SUBSTRUCTURAL DETERIORATIONS OF ALUMINIUM ALLOYS AT NORMAL SERVICE CONDITIONS

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ABSTRACT

Changes of aluminium alloys' substructure exposed to the sustained load in humid environments are presented in systematic manner. These include dislocation pile ups, hydrogen bubbles of high pressure, modifications of substructure due to hydrogenation and excessive vacancies generation as the result of metal - environment interaction. The data are considered in close connections with the latent stage of delayed fracture of different kinds.

KEYWORDS

Substructure, selective oxidation, excessive vacancies, fracture.

INTRODUCTION.

The fracture of materials under sustained stress in their service conditions is caused by different mechanisms. Before the failure occurs there are often diverse deteriorations in materials structure. At normal temperature in an active environment in the simplest case it can be some sort of corrosion - general or local - and changes in dimensions or forms of tested specimens. But additionaly to these defects commonly easily observable by naked eye or simple optical means may also appear changes at the substructural level. The latter are visible only by transmission electron microscop; or estimated indirectly according to results obtained by means of some physical metallyrgy's methods. The need to use rather sofisticated techniques for the substructure study may be the cause why these defects are not properly accounted in predictions of material's quality change and sometimes are not even well known. However in the last 30 years there was a big work in this direction. Especially large information is available for high strength aluminium alloys exploited in humid

air. The aim of this report is presentation types of defects which can form during long service of material in normal condtions and explanation of their role in delayed fracture or its preparation. We have to notice at this point that all transformations at substructural level presented and discussed in this report are thought to occur at stresses less than yield one, i.e. at stresses permited in long loaded constructions. In the final discussion there are some considerations about the meaning these phenomena can have for the other combinations material - environment.

TYPES OF DEFECTS.

Dislocation Pile ups. Formation of complanar pile ups of dislocations (Fig.1) at sustained stress σ_t less than yield one ($\sigma_{0.2}$) in high strength aluminium alloys now is almost a

Fig.1. Complanar pile ups of dislocations in Al - 5wt.%Zn - 2wt.% Mg alloy. Solution treatment at 450°C; quench in water at 20°C; ageing: 100h at 100°C. Sustained tension in laboratory air at $\sigma_t = 0.8\sigma_{0.2}$.

commnon notion of all investigators. But to our knowlege the most experimental evidencies for this alloys have been obtained after small plastic deformation. Generation and piling up of dislocations at any time of sustained loading at $\sigma_t < \sigma_{0.2}$ is to some extent problematical because in tests of high strength aluminium alloys at such stresses has been established the logariphmic character of creep (Polyanski et al, 1990). It is known that during such a creep dislocation sources are exhausted at the very initial stage (McLean, 1965). However at stress $\sigma_t > \sigma_{0.2}$ at normal temperature there is a stage of creep analogous to high temperature steady state creep (Polyanski et al, 1990). Evidently one may suppose a continued piling up of dislocations at the such conditions. Of course they are realizing at any stress concentrator, including plasticaly deformed zone ahead of crack tip, or if the Smid-Boas factor attains a critical value in some grains.

The potential danger of pile ups is at least twosided. Firstly, a pile up which is stopped befc e any barier causes high stresses in material around its heau. In accord with the theory (Cottrell, 1955) the maximum stress σ here is n times higher

than σ_t, where n - the number of dislocations in pile up. Secondly the product $n\sigma$ is reciprocally proportional to the shortest distance d between two neighbour dislocations in the head of the pile up (Stroh, 1957). If d = b where b - the Burgers vector of dislocation then forms a double dislocation, that may be regarded as an origin of a crack. Moreover as has been schown (Vladimirov and Orlov, 1969) when the values of d and b are nearby it is possible a crack initiation due to thermal fluctuations. This is of a paramount importance for any delayed fracture.

In principle a propensity to the complanar pile ups formation is structure sensitive. Dispersion hardened alloys especially valnureable to the comlanar slip when precipitations are coherent and shearable ones (Hornbogen, 1967). The meaning of complanar pile ups is more dangerous when there is other substructural defects formation due to interaction of material with an active environment.

Hydrogen Generation and Absorbtion. Gas absorbtion modifies the substructure in several aspects. If it goes from humid atmosphere in aluminium alloys in high strength conditions form hydrogen bubbles (Alani and Swann, 1977). Diameters of the latter in order of magnitude is approximately equal to the sizes of precipitations of strengthening phase. Due to high pressure of gas in the bubbles in the matrix around them arise high stresses (Fig.2), and dislocation loops are punched out (Fig.3) (Kurtasova and Polyanski, 1980). Gas saturation influences vacancies' and dislocations' structures. Hence the gas saturation of materials in active environments may be reconed as a deteriorative factor on substructural level.
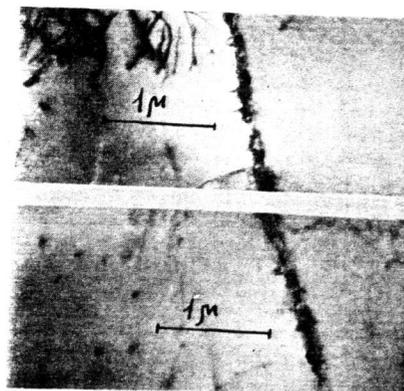

Fig.2. Contrast around HB in Al-8.6wt.%Mg alloy due to deformations in matrix stipulated by high pressure in bubbles. x20000.

Fig.3. The same area of the specimen as on Fig.2 at the different contrast conditions. Dislocation loops around HB. x20000.

As to the mechanisms of hydrogenation of materials - chemical or electrochemical one - both of them can produce a high pressure of gas in all cavities of solid spesimens when the Gibbs' free energy of corresponding chemical reaction or the applied electrode potential have enough negative values. In the

such situations the subjekt of main interest becomes kinetic factors by virtue of which the high pressure is realizable and substructural defects appear. At this place is usefull to note that simultaneously with gas generation somewhere on the surface and its absorbtion by material of specimen occurs formation of other defects, the most important of which are excesive vacancies.

Excesive Vacancies. The formation of excesive (or redundant) vacancies due to oxidation of metals and alloys is almost a common event (Bernar, ed., 1968). Hence they may be encountered in different materials exposed in active oxidazing medium. But vacancies are in size of an atomic order of magnitude. So their belonging to the substructure is indirect and is related to the aftermath the latter suffers when they appear in the specimen. The theory shows that immediatey after formation the redundunt vacancies strive to the sinks: the external surface, grain and interphase boundaries cavities, dislocations and dislocation loops. If cavities are small enough they together with two last kinds of sinks are the substructural constituents. The changes in shape and size of them are common indications of excessive vacancies presence. Indeed, by observation of transformation of straight screw dislocations in to helices (Fig.4) in thin foils of the alloy A ∪wt.% ᴍᴜ exposed in air with relative humidity 80% at 60°C for 2 days we have proven in the earlier work (Kurtasova and Polyanski, 1983) the generation of excessive vacancies in the described conditions.
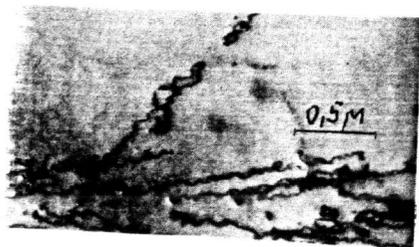

Fig.4. Helices originated from linear screw dislocations in a thin foil after its exposure in the air with relative humidity 80% at 60°C, 2 days. Alloy Al-10wt.%Mg. x28500.

The facts related to the formation of HB's - necessity of vacancies for their nucleation and their appearance in overaged alloys - have lead one of us (Polyanski, 1985) to conclusion that HBs themselves are indicators of excessive vacancies generation immediately at the exsposure time of specimens.

THE NATURE OF THE COMPLEX DEFECTS AND MECHANISMS OF THEIR FORMATION.

The theoretical calculations (Popovic and Scott, 1974) showed the large affinity between vacancy and proton in aluminium. Indirect experimental indications of formation complexes "vacancy-proton" (further presented as the symbol $(p-H^+)$) and their properties were obtained later (Larikov and Krasilnikov, 1981). All that facts gave opportunity to suggest (Polyanski, 1991) that due to simultaneous hydrogen absorbtion and excessive vacancies generation during a long time loading of specimens in humid environments, in high strength aluminium alloys are forming complexes $(p - H^+)$ i.e. the substitutionaly solved hydrogen (SSH). We have emphasized that the real cause of complex defects formation is the selective oxidation of aluminium alloys. To explain some kinetic features of the process it was suggested that oxidation goes in stages: a part of them on and another part under the oxide film. For the alloys with magnesium the whole mechanism of this element selective oxidation reaction

$$2Mg + H_2O + 1/2\ O_2 = 2MgO + H_2 , \qquad (1)$$
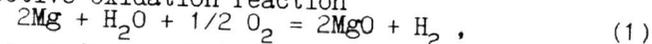
looks as follow (Polyanski and Kurtasova, 1991):

1. under a film: $Mg = Mg^{+2} + 2e + \alpha_p$;
2. tunelling of electron through a film;
3. on the external surface of a film: $1/2\ H_2O + 1/4O_2 + e = OH^-$;
4. diffusion OH^- through a film;
5. under a film : $OH^- + Mg^{+2} = MgO + H^+$;

$$(2)$$

6. under a film : $H^+ + e + \alpha_p = (1-\alpha)H + \alpha\ [(p-\ H^+) + e]$, where α – probability of a vacancy formation due to the transition of magnesium atom from an alloy into an oxide film, $0<\alpha<1$; p –the simbol of a vacancy; αe –the negative charge in a lattice screening the complex; $[(\ p - H^+) + e\ ]$ – is taken for SSH; H – is for a hydrogen absorbed on a boundary metal/oxide and instilled in solid solution.

From the succession (2) it follows, that hydrogenation of alloy, formation excesive vacancies and complexes ($p - H^+$) in it are occuring simaltaneously. It seems rather probably that complexes ($p - H^+$) are the elemental "bricks" of which HBs are bild up and that the first step in the bilding is places exchange between complex ($p- H^+$) and magnesium atom of grain boundary precipitation particles. It was shown that selective oxidation of magnesium and lithium out of aluminium alloys does go at room temperature (Varakina et al, 1979).

EFFECTS OF SSH ON DELAYED FRACTURE AND SCC MEHANISMS.

Fracture of aluminium alloys due to SCC propagates along grain boundaries. Usually two mechanisms of the phenomenon are considered: local anodic dissolution (LAD) and HE. For the former to occur the liquid electrolyte is needed at least in the tip of a growing crack. The fracture goes by dissolution of material either of narrow zones along grain boundaries or along slip planes. Dissolved areas have more negative electrochemical potential than interiour of grains due to differeces in chemical contents or in a passivity conditions. Hydrogen segregated on grain boundaries decreases the passivity of local material(Hanie and Boyd, 1969). It may be a hydrogen of

different origins: metallurgical, cathodically charged and so on. But great importance of SSH is in that that it easilly segregated and dragged by dislocations (Polyanski, 1985). It also may migrate through the lattice as simple vacancies do and in stressed specimen must move from a boundary metal/oxide to grain boundaries in perpendicular orientation to tensile stress. This mechanism is similar to that of diffusional creep. Dislocation dragging and migration in a virtual field of stress gradient are details of hydrogen transport in solids but the last of them makes SSH faster than instilled hydrogen. It is important both for LAD, HE and delayed fracture if SSH is delivered to or generated at grain boundaries. The significance of SSH consists also in that that the upper limits of its quantity may be equal to contents of elements liable to selective oxidation.

The Role of Metallurgical Factors. Schematically the distribution of alloying elements in aluminium alloys along a line normal to the grain boundary is produced on Fig.5. The intensity of selective oxidation (1,2) is proportional to concentrations of elements vulnerable to it. In accordance with sequence of events (2) the concentration of excesive vacancies and SSH are also proportional to those concentrations in the tip and on shores of a crack advancing along zones adjacent to grain boundaries. So the smallest rates of SSH generation relate to the distribution 3 on the Fig.5. The tendency for a realisation of such a distribution is the more pronounced the slower the cooling rate at quenching, the higher the temperature and the longer the time of ageing. These factors are known to increase the resistance to SCC of Al-Mg, Al-Zn-Mg-(Cu) and Al-Mg-Li alloys. Such coincidences are an implicit support of suggested ideas on connections of selectitive oxidation and SCC mechanism of aluminium alloys.
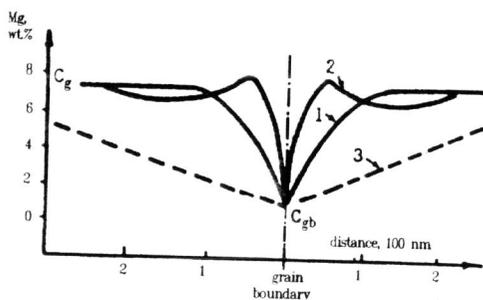

Fig.5. Schematic distribution of alloying element along a normal direction to a grain boundary in Al-Mg alloys. 1 – quenching from 520°C, short ageing at 125-275°C (Doig and Edington, 1973); 2 – quenching from 540°C (Candy et al, 1969).

SOME RELATED PHENOMENA IN DIFFERENT COMBINATIONS ALLOY - ENVIRONMENT

It is well known that titanium α and $\alpha+\beta$ alloys are characterized by patent creep behaviour at normal temperatres and at less than $\sigma_{0.2}$ stress. Besides these alloys have a propensity to absorb gases and to complanar slip, the latter at least in α-phase (Williams et al, 1980). So dislocation piling up in them may be akin to discussed for aluminium alloys. In connection with SCC and HE of steels also are known facts of hydrogen absorbtion and complanar slip. It seems usefull to look for more close ties of these structural changes with possibility of simultaneous formation of excessive vacancies due to reactions with an evironment. Obviously some search for methods of intensification the process and rules of an extension of obtained data on a real exploitation conditions must be done.

DETERIORATIVE ROLE OF SUBSTRUCTURAL DEFECTS

Aforementioned substructural defects are very deteriorative in high strength aluminium alloys . It is well known that in conditions these defects form the mechanical properties and especially ductility. worsen. Such followings may be awaited also in different combinations alloy-environment. So the approach to investigate the formation and interaction of substructural defecs of different kinds seems to be actual.

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