Al$_3$Zr and Al$_3$(Zr,Sc) Dispersoids and their Interaction with Solute Elements Investigated by Atom Probe Tomography and Scanning Transmission Electron Microscopy

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Al$_3$Zr and Al$_3$(Zr,Sc) types dispersoids are commonly used to improved the strength of many kinds of Al-based alloys. Their formation sequence has been the subject of a strong interest and is nowadays well established. Nevertheless, the interaction between these dispersoids and solute elements (e.g. Li, Mg, Cu, Zn…) leads to interesting phenomena which, according to the complexity of the system and of thermomechanical treatments, are sometimes difficult to establish. The present study reports the observations performed by Atom Probe Tomography on several systems (belonging mainly to 2xxx and 7xxx series) where clear interactions between solute atoms, hardening precipitates and dispersoids are demonstrated.

Keywords: dispersoids, Al-Zr, Atom Probe Tomography.

1. Introduction

In addition to age hardening, a high strength is achieved in Al-based alloys through a refinement of the subgrain/grain structure during forming operations like cold rolling and extrusion. However, if the alloy recrystallises during subsequent heat exposure, the strength may reduce considerably. This strength loss may be prevented by the presence of small dispersoids (with a volume fraction f and a mean radius r), which exert a retarding force (Zener drag) on migrating subgrain/grain boundaries [1]. The dispersoids are most effective when they are homogeneously distributed, coherent with the Al-matrix and present at high f/r-ratios. Before the common use of Zr as alloying addition, Mn, Cr were more generally added to form dispersoids (i.e. large particles of 0.05-0.5 μm in size) in Al-based alloys [2]. The literature related to Al$_3$Zr dispersoids or similar intermatallic compounds potentially applicable to increase the strength of Al-based alloys is very abundant. The reader may for instance read the following references [3,4], which give an excellent overview in that field.

The interaction between Al$_3$Zr type dispersoids and solute elements (e.g. Li, Mg, Cu, Zn…) may lead to interesting phenomena which, according to the complexity of the system and of thermomechanical treatments, are sometimes difficult to establish. The present study reports the observations performed by Atom Probe Tomography on several systems (belonging mainly to 1xxx, 2xxx and 7xxx series) where clear interactions between solute atoms, hardening precipitates and dispersoids are demonstrated.

2. Experiemental

2.1 Materials and heat treatments

<u>Al-Sc-Zr system:</u> The alloy has an Al-0.09at%Sc-0.045at%Zr composition. It was made by mixing appropriate amounts of Vigeland metal (99.99%Al) and master alloys of Al-10wt%Zr and Al-2wt%Sc. A well stirred melt was poured at 1033 K into a cylindrical fibre tube mould (Ø40mm x150mm) and cooled in the bottom by a large copper cylinder. The actual temperature was monitored by thermocouples during solidification, and the cooling rate was found to vary between 5-10 K/s. No grain refiner was added during casting. The different stages of Al$_3$(Sc,Zr)-formation were investigated by interrupting the precipitation annealing procedure at various temperatures. The

material was annealed from room temperature to 748 K in a Heraeus K750 forced air circulation furnace using a heating rate of 50 K/h and held at 748 K for 15 hours in order to produce a dense distribution of Al$_3$(Sc,Zr)-dispersoids.

2198 alloy: A 6mm thick 2198 alloy was provided by Alcan-CRV. The composition of alloy 2198 Is given in Table 1. The sample was solution treated for 40mn at 550°C and water quenched. It was later stored at room temperature for 7 days (natural ageing) before being stored in liquid nitrogen. It was subsequently heated up to 430K at a rate of 20K/hour and then quenched in water.

Table 1. Composition of AA2198 alloy given in wt%

AA2198	Cu	Li	Mg	Ag	Zr	Al
Min	2.9	0.8	0.25	0.1	0.04	bal
Max	3.5	1.1	0.8	0.5	0.18	bal

Al-Zn-Mg-Cu system: An alloy belonging to the 7xxx serie has also be investigated. Its composition (in wt%) is10.3%Zn, 2%Mg, and 1.6%Cu (with minor additions of Zr and Sc to control grain size). The material was subjected to a solution treatment at 471°C, followed by a water quench, 2% plastic deformation, and 6h of heat treatment at 120°C (heating ramp of 30°C/h). A reversion treatment (20 minutes at 185°C) has been carried out in an oil bath. Re-ageing heat treatments as then carried out similarly to the initial partial heat treatment, namely 6h at 120°C with a heating rate of 30°C/h. They were started immediately after the reversion step in order to avoid natural ageing between the two steps. This material will hereafter be designated as Al-Zn-Mg-Cu alloy.

2.2 Atom Probe Tomography and Scanning Transmission Electron Microscopy

For APT analyses, 0.3 x 0.3 x 20 mm^3 blanks were cut from the plates and prepared into needles by standard electropolishing in 2% perchloric acid (70%) in 2-butoxyethanol at 15 V at room temperature. Atom Probe analyses of Al-Zr-Sc samples were carried out with an apparatus of type ECOTAP. Analyses were performed at 10^{-8} Pa with a pulse fraction of 19% and a pulse repetition rate of 2.0 kHz. The tip temperature was set to 40 K. APT analyses on 2198 samples were done at 30 K with an apparatus of type LAWATAP. The femtosecond laser pulse system used was an amplified ytterbium-doped laser (AMPLITUDE SYSTEM s-pulse) with a pulse length of 350 fs. The wave length used for the analyses was 515 nm. The pulse energy was set to be equivalent to a 20% pulse fraction. Data analyses were conducted using the software developed in the University of Rouen.

Scanning Transmission Electron Microscopy (STEM) was performed with a Jeol ARM 200F. Observation was made using high angle annular dark field mode at 200kV with a probe size of 0.1 nm.

3. Al$_3$(Zr,Sc) dispersoids

After the typical heat treatment described in 2.1, it is well known that Al$_3$(Zr,Sc) dispersoids exhibit a duplex core-shell structure consisting in a Sc-rich core and a Zr-rich shell [5]. This is however not obvious when similar particles are observed in STEM using Z-contrast. In Fig. 1(a), the bright atomic columns correspond to either Sc or Zr atoms whereas Al appears with a dimmer contrast. The particular arrangement of atomic columns in the dispersoid perfectly corresponds to the L1$_2$ structure.
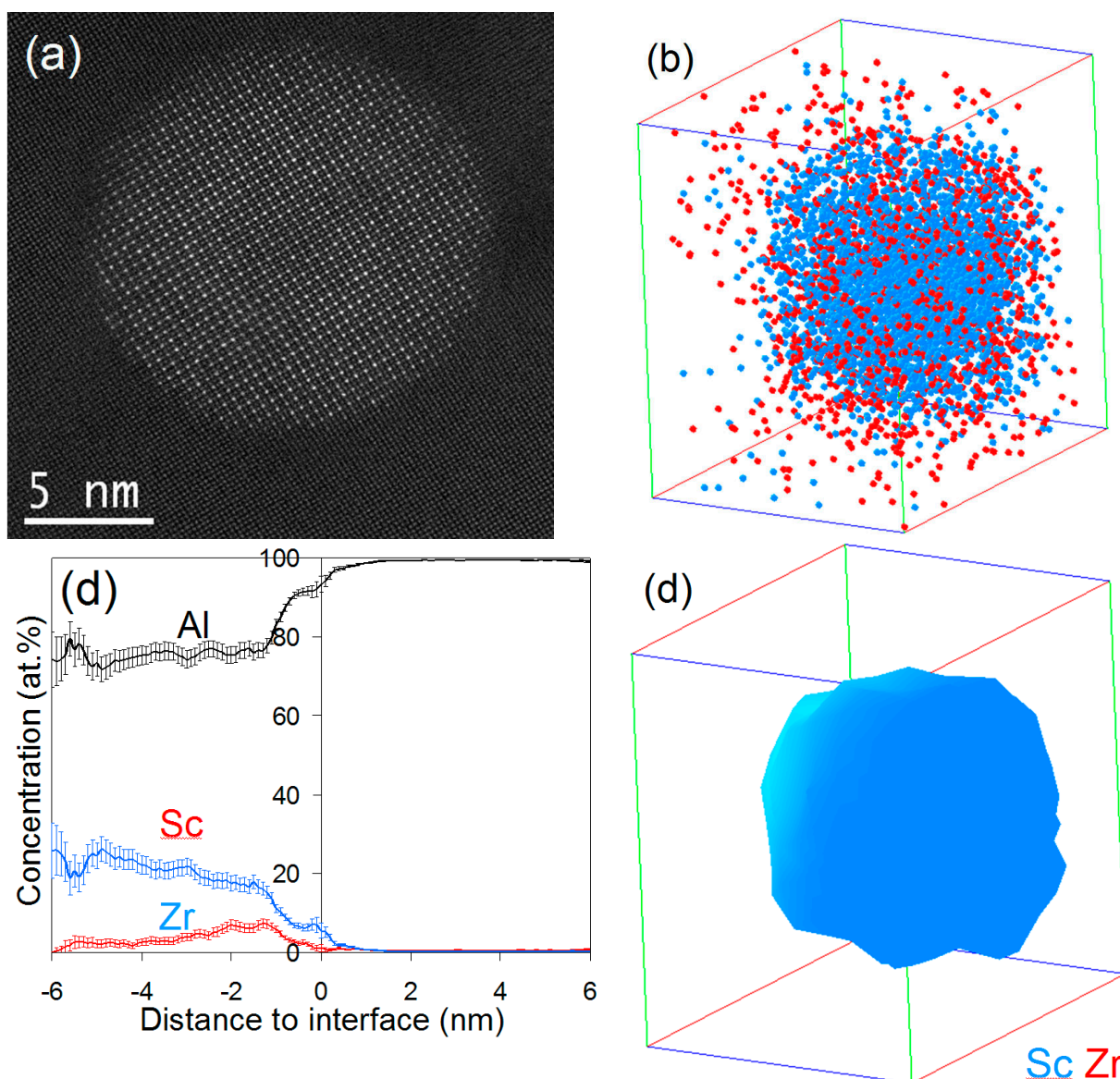
Fig. 1: Structure and chemistry of Al_3(Zr-Sc) dispersoids in the Al-Zr-Sc system after the heat treatment described in 2.1. (a) STEM HAADF observation of an Al_3(Zr-Sc) dispersoid. (b) and (d) are 20x20x15 nm^3 APT reconstructions of a single dispersoid. (b) Shows respective positions of Zr and Sc atoms while (d) shows an isosurface of 4at% Sc used to calculate the erosion profile across the dispersoids interface as shown in (d). Concentrations are given with ±σ.

Al_3(Zr,Sc) dispersoids are also used in some alloys like in the Al-Zn-Mg-Cu material investigated here in order to refine grain size. The APT analysis described in Fig.2 shows that Zn may tend to segregate at the dispersoid-matrix interface and to diffuse inside the dispersoid. On the opposite, both Mg and Cu concentrations are lower inside the dispersoid than in the matrix. According to the fact that the Al/(Sc+Zr) ratio is less than 3, it is clear that Zn may preferentially diffuse on the Al-sites of the $L1_2$ structure. Beyond possible electronic interaction which may require first principle calculation to be confirmed, the relative small size of Zn (0.134 nm) in comparison to the sizes of Al, Zr and Sc (0.143 nm; 0.160 nm and 0.162 nm respectively) may justify the substitution of Zn to Al in Al_3(Zr,Sc) dispersoids.
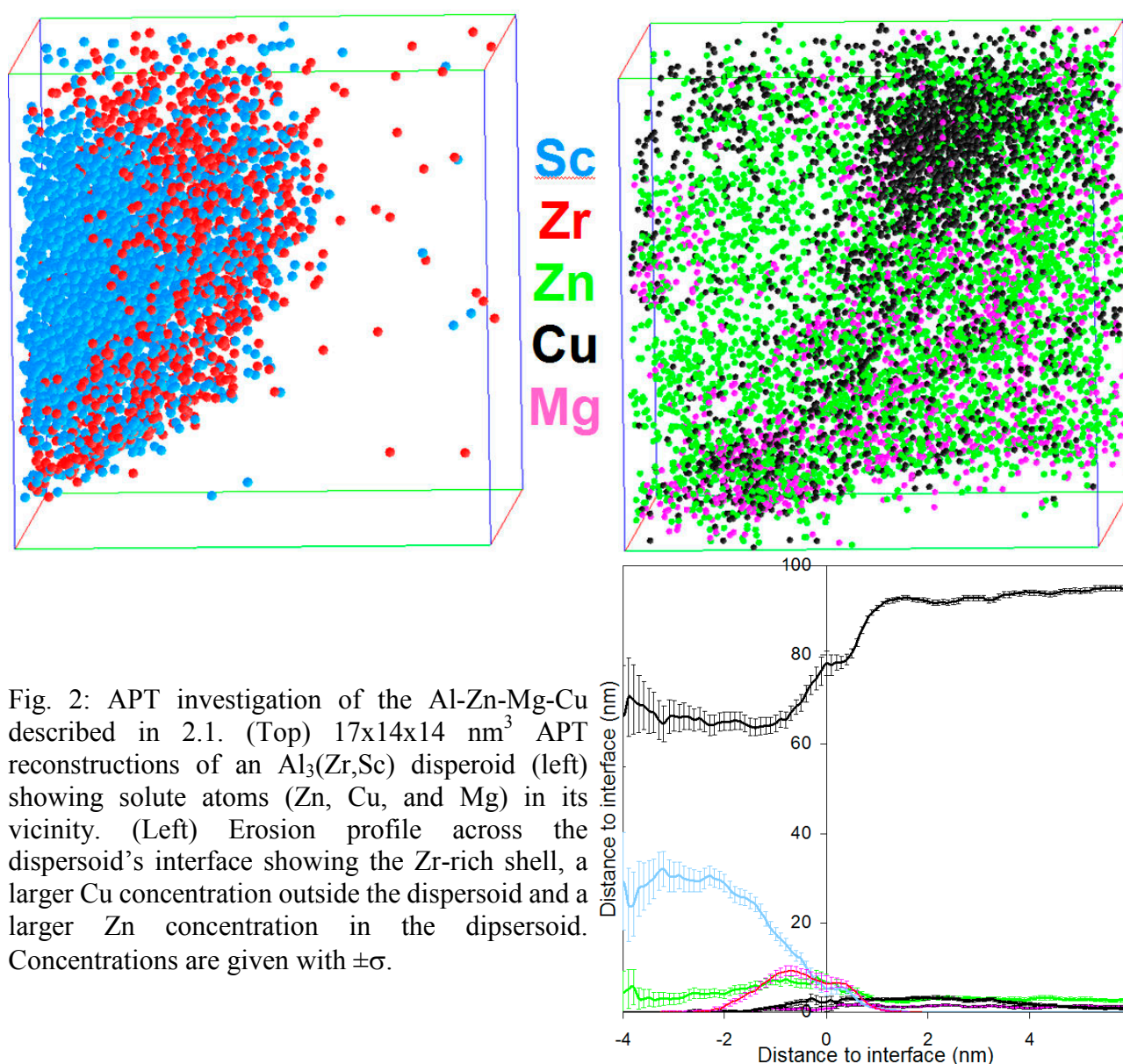
Fig. 2: APT investigation of the Al-Zn-Mg-Cu described in 2.1. (Top) 17x14x14 nm^3 APT reconstructions of an Al$_3$(Zr,Sc) disperoid (left) showing solute atoms (Zn, Cu, and Mg) in its vicinity. (Left) Erosion profile across the dispersoid's interface showing the Zr-rich shell, a larger Cu concentration outside the dispersoid and a larger Zn concentration in the dipsersoid. Concentrations are given with ±σ.

4. Al$_3$Zr dispersoids

Al$_3$Zr dispersoids are sometimes used without any addition of scandium to refine the grain size. This is easily explained by the very high price of Sc. This for instance the case for the 2198 alloy investigated here. The heat treatment applied to the alloy is not supposed to lead to a fine precipitation but to very early stages of precipitation of hardening precipitates (T1 or θ'-Al$_2$Cu). Hence, the distribution of solutes in the specimen is roughly the same that the one observed after precipitation of Al$_3$Zr. In the APT observations displayed in Fig.3, the depletion of Mg and Cu inside the dispersoid seem to be confirmed, in agreement with what was seen in the Al-Zn-Mg-Cu alloy. Strong segregation seem to be observed. Nevertheless, it is important to look first at the erosion profile calculated on the dispersoid since some well know aberrations [6] may cause wrong assertions. It is first visible that no Al$_3$Zr-Al$_3$Li core-shell structure is formed, in opposition to what was observed in ref [6]. However, it is very clear that Li concentration is significantly higher in the dispersoid. The distribution of Li appears to be homogenous inside and the erosion concentration profile of Fig. 4 clear demonstrates that dispersoids have an Al$_3$(Zr$_x$Li$_{1-x}$) stœchimetry. Li is hence supposed to share

the Zr sites of the $L1_2$ structures. It must be reminded here that Li is known to form with Al an Al_3Li-$L1_2$ compound (δ').
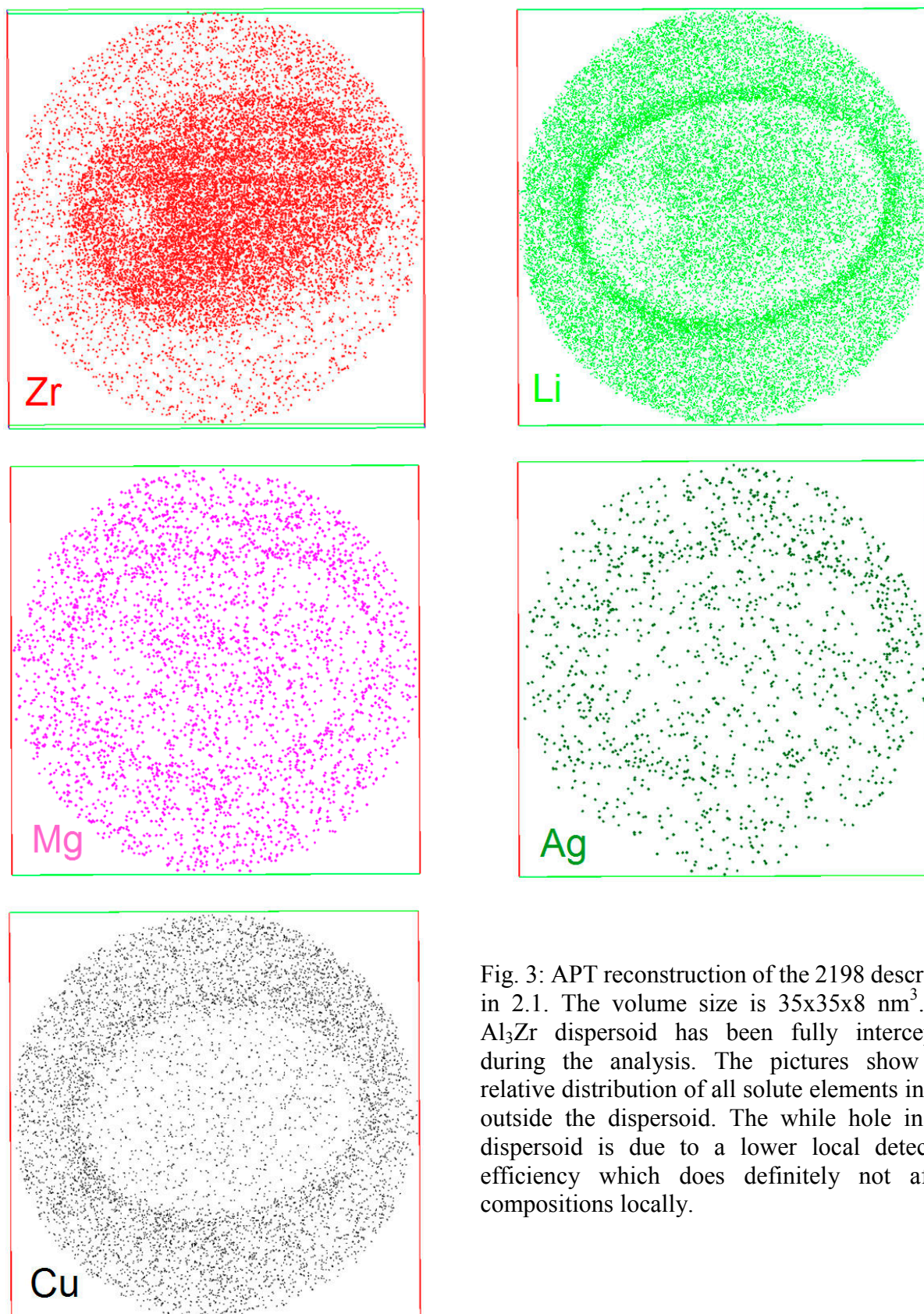

Fig. 3: APT reconstruction of the 2198 described in 2.1. The volume size is 35x35x8 nm^3. An Al_3Zr dispersoid has been fully intercepted during the analysis. The pictures show the relative distribution of all solute elements in and outside the dispersoid. The while hole in the dispersoid is due to a lower local detection efficiency which does definitely not affect compositions locally.
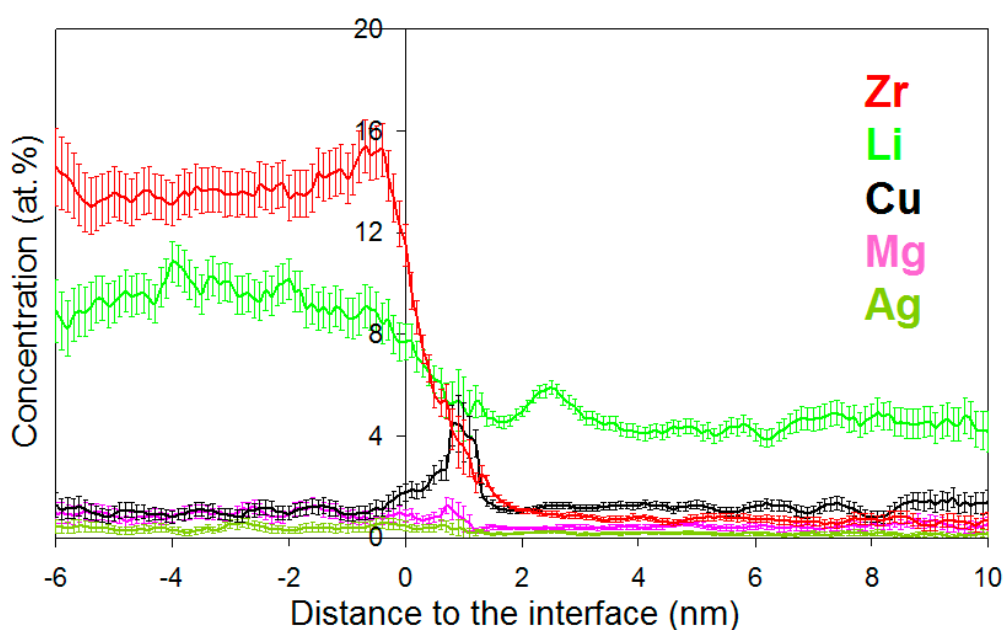
Fig. 4: Erosion profile across the interface of the dispersoid shown in Fig. 3. Concentrations are given with ±σ.

5. Conclusion

We have performed several investigation of various families of Al-based alloys mainly by Atom Probe Tomography in order to elucidate the interaction between Al_3Zr and $Al_3(Zr,Sc)$ dispersoids with usual solute additions used for precipitation hardening. We have shown that, in some cases, some solute elements may segregate to the dispersoid-matrix interface but the most stricking conclusions are that Zn substitutes to Al in Al(Zr,Sc dispersoids) whereas Li substitutes to Zr in Al_3Zr. Such substitution may mainly be due to the atomic sizes of Zn and Li.

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