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## Current positron studies of structural modifications in age-hardenable metallic systems\*

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**Abstract.** The sensitivity of positron annihilation characteristics to the structural changes occurring in supersaturated metallic systems has been demonstrated and explained since the early 1980s. This knowledge is currently applied for positron annihilation spectroscopy (PAS) investigations regarding the main phenomena that govern the structural evolution of a supersaturated alloy when various thermal treatments are applied: (a) kinetics of vacancy-type defects retained after quenching; (b) solute migration; (c) formation of solute clusters and/or GP zones; (d) precipitation. The analysis of PAS data gives information on the chemical composition, the defect structure and the density of decomposition products of nanometric size. The present article, that includes an exhaustive repertory of works published since 1987, discusses the value of the contribution that PAS studies can give to physical metallurgy in the field of age-hardenable systems. Most examples are taken from the direct experience of the authors.

### 1. Introduction

The foundations of positron annihilation spectroscopy (PAS) studies of decomposition phenomena in supersaturated metallic systems were firmly laid during the 1970s and part of the 1980s, on the basis of extensive experimental and theoretical work performed by various groups. For the period from the first observation of the effect of precipitation in an Al–Zn alloy (Sedov *et al* 1970) to the first comprehensive review papers on the subject (Dlubek 1987, Krause *et al* 1987) we count more than 60 papers related in some way or another to the interaction of positrons with the nanostructures that can be formed during the decomposition of a supersaturated alloy. As an overview of this historic material is not within the limits that we have set for the present work, we restrict ourselves to mentioning in table 1 some contributions that we regard as milestones (the choice inevitably reflects the scientific bias of the authors).

The review by Dlubek (1987) already sums up practically everything we need to know for understanding why positron annihilation characteristics are sensitive to the decomposition of a supersaturated alloy. On these grounds, Dlubek lists various subjects related to the decomposition process that one can approach by PAS techniques. All these are

\* In honour of Professor R N West's 60th birthday.

**Table 1.** A choice of milestones in PAS application to the study of age-hardenable alloys (before 1987).

Subject	Reference
Observation of positron trapping at precipitates	Sedov <i>et al</i> 1970
Measurement of vacancy–solute binding energy by PAS	Snead <i>et al</i> 1972
Observation and interpretation of effects related to positron affinities	Lock and West 1974
Theory of positron affinities to metals	Stott and Kubica 1975
Probing local chemical composition by PAS	Hautojärvi <i>et al</i> 1976
Application of PAS to the study of ageing of a commercial alloy	Johnson <i>et al</i> 1977
Observation of positron trapping by Zn-rich GP zones in Al	Dlubek <i>et al</i> 1979
Observation of vacancy clustering with solute in supersaturated Al alloys	Gauster and Wampler 1980
Observation of vacancies associated with GP zones	Kabisch <i>et al</i> 1980

subjects of great importance for understanding the mechanisms that govern age-hardening, a phenomenon of widespread technological importance that stimulates an equally high scientific attention. It may be interesting to obtain a quantitative feeling of the attention given to the study of age-hardening by noting that about 20% of the 305 papers presented at the most recent general conference on aluminium alloys, *ICAA5* (1996), was related to age-hardening. At the time of Dlubek's review, one would have easily predicted that PAS should have been included soon in the toolbox of any scientist working in the field of age-hardenable alloys. However, the history of the last ten years tells us that, so far, this has not happened. For example, if we scan again the list of the *ICAA5* papers regarding decomposition phenomena, we find works based on transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), differential scanning calorimetry (DSC) and differential thermal analysis (DTA), electrical resistometry (ER), AP-FIM (atom probe-field ion microscopy), small angle neutron scattering (SANS) and small angle x-rays scattering (SAXS), high energy synchrotron x-ray diffraction (HESXD), parallel electron energy loss spectroscopy (PEELS) etc, but not a single contribution including PAS data. We wonder whether this situation is simply due to bad communication or rather to an imperfect tuning of the subjects studied by PAS experts with the mainstream problems of materials science.

In view of the above considerations, we have set for the present work two different objectives: (a) to improve the communication, by presenting in an organized way the progress of PAS studies of the decomposition of an alloy from 1987 to the present; (b) to focus on the most fertile subjects for future studies, by discussing the actual or potential information content of selected recent work, with regards to the physical properties of the material rather than to positron physics.

Table 2 contains the repertory of PAS works regarding age-hardenable alloys or related subjects, important for interpreting PAS experiments on alloy decomposition. The authors have done their best to include every paper published since the 1987 reviews mentioned above, and apologise for possible omissions. For the convenience of readers interested in finding references to specific materials, the list is ordered on the basis of the composition of the alloys (a paper is listed more than once when it refers to different alloys; commercial aluminium alloys are designated according to the American Aluminum Association classification). The second column of the table specifies the category of phenomena studied in each paper. We have used this second classification as a guideline for organizing the presentation of the examples that we discuss below. When possible, the examples have been selected from papers published by groups including one or more of the present authors.

**Table 2.** Studies of age-hardening alloys by PAS and related subjects (since 1987).

Alloy	Subject	Reference
Al alloys	Review	Dlubek 1987
Al alloys	Review	Krause <i>et al</i> 1987
Al alloys	Review	Bharathi and Sundar 1996
Al–Ag	Kinetics (vacancies, solute clusters, GP) Composition (GP)	Bharathi <i>et al</i> 1987
Al–Ag	Kinetics (solute clustering) Composition (GP)	Bharathi and Sundar 1989
Al–Ag	Composition (GP)	Dlubek <i>et al</i> 1989
Al–Ag	Composition (GP)	Dlubek <i>et al</i> 1992d
Al–Ag	Kinetics ( $\gamma'$ ) Kinetics (vacancy and solute clustering, GP formation)	Fretwell <i>et al</i> 1992
Al–Ag	Composition (GP zones) Kinetics (GP coarsening, precipitate formation and coarsening)	Dlubek <i>et al</i> 1993
Al–Ag	Composition (GP zones)	Bischof <i>et al</i> 1996
Al–Cu	Kinetics (vacancy–solute clusters, GP, precipitation)	Dlubek <i>et al</i> 1989
Al–Cu	Positron trapping at GP (theory) Defect structure of nanoparticles (vacancies in GP)	Gläser <i>et al</i> 1991
Al–Cu	Kinetics (GP, precipitation) Defect structure of nanoparticles (vacancies at GP)	Gläser <i>et al</i> 1992
Al–Cu	Kinetics (GP, precipitation)	Cada <i>et al</i> 1995
Al–Cu	Kinetics (GP dissolution, precipitate formation and dissolution)	Schmidt <i>et al</i> 1995
Al–Cu–Mg	Kinetics (GP dissolution, precipitate formation and dissolution)	Schmidt <i>et al</i> 1995
Al–Cu–Mg (2024)	Kinetics (GP growth, reversion, precipitation)	Biasini <i>et al</i> 1997
Al–Cu–Mn	Kinetics (precipitation, rapidly solidified alloy) Defect structure of nanoparticles (vacancies at GP)	Dlubek <i>et al</i> 1991
Al–Cu–Mn (2219)	Kinetics (GP1, GP2 $\rightarrow$ $\theta'$ ) Defect structure of nanoparticles (vacancy at GP)	Abis <i>et al</i> 1992b
Al–Cu–Mn (2219)	Kinetics (GP1, GP2 $\rightarrow$ $\theta'$ )	Abis <i>et al</i> 1992a
Al–Cu–Si–Mg (2014)	Kinetics (GP2 $\rightarrow$ $\theta'$ , GP2 $\rightarrow$ S')	Abis <i>et al</i> 1992a
Al–Ge	Dilute alloy—equilibrium measurements	Kurihara and Tanigawa 1992
Al–Li	Kinetics (solute clustering)	del Río <i>et al</i> 1989
Al–Li	Kinetics (vacancy clusters)	Leighly <i>et al</i> 1989
Al–Li	Kinetics (vacancy clusters, precipitation)	de Diego <i>et al</i> 1991
Al–Li	Kinetics (vacancy clustering, precipitation)	de Diego <i>et al</i> 1992
Al–Li	Kinetics (vacancy clustering, formation of dislocation loops)	del Río and de Diego 1992
Al–Li	Positron lifetime calculations	del Río <i>et al</i> 1992
Al–Li	Defect structure of nanoparticles (precipitates with no vacancy-type defects)	Dlubek <i>et al</i> 1992a

Table 2. (Continued)

Alloy	Subject	Reference
Al-Li	Defect structure of nanoparticles (precipitates with no vacancy-type defects)	Dlubek <i>et al</i> 1992c
Al-Li	Kinetics (vacancy-solute clusters, deformed samples)	de Diego <i>et al</i> 1993
Al-Li	Kinetics ( $\delta'$ formation and decomposition) Concentration ( $\delta'$ )	del Río <i>et al</i> 1994a
Al-Li	Kinetics (vacancy clustering, formation of dislocation loops)	del Río <i>et al</i> 1994b
Al-Li	Kinetics (vacancy clustering, precipitation)	Fretwell <i>et al</i> 1995
Al-Li	Kinetics (precipitation, deformed samples)	Somoza <i>et al</i> 1995
Al-Li	Trapping at dislocations	Abdelrahman 1997
Al-Li	Kinetics (precipitation, deformed samples)	de Diego <i>et al</i> 1997
Al-Li-(Cu, Mg, Sc)	Kinetics (vacancy clustering, precipitation)	Krause <i>et al</i> 1992b
Al-Li-(Cu, Mg, Sc)	Kinetics (precipitation)	Dlubek <i>et al</i> 1992b
Al-Li-Cu-Mg-Zr (8090)	Kinetics (GP zones, deformed samples)	Abdelrahman 1996
Al-Li-Cu-Mg-Zr (8090)	Kinetics (precipitation) Concentration (precipitates)	Dlubek <i>et al</i> 1992a
Al-Li-Cu-Mg-Zr (8090)	Kinetics (precipitation) Concentration (precipitates)	Dlubek <i>et al</i> 1992c
Al-Li-Zr	Kinetics ( $\delta'$ formation and decomposition; influence of Zr)	del Río <i>et al</i> 1994a
Al-Li-Zr	Kinetics (precipitation, dissolution, composite precipitates)	Ayciriex <i>et al</i> 1996
Al-Mg-Si-RE	Kinetics (GP)	Tian Decheng <i>et al</i> 1989
Al-Mn	Kinetics (vacancy clustering)	Szeles and Vértes 1992
Al-Sc	Kinetics (vacancy clustering, precipitation)	Krause <i>et al</i> 1992a
Al-Zn	Annihilation characteristics in solute clusters (theory)	Bharathi and Chakraborty 1988
Al-Zn	Kinetics (cellular precipitation)	Bharathi <i>et al</i> 1988
Al-Zn	Positron trapping by GP zones (theory)	Gläser and Dlubek 1989
Al-Zn	Composition (GP)	Dlubek and Gerber 1991
Al-Zn-Mg-Cu (7012)	Kinetics (solute transport)	Dupasquier <i>et al</i> 1995
Al-Zn-Mg-Cu(Mn) (7012 and 7005)	Kinetics (GP formation, reversion, GP2 $\rightarrow$ $\eta'$ )	Ferragut <i>et al</i> 1996
Al-Zn-Mg-Cu (7012)	Kinetics (GP, precipitation)	Abis <i>et al</i> 1989a
Al-Zn-Mg-Cu (7012)	Kinetics (GP, precipitation)	Abis <i>et al</i> 1989b
Al-Zn-Mg-Cu (7012)	Kinetics (GP $\rightarrow$ $\eta'$ )	Abis <i>et al</i> 1992b
Al-Zn-Mg-Cu(Mn) (7012 and 7005)	Kinetics (GP formation, reversion, precipitation, solute transport)	Somoza 1997
Al-Zn-Mg-Mn (7012 and 7005)	Kinetics (GP formation, reversion, precipitation, solute transport)	Ferragut <i>et al</i> 1998
Al-Zn-Mg-Mn(Cr)	Kinetics (precipitation in rapidly solidified alloys)	Czurratis <i>et al</i> 1989
Au-Pt	Kinetics (precipitation) Defect structure of nanoparticles (open volume at phase boundary)	Pahl <i>et al</i> 1995
Cu-Ag	Kinetics (precipitation)	Mikhalekov <i>et al</i> 1995
Cu-Be	Kinetics (precipitation)	Pahl <i>et al</i> 1992
Cu-Be	Defect structure of nanoparticles (open volume at phase boundary)	Gröger <i>et al</i> 1995
Cu-Be-Co	Kinetics (GP formation, precipitation)	del Río <i>et al</i> 1997b
Elemental metals	Positron affinities to metals (theory)	Puska <i>et al</i> 1989

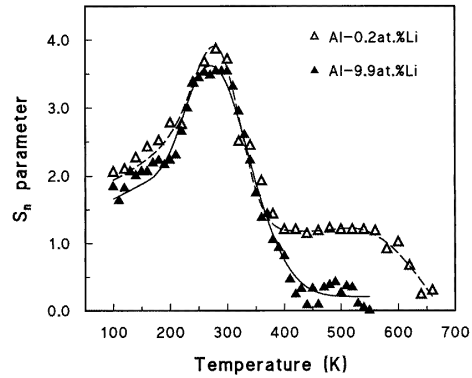
Table 2. (Continued)

Alloy	Subject	Reference
Fe–Cu	Kinetics (vacancy migration)	Sebti <i>et al</i> 1992
Fe–Cu based	Kinetics (vacancy–solute clusters, precipitation)	Phythian <i>et al</i> 1993
Fe–Cu–Ni	Kinetics (vacancy migration)	Sebti <i>et al</i> 1992
Mg–Li	Kinetics (vacancy–Li complexes, vacancy clusters)	del Río <i>et al</i> 1997a
Ni(Pb, Zn, In, Ge, Sb)	Positron trapping at precipitates	Michno and Gorecki 1987
Ni–Pb(Zn, In, Sb)	Positron trapping at precipitates	Michno and Gorecki 1989
Pb–Sn	Kinetics (vacancy formation during precipitation)	Leighly and Belaidi 1997
Ti–Al	Kinetics (vacancy clustering)	Wang <i>et al</i> 1997

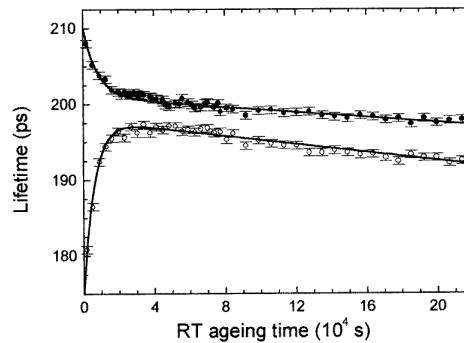
## 2. Decomposition kinetics

### 2.1. Vacancy clustering

The decomposition of an alloy, initially prepared in the form of a supersaturated solid solution (SSSS), is a complicated phenomenon controlled by thermodynamical factors (phase stability) as well as atomistic processes (solute transport). The vacancies play a fundamental role not only in the transport of the solute, but also by contributing to the energetic balance of the phases in which they are included as structural constituents. Since ageing treatments (i.e. treatments that are given to an alloy to modify its microstructure in order to obtain technologically desirable properties) are normally carried out at temperatures low enough to avoid significant production of vacancies in thermal equilibrium, non-equilibrium vacancies (vacancies retained after quenching or produced by cold work) are specially important. The experts of physical metallurgy know very well that the decomposition process can be to some extent controlled by modifying the initial vacancy distribution through different quenching procedures, plastic deformation at low temperature or tailored additions of minority elements. However, the common knowledge in this field is mostly inferred from indirect evidence, gathered from ER (see, for instance, Panseri and Federighi 1963) and from TEM observations of the dislocation loops left after the collapse of the clusters (see, for instance, Westmacott *et al* 1961), although the potential of PAS for measuring vacancy formation energies, as well as vacancy–solute binding energies, is fully recognized in many textbooks of physical metallurgy. We do not review here this subject, which is important, but not specific, to age-hardenable alloys. In contrast, we need to emphasize the importance of PAS for the direct observation of the effect of solute elements on vacancy clustering as a first step of decomposition. After the pioneer works by Gauster and Wampler (1980) and Alam and West (1982), in the period considered in this review the subject has been reconsidered for a variety of alloys and by several authors (see table 2). An example is shown in figure 1, that refers to the formation and dissolution of vacancy clusters during the isochronal annealing of Al–Li, after initial 23% deformation at 77 K (de Diego *et al* 1993). The shape parameter  $S_n$  used in this work (see the definition in the original paper) discounts pure thermal expansion effects. The evolution of  $S_n$  indicates that isolated vacancies generated by cold work form clusters as in pure Al, but that the dissolution stage is moderated by Li. The effect is clearly observed for both a dilute (0.2 at.%) and a concentrated (9.9 at.%) alloy. In a similar way, PAS has also proved the ability of Li to stabilize small quenched-in vacancy clusters (del Río *et al* 1994b) that coexist with the vacancy loops that can be observed by TEM (Ceresara *et al* 1977).



**Figure 1.** Evolution of the Doppler-broadening parameter  $S_n$  during isochronal annealing post 23% deformation at 77 K, for a diluted and a concentrated Al–Li alloy. (Redrawn, after de Diego *et al* 1993.)



**Figure 2.** Evolution of the positron lifetime during room temperature ageing of Al–4 wt% Cu–0.3 wt% Mg. Solid symbols: as quenched. Open symbols: quenched and immediately aged at 180 °C for 30 s. (After Dupasquier *et al* 1998.)

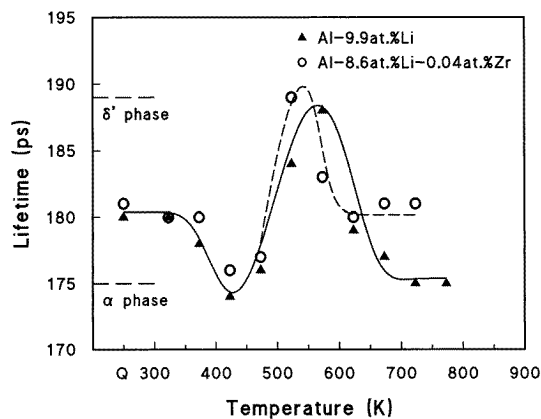
## 2.2. Solute transport

Solute transport occurs in a solid solution by migration of small vacancy–solute complexes. These are formed from quenched-in vacancies or from vacancies released by particles dissolved during ageing treatments. Every stage of a decomposition sequence is governed by solute transport. In most cases, the process is slow enough to be possibly observed by PAS during its evolution. An example is given in figure 2 (Dupasquier *et al* 1998). The phenomenon displayed in this figure is the formation of vacancy-rich solute clusters or GP zones during RT ageing of Al–4 wt% Cu–0.3 wt% Mg alloy.

The two curves refer respectively to a quenched sample (solid symbols) and to a sample quenched and immediately aged for 30 s at 180 °C. The initial conditions, that are determined by the balance of different contributions due to mobile vacancy–solute pairs and to solute clusters, are clearly different, but the species that is temporarily formed at RT is probably the same and the transformation characteristic times (time constants of an exponential fitting to the first part of the curves) are also similar (a few hours). We interpret this behaviour as due to a similar level of vacancy supersaturation of the matrix in the initial stage. It is also clear that this supersaturation decreases as far as more mobile vacancy–solute pairs are trapped at the newly formed metastable phase; thus, the further evolution (probably the increase of the Cu concentration in the clusters) is considerably slower than the initial stage (time constants of a few days). On the basis of curves like those shown in this example, taken *in situ* at different moderate temperatures (or at room temperature after isothermal treatments of increasing duration), it is possible to obtain the migration energy of the diffusing species, that may change in different stages of decomposition and be affected by minority alloying elements. The Milano–Tandil collaboration has given special attention to these aspects of the decomposition kinetics (Dupasquier *et al* 1995, Ferragut *et al* 1996, 1998). There are other ways of observing the time evolution of ageing phenomena (the classical method is ER; also Vickers micro-hardness (VMH) measurements can be useful), but none like PAS that gives at the same time information on the nature of the particles that are being formed.

### 2.3. Formation and dissolution of GP zones and precipitates

The classical technique for the study of the decomposition sequence of a supersaturated alloy is DSC, complemented by VMH. Electron microscopy and diffraction studies are essential for assessing the morphology of the decomposition products. Sometimes the interpretation of a DSC curve (thermogram), that reflects not only the thermal stability (essentially, equilibrium properties) but also kinetic properties (non-equilibrium evolution), may be uncertain. Alternative methods thus may find room. Like DSC thermograms, also the curves representing the evolution of PAS parameters (from lifetime as well as Doppler broadening measurements) during the isochronal anneal of a quenched sample display structures corresponding to different stages of decomposition. In particular, it is possible to see effects related to formation and dissolution of those species of solute clusters, GP zones and precipitates that are able to trap positrons either because they are associated with open volumes (structural vacancies, misfit surfaces) or because the difference of positron affinities between particles and matrix favours the localization of the positrons into the particles. It is also required that these particles are finely dispersed (mean distances below  $\approx 0.1 \mu\text{m}$ ).



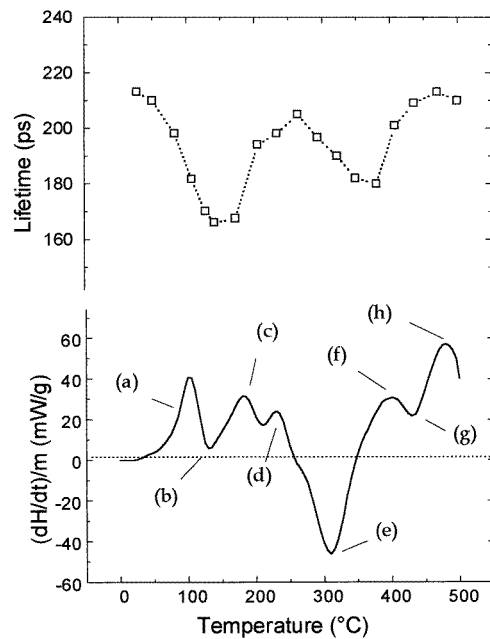
**Figure 3.** Evolution of the positron lifetime during isochronal annealing of Al-Li and Al-Li-Zr (Redrawn, after del Río *et al* 1994a).

Figure 3, after del Río *et al* (1994a), gives an example of positron lifetime variations occurring during an isochronal annealing. The example refers to Al-9.9 at.% Li and Al-8.6 at.% Li-0.04 at.% Zr. Taking into account that the calculated positron lifetime  $\tau$  is 175 ps for annihilation in the Al-Li solid solution ( $\alpha$ -phase) and 189 ps for the  $\text{Al}_3\text{Li}$  composition, the information contained in these data can be quickly read as follows. *As-quenched state*: the result  $175 \text{ ps} < \tau < 189 \text{ ps}$  indicates the presence of Li-rich particles; this is in agreement with the selected area diffraction pattern (SADP) observation of the  $\delta'$ -phase ( $L1_2$  structure,  $\text{Al}_3\text{Li}$  composition) and HRTEM observations of ordered domains with a radius  $R = 2.5 \text{ nm}$ ; the analysis of the PAS data, guided by the HRTEM results, enables the authors to evaluate the density of the  $\delta'$  particles (comments on density determinations by PAS are made below). *Minimum at  $\approx 450 \text{ K}$* : the result  $\tau \approx 175 \text{ ps}$  indicates the almost complete dissolution of the particles formed during quenching or after very brief ageing at RT; this is in agreement with DSC evidence of an endothermic stage around 430 K, but it also tells us something that DSC cannot tell, i.e. that the density of the particles drops to a very low value (below PAS sensitivity). *Peaks at 520 K (Al-Li-Zr alloy) and at 550 K (Al-Li alloy)*: the result  $\tau \approx 190 \text{ ps}$  indicates a density of  $\text{Al}_3\text{Li}$  particles above or near to the saturation limit of PAS; the presence of these particles is consistent with SADP



observations of  $\delta'$  phase and with TEM observations of particles with a radius  $R = 30$  nm; PAS results confirm the well known accelerating effect of Zr on the formation kinetics of the  $\delta'$  particles. *Plateau above 700 K*: PAS indicates that Zr stabilizes the presence of finely distributed Li-rich particles (composite  $\text{Al}_3\text{Li}-\text{Al}_3\text{Zr}$  precipitates, distinctly visible by TEM), while in the binary alloys the particles density is below the sensitivity limits of PAS.

DSC and PAS are not to be considered alternative methods for obtaining the same information. The selective sensitivity of the positrons to the composition and to the distribution of the decomposition products can be exploited for isolating specific processes. Figure 4 shows a comparison between a DSC thermogram and the evolution of the mean positron life during an isochronal run. This example refers to Al-4.5 wt% Cu-0.56 wt% Mg; the data reported in the figure are taken from Schmidt *et al* (1995).



**Figure 4.** Comparison between the evolution of the positron lifetime  $\tau$  during isochronal annealing of Al-4.5 wt% Cu-0.56 wt% Mg quenched at liquid nitrogen temperature (upper curve), and a DSC thermogram for the same system (lower curve): (a) dissolution of GPZ formed at RT; (b) intensive reformation of GPZ; (c) dissolution of GPZ and formation of  $\theta''$ ; (d) dissolution of  $\theta''$ ; (e) formation of  $\theta'$ ; (f) dissolution of  $\theta'$ ; (g) formation of  $\theta$ ; (h) dissolution of  $\theta$ . (Redrawn, after Schmidt *et al* 1995).

It is clear, however, that the interpretation of PAS results in terms of a decomposition sequence needs the support of previous knowledge drawn from DSC and from various microscopies. This weakness may be one of the reasons why PAS has not been yet accepted in the number of standard techniques for assessing the sequence of decomposition stages of age-hardenable alloys. On the other hand, when the signature of a stage has been identified on a isochronal or isothermal curve, one can go further in the analysis of PAS data to look into quantitative details of the decomposition kinetics. The present authors have gained some experience in drawing information from isothermal curves. One aspect, already discussed above, is the time dependence of the process at a given temperature. A second one refers in particular to formation of semicoherent precipitates, that occurs by partial loss of coherency when a critical size  $R$  is attained. The gradual change of PAS parameters that occurs during the transformation from small coherent particles to bigger semicoherent precipitates reflects the increasing number of particles that reach the critical size, and therefore is related to the time-dependent size distribution  $p(r, t)$ . This idea has been pursued in several works by some of the present authors (Abis *et al* 1989a, b, 1992a, b, Pahl *et al* 1995). Let us discuss,

as an example, the transformation GP  $\rightarrow$  spherical Pt precipitates occurring in Au–Pt (Pahl *et al* 1995). This is a simple case, since GP zones do not trap positrons (no structural vacancies, wrong sign of the positron affinity difference) while precipitates do, because of the misfit at the incoherent phase boundary that leaves some open volume. In this situation, the measured positron trapping rate  $k_{meas}$ , which is a function of the ageing time  $t$ , can be written as a weighted average of the size-dependent trapping rate  $k(r)$  as follows:

$$k_{meas}(t) = \int_R^\infty k(r)p(r,t) dr. \quad (1)$$

In a coalescence regime the size distribution can be scaled to a time-independent function  $g(x)$  by using a reduced radius  $x = r/\langle r \rangle$ ; furthermore, the mean radius increases with the ageing time as given by:  $\langle r \rangle = at^{1/3}$ . The appropriate expression for  $k(r)$  depends on the trapping regime; for a fixed volume fraction of the precipitates, one has  $k \propto r^{-2}$  in the case of the diffusion-limited trapping regime and  $k \propto r^{-1}$  for a transition-limited regime. By taking a general expression of the form  $k = br^{-m}$ , equation (1) becomes:

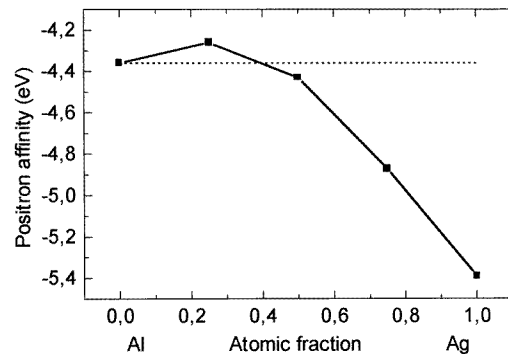
$$k_{meas}(t) = k(\langle r \rangle) \int_{x=R/\langle r \rangle}^\infty x^{-m} g(x) dx. \quad (2)$$

It is a feasible mathematical exercise to invert equation (2) to obtain  $g(x)$  in terms of  $k_{meas}(t)$ . The alternative chosen by Pahl *et al* was, however, to assume a model form of  $g(x)$  with adjustable parameters, to be determined by a best fit of equation (2) to PAS data. The final result was a distribution with a width in reasonable agreement with the classical theory of coalescence during Ostwald ripening (Lifschitz and Slyozov 1959, Wagner 1961).

### 3. Chemical composition of nanoparticles

Excluding the case of light elements, the chemical composition of a particle bigger than  $1 \mu\text{m}$  can be easily determined by energy dispersive analysis by x-rays (EDAX). With special care, the range of dimensions can be extended down to  $\sim 0.5 \mu\text{m}$ , but the real problem is the determination of the composition of nano-sized particles. At this dimension scale, the most powerful technique is AP–FIM, that combines the advantages of imaging at atomic resolution with the analytical potential of a mass spectrometer. The limitations of the technique come only from the smallness of the volume that can be explored, that reduces the statistical significance of the information and the application only to high concentrations of nanoparticles. Since about  $10^5$  atoms are collected in an accurate AP–FIM run, detecting on average one particle formed by  $\sim 10$  solute atoms per run requires a concentration of the order of  $10^{-4}$  or larger. AP–FIM has in common with other advanced microscopy techniques the difficulty of preparing good samples. Statistics and sample preparation problems are overcome by non-destructive volume techniques like SAXS, SANS, PAS. The potential of SAXS and SANS for estimating the composition of a scattering centre depends on the contrast between the components of the particle. PAS can be a useful alternative (see Dlubek 1987, Krause *et al* 1987 and references therein) for determining the chemical composition of solute clusters and defect-free Guinier–Preston (GP) zones of nanometric size under two conditions: (a) the positron needs to have a higher affinity for the particle than for the matrix; (b) the size of the cluster must be sufficiently large to allow the formation of a bound state. Predictions regarding positron annihilation parameters enable one to check the consistency of a model of the composition and the size of a particle with the experimental result. From the methodological point of view, recent progress has been made in the development of first-principles calculations of positron affinities and electron–positron combined densities in mixed composition systems (Puska and Nieminen 1983, Seitsonen *et al* 1995; for a review,

see Puska and Nieminen 1994). In the period of time covered by the present review, PAS has been applied to chemical composition studies in a few systems (Al–Ag, Al–Zn, Al–Li). A recent work (Bischof *et al* 1996) emphasizes the importance of the accurate evaluation of the positron affinity differences between a particle and the matrix. For particles of mixed composition, the affinity has been often calculated as a linear combination, weighted on the atomic concentrations, of the affinities of the pure constituents taken from a well known work by Puska *et al* (1989). However, the specific calculation for the Al–Ag system (the results by Bischof *et al* are shown in figure 5) indicates that this approximation can be inaccurate.



**Figure 5.** Positron affinity as a function of the atomic fraction for the Al–Ag system. (Redrawn, after Bischof *et al* 1996.)

On the basis of their calculations, the above authors argue that particles with a concentration of 30% silver would not trap positrons, and that observed lifetimes differences are possibly due to the different dimensions of the particles rather than to composition changes. Thus, in contrast with previous studies, they assign the same chemical composition (60% Ag) to both types of GP zone formed in Al–Ag ( $\eta$ , formed below 170 °C and  $\varepsilon$ , formed above 170 °C).

#### 4. Defect structure of nanoparticles

The direct observation of lattice disorder associated with nanoparticles formed during decomposition (structural vacancies and misfit surfaces) is possible by means of microscopy techniques at atomic resolution (HRTEM and FIM). The common problems are the same as we have mentioned before: statistics and sample preparation. In HRTEM there are additional problems due to a contrast depending on the depth of the particle and, in a critical way, on the condition of image formation. In favourable conditions, PAS can really help. We recall that the possibility of using PAS to detect vacancies associated with solute clusters and GP zones is well established (see Dlubek 1987, Krause *et al* 1987 and references therein). We have listed in table 2 four papers that mention this kind of evidence. The detection of vacancies associated with nanoparticles is a real point of force of PAS, and there is further room for enhancing its potential as far as it regards the determination of the number of vacancies and of the chemical composition of their environment. Although a rough indication in this direction can be obtained by comparing lifetime and Doppler-broadening data with those known for the constituents of the alloy in their pure form, modern calculation methods of positron affinities and annihilation parameters can provide a better gauge for checking the consistency of a model with the experiment.

A new point that has recently been brought out is the characterization of the degree of misfit at internal surfaces (interphase boundaries). One aspect of the morphology of the

misfit surface is the free volume locally probed by trapped positrons, which is correlated with the positron lifetime  $\tau_{trap}$ . Room temperature values of  $\tau_{trap}$  normally reflect the deepest traps that a positron encounters onto the surface, but low temperature measurements might give information on the distribution of small open spaces (shallow traps). A second aspect of the disorder at a misfit surface is the free volume probed by a free positron that hits the surface. Since a thermal positron at room temperature is a wave packet of about 7 nm, trapping is governed by the average free volume rather than by the local free volume that determines the annihilation parameters of the trapped state. Pahl *et al* (1995) have shown that quantitative information on these regards can be obtained when positron trapping is controlled by the morphology of the surface (transition-limited trapping regime) rather than by purely geometrical factors (diffusion-limited trapping regime). This condition sets a lower limit for the internal surface contained in a unit volume (specific internal surface)  $\sigma$  as given by the relationship  $\sigma_{min} \cong 3/L_+$ , where  $L_+$  is the positron diffusion length. For most metals ( $L_+ \approx 0.1 \mu\text{m}$ ),  $\sigma_{min} \cong 3 \times 10^7 \text{ m}^2 \text{ m}^{-3}$ . This is not an unrealistically high limit; for instance in the situation analysed by Pahl *et al*, where the internal surface was the boundary between the matrix (an Au–Pt solid solution) and nearly spherical precipitates of 98% Pt, the actual numbers were: volume fraction of the precipitates  $f \cong 9\%$ , radius  $r \cong 2 \text{ nm}$ , specific surface  $\sigma = 3f/r \cong 1.3 \times 10^8 \text{ m}^2 \text{ m}^{-3}$ . Depending on the value of  $\sigma$ , the appropriate model for the analysis of PAS data may be the standard trapping model (STM) or may need explicit account of diffusion (diffusion trapping model, DTM; see, for instance, Nieminen *et al* 1979, Dupasquier *et al* 1993). In any case, the analysis leads to the determination of the trapping rate per unit specific surface  $\nu_s$ , a parameter with the dimension of a velocity that characterizes the average free volume at the misfit surface (for spherical particles of radius  $R$ ,  $\nu$  would be related to the specific trapping rate per number density  $\mu$  by the equation  $\mu = 4\pi R^2\nu$ ). The result  $\nu_s = 70 \pm 7 \text{ m s}^{-1}$  found by Pahl *et al* for the Pt precipitates, when compared to  $\nu_s$  values typically found for grain boundaries (from 200 to 3000  $\text{m s}^{-1}$ , Dupasquier *et al* 1993), reasonably indicates a smaller degree of disorder for an interface that is developed from a gradual loss of coherency between regions with the same orientation and with a small lattice misfit in comparison to an interface between microcrystals of random orientation.

## 5. Concentration of nanoparticles

Quantitative analysis, leading the determination of the density of decomposition products of nanometric size, is normally carried out on TEM micrographs. Reaching an acceptable statistics with nanoparticles requires the analysis of a relatively extended volume (for obtaining 20% accuracy in the determination of a volume fraction of 1% of 10 nm particles, it is necessary to scan a volume of at least  $10^{-20} \text{ m}^3$ , which means more than 10 micrographs (Goodhew 1992). The accuracy is not limited by statistics only, but also by the imperfect knowledge of the non-uniform thickness of the samples. Alternatives to TEM, like scattering techniques, are also used. The possibility of exploiting PAS sensitivity to nanoparticles for quantitative concentration measurements obviously also exists. However, in the list of table 2 there are only a few contributions in this direction. The reason is that, in most cases, positron trapping is so intense that saturation conditions (trapped fraction  $\approx 100\%$ ) are encountered and the sensitivity to the concentration is lost. The issue of concentration limits is important for having a clear idea of what can and what cannot be obtained, and of the correct version of the positron trapping model to be used for interpreting PAS data in terms of trap density. To begin discussing this point, we need to make a distinction between particles characterized by a high specific trapping rate  $\mu$  (for instance, large particles with

an affinity difference with the right sign for capturing positrons), that for simplicity we call here ‘black particles’, and those with a comparatively smaller specific trapping rate (for instance, precipitates that trap positrons only at the interface with the matrix), henceforth called ‘grey particles’. Below we shall be more precise for a quantitative distinction between ‘black’ and ‘grey’. Of course, ‘white particles’ ( $\mu = 0$ ) cannot be detected by PAS, thus are not interesting for us in this context. The lower limit of measurable concentrations is set by the condition that at least a small fraction (say, 1%) of the positrons thermalized in the sample hits a particle (black or grey; at this point of the discussion it does not matter). For extended particles (radius  $R$  of the order of the positron de Broglie wavelength or bigger), the positron current hitting the surface of the traps can be evaluated by means of the classical diffusion approximation; this gives  $N_{min} \approx 10^{-2}/(4\pi L_+^2 R) \cong 10^{19} \text{ m}^{-3}$  for  $R = 10 \text{ nm}$ . Between this limit and the upper limit set by saturation, the trapping rate  $k$  can be obtained from the analysis of PAS data. In the case of black particles, one can use the STM for obtaining the trapping rate from PAS data, hence the number density  $N$  of traps from the well known approximation  $k = (4\pi D_+ R)N$  (where  $D_+$  is the positron diffusion constant). In the case of grey particles,  $N$  can still be obtained, but one has to be careful in the choice of the right model for analysing PAS data (STM in conditions of the extreme transition limited regime, DTM in any other case). Saturation conditions occur when  $k$  exceeds by at least an order of magnitude the bulk annihilation rate  $\lambda_b$ . For black particles, this situation typically occurs at  $N_{sat} = 10\lambda_b/(4\pi R D_+) \cong 10^{22} \text{ m}^{-3}$  when  $R = 10 \text{ nm}$ . For grey particles, the same criterion sets saturation at  $N'_{sat} = 10\lambda_b/\mu$ . One may assume, for a practical definition of grey particles, the condition  $N'_{sat} > N_{sat}$ ; it follows that a particle must be considered grey when  $\mu < 4\pi R D_+ \cong 10^{-11} \text{ m}^3 \text{ s}^{-1}$  for  $R = 10 \text{ nm}$  (for orientation on typical orders of magnitude for  $\mu$ , we recall that for monovacancies in metals one has typically  $\mu \approx 10^{-14} \text{ m}^3 \text{ s}^{-1}$ ; for a spherical particle with a surface specific trapping rate  $\nu \approx 10^2 \text{ m s}^{-1}$  and  $R = 10 \text{ nm}$ , one calculates  $\mu \approx 10^{-13} \text{ m}^3 \text{ s}^{-1}$ ). Above saturation, the absolute determination of the trapping rate from PAS data is impossible. It is still possible, however, to obtain the ratio of the trapping rates of two species of trap in competition, which corresponds to the ratio of the weights of the respective contributions to linear annihilation parameters (e.g. mean lifetime and Doppler broadening shape parameters). The trapping rate ratios, in turn, gives the density ratio through the relationship  $k_a/k_b = \mu_a N_a/\mu_b N_b$ . Note that this equation applies to black as well as to grey particles; indeed, above saturation, trapping is not at all limited by transport, thus the competition between different traps is controlled only by the transition rates.

## 6. Final comments

The number of papers listed in table 2 demonstrates that, after almost 30 years of PAS studies of decomposition phenomena in age-hardenable alloys, this is still a very flourishing field. The list includes a few contributions of lasting methodological value in the area of the interpretation of PAS data. Most of the work, however, uses accepted interpretation schemes for addressing physical metallurgy problems. Increasing attention is being given to commercial alloys, as several studies have shown that the sensitivity of positron annihilation to the microstructural transformations is not lost in the presence of a complicated chemical composition. This sort of transition from pure physics to materials science is a perfectly physiological evolution of a field that must be considered scientifically mature. On the other hand, as already noted in the introduction, the transition is less rapid than one would have expected. This is due to the dominant role that other well established techniques play in the field of microstructural analysis. Above we have discussed the points where the

limits of the other techniques seem to leave room for an expansion in the application of PAS. In particular, we have called attention to the properties of the material that can be characterized in a quantitative manner (in general, time constants and activation energies of vacancy-controlled processes; in favourable conditions, also chemical composition, defect structure and density of the decomposition products). A consistent effort in this direction is, in our opinion, the correct way for reinforcing the roots of PAS in the field of physical metallurgy.

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