

# Dissociative Mechanism of Scales Growth on Metals and Alloys

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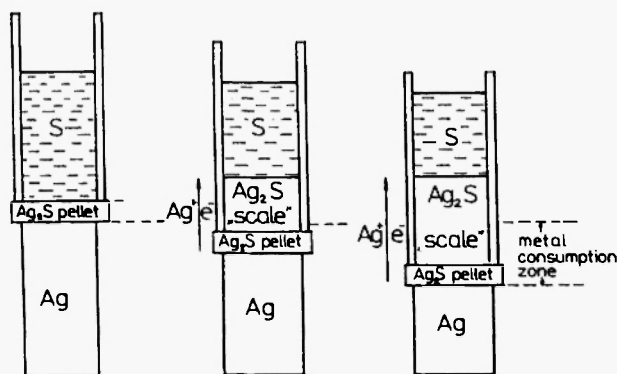
## ABSTRACT

The present paper is an attempt to reconsider the theoretical background of the formation of micro-porosity in scales on metals and to present convincing experimental proofs of the validity of dissociative growth theory, explaining the mechanism of this phenomenon. This theory is based on the assumption that, due to limited dimensions of the oxidized samples, the metal consumption zone cannot be continuously compensated by the plastic flow of the scale growing owing to the outward diffusion of cations. As a consequence, a crack develops at the metal-scale interface, following the decomposition (dissociation) of the primary compact scale layer and the formation on the metal surface a porous inner layer. The dissociation of the outer layer proceeds mainly along the perpendicular-to-the-core grain boundaries of large columnar crystals of this layer, resulting in the formation of dissociation fissures, enabling eventually the inward diffusion of the oxidant.

Direct experimental proofs of the formation of dissociation fissures and of the mechanism of double-layer scale growth on metals and binary alloys, obtained with the use of radioactive isotope of sulphur  $^{35}\text{S}$  and stable isotope of oxygen  $^{18}\text{O}$ , have been presented. All these results may be considered as an ultimate demonstration that the specific micro-porosity in scales growing by the outward diffusion of cations has nothing in common with mechanical stresses developed in metal-scale-oxidant system during the reaction.

## 1. INTRODUCTION

Wagner's theory of metal oxidation [1], being a milestone in the development of the theory of gas corrosion of metallic materials, was based on the assumption that the matter transport in the growing single-phase oxide or sulphide scale on metals proceeds through point defects, i.e., by volume diffusion, this process being the slowest step in the overall reaction rate (parabolic kinetics). This main assumption is perfectly true only in the case when the scale is compact and well adherent to the metallic core during the whole reaction time and grain boundary diffusion may be neglected. As the activation energy of volume diffusion is generally much higher than that through grain boundaries, at high temperatures the last process is, in fact, unimportant. Since transition metal oxides and sulphides show as a rule predominant point defects in cation sublattice [2,3], from Wagner's theory it follows that in all those cases oxide and sulphide scales on metals should grow by the outward diffusion of cations. In his well known experiments carried out with the so called pellet method (Fig. 1) Wagner has demonstrated that the sulphide scale on silver grows, as expected, exclusively owing to the outward diffusion of cations. However, the process of scale formation in the "pellet system" does not simulate properly any real metal-scale-oxidant system, since the "scale" grown into the reaction tube can freely move down together with the pellet, following the receding metal surface, as a result of which metal consumption zone is fully compensated



**Fig. 1:** Scheme of the Wagner's pellet method.

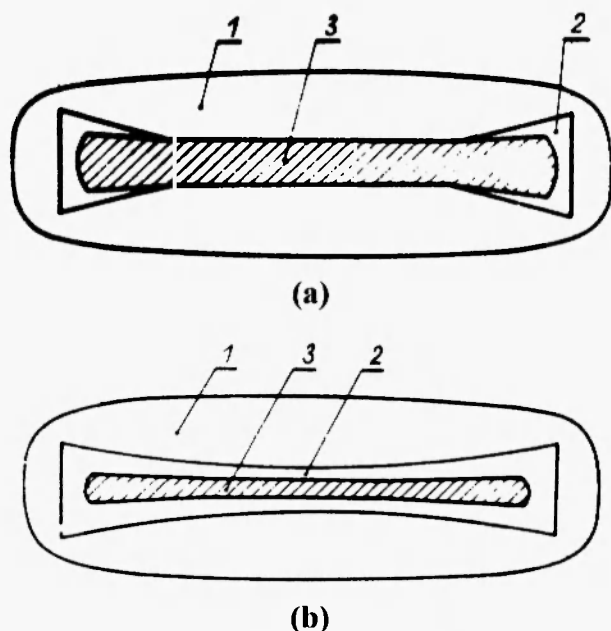
without any restrictions. In conventional sulphidation and oxidation experiments the situation is much more complex because the metal consumption zone can be compensated only to some extent owing to the plastic flow of the scale. In fact, numerous studies have shown that the single-phase scales are generally composed of two layers with the marker located in the interior of the scale, indicating that the inner porous scale layer is growing as a result of inward diffusion of the oxidant. However, in some cases it has been found that under the same reaction conditions the scale may be compact and single-layer with the marker located close to the metal-scale interface, clearly indicating that in agreement with Wagner's approach such a scale does form virtually only by the outward diffusion of cations. A number of hypotheses have been put forward in the literature concerning possible mechanisms of the formation of single-phase double-layer scales, criticizing Wagner's theory, but none of them could give a convincing and consistent explanation of this fundamental – from a scientific and practical point of view – problem in question.

About 35 years ago, basing on a number of experimental results and theoretical considerations, the author of the present paper showed /4/ that the main reason for the inconsistency of Wagner's theory with experimental results mentioned above is only apparent and results from secondary dissociation processes which may or may not occur at the metal-scale interface, depending on the size and shape of the oxidizing element (sample) and the time of reaction. This "dissociative growths theory" has been accepted in the

literature, but several years later some authors postulated that the specific micro-porosity in scales growing owing to the outward diffusion of cations results rather from mechanical stresses developed during the reaction in the metal-scale system and not due to secondary dissociation processes. These mental reservations seem to result from the fact that the experimental proofs of the discussed theory have been spread over a number of papers published in different journals /5-20/ and only the first paper /4/, describing merely the theoretical basis, was the subject of the above-mentioned criticism. Considering these misunderstandings, the author of the present paper arrived at the conclusion that it would be reasonable to summarize the most important experimental results (published and not yet published) and on the basis of theoretical background explain that the mechanism of the formation of specific porosity in scales on metals and alloys has nothing in common with mechanical stresses but results from secondary anisotropic dissociation processes.

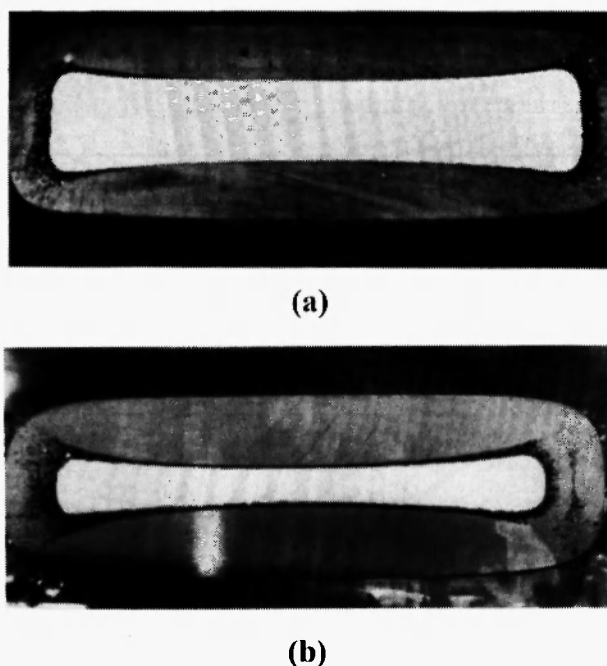
## 2. THEORETICAL BACKGROUND AND EXPERIMENTAL PROOFS

The favourable conditions for plastic flow of the scale, growing by the outward diffusion of cations, exist on sufficiently large flat surfaces but limited dimensions of the sample make it the more difficult the thicker is the scale and the less plastic is the reaction product. The system is, namely, rigid on edges and curvatures of the oxidizing element and it is there where the scale loses its full contact with the metallic core already in the very beginning of the reaction. In this stage the scale is single-layer and adherent to the substrate in flat regions of the sample and double layer and porous on edges. With the reaction progress, detachment of the scale from the substrate extends gradually over flat regions of the oxidizing sample and the scale becomes double-layer all over the surface of the metallic core. The scheme of scale morphology in these two stages of the reaction is depicted in Fig. 2, and in Fig. 3 this situation is illustrated by two cross-sections of flat silver samples, having the same dimensions, but sulphidized for two different times.



**Fig. 2:** Schemes of scale morphology formed on flat metal samples; (a) – in early stages of the reaction; (b) – in later stages; 1 – outer compact scale layer; 2 – inner porous layer; 3 – metallic core.

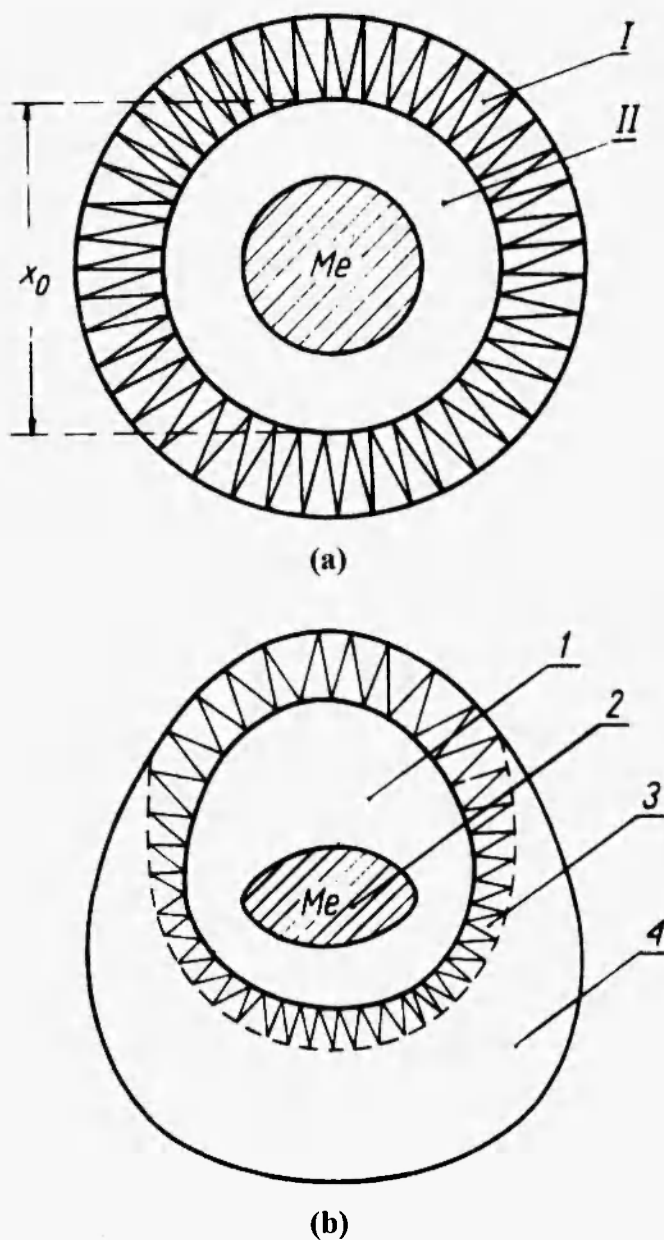
Ag - S and Cu - S systems have been chosen as the most suitable models for studying the mechanism of single-phase scale formation, because  $\text{Ag}_2\text{S}$  and  $\text{Cu}_2\text{S}$  sulphides, defected virtually only in cation sublattice, are extremely plastic even at room temperatures and consequently, the formation of cracks and fissures in these scales due to mechanical stresses can absolutely be excluded [2,3]. From the photographs presented in Fig. 3a it follows that in agreement with the scheme in Fig. 2a,  $\text{Ag}_2\text{S}$  scale on silver in flat regions of the sample is initially compact and well adherent to the substrate, clearly indicating that in this region the metal consumption zone was fully compensated by the plastic flow of the scale, growing by the outward diffusion of cations, like in the model-pellet-system (Fig.1) representing, in fact, infinitely large flat surface. In the vicinity of edges, on the other hand, where the system was rigid and the plastic flow of the scale was impossible, the porous, double-layer scale was formed (Fig.3a). In these regions then, the scale was growing as a result of outward lattice diffusion of cations and the



**Fig. 3:** Cross-sections of sulphide scales formed on two flat silver samples of the same dimensions at 712 K. (a) – reaction time 5 min., (b) – reaction time 10 min.,  $X_0$  - initial thickness of the sample [15].

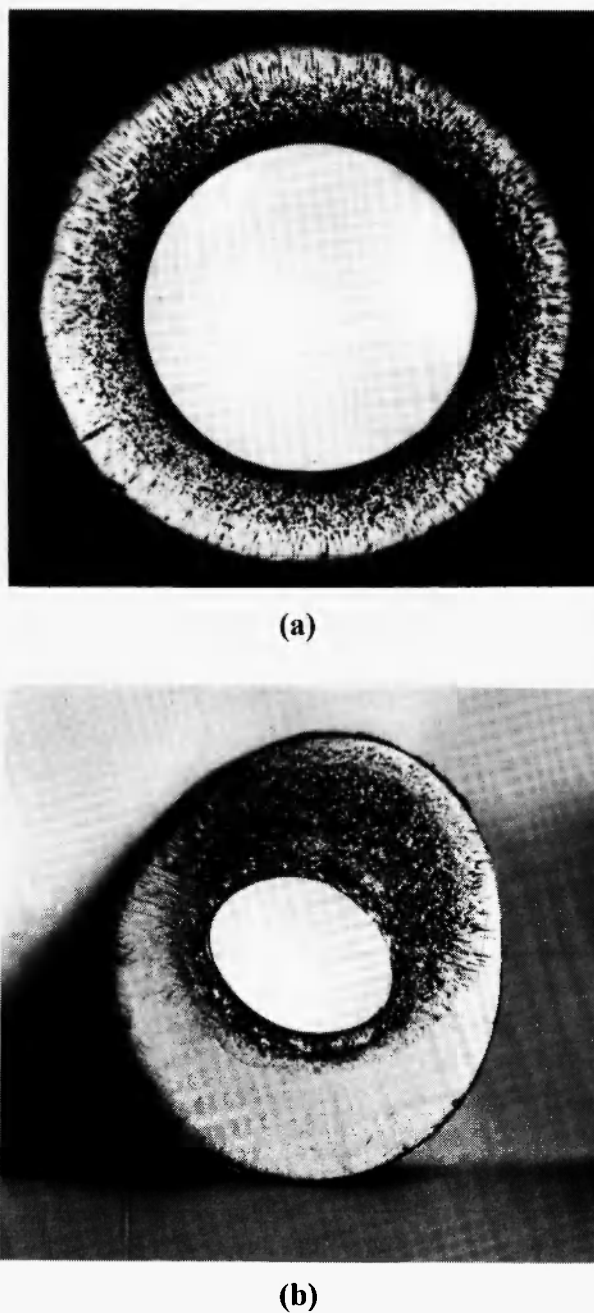
inward diffusion of sulphur, from the very beginning of the sulphidation process. In later stages, finally, when the scale becomes thicker, the inner porous layer starts to be formed also in flat regions of the metallic core, because the plastic flow of the reaction product cannot continuously compensate fully the metal consumption zone (Fig. 3b).

The least favourable conditions for plastic deformation of the scale exist on round-shaped samples (wires, cylinders) because in this case the system is rigid all over the surface. One may then anticipate that the scale on a wire should be double-layer and porous over the whole surface, as depicted schematically in Fig.4a. However, when the wire is sulphidized (or oxidized) in horizontal position, the metallic core in the rigid shell of the scale can move down under its weight, compensating to some extent metal consumption zone (Fig. 4b). Two cross-sections of copper wires sulphidized in different positions confirmed this type of reasoning (Fig. 5a and b). As can be seen, the scale on



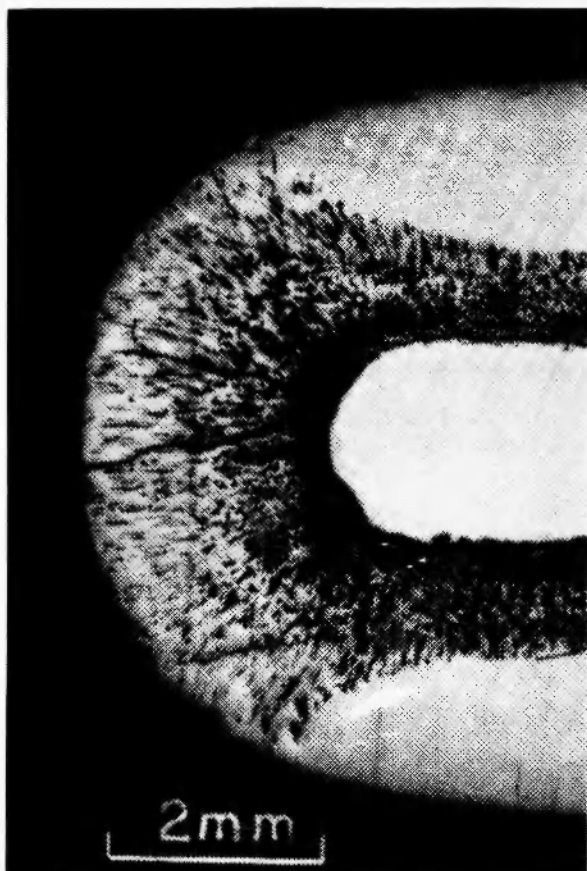
**Fig. 4:** Schemes of scale morphology formed on round-shaped metal samples (wires); (a) – sulphidized in vertical position; (b) – sulphidized in horizontal position; 1 – inner porous layer; 2 – metallic core; 3 – intermediate porous layer; 4 – outer compact layer.

the wire sulphidized in vertical position (Fig. 5a) was double-layer and porous over the whole surface of metallic core and shown analogous morphology to that observed on edges of flat copper sample sulphidized



**Fig. 5:** Cross-sections of copper wires sulphidized at 712 K; (a) – in vertical position; (b) – in horizontal position.

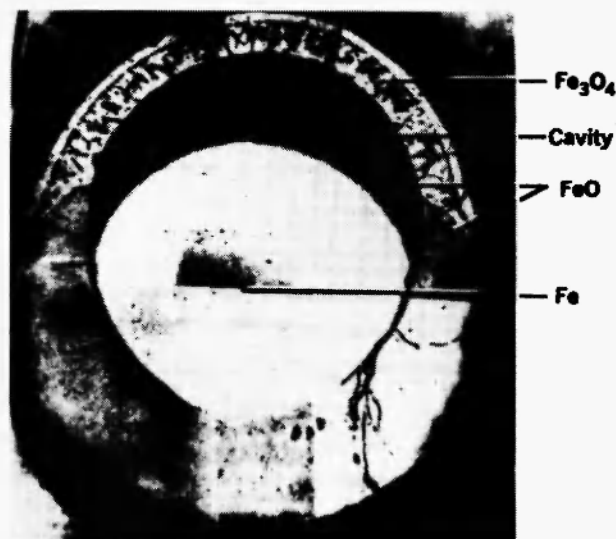
under the same experimental conditions (Fig. 6). On the other hand, the scale morphology on the wire sulphidized in horizontal position is completely different (Fig. 5b). It is clearly seen that in the bottom part a double-layer scale has been formed, with the thick, compact outer layer and the thin inner one, owing



**Fig. 6:** Cross-section of the corner-fragment of flat copper sample sulphidized at 712 K.

to partial compensation of metal consumption zone by moving down of the metallic core, like in the case of sulphidation of flat specimen (Fig. 3b). On the other hand, in the upper part a very thick inner porous layer was formed with a thin and also porous outer scale layer. An analogous situation is observed in the case of oxidation (Fig. 7).

The question then arises, what is the rational explanation of the mechanism of double layer scale formation with predominant cation disorder. First of all it may be stated that, from the above discussion it follows that the influence of mechanical stresses on the formation of such specific micro-porosity in these scales can *a priori* be ruled out. On the other hand, the explanation of this phenomenon follows directly from dissociative growth theory under discussion. The thermodynamics and kinetics of secondary processes



**Fig. 7:** Cross-section of an iron wire oxidized at 1023 K in horizontal position.

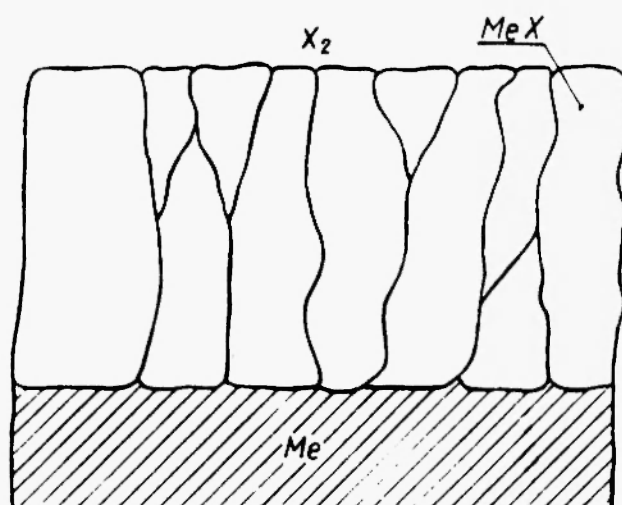
leading up to the formation of dissociation fissures and consequently to the development of double-layer scales with predominant cation disorder, have been described elsewhere [4,20]. In the present paper the main assumptions of this theoretical approach will only be recalled and the most convincing experimental proofs, already published and not yet published, will be demonstrated.

From the above discussion it follows that the process of scale formation can be regarded as consisting of two stages in which compact, mono-layer scale, well adherent to the substrate, is formed in the first stage. In agreement with Wagner's theory the rate determining step of the reaction in this stage is the outward diffusion of cations (parabolic kinetics) [22,23]. Thus, a constant difference of chemical potential of the oxidant is established in the growing scale with its lowest value at the metal-scale interface, determining the dissociation pressure of the reaction product (local thermodynamic equilibrium at the metal-scale interface). As the reaction proceeds the thickness of the scale exceeds a certain critical value at which metal consumption zone cannot be further fully compensated by plastic flow of the scale layer and the process passes into the second stage. Between the metallic phase and the reaction product a crack starts to develop, hindering the transfer of cations from the metal to the scale. As the outward diffusion of

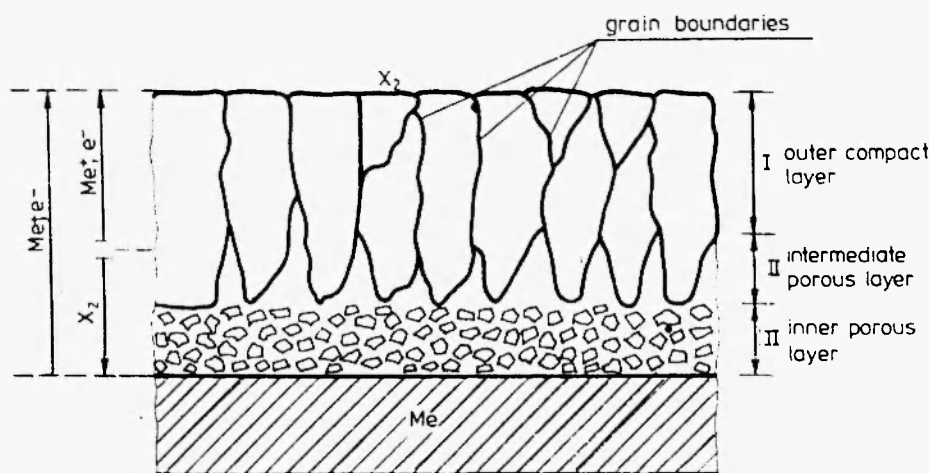
cations is still continued, this leads to the rise of chemical potential of the oxidant at the inner surface of the scale and thereby the oxidant pressure in the crack increases. The conditions are then created for secondary formation of the reaction product on the metal surface. As a consequence, a gradient of oxidant pressure in the crack is established, resulting in the formation of the inner porous layer of the same phase composition. The loss of the oxidant in the crack due to this reaction is followed by gradual decomposition (dissociation) of the primary outer layer and ions and electrons liberated in this process diffuse outward.

From these short remarks it follows that the formation of the single-phase, double layer scales on metals may form without the participation of the inward diffusion of the oxidant from outside. However, it is well known that the scales growing by the outward diffusion of cations show highly developed growth texture, characterised by long columnar crystals, as illustrated schematically in Fig. 8. Such an anisotropic character of crystal growth clearly indicates that the reverse process of decomposition (dissociation) must proceed with the highest rate on crystal planes with slowest growth rate, i.e., along the perpendicular-to-the-core grain boundaries. As a result of this, primary scale layer begins gradually to lose its compactness and a triple-layer scale is formed, built of two porous layers and the outer compact one, which is a part of primary scale not yet affected by dissociation processes, as

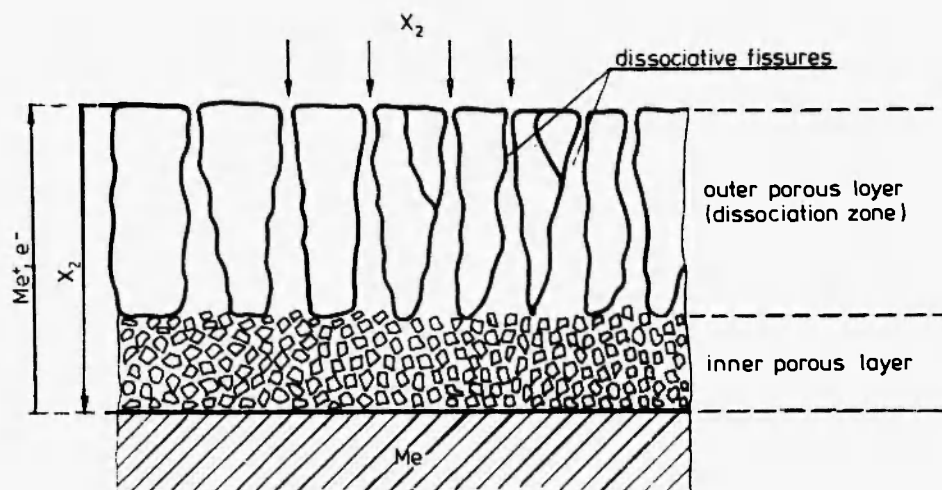
shown schematically in Fig. 9. The relative thicknesses of both porous layers depend on the shape and dimensions of the oxidized sample because of different conditions for the plastic flow of the scale. In the vicinity of edges of flat specimens and over the whole surface of round-shaped samples (wires, cylinders) the metal consumption zone remains virtually uncompensated and therefore dissociation processes begin to operate right at the beginning of scale formation and lead to immediate perforation of a very thin primary scale layer, i.e., to the formation of porous, double-layer



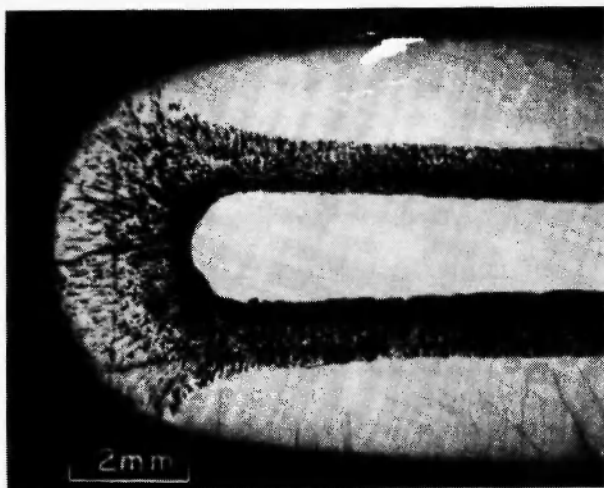
**Fig. 8:** Scheme of the scale morphology formed on a flat metal sample by the outward volume diffusion of cations. Me – metal; X – oxidant.



**Fig. 9:** Scheme of the growth mechanism of a single-phase, triple-layer scale on metals (regions of flat sample surface).



**Fig. 10:** Scheme of the growth mechanism of a single-phase, double layer scale on metals (regions of edges or curvatures of the sample).



**Fig. 11:** Cross-section of a flat copper sample sulphidized at 712 K /15/.

scale, growing by simultaneous diffusion of both reactants (Fig. 10). In the middle regions of flat specimens, on the other hand, triple-layer scale is growing as a result of the outward diffusion of cations, only (Fig. 9). From the photograph presented in Fig. 11 it follows clearly that on one and the same flat specimen double- and triple-layer scale can be formed by the two different mechanisms discussed above, and in early stages even single-layer scale may be observed (Fig. 2a and 3a).

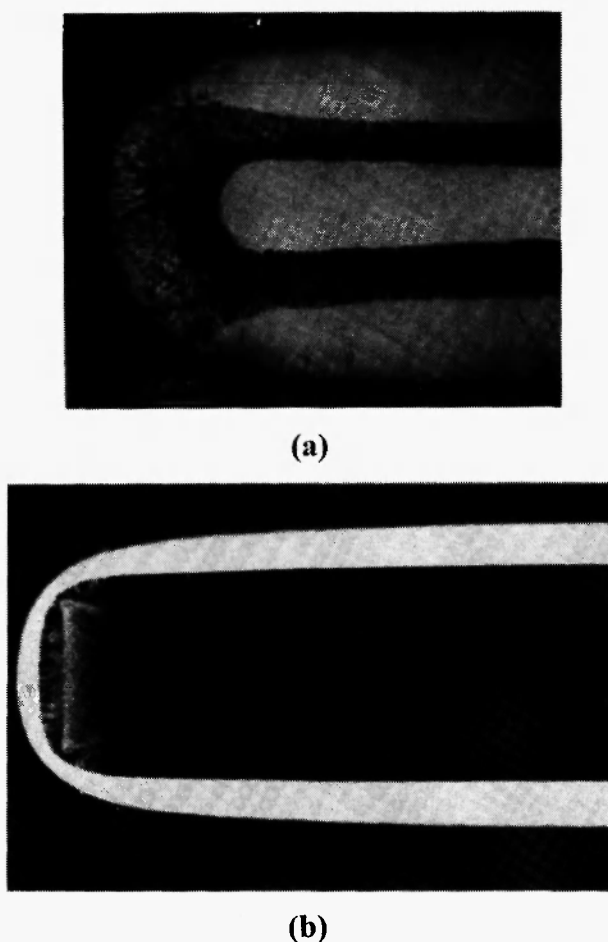
### 3. TWO-STAGE SULPHIDATION AND OXIDATION METHOD

In order to get direct, convincing proofs of the decisive influence of secondary dissociation processes on the growth mechanism of sulphide and oxide scales on metals a number of experiments have been carried out using radioactive isotope of sulphur  $^{35}\text{S}$  and stable, heavy isotope of oxygen  $^{18}\text{O}$ . The original, two-stage sulphidation (or oxidation) methods /13,16,18/, applied in these investigations, consisting in sulphidizing (or oxidizing) of a given metal sample, first in normal atmosphere and then, without breaking up the reaction, in the environment containing the radioactive sulphur- or stable oxygen isotope. After terminating the sulphidation reaction the distribution of the radioactive sulphur isotope in the cross-section of the scale was determined autoradiographically. In the case of oxide scales the distribution of stable oxygen 18 was examined by sectioning and autoradiographic methods /16/ with the use of two nuclear reactions:  $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$  and  $^{18}\text{O}(p, n)^{18}\text{F}$ . In the former method the scale surface was irradiated with alpha particles and the emitted neutrons were registered. Then, the thin scale layer was ground parallelly to the surface and the whole procedure was repeated until complete removal of the scale. The autoradiographic method consisted in proton irradiation of the scale cross-section, which resulted in transformation of oxygen 18 into radioactive fluorine,



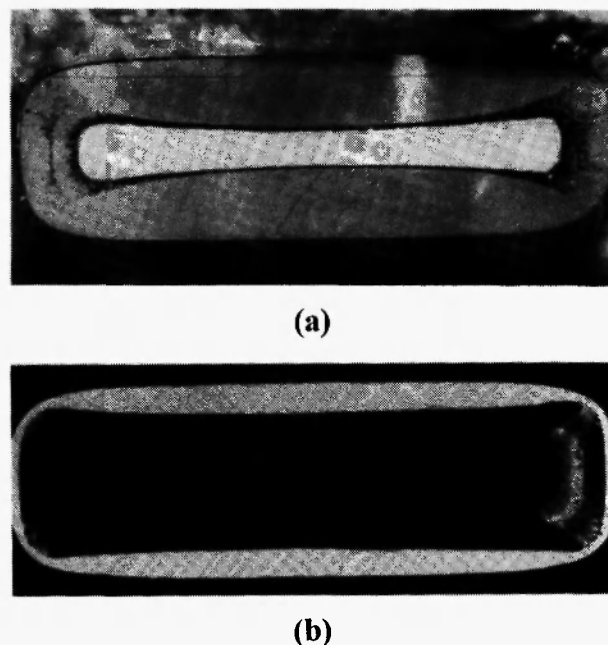
$^{18}\text{F}$ , and its distribution in the scale cross-section was determined autoradiographically.

The experiments with oxygen isotope were only fragmentary because it has been found that the secondary dissociation processes play exactly the same role in the formation of sulphide and oxide scales, and much more clear and illustrative results could have been obtained in the case of sulphidation. Fig. 12 shows, for illustration, an autoradiogram and the photograph of the cross-section of the sulphide scale formed on a flat copper sample, during two-stage sulphidation experiment. As can be seen, on edges of the sample, where no plastic flow of the scale did occur, it became



**Fig. 12:** Photograph (a), and autoradiogram (b) of the cross-section of the sulphide scale formed at 712 K on a flat copper sample in two-stage sulphidation experiment; 5 min. in non-radioactive, and 15 min. in radioactive sulphur /15/.

perforated and therefore sulphur diffused inwardly (the radioactive isotope of sulphur was present in the entire cross-section of the reaction product). In contrast, in the region of flat surfaces, where the dissociation began much later and did not result in scale perforation, the growth of the scale proceeded without the participation of inward diffusion of sulphur from the ambient atmosphere (the  $^{35}\text{S}$  isotope is present only in the outer part of a compact layer, formed during the second stage of the reaction). Analogous results have been obtained in two-stage sulphidation of silver (Fig. 13) and iron (Fig. 14) at different temperatures.

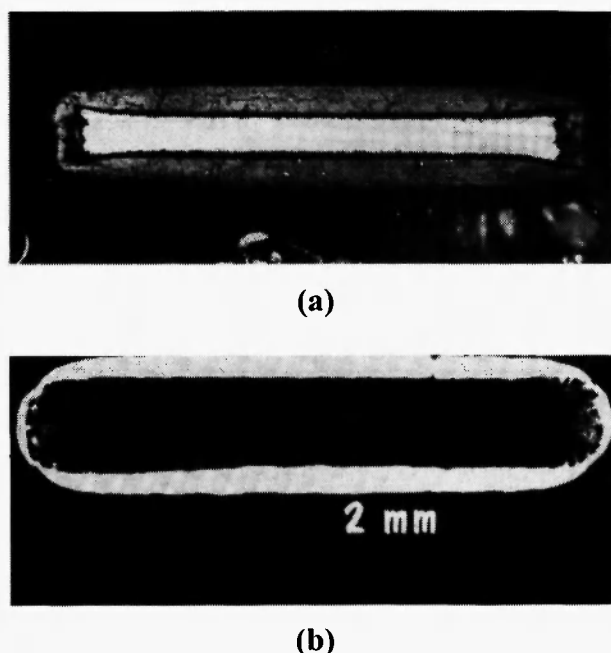


**Fig. 13:** Photograph (a), and autoradiogram (b) of the cross-section of the sulphide scale formed on a flat silver sample at 712 K in two-stage sulphidation process; 2 min. in non-radioactive and 4 min. in radioactive medium /10/.

#### 4. THE EFFECT OF THE SHAPE AND SIZE OF THE OXIDIZED SAMPLE

The effect of sample geometry on the growth mechanism of single-phase scales on metals is very well illustrated in Fig. 15, showing photographs and autoradiograms of two cross-sections of sulphide scales

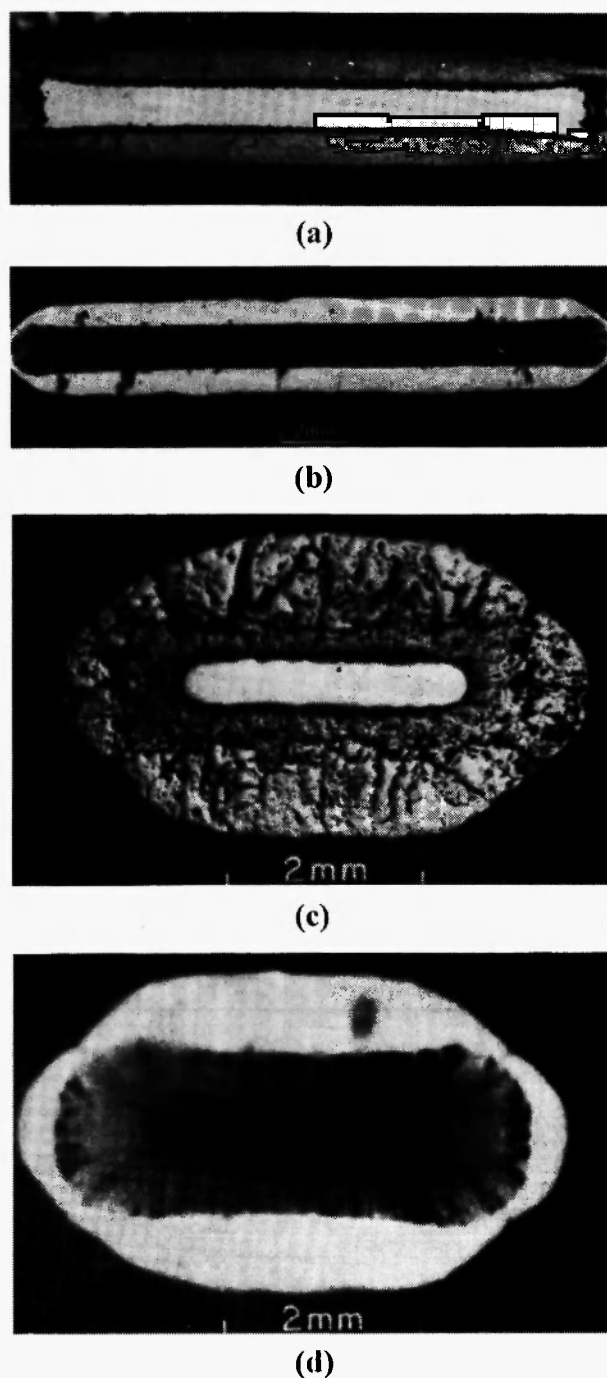




**Fig. 14:** Photograph (a) and autoradiogram (b) of the cross-section of the sulphide scale formed on a flat iron sample at 710 K in two-stage sulphidation process /9/.

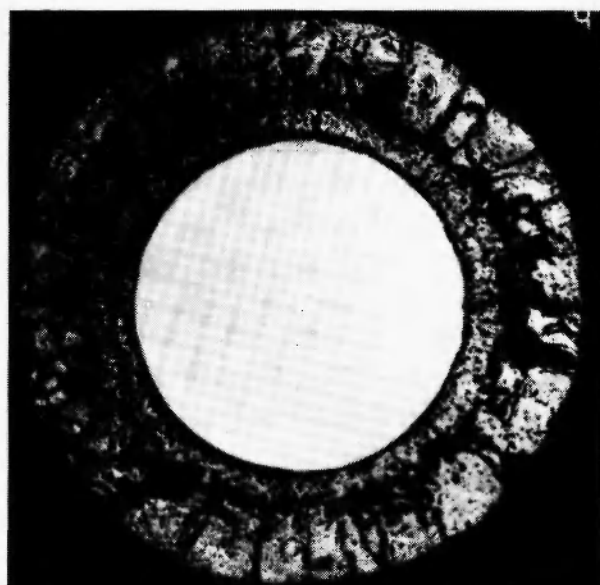
formed under the same experimental conditions on two flat iron samples of different dimensions but of equal thickness. It is clearly seen that the perforation of the scale on a bigger sample (Fig. 15a and 15b) occurred only near the edges, whereas on the smaller specimen (Fig. 15 c and d), where the influence of edges was greater, the dissociation of the scale led to its perforation over the whole surface, although it began later in the region of flat surfaces (lower concentration of the  $^{35}\text{S}$  isotope in the inner layer than near the edges). It should be stressed that the autoradiographic images of both samples correspond well with the morphology of scales. On the bigger sample, namely, the scale in flat regions consists virtually only of a single layer, whereas on the smaller specimen two scale layers are well visible.

As already pointed out, the least favourable conditions for plastic flow of the scale exist on round-shaped samples (wires, cylinders), and consequently a porous, double-layer scale is formed (Figs. 4 and 5) by simultaneous diffusion of both reactants. This conclusion is in full agreement with the results obtained in two-stage sulphidation experiments, shown in Fig.

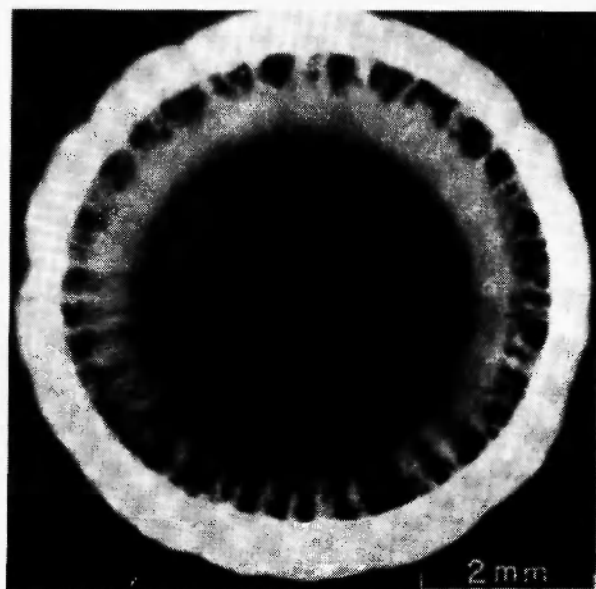


**Fig. 15:** Photographs (a and c) and autoradiograms (b and d) of the cross-sections of sulphide scales, formed in two-stage sulphidation process, on two flat iron samples of the same thickness but of different dimensions /9/.

16. From the photograph and autoradiogram of the scale formed on iron wire it follows that because of the rigidity of the system the boundary between both porous



(a)



(b)

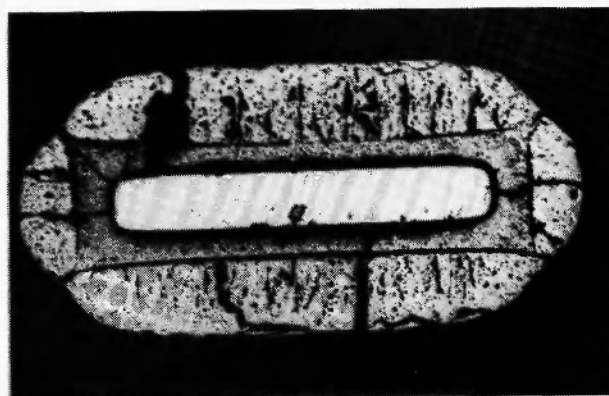
**Fig. 16:** Photograph (a), and autoradiogram (b) of the cross-section of the sulphide scale formed on iron wire ( $\phi = 4,85$  mm) in two-stage sulphidation process at 710 K [9].

layers corresponds strictly with the initial thickness of the wire and the inner layer was growing owing to the inward diffusion of sulphur. In addition, from the autoradiogram it follows clearly that the inward diffusion of sulphur proceeded along the favourable

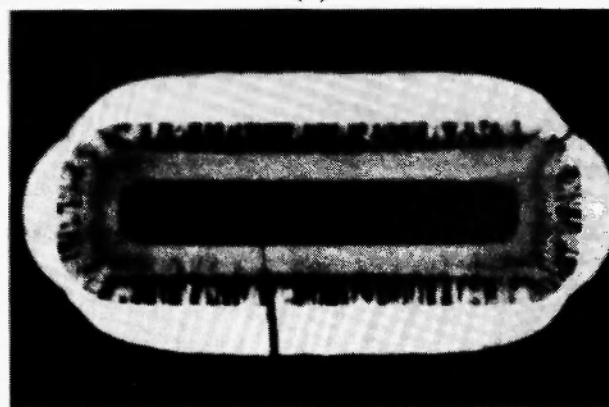
diffusion paths, corresponding to grain boundaries of the outer layer, i.e., through dissociation fissures.

### 5. THE EFFECT OF IMPURITIES ON THE GROWTH MECHANISM OF SCALES ON METALS

The above results concerned spectrally pure metals. When, however, the substrate contains small amounts of impurities that do not form solid solution with the reaction product, the morphology of the scale and its growth mechanism is completely different. This phenomenon is well illustrated by the photograph and autoradiogram of the cross-section of the sulphide scale formed in two-stage sulphidation process on flat sample of ARMCO iron containing 0.4 % of impurities (Fig. 17). As can be seen, in this case the scale consists of



(a)



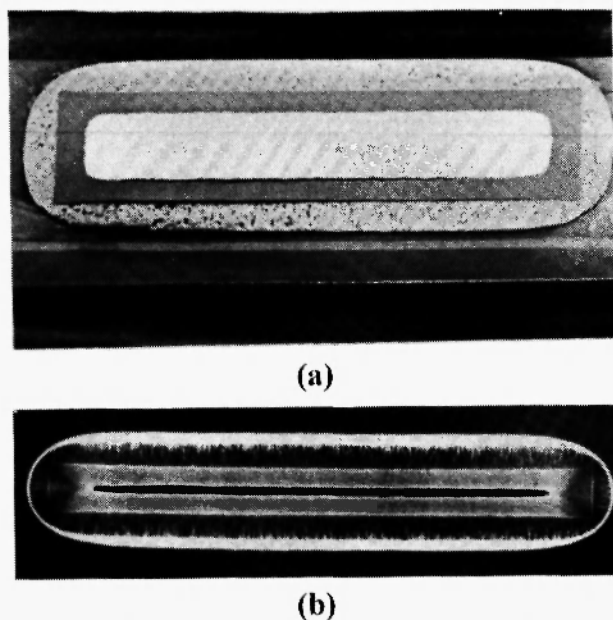
(b)

**Fig. 17:** Photograph (a), and autoradiogram (b) of the cross-section of the sulphide scale formed on a flat ARMCO iron sample at 710 K in two-stage sulphidation process. 25 min. in non-radioactive, and 200 min. in radioactive sulphur [9].

two layers with distinctly visible boundary between them, corresponding with the initial thickness of the metal sample (Fig. 17a). From the autoradiogram (Fig. 17b), in turn, it follows that the inner scale layer grew by the inward diffusion of sulphur from the surrounding atmosphere, like on edges of flat samples, or on the whole surface of round-shaped specimens of pure metals. Such mechanism of scale growth is due to the restricted plastic flow of the scale, caused by the impurities accumulating at the metal-scale interface and worsening the contact between the scale and the metallic core. Thus, the impurities insoluble in the reaction product play the same role as the curvatures of the sample in the case of pure metal sulphidation (or oxidation).

## 6. SULPHIDE SCALES ON ALLOYS

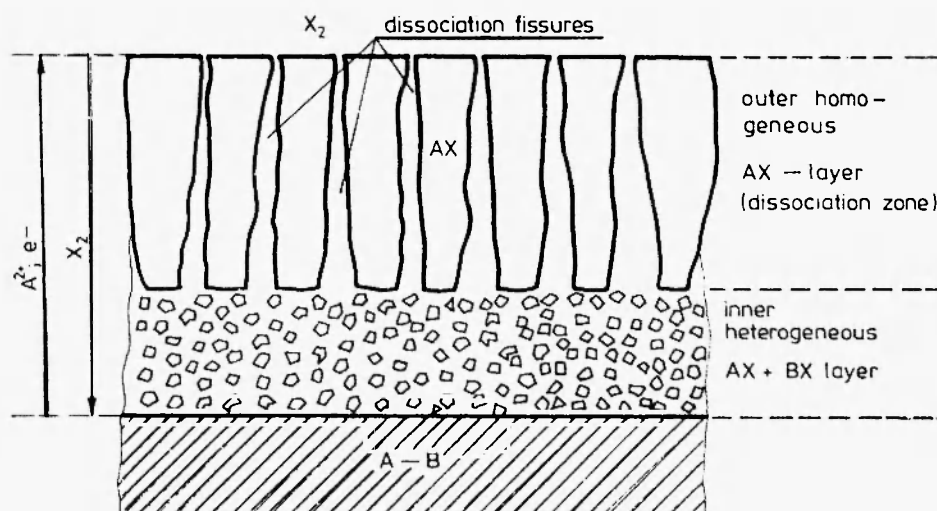
This phenomenon is still more distinct in the case of alloy sulphidation, the components of which do not form intersoluble sulphides. Fig. 18 shows, for



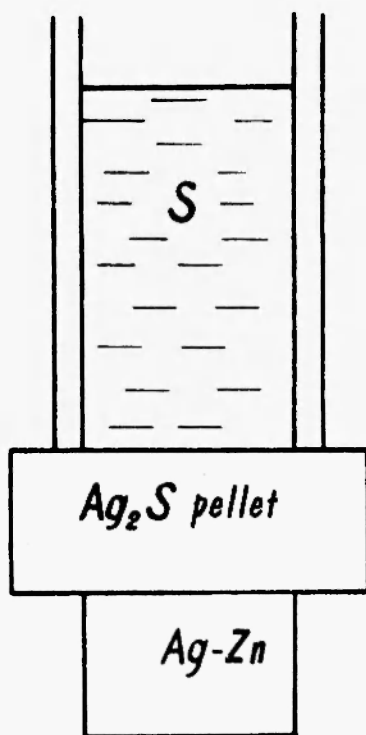
**Fig. 18:** Photograph (a) and autoradiogram (b) of the cross-section of sulphide scale formed in two-stage sulphidation process on a flat Cu-9%Zn alloy sample; 60 min. in non-radioactive and 60 min. in radioactive sulphur.

illustration, the photograph (a) and the autoradiogram (b) of the cross-sections of sulphide scale formed on a flat sample of Cu-Zn alloy containing 9at.% Zn. It follows clearly from these pictures that in this case the inner heterogeneous  $\text{Cu}_2\text{S} + \text{ZnS}$  scale layer fills the metal consumption zone not only near the edges but also in flat regions of the sulphidized sample, the boundary between both scale layers corresponding strictly with the initial surface of the alloy sample (Fig. 18a). This means that, in contrast with pure copper (or silver) sulphidation (Fig. 12 and 13), the scale did not undergo plastic deformation anywhere during its growth and consequently, the inner layer had to be formed by the inward diffusion of sulphur. This conclusion is fully confirmed by the autoradiogram of the cross-section of the scale (Fig. 18b), from which it follows that due to perforating dissociation the radioactive sulphur isotope, introduced into the sulphidizing atmosphere in the second stage of the reaction, is present in the whole cross-section of the scale. In addition, it is clearly seen that the inward transport of sulphur through the outer scale layer proceeded along the favourable paths (dissociation fissures) both near the edges and in flat regions of the sample. Such a growth mechanism of double-layer, heterogeneous scales on binary alloys is always observed when the inner layer is heterogeneous. The scheme of the discussed mechanism of double-layer scale formation on binary alloys is shown in Fig. 19.

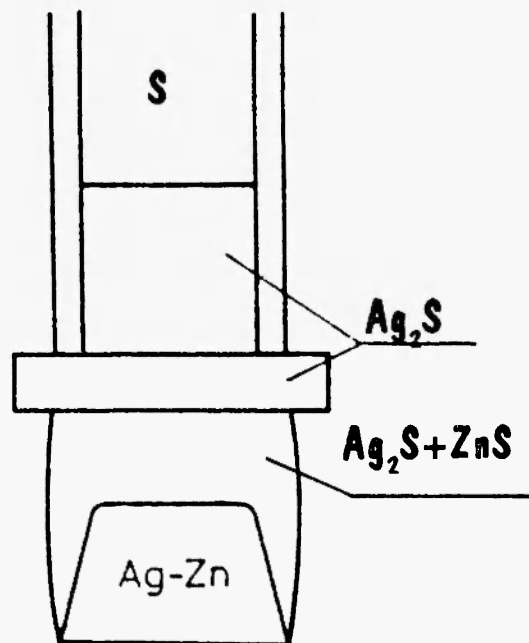
In order to obtain a direct proof that the plastic deformation of the scale is impeded by the formation of dispersed phase of the second reaction product in the inner layer, the Wagner's pellet method was applied, using radioactive sulphur isotope [17]. These experiments were performed on the model system, consisting of Ag-Zn rod covered by the  $\text{Ag}_2\text{S}$  pellet, on the surface of which the quartz tube with molten sulphur was located (Fig. 20). As expected, the pellet together with the loaded ( $5 \times 10^4 \text{ kg/m}^2$ ) reaction tube did not move down following the receding alloy surface, like in the case of pure silver sulphidation (Fig. 1) but remained in its initial position, and under the surface of the pellet, in the metal consumption zone, a heterogeneous  $\text{Ag}_2\text{S} + \text{ZnS}$  layer was formed (Fig. 21). It is important to note that this sulphide layer appeared not only between the pellet and the alloy surface but also on the sides of the alloy bar. It becomes



**Fig. 19:** Scheme of the growth mechanism of a double-layer, heterogeneous scale on binary alloys. A - more noble base metal; B - less noble alloying component.



**Fig. 20:** Scheme of the Wagner's pellet method applied to the sulphidation of an Ag - Zn alloy.

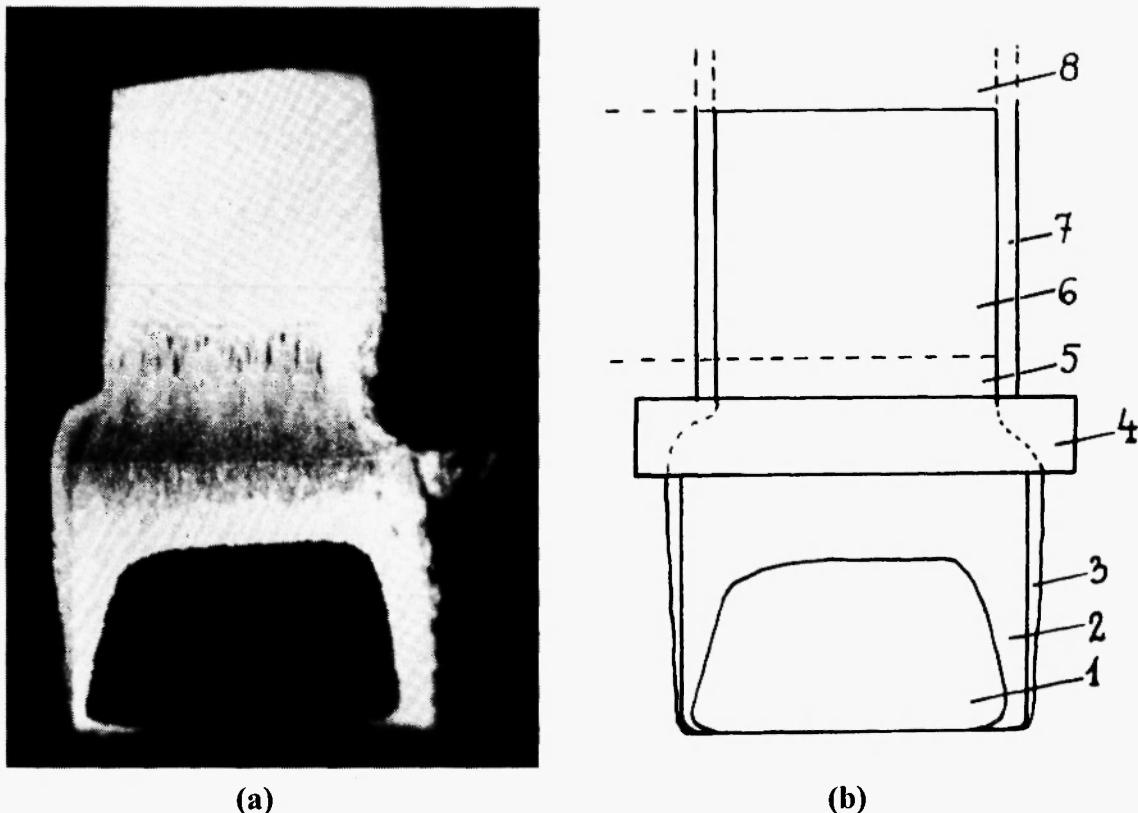


**Fig. 21:** The situation observed after sulphidation of Ag - Zn alloy in Wagner's pellet system (schematic).

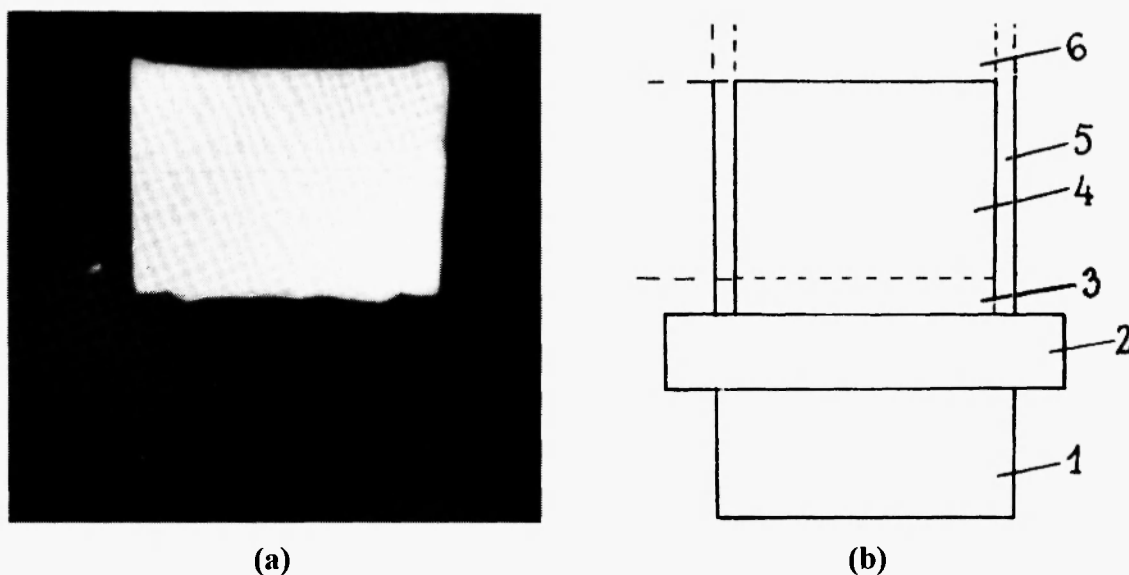
conceivable if one considers the fact that the lack of full contact between the  $\text{Ag}_2\text{S}$  phase and the alloy, caused by the formation of a dispersed  $\text{ZnS}$  phase, brings about an increase in the chemical potential of sulphur and consequently, in the dissociation pressure of the pellet. Thus, the process of alloy sulphidation under these conditions could occur also on the parts of the alloy bar being not in the direct contact with the pellet, at the expense of  $\text{Ag}_2\text{S}$  phase dissociation.

Taking into account the fact that the dissociation of the outer compact scale layer occurs along the perpendicular-to-the-core grain boundaries, one could expect that the dissociation of the pellet and of silver sulphide grown into the reaction tube would result in the formation of micro-fissures, enabling inward diffusion of sulphur. In order to verify this conclusion, after a certain reaction time a radioactive sulphur isotope was

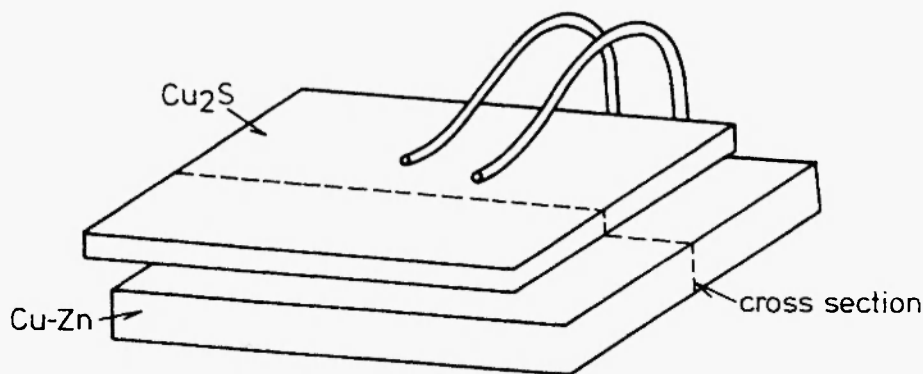
introduced into the reaction tube and after terminating the reaction the whole system was cut along the axis of the tube. A scheme of this cross-section and its autoradiogram is shown in Fig. 22. The broken line on the scheme indicates the thickness of the reaction product grown into the tube at the moment of letting in the radioactive sulphur isotope. For comparison, an analogous two-stage sulphidation experiment has been carried out in the system: pure silver bar -  $\text{Ag}_2\text{S}$  pellet - sulphur, and the scheme of the cross-section (a) and its autoradiogram (b) are shown in Fig. 23. It follows clearly from these two experiments that in the case of pure silver sulphidation the "scale" was growing exclusively as a result of outward diffusion of cations, because the pellet together with the reaction tube could freely move down following the receding metal surface (see also Fig. 1) On the other hand, during alloy



**Fig. 22:** Autoradiogram (a) and the scheme (b) of vertical cross-section of Ag-Zn alloy- $\text{Ag}_2\text{S}$  pellet-sulphur system after two-stage sulphidation at 710 K. Broken line on the scheme marks the thickness of the "scale" grown into the reaction tube at the moment of introduction of radioactive sulphur isotope /17/. 1 - Ag-Zn alloy; 2 -  $\text{Ag}_2\text{S} + \text{ZnS}$ ; 3 -  $\text{Ag}_2\text{S}$ ; 4 -  $\text{Ag}_2\text{S}$  pellet; 5 -  $\text{Ag}_2\text{S}$  formed in the first stage; 6 -  $\text{Ag}_2\text{S}$  formed in the second stage; 7 - reaction tube; 8 - liquid sulphur.



**Fig. 23:** Autoradiogram (a) and the scheme (b) of vertical cross-section of reacting pellet system after two-stage sulphidation of pure silver at 673 K /17/. 1 – Ag rod; 2 –  $\text{Ag}_2\text{S}$  pellet; 3 –  $\text{Ag}_2\text{S}$  formed in the first stage; 4 –  $\text{Ag}_2\text{S}$  formed in the second stage; 5 – reaction tube; 6 – liquid sulphur.

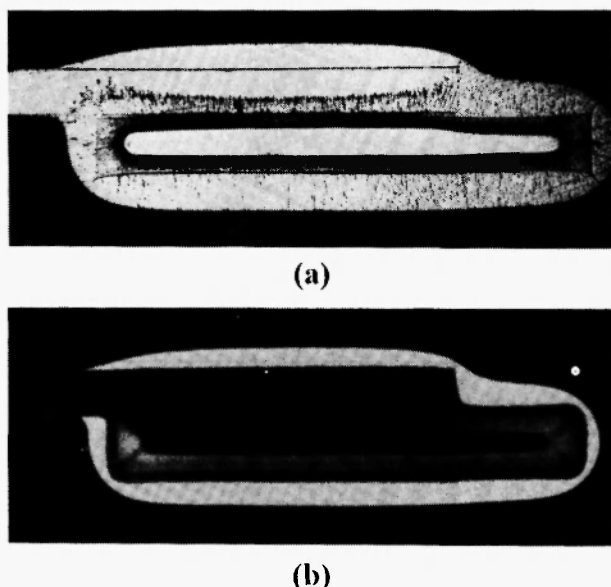


**Fig. 24:** Scheme of the system: flat Cu - Zn alloy sample partially covered by the compact  $\text{Cu}_2\text{S}$  scale obtained during sulphidation of flat copper sample. The broken line marks the plane along which the system was cut after the reaction.

sulphidation the movement of the pellet and the reaction tube was impossible and under the pellet the second (inner) scale layer was formed by the inward diffusion of sulphur.

The anisotropic character of the discussed dissociation processes has been confirmed once again in a very interesting experiment carried out in the following way. A part of flat Cu-Zn alloy sample was covered with the plate of a compact  $\text{Cu}_2\text{S}$  scale obtained on pure copper, as depicted schematically in Fig. 24.

The system prepared in this way was then subjected to two-stage sulphidation and, after terminating the reaction, it was cut along the plane indicated on the scheme by the broken line. A photograph and autoradiogram of that cross-section is shown in Fig. 25. It follows from these data that the mechanism of scale growth in the region covered with  $\text{Cu}_2\text{S}$  plate differed considerably from that on uncovered fragments of the metallic core. On covered surfaces, namely, the scale grew without any participation of the inward diffusion



**Fig. 25:** Photograph (a) and autoradiogram (b) of the cross-section of the scale formed at 710 K in two-stage sulphidation process on a flat Cu - Zn alloy sample, covered in part with compact  $\text{Cu}_2\text{S}$  scale layer prior the reaction. 5 min. in non-radioactive and 40 min in radioactive sulphur /10/.

of sulphur from the environment, whereas on uncovered regions it was formed due to simultaneous diffusion of copper and sulphur in opposite directions, as already described previously. However, under the  $\text{Cu}_2\text{S}$  plate there was also formed a heterogeneous  $\text{Cu}_2\text{S} + \text{ZnS}$  inner layer, which grew as a result of sulphide plate dissociation rather than due to the inward diffusion of sulphur from outside. This conclusion follows equally well from the morphology of  $\text{Cu}_2\text{S}$  plate (Fig. 25a) and from the lack of radioactive sulphur isotope under the plate (Fig. 25b). The above-mentioned differences result from the fact that on uncovered surfaces the dissociation of the outer scale layer began directly after its formation and consequently led to its immediate perforation (see also Fig. 18). On covered surfaces, on the other hand, there existed already the artificially-formed compact outer scale layer, and the dissociation process, in spite of its anisotropic character, did not result in plate perforation but destroyed only a part of its compactness (Fig. 25a). The situation in this part of the sample is therefore similar to that encountered during the

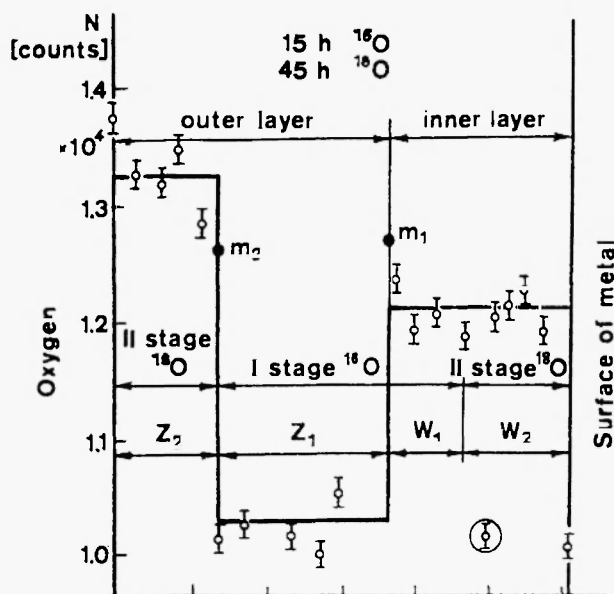
formation of inner scale layer on the flat samples of pure metals where, owing to the plastic flow of the scale, the loss of full contact between the primary compact scale layer and metallic core occurs later than near the edges (Figs. 11 and 12).

## 7. OXIDE SCALES ON ALLOYS

From the results described above it follows clearly, that secondary processes of dissociation play a very important role in the growth mechanism of sulphide scales with predominant cation disorder. The question then arises whether these processes are equally valid and important in the case of oxide scale formation with the same predominant lattice disorder. It has been suggested in the literature that in the case of oxidation the discussed secondary dissociation processes may play a much less important role than in the mechanism of sulphidation, because metal oxides are generally more thermodynamically stable than corresponding sulphides and consequently, dissociation must proceed with much lower rate, playing thus unimportant role in the formation of the inner scale layer, and thereby in the whole process of high temperature corrosion. However, in these considerations the most important fact – the **anisotropic character** of dissociation – was overlooked. In contrast with this it has been shown in convincing radioactive experiments and morphological studies described above, that the scale dissociation proceeds virtually only along perpendicular-to-the-core grain boundaries of columnar crystals of the scale, resulting in the formation of micro-porosity and thereby in the increase of dissociation area by several orders of magnitude. Thus, even if the dissociation pressure is very low the supply of the oxygen to the surface of the metallic core may be sufficient not only for the perforation of the outer scale layer but also for the formation of the inner porous layer. In fact, the results obtained with heavy oxygen isotope using two-stage oxidation method confirmed this conclusion. Finally, the outstanding and very elegant *in situ* oxidation experiments, carried out by Rapp *et al.* /24,25/ in hot stage scanning electron microscope, have unequivocally demonstrated the perforating dissociation during the formation of the oxide scale on copper. Some of these

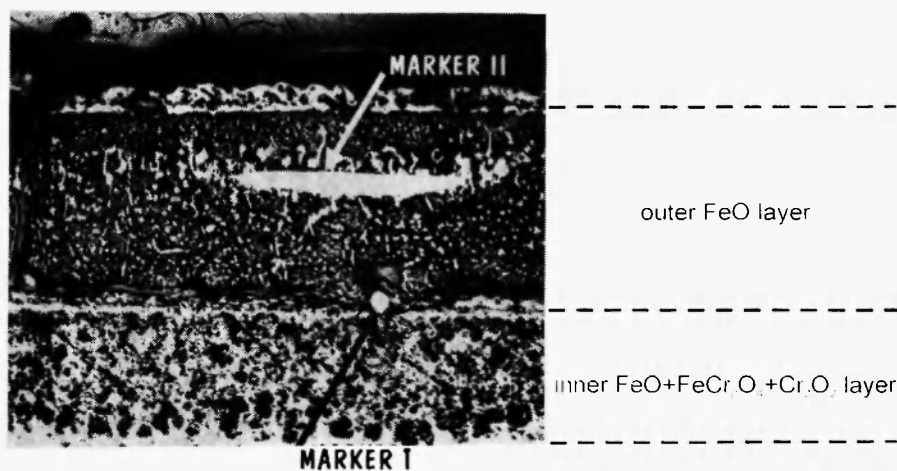


results will shortly be discussed below. Fig. 26 shows the distribution of oxygen isotope  $^{18}\text{O}$  in the oxide scale

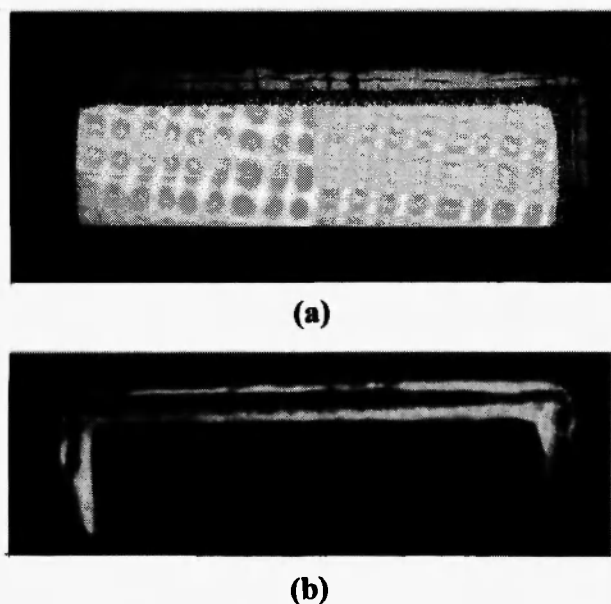


**Fig. 26:** Distribution of  $^{18}\text{O}$  isotope concentration in the oxide scale formed during two-stage oxidation of Fe – 3.5at.%Cr alloy at 1273 K.  $Z_1$ ,  $Z_2$ ,  $W_1$  and  $W_2$  denote sections of outer and inner scale layers, respectively. The indices I and II correspond to the first and the second reaction stage, respectively;  $m_1$  and  $m_2$  - positions of platinum wire markers in the scale [16].

on Fe-Cr alloy obtained in two-stage oxidation process. These results have been obtained with the first, sectioning method, described in Section 3. Fig. 27, in turn, demonstrates the cross-section of the other side of the same sample, the surface of which before the reaction was marked with thin platinum wire (marker I). The second marker (marker II) was placed on the scale surface at the moment of introduction of oxygen 18 into the reaction atmosphere. From the comparison of these two figures it follows (Figs. 26 and 27) that the inner, heterogeneous ( $\text{FeO} + \text{FeCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3$ ) scale layer, formed beneath the marker I, grew owing to the inward diffusion of oxygen. In addition, the distribution of  $^{18}\text{O}$  isotope in the scale indicates that the transport of oxygen did not proceed by lattice diffusion but along the favourable diffusion paths (dissociation fissures). When passing, namely, from the outer to inner scale surface the concentration of oxygen 18 decreases abruptly to a very low value at the boundary traced by the marker II, and then increases again beneath the marker I (see Fig. 26). This conclusion is in full agreement with the autoradiogram (Fig. 28b) of the cross-section, obtained with the second method described in Section 3. It should be noted that, in the case under discussion, the heterogeneous inner scale layer fills up the metal consumption zone (Fig. 28a) which implies that, similar to the case of sulphidation of Ag-Zn and Cu-Zn alloys, the scale did not undergo any



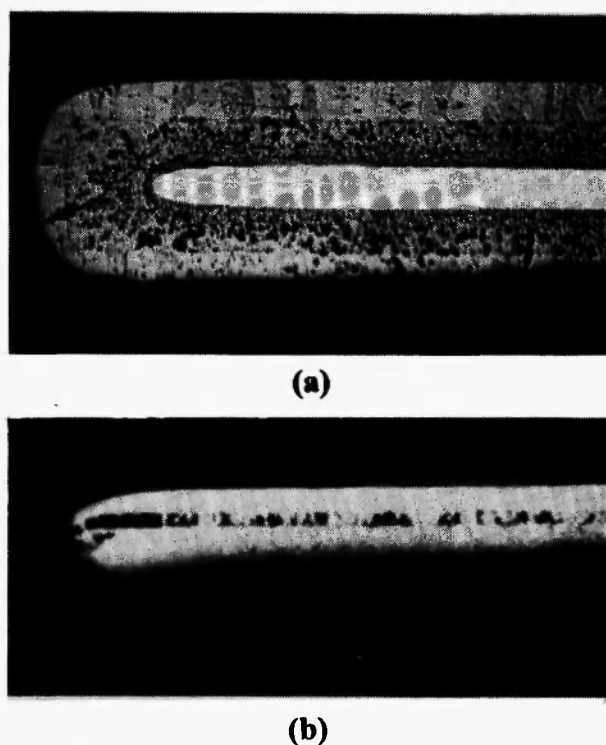
**Fig. 27:** Photograph of the cross-section of the oxide scale formed on the other side of Fe-Cr alloy sample marked before the reaction by platinum wire (marker I) and subsequently by second marker (II) at the moment of introduction of oxygen 18 into the oxidizing atmosphere [16].



**Fig. 28:** Photograph (a) and autoradiogram (b) of the cross-section of the oxide scale formed on the flat Fe - 3.5 %Cr alloy sample at 1273 K in two-stage oxidation process. First stage 15 h second stage 45 h /16/.

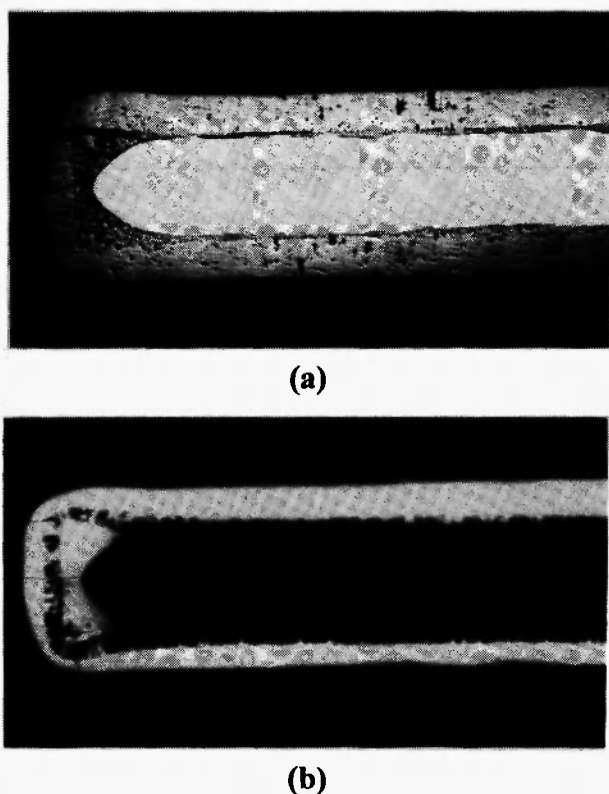
plastic deformation and consequently, anisotropic dissociation led to its immediate perforation.

Analogous results have been obtained with Co-Cr and Ni-Cr alloys. For illustration, Fig. 29a shows the cross-section of a double-layer oxide scale on Co-Cr alloy from which it follows that in this case too the inner, heterogeneous ( $\text{CoO} + \text{CoCr}_2\text{O}_4 + \text{Cr}_2\text{O}_3$ ) layer fills up the metal consumption zone, i.e., the scale did not undergo plastic deformation. From the autoradiogram, in turn, shown in Fig. 29b, it follows clearly that the inner scale layer did form owing to the inward diffusion of oxygen through favourable diffusion paths (dissociation fissures). On the other hand, in the case of pure cobalt and nickel oxidation the mechanism of scale formation has been found to be perfectly analogous to that of pure metal sulphidation. This conclusion is well illustrated in Fig. 30 by the photograph (a) and the autoradiogram (b) of the cross-section of the oxide scale formed in a two-stage oxidation process on a flat cobalt sample. As can be seen, in flat regions the metal consumption zone was largely compensated by plastic flow of the scale and in the vicinity of edges, where the system was rigid, a

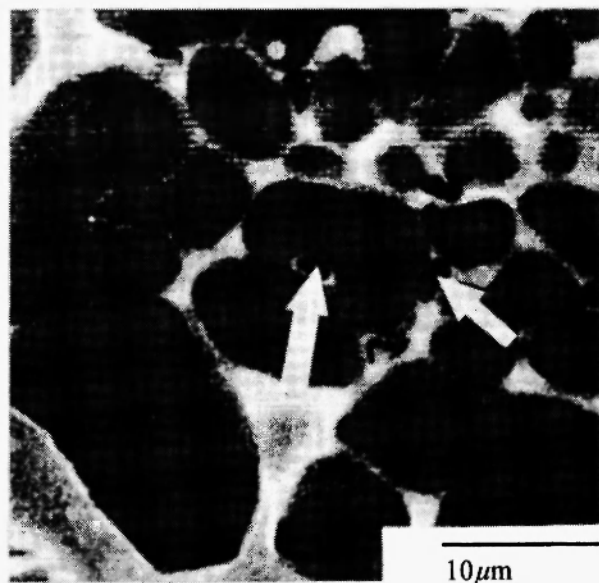


**Fig. 29:** Photograph (a) and autoradiogram (b) of the cross-section of the oxide scale formed on flat Co - 4% Cr alloy sample in two-stage oxidation process at 1273 K. First stage 21 h; second stage 72 h /21/.

thick inner scale layer was formed (Fig. 30a). From the autoradiogram, in turn, it follows that, as in the case of pure metal sulphidation, in the regions of flat surfaces the scale grew without the participation of inward diffusion of oxygen, whereas on edges the said process took part in the formation of the inner porous scale layer (Fig. 30b). The final, excellent experimental proof of the formation of dissociation fissures in the growing oxide scale on metals has been obtained, as already pointed out, by Rapp /24,25/ in his *in situ* oxidation studies of copper, carried out with a hot stage scanning electron microscope. The micro-photograph of the surface of the  $\text{Cu}_2\text{O}$  scale obtained during its formation is shown in Fig. 31. The outlets of dissociation fissures, located at grain boundaries of oxide crystals, are clearly visible.



**Fig. 30:** Photograph (a) and autoradiogram (b) of the cross-section of the oxide scale formed on pure cobalt at 1273 K in two-stage oxidation process /21/.



**Fig. 31:** Photograph of the surface of the  $\text{Cu}_2\text{O}$  scale formed on copper at 1123 K. Dissociation fissures indicated by arrows /24/. The picture obtained *in situ*, during oxidation process.

## 8. CONCLUSIONS

The experimental results and theoretical considerations described in this paper allow the following conclusions to be formulated.

Single-phase scales with predominant cation disorder, formed at high temperatures on pure metals, may be composed of one, two or even three layers. The different morphological structure of such scales is related to the effect of geometry of the metal-scale system and can be observed on one and the same oxidized sample.

These differences in scales morphology and thereby in their growth mechanisms result from restricted possibilities for the compensation of metal consumption zone by the plastic flow (deformation) of the growing layer of reaction product. When this zone is fully compensated, a single-compact-scale layer is formed as a result of the outward diffusion of cations, in agreement with Wagner's theory of metal oxidation. However, such a possibility exists without any restrictions only in artificial metal-scale-oxidant system created in Wagner's pellet method (Fig. 1), representing, in fact, an infinitely large flat surface. In real systems metal consumption zones can only be compensated to some extent, or even cannot be compensated at all. In the regions of appropriately large flat surfaces a compact, single scale layer can form so long as the consumption of the metal is fully compensated by its plastic flow. When the thickness of the scale exceeds some critical value it begins to lose the full contact with the metallic core and the local thermodynamic equilibrium at the metal-scale interface starts to be disturbed, resulting in the increase of chemical potential of the oxidant and thereby of its pressure in the forming crack. The conditions are then created for the secondary formation of porous reaction product on the metal surface, following by gradual decomposition (dissociation) of the primary compact scale layer. This process proceeds mainly along the perpendicular-to-the-core grain boundaries of large columnar crystals typical for the outward lattice diffusion of cations. Such an **anisotropic** process of dissociation of the outer scale layer leads to the formation of a second, intermediate porous layer, built of partially destructed primary outer scale. Thus, in this

stage of the reaction, in flat regions of the oxidized sample, the triple-layer scale may be formed, growing by the outward diffusion of cations only. In later stages of the reaction dissociation fissures may reach the outer surface, destroying the compactness of the primary outer layer in its whole cross-section and from that moment on double, porous scale layer is growing by simultaneous diffusion of both reactants in opposite directions.

The situation is different in the vicinity of edges of flat specimens and on the whole surface of round-shaped samples (wires, cylinders) because the system is rigid and the metal consumption zone cannot be compensated by the plastic flow of the scale, at all. Thus, anisotropic dissociation of primary, very thin scale layer leads virtually immediately to the destruction of its compactness (perforating dissociation) and the porous, double layer scale layer is growing from the very beginning by simultaneous diffusion of both reactants. Experimental results presented in this paper have clearly demonstrated that the influence of geometrical parameters on the mechanism of scale growth is equally valid for oxide and sulphide scales.

The second important factor which may considerably influence the mechanism of scale growth constitute small amounts of impurities insoluble in the reaction product. Accumulating at the metal-scale interface they form an obstacle to the plastic flow of the scale and consequently, act in the same way as curvatures or edges in the case of pure metal oxidation or sulphidation.

In the case of alloys which form double-layer scales with a heterogeneous inner layer, the mechanism of the reaction is analogous to that governing oxidation or sulphidation of metals containing insoluble impurities. The dispersed phase of slower growing product of less noble metal with the oxidant accumulates in the inner layer, making the plastic flow of the scale impossible and as a result of perforating dissociation the scale is growing by simultaneous outward diffusion of more noble base metal and the inward diffusion of the oxidant.

Summing up these conclusions it should be stressed once again that different types of specific micro-porosity observed in scales on metals and alloys result as a rule from secondary dissociation processes and not

from mechanical stresses developed during the reaction. Certainly, in some cases these stresses may cause scale cracking, breakdown or spalling. However, in those cases the scale morphology is completely different and considerable deviations from parabolic kinetics of the reaction take place. On the contrary, secondary processes of scale dissociation do not affect parabolic kinetics because still the rate-determining step of the reaction is the outward diffusion of cations.

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