MECHANICAL PROPERTIES AND STRUCTURAL TRANSITIONS IN SPLAT-COOLED Al-Mn AND Al-Fe ALLOYS

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Abstract

Molten droplets of Al-Mn and Al-Fe were quenched by the splat cooling technique in order to obtain α Al supersaturated solid solutions. The solid solubility of these transition elements can be extended to approximatively 5 at.%.

A substantial hardening effect is observed only in Al-Fe alloy; the hardness of the Al-Fe 3 at.% alloy is three times higher than that of usual aluminium alloys. We show that Al-Fe samples are not homogeneous solid solutions : the splat-cooling technique produces a very fine dispersion of "clusters" which deform the aluminium matrix.

Introduction

The splat cooling technique of droplets of molten metal (1,2) has been used to obtain solid solutions of Al with the first series transition elements (3, 4, 5). The solubilities of these elements can be considerably extended up to approximatively 5 at.% while the maximum equilibrium solubility of Fe in Al is known to be less than 250 ppm at 650°C.

We have studied the structural transitions and the mechanical properties during the transformation of the Al-Fe and Al-Mn solid solutions into the equilibrium phases. It was decided to study these systems in order to get information on the nature of the metastable structures in new splat-cooled aluminium alloys, since at the beginning of this work only very limited data (Moss in Al-V system) were available.

The most striking effect was recently pointed out by H. Jones (6). The hardness of the Al-Fe 3 at.% is three times higher than that of usual hardened alloys, while that of Al-Mn 3 at.% alloy is quite of the same order.

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Experimental procedure

Splat-cooled specimens are prepared by the anvil and piston technique. They are foils of less than a few μ thickness and a few mm^2 area. There is an inverse relationship between specimen thickness and cooling rate. Thus homogeneous phases are only obtained when the thickness is less than 20μ for Al-Fe 3 at.% and 35μ for Al-Mn 3 at.%.

This phase has the F.C.C. aluminium structure with a shift of the parameter ($a = 4.032$ Å for Al-Fe 3 at.% and Al-Mn 3 at.%). Furthermore the matrix of this phase is distorded as shown by X-ray line broadening.

Since the samples are too small and hence inadequate for any tensile measurements we have measured the microhardness of these alloys. The weak load used on Reichert equipment, produces indentations the depths of which are less than the tenth of the thickness of the sample.

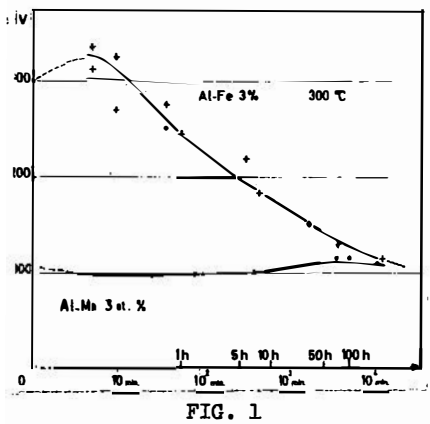

FIG. 1
μ-hardnesses after anneal. 300°C.

On FIG.1 microhardness results are plotted as a function of the time of the isothermal annealing at 300°C of Al-Mn and Al-Fe alloys respectively. The phases and the structures were investigated by X-ray diffraction and by electron microscopy.

The transformation of the two alloys during annealing at 300°C is different until precipitation is very advanced (100 h, 300°C) when the hardness of the two alloys becomes equal. Therefore, in that state the metallographic structures are not exactly similar (FIG.6 7).

Experimental results

The Al-Fe solid solution annealed for one hour at 300°C has completely disappeared, but no intermetallic phase is yet detected by X ray diffraction-However, for the first times of annealing on the heating stage of the electron microscope we observe the formation of precipitates at the grain boundaries as well as small dark globular areas uniformely distributed throughout the grain. These clusters or micro-precipitates are surrounded by a strained region of the matrix. In that state the microhardness shows a small increase which is relatively not very important when compared to the high initial value (10%).

On the other hand the micrographs show that the images of micro-

precipitates pass from white to black when a thickness dark fringe is crossed. That is a situation opposite to the transition of intensity observed for the G.P. zones in Al-Ag system. From this observation we may conclude that in Al-Fe the micro-precipitates are of the "hole type", where as in Al-Ag they correspond to the increase of the factor structure correlative to the substitution of Ag atoms in the Al matrix.

The similarity of the FIG.4 (Al-Fe) with the FIG.5 (Al-Ag) could suggest the existence in Al-Fe, of G.P. zones, analogous to those of the Al-Ag system. That is silver-enriched domains formed by the replacement by the solute atoms of the aluminium atoms in the matrix lattice. Furthermore this substitution does not produce any significant distorsion because of the equality of atomic radii.

But in splat-cooled Al-Fe alloy, the structure of the iron enriched domains seems to be much more different from the structure of the matrix. That is shown by the "hole type" image of these zones and the strains apparent on the electron micrographs. So we prefer to call these first clusters, micro-precipitates instead of G.P. zones, because these structures, although not well defined and still coherent with the matrix, may be considered as a first step towards the structure of a crystallized precipitate Al_6Fe. This precipitate which is not yet the equilibrium precipitate Al_3Fe, becomes visible on the D.S. diagrams when the annealing treatment is continued either for a longer time at 300°C or a higher temperature between 300° and 470°C. After a treatment above 480-490°C the phase Al_6Fe disappears and the stable phase Al_3Fe is formed.

The evolution of Al-Mn alloy is definitely distinct from that of AlFe: during annealing at 300°C the supersaturated solid solution disappears progressively; that is shown on the diffraction pattern by the splitting of the Bragg reflections of the F.C.C. lattice. New lines of the α-equilibrium phase appear on the film besides the lines of solid solution which becomes weaker. After annealing for 100 hours at 300°C, the solid solution reflections have not yet disappeared. The intermetallic phase is a very fine precipitate dispersed in the matrix in the shape of thin plates.

Hence the as-quenched alloy Al-Mn 3 at.% seems to be near to a perfect solid solution without any large distortion in the matrix. The use of Guinier law to calculate the radius of clusters from the S.A.S.(s→o) leads to a size of 7,8 Å after annealing for five hours at 300°C (11). After this treatment, Al_6Mn Bragg reflections are seen on the diagram as well as intense reflections of the solid solution Al-Mn.

The segregation in this system occurs by growth of the equilibrium phase which is non-coherent.

The more important difference between Al-Mn and Al-Fe is the large difference between the hardness of the two alloys. (AlFe is harder by a factor 3). Furthermore electron micrographs(FIG.2 and 3) exhibit some essential differences.

The thinned specimen of Al-Fe (FIG.2) contains a micro-structure throughout the grain, with a spacing about 100 Å, - as Matija and al.(8) have previously reported for splat-cooled Al-Fe 1 at.% -, while the micro-structure is absent in Al-Mn sample (FIG.3).

We think that very small groups of iron atoms are bound with aluminium atoms by no-metallic bonds and hence form stable nuclei of imperfect structure, very different from the aluminium lattice. These regions produce contrasts on the micrographs. They are coherent with the matrix; hence they shift the average lattice parameter and produce considerable distortion.

That would be the origin of the hardness; it is thus understood that it is exceptionnal since the primary cause involves the particular bonds between Al and Fe different from that between Al and the other first series transition metal, Mn.

The general state of distortion in the matrix explains the absence of contrasts of dislocations on the electron micrograph of the as-quenched Al-Fe alloy(FIG.2) : the strains around the dislocation core do not produce a sufficient contrast, distinguishable from the general background due to the other distortions spread out in the matrix.

These ideas are consistent with the existence of clusters on the "solid solution", probably present immediately after solidification. Janot and Lelay (10) detect such stable nuclei in Al-Fe 200 ppm, by the analysis of "Mossbauer spectrum, as Leroux (11) in the splat-cooled Al-Mn system, by X-ray Small Angle Scattering data on the device of A.M. Levelut(9 .

Unfortunately it has not been possible to use this last device which is able to detect the presence of small clusters. But this apparatus uses CuKα radiation which excites the fluorescent emission of FeKα radiation, intense enough to mask scattering which is researched.

Recently Höhler and Steeb (12) have measured the S.A.S. produced by the Al-Sn liquid alloy. Their results prove the existence of clusters at the temperature of 1000°C. Hence in this last alloy as probably in the Al-Fe alloy it is not possible to obtain homogeneous solid solution from the

molten alloy where solute atoms are just substituted in place of alumum atoms.

Conclusion

We conclude that the as-quenched "solid solution" is not perfectly homogeneous. That is consistent with the very low reported solubility of Fe in Al (240 ppm at 650°C, HANSEN). The splat-cooling technique produces a very fine dispersion of iron atoms in very small clusters. Since the diffusion coefficient of Fe in Al (13) crystal is particularly low the segregation begins at a high temperature (300°C) for an aluminium alloy.

Acknowledgments

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FIG.
Al-Fe 3 at.% (unannealed)

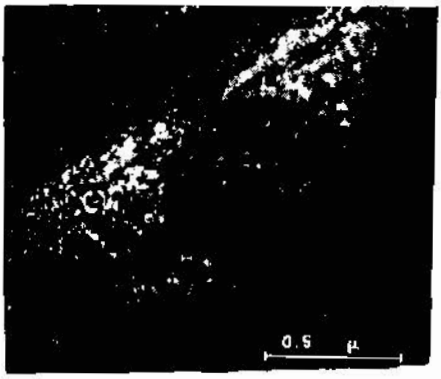

FIG. 3
Al-Mn 3 at.% (unannealed)

FIG. 4
Al-Fe 3 at.% (30' 320°C)

FIG. 5
Al-Ag 8 at.% (48 h. 150°C)

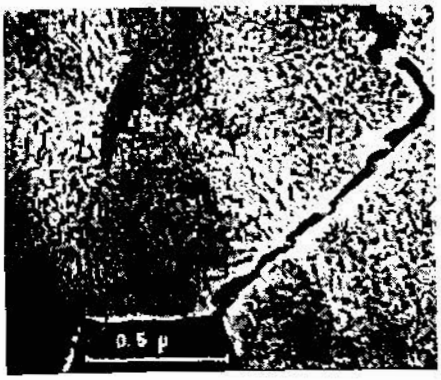

FIG. 6
Al-Fe 3 at.% (100 h. 300°C)

FIG. 7
Al-Mn 3 at.% (100 h. 300°C)

DISCUSSION

H. Warlimont : As a general, concerning the terminology used for coherent precipitates I should like to point out that there is no definition of a thermodynamic difference between disordered zones and disordered coherent precipitates (or ordered zones and ordered coherent precipitates, respectively): both of these transformation products are characterized by nucleation, growth and coarsening, thus indicating a decrease in the system of chemical free energy by the process. An apparent dissimilarity arises in cases such as zones in Al-Cu where, because of the large coherency strains, the next (transitional) phase begins to form before the zones exceed atomic dimensions (in thickness). But compared to other disordered coherent precipitates (such as in the Cu-Ni-Co and Cu-Ni-Fe systems, for example) this is only a quantitative rather than a qualitative difference (apart from the metastable and stable nature of the phases which is immaterial in this respect).

G.W. Lorimer : I support the plea of Dr. Warlimont to halt the proliferation of terms used to describe the first phase that is detected during the breakdown of a solid solution by a homogeneously distributed nucleation and growth mechanism. Clusters, microprecipitates and G.P. zones, are all terms which describe the first phase to form. The term G.P. zones has served well in the past and I see no reason why it should not continue to do so in the future.