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Abstract

Secondary ageing is a phenomenon in which precipitation hardening is observed to continue in alloys at relatively low temperatures after they have first aged at significantly higher temperatures. This process is reviewed in high-purity and commercial aluminium alloys. Experimental results will be presented regarding the effects of residual supersaturation, the role of vacancies, chemical effects, precipitates formed during secondary ageing, and practical outcomes of secondary ageing.

1. Introduction

Tailoring to design the microstructure of precipitation hardenable alloys is the nonimpossible dream of the physical metallurgy of the current days that is actively pursued in many laboratories by using powerful spectrographic techniques to investigate at atomic level on the factors that control solute aggregation processes. An effective method for controlling the morphology and the composition of the particles formed during the evolution of an alloy is to adopt multi-stage heat treatments. A contribution along this direction has been given recently by Lumley, Morton and Polmear [1-4], who have obtained significant improvements of mechanical properties for a wide range of alloy compositions by heat treatments that include secondary ageing, i.e. a stage at a relatively low temperature after another stage at higher temperature. This application has raised new interest in secondary ageing phenomena, which were observed several years ago in Al-Mg-Si, Al-Zn and Al-Zn-Mg alloys [5-7], also more recently in Al-Cu-Mg and Al-Cu-Mg-Ag by Somoza et al. [8,9]. Latest investigations on this subject can be found in Refs. [10-19]. The present work seeks to combine results gathered so far in an attempt to build a concise but comprehensive picture of the factors that control secondary ageing and of the microstructure that can be formed.

2. Experimental Techniques

The results that will be discussed below were obtained by combining measurements of mechanical properties (essentially, microhardness measurements) with imaging,

calorimetric and spectroscopic methods. It may be safely assumed that most of the readers of these Proceedings are familiar with the majority of the techniques that were used in the experiments discussed below, such as Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC) and Small Angle X-ray Scattering (SAXS). However, a short introduction to Positron Annihilation Spectroscopy (PAS) can be useful to many experts of physical metallurgy.

PAS is a group of techniques based on the spectroscopy of the annihilation radiation that is emitted when positrons are implanted in matter and react with electrons. All PAS variants have an extremely high sensitivity for cavities in the sub-nanometric range (lattice vacancies and open spaces in disordered regions) that comes from the electrostatic repulsion between positrons and positive atom cores, which confines positrons in any site where one or more atoms are missing. Therefore PAS is suitable to follow, in situ or ex situ, structural evolutions that imply association of vacancy with solute atoms or formation of disordered regions at the interface of precipitates with the matrix. The PAS technique that has been most widely applied to the study of secondary ageing is PALS (Positron Annihilation Lifetime Spectroscopy). PALS measures positron lifetime spectra, from which the positron mean life in the sample and other statistical parameters can be calculated. The positron mean life depends on the local electron density; it turns out to be longer for positrons trapped in open volumes than for free positrons moving in the bulk metal and is also sensitive to the chemical composition at the annihilation site. Further reading on PAS techniques can be found in [20] and references therein.

3. Features of Secondary Precipitation

3.1 Residual Supersaturation

When the phases formed during the high-temperature (HT) stage are stable or metastable at low temperature (LT), secondary ageing is promoted by the presence of residual supersaturation. All secondary ageing effects become weaker with the increase of the HT stage duration, concomitantly with the reduction of the residual supersaturation. An example is shown in Figure 1, depicting PALS results [13] for the alloys Al-4Zn-3Mg and Al-4Zn-3Mg-0.3Ag (here and below, concentrations in wt. %), where it may be clearly seen how the positron lifetime variations occurring during secondary ageing become progressively weaker with increasing HT exposure time.

Figure .Positron 1: lifetimes for AI-4Zn-3Mg-(0.3Ag) first aged at 150°C, prior to ambient exposure. temperature The change in lifetimes becomes weaker as the exposure time of ΗT increases [13].



It must be noted, however, that lowering the secondary ageing temperature increases the effective supersaturation due to the decreasing solid solubility of the solute with temperature according to the relevant phase diagram; this may be sufficient for promoting

additional precipitation even after long HT stages. This effect has been observed to cause embrittlement in peak-aged alloys based on the Al-Li system [eg.21]. The decreased solid solubility with reduced temperature may also increase the rate of precipitation as shown, for example, with the alloy 8090 (AI-2.4Li-1.3Cu-0.9Mg-0.1Zr) shown in Figure 2. In this experiment, artificial ageing was conducted at 185°C for 2, 4 or 6 hours and the alloy was then rapidly quenched, prior to ageing at 65°C. As demonstrated for the hardness evolution depicted in Figure 2. secondary precipitation of δ' (Al₃Li) at 65°C is faster for several hours than if ageing was continued at 185°C.



Figure 2: Secondary ageing at 65°C for alloy 8090, first aged at 185°C for 2, 4 or 6 hours and then rapidly quenched. The initial rate of secondary ageing (broken lines) at 65°C after first ageing at 185°C is greater than the rate of ageing if continued at 185°C for the T6 condition (solid line).

3.2 Role of Vacancies

Vacancy-assisted diffusion is the main mechanism that governs solute diffusion inside the matrix. In this respect, the presence of vacancies above thermal equilibrium concentration is an important factor for controlling the rate of solute aggregation. The excess concentration of vacancies that is contained in the material after quenching from the solution treatment temperature is reduced during underageing at the HT. This may reduce the rate of secondary ageing at the LT when compared with the primary rate of ageing at this temperature. For example, Massazza et al. [11] observed that Al-4.5Cu-0.6Mg during secondary ageing at RT (after 7 min at 190°C) reaches asymptotically the same hardness value attained by natural ageing, but that the process is slower by a factor near to 15.

However, this behaviour is not general and does not occur with the alloy Al-[15]. 4.8Zn-1.3Mg important An contribution to solute transport may come from vacancies that are temporarily trapped inside the solute aggregates formed during the HT stage, and become available to assist diffusion during the LT dwell period. An indication in this direction comes from PAS experiments on Al-Cu-Mg and AI-Zn-Mg alloys [8-14]. In all these systems, the positron mean lifetime HT measured after а treatment the interrupted before onset of precipitation of semicoherent or incoherent particles indicates



Figure 3: RT evolution of the positron lifetime in Al-4Cu-0.3Mg after heating at 180°C for various times. [8].

predominant association of vacancies with Mg-free Cu or Zn clusters. On the other hand, PAS investigations on binary alloys AI-Cu and AI-Zn show that GP zones do not retain

vacancies. Therefore, the vacancies trapped in Cu or Zn clusters without being stabilised by a neighbouring Mg atom will be gradually released in the matrix when these clusters evolve toward ordered GP zones.

3.3 Chemical Effects

In ternary alloys, differences in the temperature dependence of the solubility of the solutes and in their affinity to vacancies affect the clustering rate of the solutes. This leads to the change of the average chemical composition of the solute aggregates. A typical example of this behaviour is in Figure 3, which shows the evolution of the mean positron lifetime at RT after heating at 180 °C. The solid lines in this figure are best-fit curves calculated on the basis of the following interpretation: a) the initial lifetime value (approximately the same for all curves) is determined by positron trapping at vacancies embedded in Mg-free Cu clusters; b) when the temperature drops, the Mg supersaturation increases and Mg clustering takes place at a rate faster than Cu which causes a steep initial rise in the lifetime curves and reveals the formation of mixed Cu-Mg clusters; c) if the Cu supersaturation is not entirely consumed during the high temperature stage, the average Mg/Cu ratio in the clusters reaches a maximum and then decreases slowly by further aggregation of Cu; in this case the lifetime curve develops a descending branch.

3.4 Precipitates Formed during Secondary Ageing

Further aggregation of solute to pre-existing precipitates would produce growth. This form of secondary precipitation probably occurs if the HT treatment is interrupted so early that only diffuse nucleation of small solute clusters has taken place. Alternatively, it may become dominant in the latter stages of secondary ageing, if matrix diffusion is

suppressed by the absence of vacancies and interfacial diffusion becomes the most effective mechanism. The transport experimental evidence gathered so far by TEM [3,18], DSC [11,15], and SAXS [14] usually indicates independent nucleation of new precipitates rather than the growth of existing ones. Microstructures and diffraction patterns observed by TEM analysis of AI-4Cu [3] and of the Al-Mg-Si alloy 6061 (Al-1Mg-0.6Si-0.3Cu) [18] show the nucleation and growth of new GP zones within matrix material. DSC calorimetric AI-4.5Cu-0.6Mg traces taken for after preliminary ageing at 190°C and secondary ageing at RT [11] show an endothermic peak that does not appear when the secondary ageing stage is omitted. This peak reveals formation at RT of solute clusters or GP zones that occurs independently of the presence of the more stable precipitates formed at 190°C. SAXS results for AI-4.8Zn-1.3Mg are displayed in Figure 4 in the form of an Iq^2 plot (*I* is the scattered intensity and q the scattering parameter). Panel (a) shows the effect of exposure at 150°C. The broad peak centred at



Figure 4: SAXS results for Al-4.8Zn-1.3Mg aged at 150°C (upper panel) and at room temperature after 30 min at 150°C (lower panel)[14].

about 4 nm⁻¹, that is already present at the beginning of the HT treatment, may be attributed to small solute clusters (Guinier radius around 0.5 nm) formed during quenching

and a few minutes of exposure to RT. These clusters are strongly reverted in less than 1.5 min at 150°C; concomitantly, new and bigger scattering centres are formed (peak centred at about 1 nm⁻¹, Guinier radius increasing from 1.3 to 1.8 nm). As shown in panel (b), when the sample is then exposed at RT, the peak due to small centres returns and moves slightly to the left of 4 nm⁻¹ (representing a more moderate size increase). The peak at 1 nm⁻¹ survives without any evident change in either the position or the intensity.

3.5 Practical Effects of Secondary Ageing

Secondary ageing may have notable effects on the mechanical properties of age hardenable aluminium alloys [1-4]. Where secondary ageing alone is conducted for appropriate durations following short periods of underageing at HT (designated as the T6I4 temper [2]), alloys are found to display tensile properties close to and occasionally exceeding those of the T6 condition (Table 1). At the same time, most alloys display significant increases in fracture toughness. These changes in mechanical properties can be obtained with reduced times of HT ageing which may lower heat treatment costs. If interrupted ageing is conducted whereby a typical T6 ageing cycle is interrupted by a low temperature dwell period (designated as the T6I6 temper [1,3,4]), the hardness, yield strength, tensile strength and fracture toughness of most age hardenable aluminium alloys are increased simultaneously (Table1).

In interrupted ageing, secondary precipitation is utilised to initiate nucleation of new GP zones, which, after further high temperature ageing, may stimulate formation of a higher density of finer precipitates within the matrix aluminium. The timeframe of secondary ageing required in these instances may range from a few hours to several days, since the critical size and dispersion of precipitate phases required to avoid regression and maximise strengthening in the final stage of ageing varies from alloy to alloy.

Alloy	Treatment	0.2% Proof	UTS (MPa)	% Elongation	S-L Fracture
		Stress (MPa)			Toughness (MPa√m)
7050	Т6	546	621	14	37.6
	T6I4	527	626	16	52
	T616	574	639	14	41.1
2214	Т6	386	446	14	26.9
(var. 2014)	T6I4	371	453	13	27.1
	T616	416	483	16	36.2
6061	Т6	267	318	13	36.8
	T6I4	302	341	16	43.2
	T616	299	340	13	58.4
357	Т6	287	340	7	25.5
	T6I4	280	347	8	35.9
	T616	341	375	5	26

Table 1: Comparative mechanical properties of alloys treated to the T6, T6I4 and T6I6 tempers.

In some instances such as in the alloy 2014 (Al-4.5Cu-0.5Mg-0.8Si-0.8Mn), which typically contains precipitates of θ ' (Al₂Cu) and S phase (Al₂CuMg), the proportion of the S phase is found to be increased by 75% over that contained within the T6 tempered alloy [12]. This suggests that secondary ageing has the potential to produce microstructures that are specifically tailored for engineering performance, when the treatment favours nucleation of a particular phase.

4. Conclusions

- The process of secondary precipitation is affected by the residual supersaturation of solute and vacancies that are retained on quenching to the lower ageing temperature. In some alloys, this can stimulate faster rates of precipitation at this lower temperature than would occur if ageing was continued at the higher temperature.
- 2. Secondary precipitation is facilitated by the presence of vacancies within the aluminium. Vacancies may be trapped in aggregates formed at elevated temperature and then released during the subsequent ageing at a lower temperature.
- 3. Chemical species present in aluminium alloys during the low temperature secondary age display specific solute/vacancy binding energies that may be revealed by PALS. These binding energies control diffusivity of solute and their ability to form clusters.
- 4. Precipitation during secondary ageing is typically observed to occur by the formation of GP zones or other solute clusters.
- 5. Utilisation of secondary precipitation in T6I4 and T6I6 tempers may result in significant changes to the mechanical properties of aluminium alloys through manipulating the size, density and proportions of phases present within the material. Studies of a wide range of alloys have shown that tensile properties may be increased by an average of 10% with concomitant improvements in fracture toughness.

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