

Defect interpretation by Auger spectroscopy in problems arising in lubricating and degreasing steels

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Abstract

The use of certain lubricants, lubrication additives and detergents generally containing chlorine atoms in the molecule, although very effective, is not recommended for components in ferrous alloys subjected to periodic stresses since, although there is no manifestation which can be detected macroscopically or microscopically, their service life (or fatigue limit) is considerably reduced.

Numerous investigations, using various Auger techniques, show that, in ferrous alloy polycrystals i.e. in most metal materials of interest for mechanical engineering, there exists, even at ambient temperature, in surface layers less than one μm thick, a very high degree of mobility of ions foreign to the matrix, particularly if they have a considerable chemical affinity for the latter, as in the case of chlorine, oxygen and sulphur in an iron matrix at grain boundaries.

This very high degree of mobility of grain boundary ions, even at ambient temperature, seems a very appropriate explanation of the cause of damage to steel mechanical components arising from contact with chlorinating substances, even for only a short time, as in the case of degreasing.

Riassunto

Interpretazione di anomalie nei problemi di lubrificazione e di sgrassaggio degli acciai mediante spettroscopia Auger.

L'impiego di alcuni lubrificanti, additivi di lubrificazione e detergenti, generalmente contenenti atomi di cloro nella molecola, benché di grande efficienza, viene sconsigliato per gli organi in leghe ferrose soggetti a sollecitazioni periodiche in quanto, pur senza alcuna manifestazione rilevabile macro o microscopicamente, ne riducono sensibilmente la durata (o il limite di fatica).

Numerose serie di esperienze, eseguite con varie tecniche all'Auger, indicano che, nei policristalli di leghe ferrose, cioè nella gran parte dei materiali metallici di interesse meccanico, esiste, già a temperatura ambiente, in strati superficiali di spessore inferiore al μm , una grandissima mobilità di ioni estranei alla matrice, specie se aventi per essa notevole affinità chimica, come nel caso degli ioni di cloro, ossigeno e zolfo in matrice ferrosa al bordo dei grani.

Questa grandissima mobilità di ioni a bordo grano, anche a temperatura ambiente, appare molto adatta ad interpretare la causa del danneggiamento degli organi meccanici ferrosi, derivanti dal contatto con sostanze cloruranti, anche se di breve durata, come nel caso dello sgrassaggio.

Introduction

It is well known that the rate of diffusion in a polycrystal, particularly with respect to substitutional ions, is determined by the rates of diffusion through the "grain boundary junctions", the "axes of dislocations" and the "bulk" (activated by point defects), the last, with equal section, being of much less magnitude than the first two (1-4).

Proof of this can be obtained, at least as regards "grain boundary junction" diffusion, from any simple examination, through the section, of polycrystals subjected to diffusion (for example: components in case-hardened or decarburised steel).

It would seem to be important, not only from a theoretical viewpoint but also for an immediately practical aspect, to be able to ascertain separately the coefficients relating to the first two processes, since it is their high value that might account for the diffusion which tends to occur through metal materials even at ambient temperature.

Measurements of the various coefficients of diffusion are not easy, however, because of the continuous interaction between the various processes, and have only been undertaken by few workers (1,2,4,5).

Results from such investigations are in agreement, however, in giving the grain boundary diffusion coefficient a value 10^3 to 10^4 times the value of the coefficients for mass diffusion and, on the "surface", a value about 10^3 times greater (3-4).

It is also well-known that exposure of steel components to certain environments, even though apparently not very aggressive, can have an adverse effect on the service life or fatigue strength (7, 9-11, 13).

This sometimes happens a very long time after the moment of exposure, and even without any surface

deterioration which can be detected at macroscopic or microscopic level, as in the case of steel mechanical components lubricated, or simply degreased, with organic solvents containing atoms of sulphur, phosphorus and, in particular, chlorine (chloroform, trichloroethylene etc).

Clearly this happens because, even within the brief period of exposure necessary for degreasing, irreversible damage occurs. This damage is naturally increased as a result of repeated stresses, particularly if exposure to the aggressive environment continues (5-9).

However, for lubrication under E.P. (extreme pressure) conditions, i.e. conditions where material is subject to high compressive stressing:

- lubrication itself is sometimes entrusted precisely to products which have been sulphurised or chlorinated; and, in general,
- the coefficient of friction of the ferrous materials is determined by the presence of oxygen in the environment (so that, in the absence of oxygen, it may become equal to infinity, as a result of seizing).

In particular, in all cases where chlorinated lubricants are used it is essential to operate in an absolutely anhydrous environment.

All these experimental results, particularly those relating to E.P. conditions, can be interpreted as a consequence of reactions between the metal matrix (in particular, the iron matrix) and sulphur, chlorine and oxygen. These elements may form films (even monomolecular) of compounds (according to some authors, even complex compounds, such as

mercaptans) on the surface of metal components (Fig. 1) (7, 10-13).

To demonstrate that these hypotheses were correct it was necessary to have the means to carry out examinations of very thin surface layers, even monomolecular ones.

Auger spectroscopy, since it permits examination of a few monolayers, is particularly suitable for an investigation of this type, both on the external surface and on any fracture surfaces.

Investigations have therefore been carried out with various types of set-up in order to verify whether the results obtained might confirm the fact that, for steel polycrystals, even at ambient temperature, there is a "mobility of elements" along the preferential areas (naturally, in particular, along "grain boundaries").

— results already obtained experimentally and hypotheses to be proved

a) taking into account the liability of structural metals (iron, copper etc.) to cover themselves with films by chemisorption or adsorption of reactive elements such as chlorine, sulphur etc., to test the actual formation of such films (possibly, even as monomolecular films);

b) whether these films, on polycrystalline solids, form in a continuous and uniform manner, in accordance with the usual tribological representation,

independently of the crystalline structure of the underlying metal, in the form of monomolecular films (or films with only a few layers); or whether, is a preferential reaction at the grain boundaries and thus a consequent tendency on the part of foreign atoms to penetrate preferentially along grain

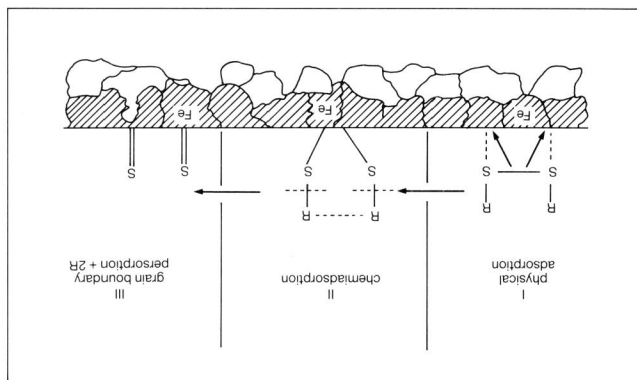


Fig. 1 - Grignard-type reaction, catalyzed by metallic surfaces.

Experimental results and discussion.

1. Mobility of oxygen on fracture surfaces.

Examining the fracture surfaces of bars of various types of steel by Auger spectroscopy, the presence of oxygen in quantity variable with time was noted on grain boundary surfaces. The simplest explanation, i.e. that the oxygen came from the gases in the residual vacuum in the experimental chamber (a vacuum which varied from 10^{-9} to 10^{-10} torr), did not seem satisfactory as the rate at which these surfaces were covered seemed too high in relation to the oxygen

It was therefore decided to carry out two types of investigation:

- preparation of plain carbon steel test specimens (so as to avoid complications due to grain boundary segregation of the alloy elements) in order to verify whether the metal had a tendency to break the organic molecules and become covered with chemisorbed films (particularly in the vicinity of grain boundary junctions);
- deep-ranging examinations, but always starting from the outer surface, in order to verify the tendency of foreign atoms (chlorine, oxygen, etc.) to "penetrate deeply" along the grain boundary.

For this purpose it was necessary to carry out investigations capable of showing:

- the tendency of iron polycrystal surfaces to become covered with adsorbed or chemisorbed chlorine - sulphur - or oxygen-based films, even removing those atoms from the organic molecules of the lubricants, additives, or degreasing agents;
- the ability of these foreign atoms to penetrate into the polycrystal along the grain boundary;
- the ability of these atoms to "flow" under suitable conditions, even at very low homologous temperatures, along the grain boundary.

the order of $0 = 0.2 \pm 0.3$.

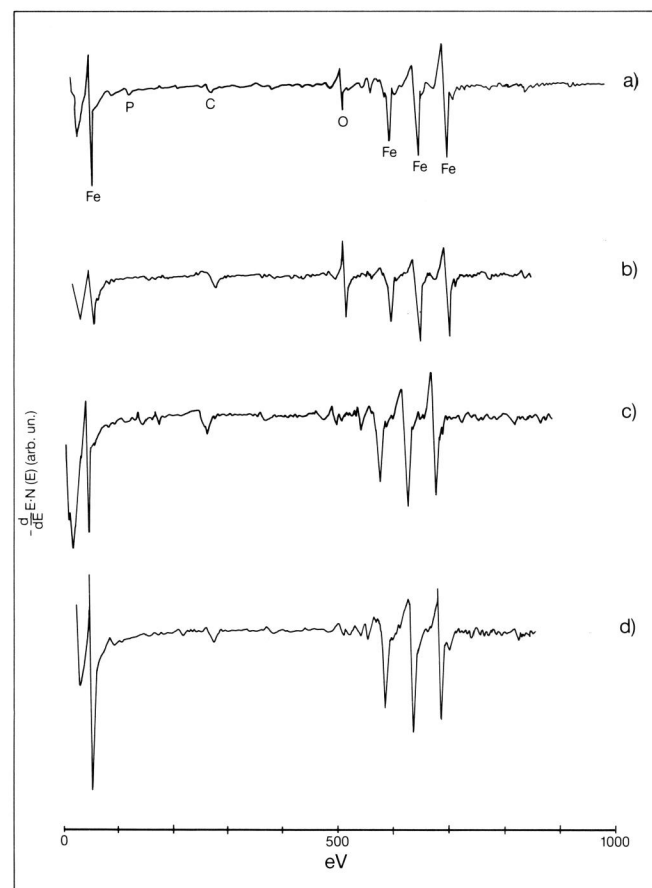
foreign atoms, even at homologous temperatures of existence, at grain boundaries, of a "flow" of by Henry (8) about twenty years ago on the possible preferential penetration at grain boundaries were found, this would confirm the hypothesis formulated. Further, if, under experimental conditions, exposure, repeated stresses, even a considerable time after reduction in the resistance of components to correct, it would be easy to account for the correct, if this last hypothesis is found to be stretched, but fastened to the latter).

boundaries (thus forming films not uniformly

partial pressure. Further, it was definitely established that it was not an adsorption phenomenon, from the fact that the quantity of oxygen present on these surfaces tended to become nil after a certain time.

From Fig. 2 (a, b, c, d.), showing Auger charts relating in each case to the same point on the surface, it can be seen that, on a fracture surface where, initially (a), a little oxygen quantity is present, this increases after a few minutes (b) and then, as time passes it decreases (c), and practically disappears after 12 hours (d). The hypothesis that the oxygen could come from other surface areas not subjected to ionic bombardment was rejected, however, because such surface mobility of oxygen was never found, at least in the case of steels. In fact, in Auger spectroscopy, a steel surface cleaned of oxides by means of ionic bombardment in high vacuum remains so throughout the period for which the specimen is exposed under vacuum conditions (14).

Fig. 2 - Auger spectra showing the evolution of oxygen content in a point of a fracture surface during time:
a) immediately after ion etching; b) after exposition under vacuum and with the electron beam on, after a few minutes; c) id. after six hours; d) id. after twelve hours.



Having ruled out the hypotheses of adsorption and surface diffusion, what essentially remained was the hypothesis that the oxygen came from inside the steel studied i.e. due to fracture of the bar, oxygen trapped at the grain boundary was freed, remaining for some hours simply absorbed on the surfaces created in the course of the fracture. This hypothesis was confirmed because, with time, the oxygen tended to disappear (Fig. 2d) while, as is well known, the oxides of iron are rather stable compound which do not readily separate out under vacuum.

2. Evidence of unforeseen elements, in analysis, made mobile by mechanical abrasion under vacuum.

Using ionic bombardment with Auger spectroscopy, it is possible to have a calibration of the system under examination, thus avoiding problems which, in some cases (not that of steel) may be quite serious. Studying various steels, the presence of elements, which are normally present only in minimum quantities, or quantities which are considered not to be present in these alloys, was discovered.

Mechanical abrasion of surfaces (scraping) under vacuum is also employed at the same purpose. This method allows examination of the mean composition of a thickness located close to the surface, but quite thick, without the alterations and loss of time connected with abrasion by ionic bombardment.

Various specimens have been examined in this way. On many abraded surfaces, not only were considerable quantities of elements found which, as a rule, are not part of their composition, but it was also possible to show that, with time, their quantity varied over the surface examined; therefore, like the oxygen in Fig. 2, they had to be considered "mobile".

The specimen, degreased and placed inside the vacuum chamber, was abraded using a sufficiently hard vanadium steel milling cutter which had been carefully degreased. In this way, craters 1 mm in diameter and about 10 μm deep were obtained. The surfaces were examined at the same point, before and after the scraping operation.

The presence, on the Auger chart, of new elements after abrasion was therefore attributed to the presence of these elements inside the metal.

3. Evidence of oxygen, obtained by mechanical abrasion under vacuum conditions

It should therefore also have been possible to see grain boundary oxygen in this way because, as a result of abrasion, obviously both the structure of the material in the crystal and the grain boundaries underwent profound alterations.

One spectrum relating to a steel surface which had been previously abraded (Fig. 3) shows, in fact, the

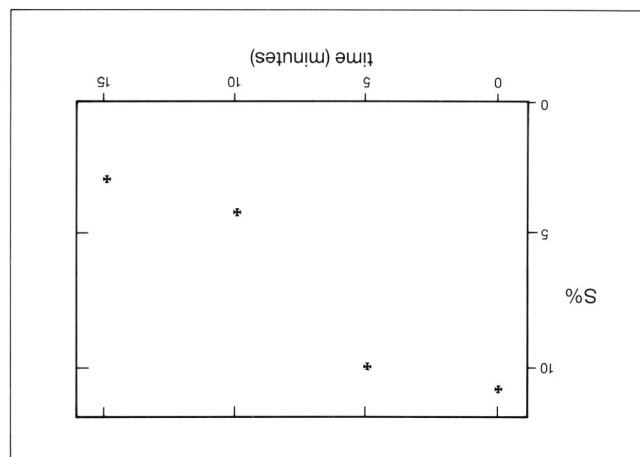


Fig. 4 - Evolution of sulphur content in Auger spectra vs. time.

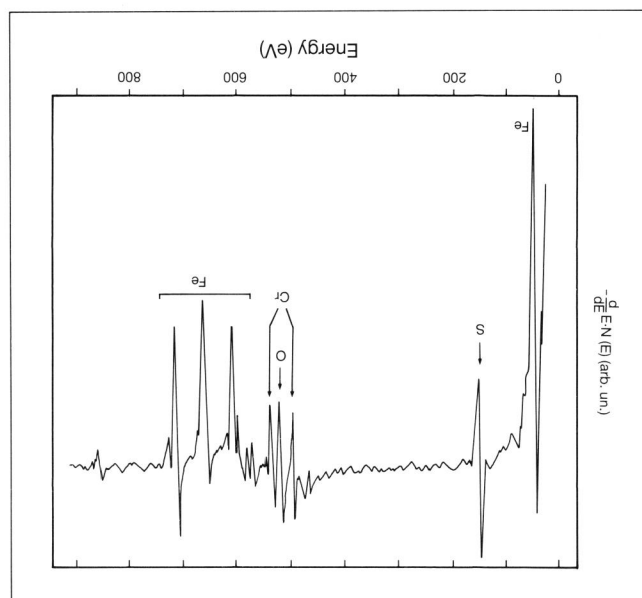


Fig. 3 - Auger spectrum obtained on a mechanically scraped surface of an AlSi 316 L steel, showing sulphur and oxygen presence.

In addition to oxygen, a considerable quantity of sulphur has been found in some austenitic chromium nickel steels (AlSi 316L), on the abraded surface (Fig. 3). As regards sulphur, it is known that, apart from exceptional cases this is tolerated in steels only to the extent of some tens p.p.m. in the mass. On the other hand, in Auger spectra, an element is only shown when it is present on the surface being examined in quantities of at least some points percent.

4. Evidence of the presence of sulphur and its mobility

presence of oxygen.

by various authors have shown a considerable presence of sulphur at grain boundaries, we can deduce that, once the grain boundary surfaces are destroyed or much distorted by abrasion, a considerable quantity of sulphur emerges and remains for a certain time absorbed on the outer surfaces. The mobility of sulphur is confirmed by the fact that its percentage decreases more rapidly as the intensity of current in the electron beam from the Auger spectrometer gun increases, probably due either to localised heating at the point where the beam arrives, or to the over-abundance of electrons in the area. A typical case of change in the quantity of sulphur present in an area examined by the Auger process is shown in Fig. 4, (15).

5. Evidence of the presence of chlorine and its mobility

Further experimental evidence was obtained using samples which, before being placed in the experimental chamber, were degreased in Freon 2 ($C_2Cl_3F_3$) is widely used to clean steel surfaces as it is an excellent degreasing agent. Only in these samples, a considerable quantity of chlorine was found on the surfaces abraded under vacuum conditions, and the chlorine behaved very much like sulphur. This prompted the hypothesis that the chlorine came from within. Further experimental evidence favouring this hypothesis was obtained by bombarding these abraded surfaces, rich in chlorine, with argon ions. After the bombardment, no chlorine was found to be present, which indicated that the chlorine was only present in the form of one or few monolayers. With the passing of time, however, the surfaces – still in vacuum – again became enriched with chlorine. Spectra of one of these surfaces rich in chlorine are shown in Fig. 5, and variations in the quantity of chlorine present on a surface which, initially rich in chlorine, was cleaned almost completely by ionic bombardment, are shown in Fig. 6. In the case of chlorine, what has already been stated for oxygen appears even clearer since, inside the experimental chambers, there are certainly no chlorine sources present, and even the possible presence of chlorine on the surface in other zones of the sample which was not bombarded is too low to explain the very high chlorine content on these abraded surfaces.

Conclusions

In conclusion, application of the method comprising mechanical abrasion under vacuum, allowing examination of the mean composition of a thickness located close to the surface, but quite thick, without the

Fig. 5 - Auger spectra of a C50 steel, previously degreased with Freon 2, after scraping, showing the evolution of chlorine content during time:
a) immediately after scraping; b) after a light ion bombardment; c) id. after 12 min exposure under vacuum and with the electron beam on.

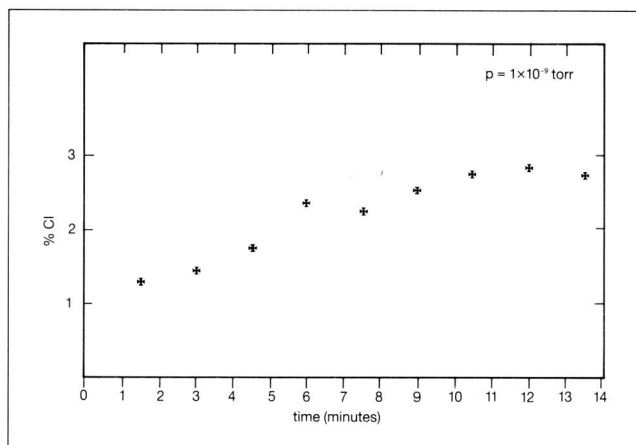
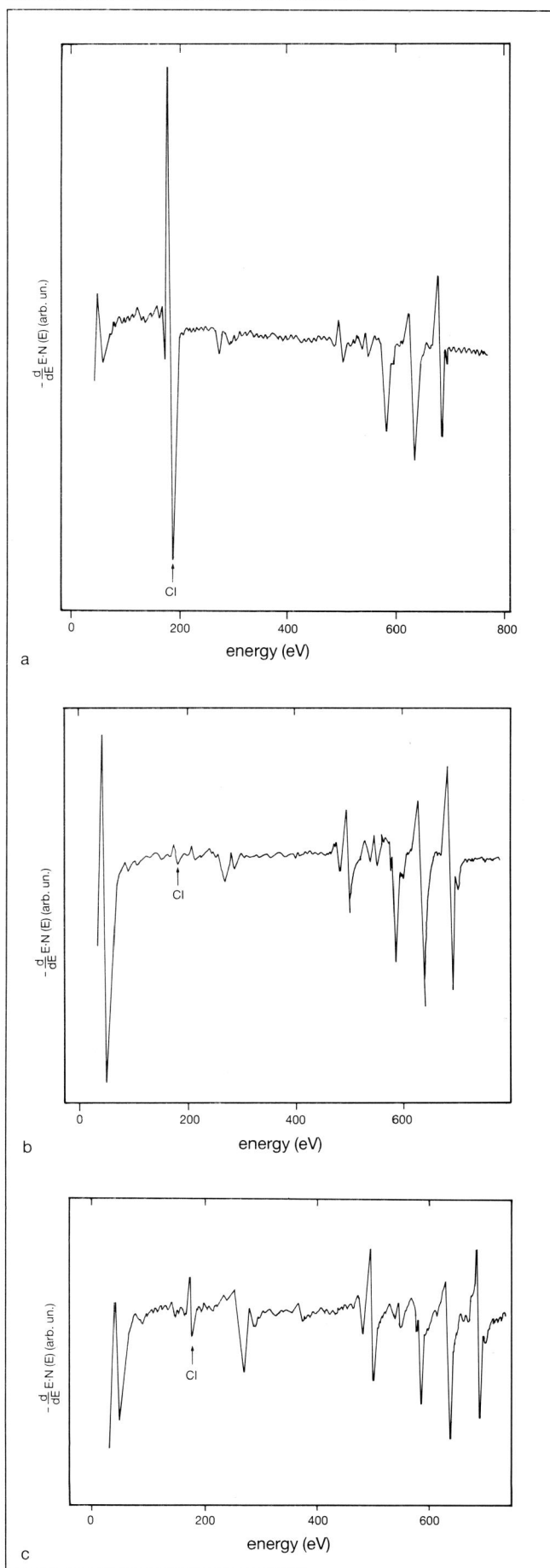


Fig. 6 - Evolution of chlorine content in Auger spectra Vs. time.

alterations and loss of time connected with abrasion by ionic bombardment, has shown that, at least in the case of steel:

- if it is in contact with an organic compound containing chlorine, not only does a chemisorbed film of chlorides form but also, possibly with very brief contact, and at a very low homologous temperature, chlorine atoms penetrate to a considerable depth (inevitably at grain boundaries);
- at grain boundaries, there is considerable mobility of chlorine atoms and, similarly, of oxygen and sulphur atoms.

The evidence of this high mobility (at grain boundaries) provides an easy explanation of the damage which may be done to steel mechanical components by contact, even brief, with substances which contain chlorine or sulphur in their molecule.

In this case, by hydrolysis or, more generally, by a reaction of the Grignard type, initial persorption of chlorine or sulphur ions may occur at grain boundaries (Fig. 1) which, by a single contact, promotes the creation of microcracks (of dimensions close to those of the grain) capable of acting as starting points for fatigue crack and, by a continuous contact, as in the case of a lubricant, exerts an action synergic with the periodic tensile stresses in promoting rapid crack development.

In particular, with reference to oxygen, the evidence of its considerable mobility along grain boundaries, even at very low homologous temperatures, prompts a revision of the interpretation, generally accepted, according to which the large increase in the endurance of ferrous materials subjected to periodic alternating stresses, noted under experimental conditions when the ambient pressure becomes less than 10^{-8} torr is due to the absence of interactions between the gases in the atmosphere and the "intrusions/extrusions" caused by the intragranular movement of the

dislocations (16). In fact, it seems much easier to consider the cessation of the synergic action, of stress and persorption of oxygen from the environment, along grain boundaries, as the cause of the phenomenon. However, these are only some examples of the range of theoretical and practical considerations which may arise from the evidence of the very high mobility of foreign ions along grain boundaries, even though only relating to layers of very small thickness close to the surface.

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