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# EFFECT OF DIFFERENT VARIABLES ON THE PRECIPITATE FREE ZONES ADJACENT TO GRAIN BOUNDARY REGIONS IN CONVENTIONALITY QUENCHED AND AGED Al-Zn-Mg ALLOYS(*)

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Agehardenable Aluminium alloys are noted for their high strength to weight ratio. Interest in the agehardenable alloys based on the aluminium - zinc - magnesium system stems from the fact that they have the highest static strength of known Aluminium alloys; a noticeable feature of this alloy is the "precipitate-free zone" formed adjacent to grain boundaries. Electron microscopic studies have shown that the stress-corrosion susceptibility and the lack of ductility of aged Al-Zn-Mg alloys are normally associated with these soft precipitate - free zones adjacent to grain boundaries. When the alloys are deformed, the precipitate-free zones serve as favourable sites for dislocation movement and this may lead to preferential flow in these regions and ultimately to intercrystalline failure.

The problem of stress-corrosion cracking, therefore, arises in alloys aged to maximum tensile strength, where there is maximum grain boundary embrittlement. The solution to this problem is, thus, to eliminate the precipitate-free regions next to grain boundaries, whilst at the same time retaining a high mechanical strength. Some possible ways of doing this are:-

(1) to use single crystals, which of course, is impossible for engineering structure.

(2 ) to reduce the width of the precipitate-free zone to a great extent by the help of proper heat treatment, i.e., proper control of solution treatment temperature, ageing temperature, ageing time, quenching rate etc.

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(3) to study the effects of some alloying additions.

(4) to fill up the existing precipitate-free regions with the introduction of dislocations which may act as new nuclei for the precipitates. This may be achieved by plastic deformation prior to ageing.

(5) to modify, by the addition of trace elements, the structure of the precipitate phase so that it is nucleated coherently and does not require vacancies.

(6) to stabilise, by the addition of trace elements, the vacancy clusters near the grain boundary and to prevent the formation of a vacancy-free zone.

PRECIPITATE-FREE ZONE - ITS MEANING AND CAUSES OF ITS FORMATION:

The classical theory of heterogeneous nucleation shows that the grain boundary precipitate is in a lower energy state than the zones or intermediate precipitates formed within the grain and it will, therefore, tend to increase in size during ageing at the expense of intragranular precipitates. In addition, the grain boundary precipitate is frequently nucleated before the intragranular precipitate and is able to draw solute atoms from within the grains. Classical precipitation theory have assumed that these two effects are the cause of the "denuded zone" near grain boundaries. Electron microscopy has shown that this is not always true. In case of Al-Si alloys it has been established that the width of the precipitate-free zone increases with decreasing quenching rate although the amount of grain boundary precipitation is hardly affected and that precipitates on the edge of the precipitate-free zone are larger than those within the grains suggesting that they are able to draw excess solute atoms from the zone. It has also been observed that if the alloy is deformed before ageing, precipitation occurs near the boundary and there is no precipitate-free zone.

It may, therefore, be concluded that in this alloy the "denuded zone" is only denuded of nucleating sites for precipitates and that the solute concentration is the same as that in the supersaturated solid solution within the grains. Therefore, the "denuded zone" is in fact only denuded of vacancies and the phrase "precipitate-free zone" is a better description.

After quenching from the solution treatment temperature an alloy will be supersturated with respect to both solute atoms and vacancies, except in the vicinity of vacancy sinks. That the grain boundaries act as vacancy sinks has been demonstrated by the absence of dislocation loops in regions adjacent to the boundaries in drastically quenched aluminium. So, the concentration of vacancies in the vicinity of grain boundaries immediately after quenching from solution treatment temperature is low compared to that within the grains.

A critical concentration of vacancies is always necessary for the nucleation of precipitate under fixed conditions of ageing. As the concentration of vacancies near the grain boundary regions is low, there will be no precipitates in these regions but nucleation will occur within the grains.

EFFECT OF HEAT TREATMENT

It is known that in addition to point defects formed by thermal fluctuations, point defects may be created in the crystal by other means. One method of producing an excess number of point defects is by quenching from a higher temperature. If temperature is lowered fast enough in the quench, some of the defects in equilibrium at higher temperature may be retained at lower temperature. An increase of the solution treatment temperature will, therefore, increase the concentration of vacancies. On the other hand, a slower quenching rate leads to a greater diffusion distance during quenching and hence acts in the opposite way. The reduction in the width of the precipitate-free zone at lower ageing temperatures may be attributed to the fact that the critical concentration of vacancies required for nucleation at lower ageing temperatures will decrease. So, it is evident that a higher solution treatment temperature, a slower quenching rate and/or a lower ageing temperature will lead to the formation of a narrower precipitate-free zone. A longer ageing time below the G.P. Zone solvus results in the formation of a fine dispersion of the precipitates and a narrow precipitate-free zone.

EFFECT OF ALLOYING ELEMENTS

Various alloying elements such as copper, manganese, chromium, titanium, silver etc. have been added to Al-Zn-Mg alloys in an attempt to reduce the susceptibility of these alloys to stress-corrosion cracking. It has been observed that the addition of silver to Al-Zn-Mg-Cu alloys leads to the removal of the precipitate-free zone completely after proper ageing at a suitable temperature and this results in an increased resistance to stress-corrosion cracking. It has been reported that the addition of copper, chromium and manganese is responsible for the improved stress-corrosio cracking. It has been reported that the addition of copper, chromium and manganese is responsible for the improved stress-corrosion performance of Al-Zn-Mg alloys but when manganese is added in the absence of chromium it has no effect on stress-corrosion properties; manganese in presence of copper, however, restricts the precipitate-free zone and hence results in better stress-corrosion properties. The beneficial effect of Ti on the properties of Al-Zn-Mg-Cu alloys has also been reported.

Effect of Cold Work

Deformation either prior to or during the ageing process may be employed to minimise the deleterious effects of precipitate-free regions. The deformation introduces additional nucleation sites for precipitates and hence causes the precipitation to occur close to the grain boundaries, thus tending to eliminate the depleted grain boundary regions. Another beneficial effect of cold working results from the mechanical strengthening of grain boundary regions through work hardening and through the creation of jogs along grain boundaries which reduce the free slip distance.

CONCLUSION

From the above discussions it is evident that the possibilities of improvement of stress-corrosion behaviour in otherwise suitable Al-Zn-Mg alloys warrant attention. While the exploitation of possible ways of (1) finding out a suitable heat treatment procedure (2) examining the effect of cold work prior to ageing or (3) finding out a suitable combination of alloying elements seems to be promising, the present state of knowledge is too inadequate to give us a suitable method for the improvement of the stress-corrosion properties of Al-Zn-Mg alloys. However, the authors believe that of the methods cited above the addition of suitable alloying elements and the control of their quantities have a great influence on the reduction of the precipitate-free zone adjacent to grain boundaries and hence this would probably be of great significance so far as the direct industrial application of these alloys is concerned.

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