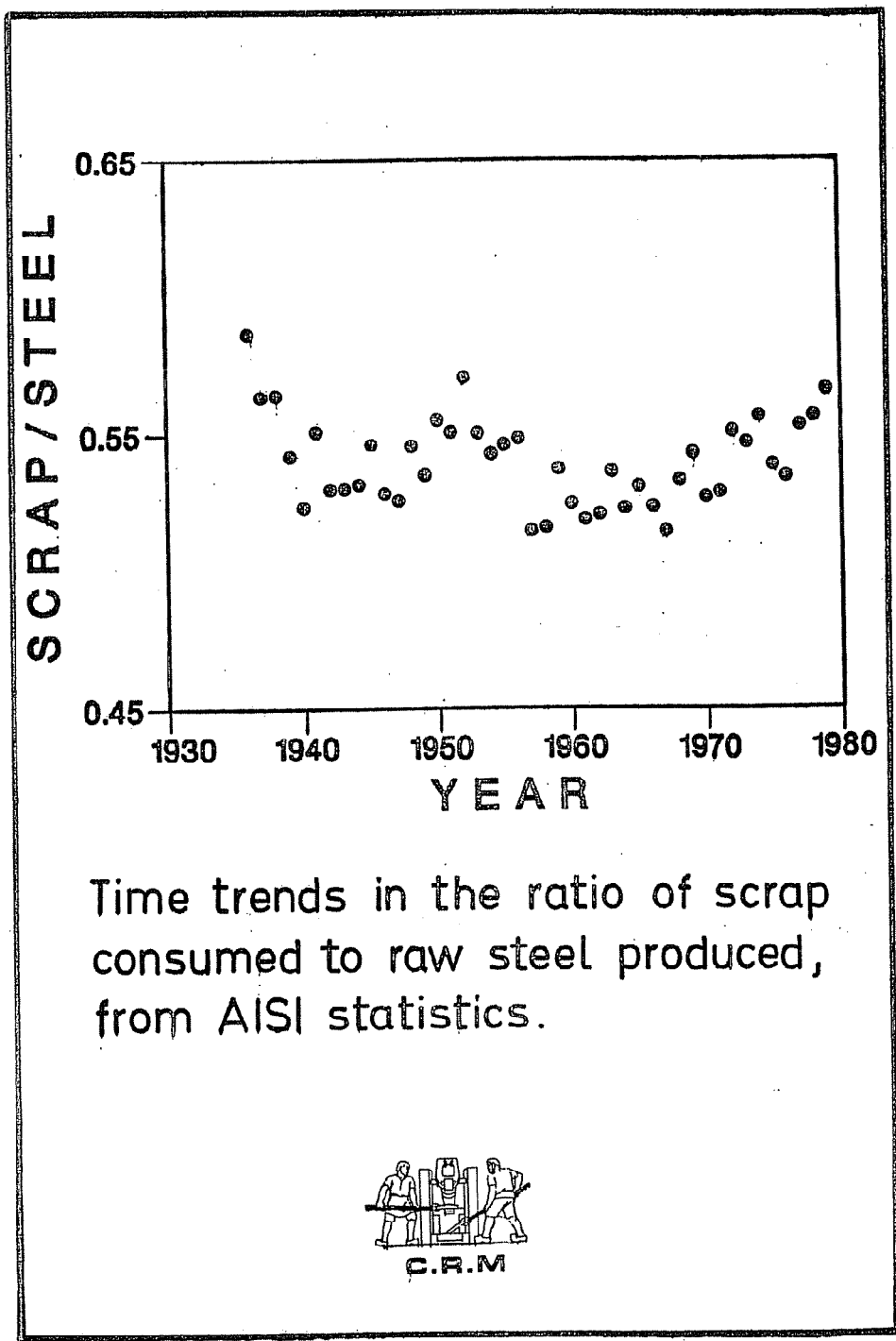


Fig.2.

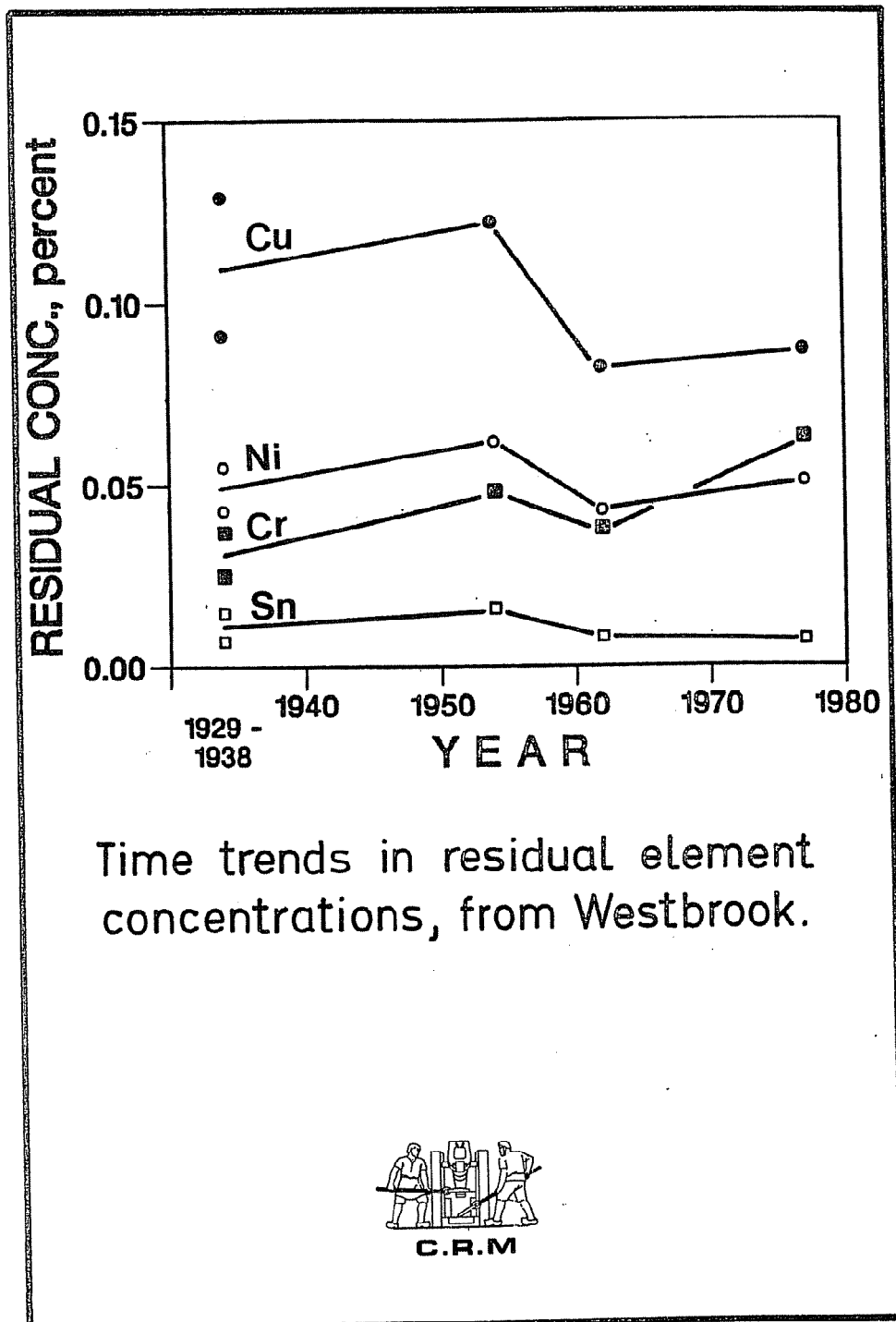
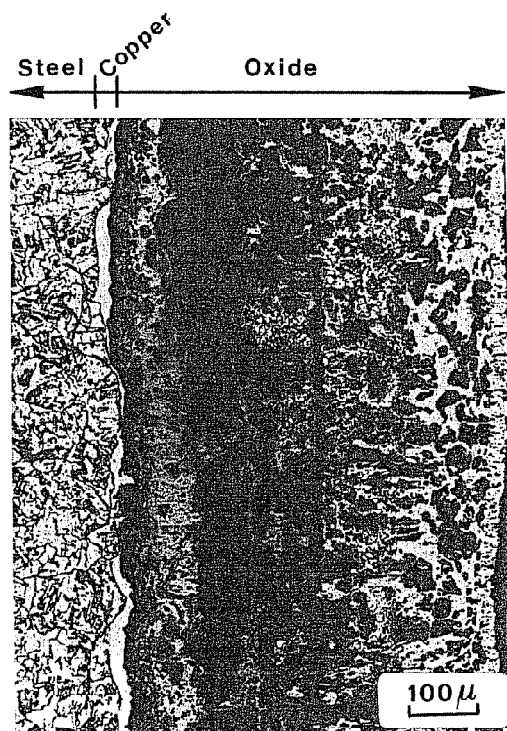


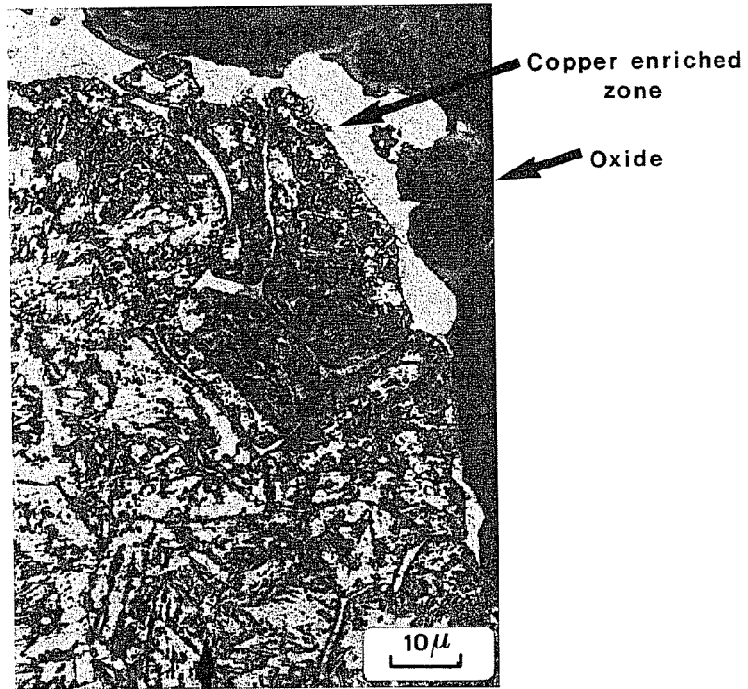
Fig.3.



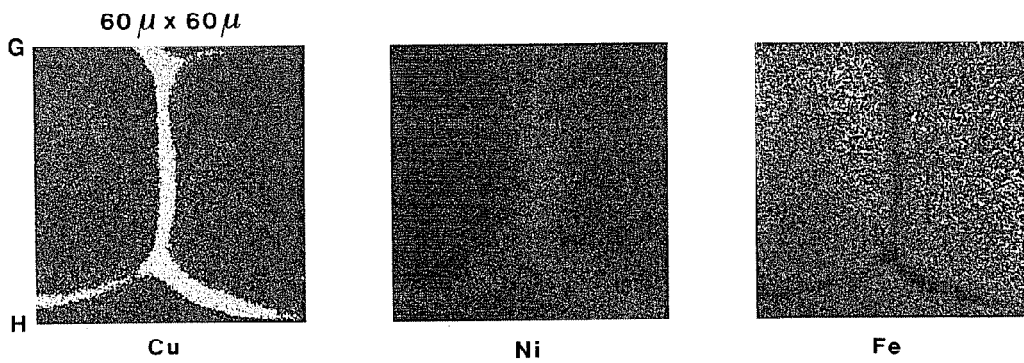
1100°C - 3h

Fig. 4.

Steel S4 - 1100°C - 6h



Base Metal



Microprobe X-ray picture

Fig. 5.

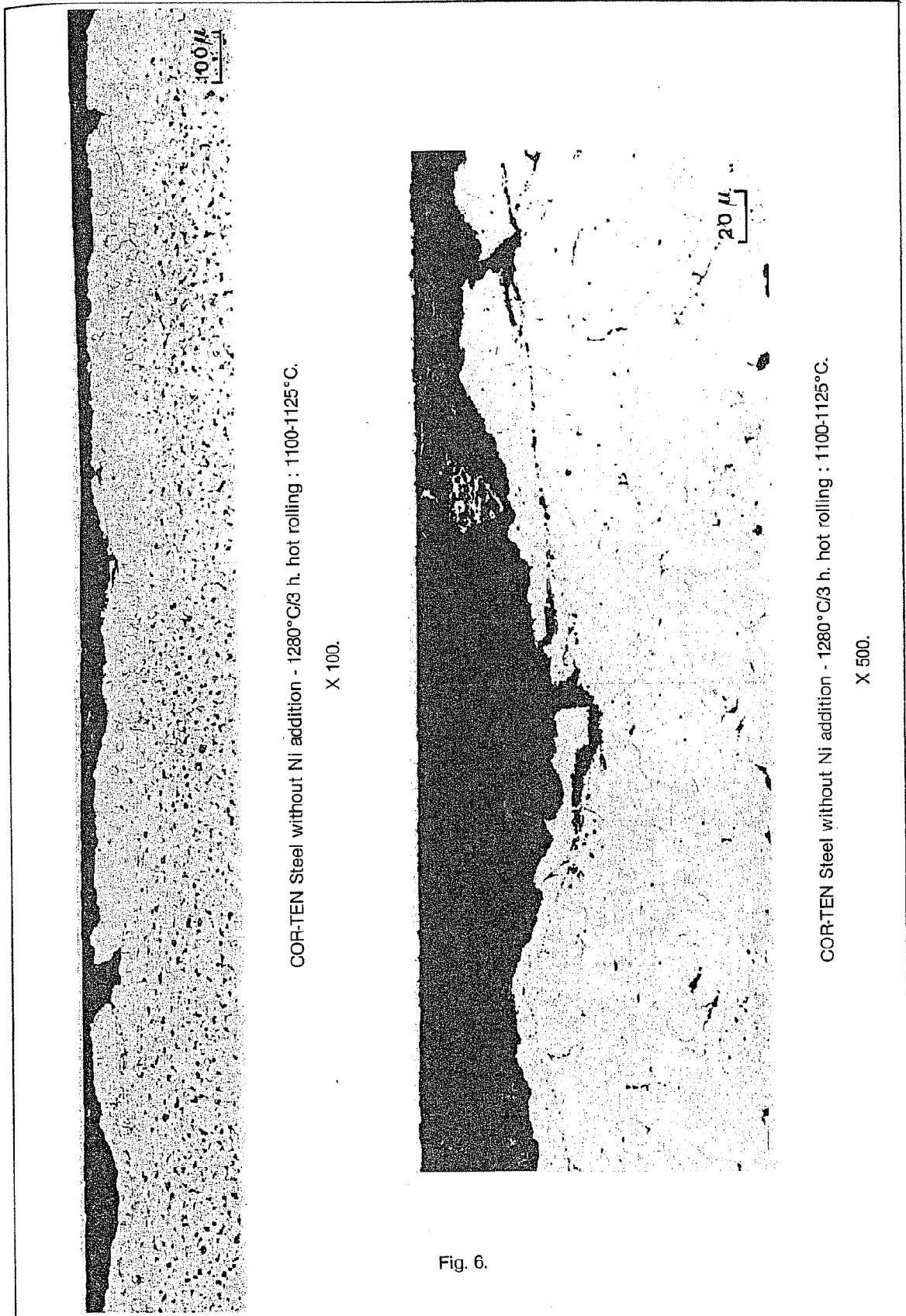


Fig. 6.

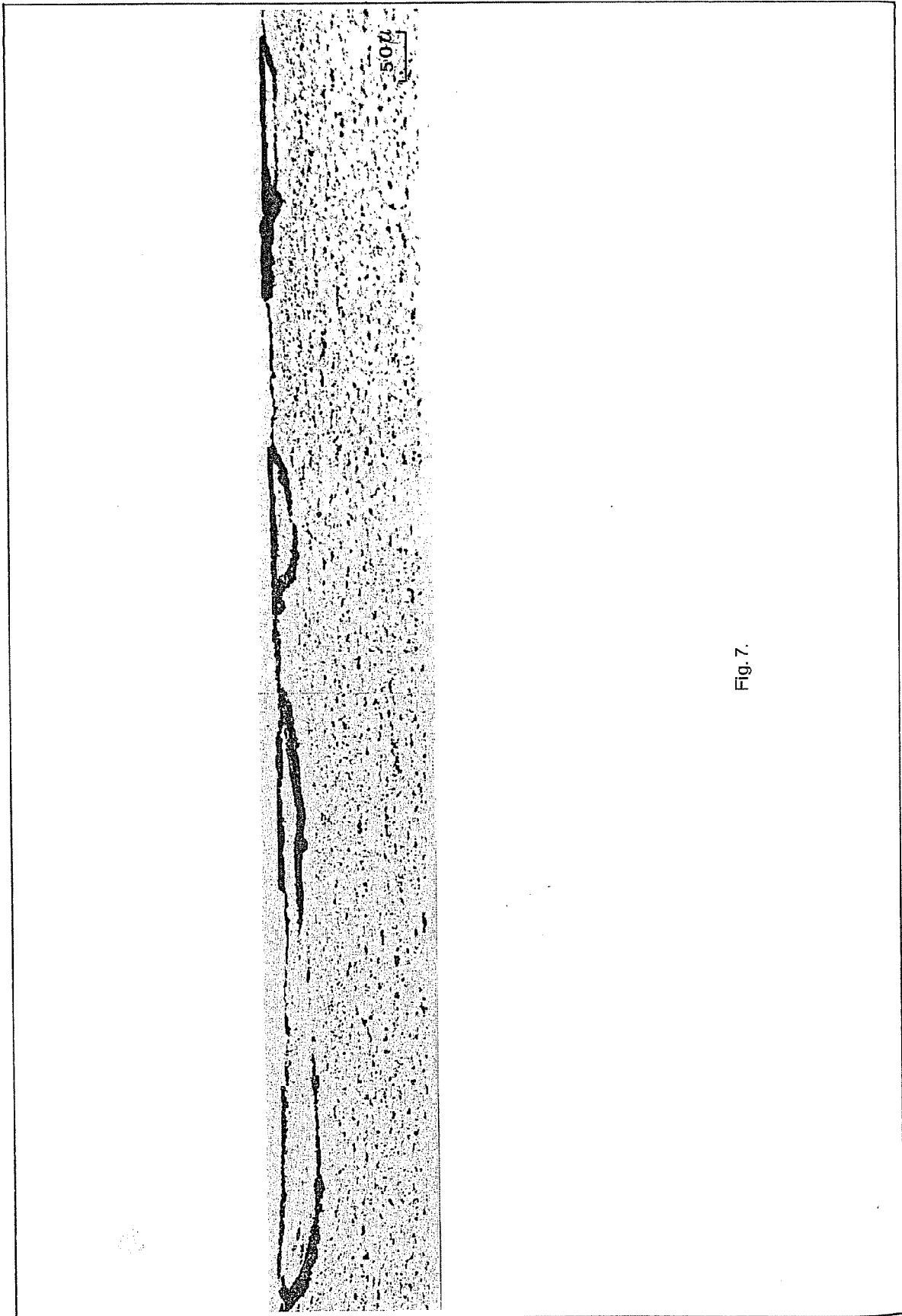


Fig. 7.

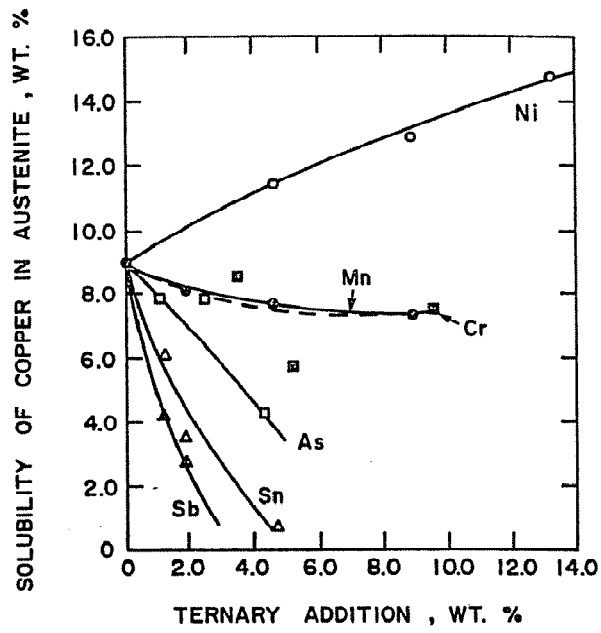


Fig. 8.

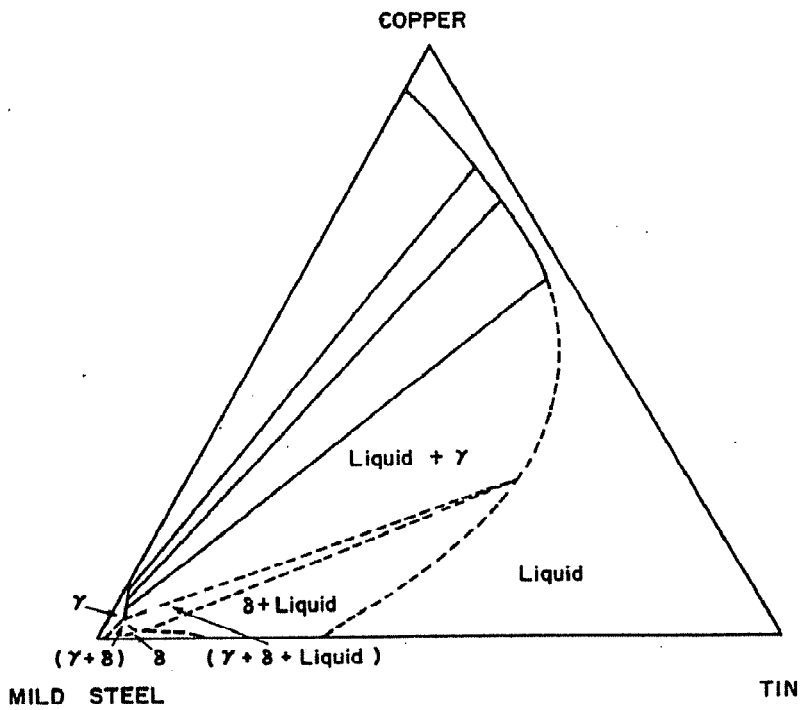


Fig. 9.

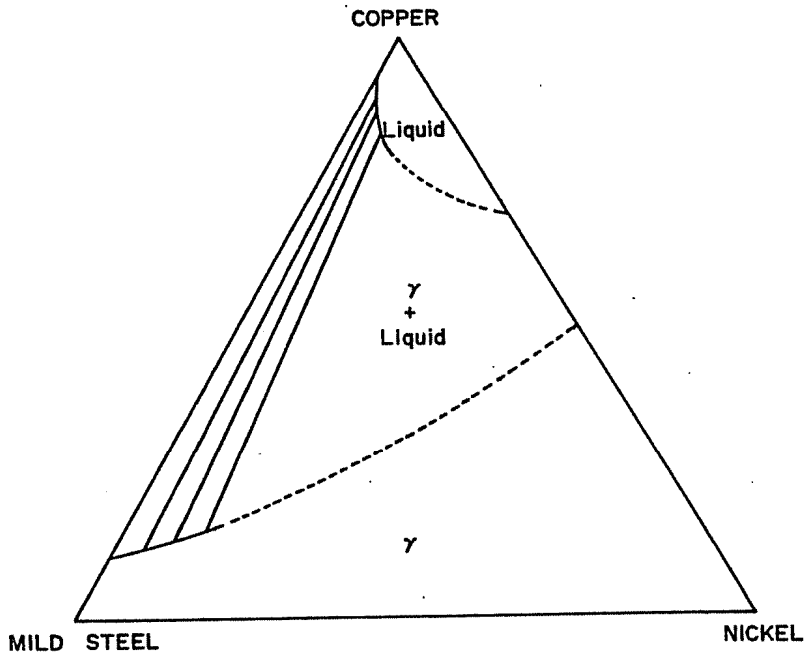


Fig. 10.

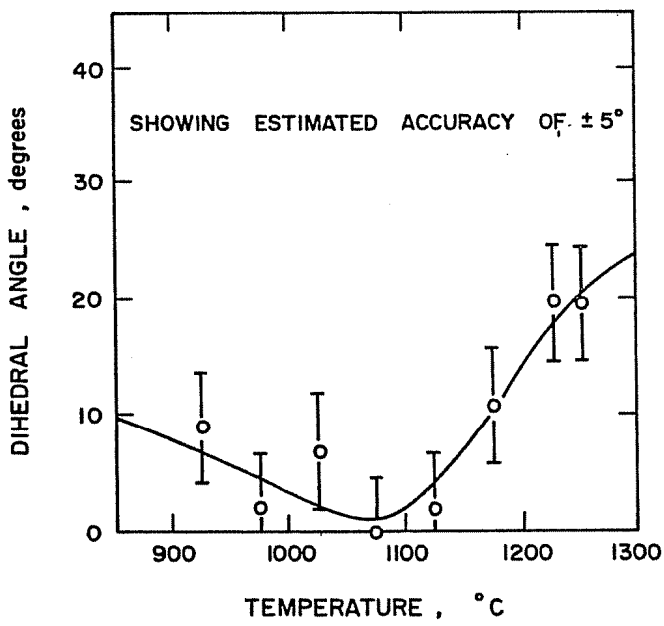


Fig. 11.

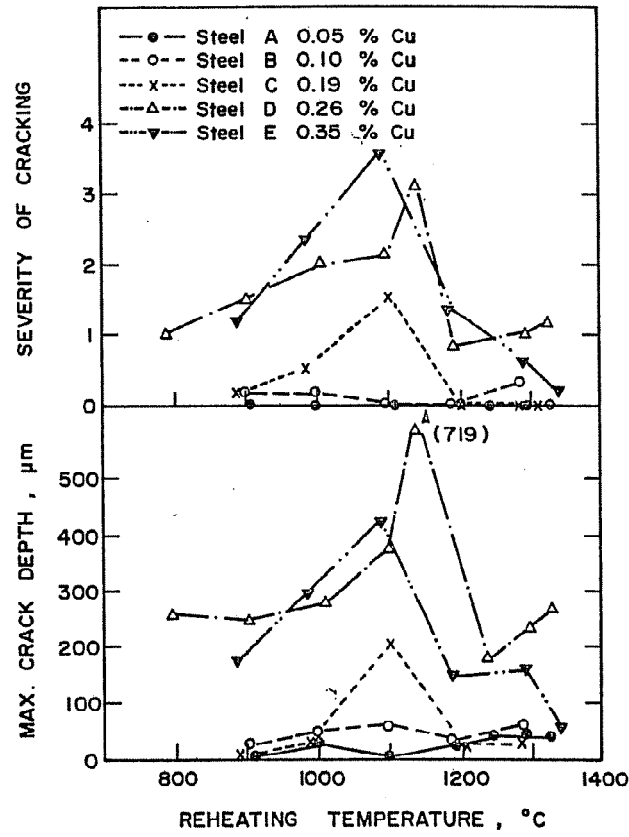


Fig. 12.

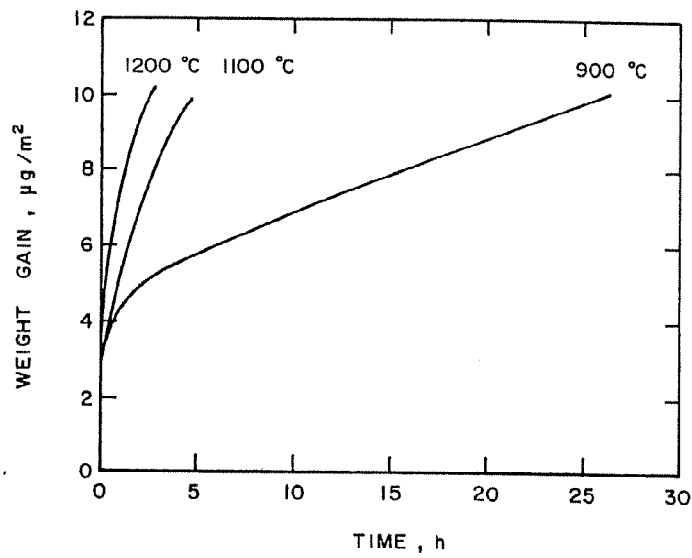


Fig. 13.

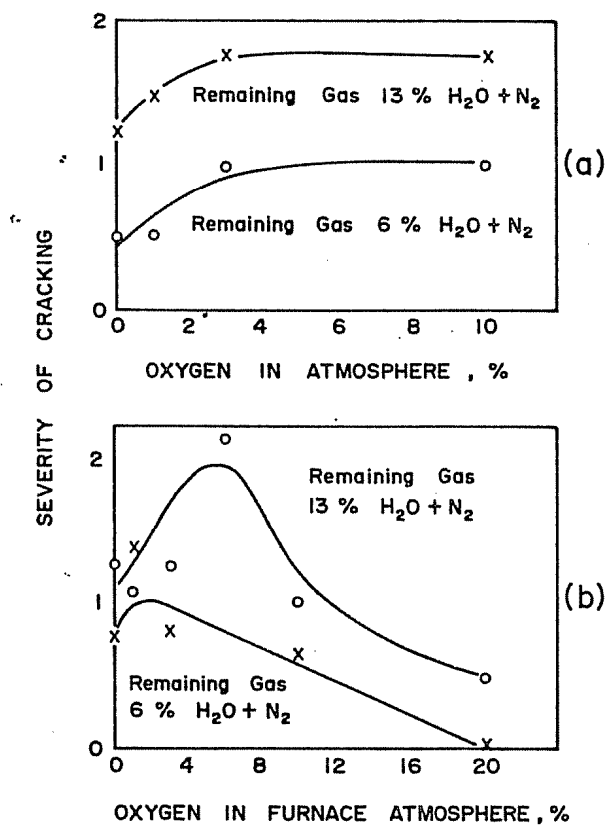


Fig. 14.

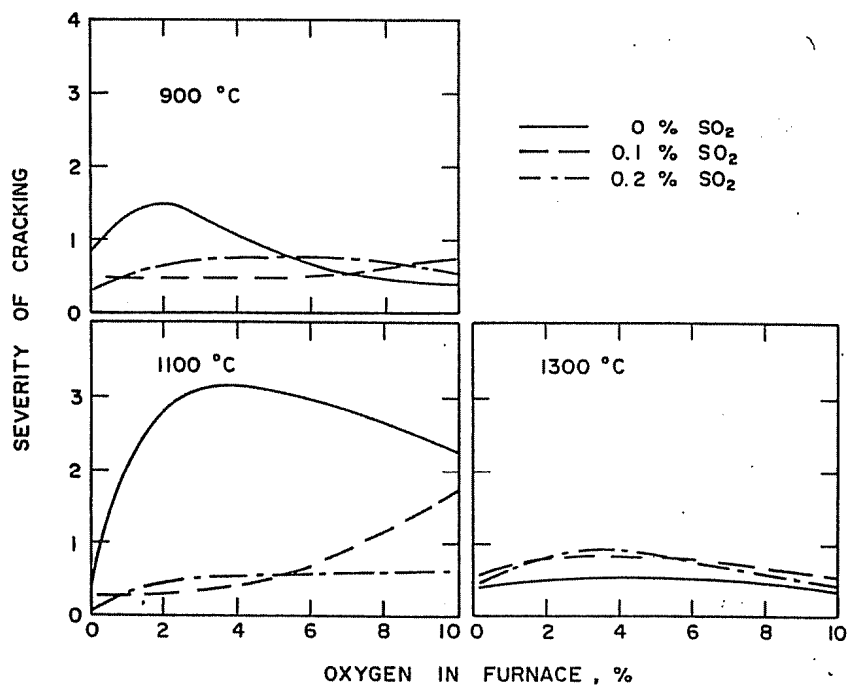


Fig. 15.

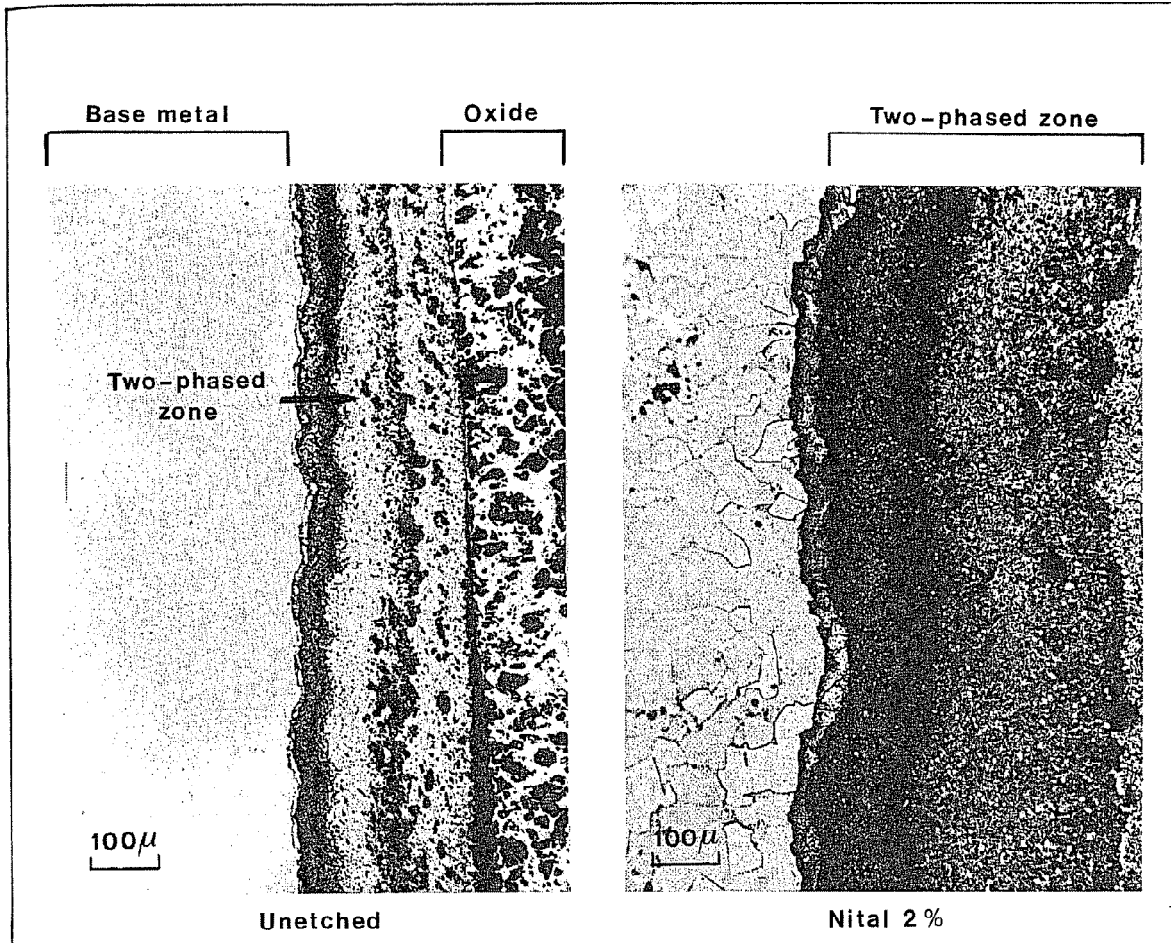


Fig. 16.

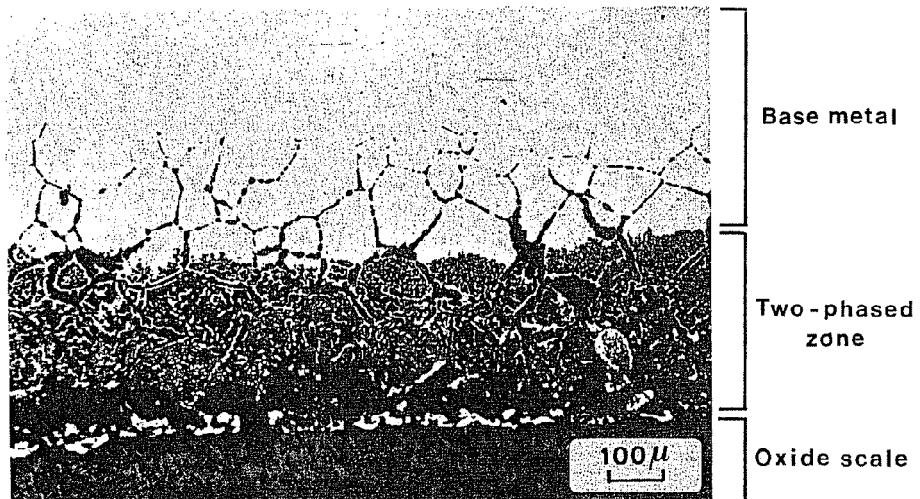


Fig. 17.

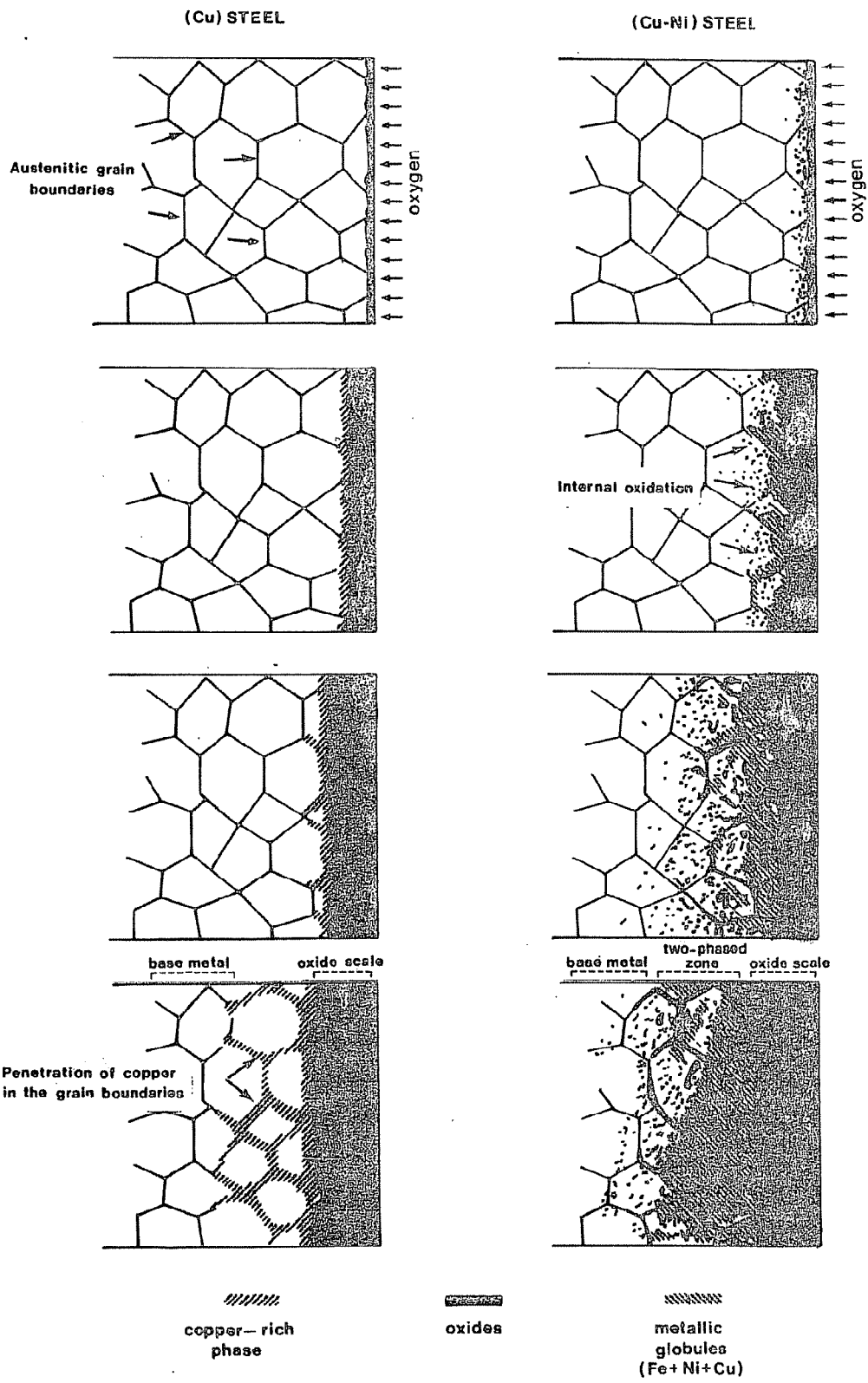


Fig.18.

Process of oxidation at high temperatures [T = 1100 °C]