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Structural Characterization: Al_2Cu Nanoprecipitates from TEM to DFT

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Mechanical strengthening of commercial aluminum alloys by micro-and nano-precipitation of binary or even intermetallic phases has been widely and successfully used in materials science and industrial applications [1]. There are publications on many alloys and their subsequent chemical modification, followed by time and temperature conditions within heat treatment schemes that trigger the precipitation mechanisms. On the other hand, our understanding of the atomic or fundamental interactions that govern these atomic diffusion processes and the self-assembly of precipitated phases remains incomplete. One of the most widespread efforts to add information in this respect has been developing and applying computational theoretical methods known as ab-initio, in particular density functional theory (DFT). DFT has been a tool used with experimental results on crystalline solids, polymers, crystalline defects, and interfaces. The latter system, interfaces, has the technical limitation that requires a large number of atoms to represent an accurate model comparable to reliable experimental observations.

In the present investigation, we report the structural characterization of the binary phase Al_2Cu (θ') precipitated in the commercial aluminum alloy 319 (AA319) modified with Ni. The AA319 alloy was modified using Al-20Ni feedstock blocks to obtain Al-2%Ni. The melting process was carried out inside a crucible in an electric furnace and degaussed with Ar. The heat treatment used was T6: solubilization at 495°C for 5h and artificial aging at 220°C for 3h. Structural characterization was performed by high-resolution scanning transmission electron microscopy (HR-STEM). While the computational characterization was performed using Density Functional Theory (DFT) coupled with numerical tabulated bases (NAOS) and also with maximally localized Wannier functions (MLWF) [2].

Figure 1a) shows θ' precipitates by HR-STEM at a scale of 50 nm. It can be observed that this area of the alloy θ' needles is in the same orientation as the θ' needles are parallel to the [001] direction of the Al matrix, which we had previously published as an effect of Ni addition [3]. The thickness of the needles in 1a) ranges from 1.4-0.3 nm and lengths from 1.2-10.3 nm. The variability in dimensions and aspect ratio of the θ' phase is a feature that cannot be decreased in the thermal process employed in the present study as in industrial processes. However, the variability in dimension is essential for the mechanical reaction of the material to different stresses and material fatigue conditions. Figure 1b) corresponds to a higher magnification that contains two interfaces of the θ' phase with the aluminum matrix. The clarity of the image is due to the use of the Fourier transform to remove some of the noise in the signal capture. It can be seen that there are dislocations in the Al matrix due to the difference in dimensions of the lattice parameters. However, it is notable that these correspond to the planes parallel to the θ' needles

and not the perpendicular ones. It can also be observed that inside the nanoprecipitation θ', there is an excellent uniformity of the atoms in the different planes. However, interplanar bonding is also at different distances from the Al matrix and on the shortest side when approaching the needle boundary.

To mimic the needle morphology of the θ' phases for the computational experiments, an interface was created between the Al matrix and the θ' precipitates (Al_2Cu) until a precipitate embedded by the 6 planes inside the Al matrix was obtained. DFT and NAOS [4] calculations allow the creation of the precipitate and the Al matrix in combination with boundary conditions imposed by the unit cell. In addition, NAOS bases allow increasing the system size to 577 atoms at a computational cost of 256 nuclei. Figure 1 c) shows the precipitate in the initial structure; the precipitate configuration is based on the relaxed structure of the Al_2Cu cell corresponding to the bulk. The right side of Figure 1c) shows the precipitate after structural relaxation in the supercell containing the precipitate. In both cases, the aluminum matrix atoms present at the interfaces were hidden for clarity. The relaxed structure presents essential changes concerning bulk; the distance of the Cu-Cu bonds is reduced in the long axis at the interfaces with the Al matrix while exchanging places with the precipitate Al atoms. This atomic diffusion makes it possible to create an interface with less deformation towards the Al matrix and lower energy. This DFT simulation result is in good agreement with the HR-STEM micrograph. The Al_2Cu precipitate was fractionated into 3 similar zones, separated by increased distances between sub-clusters of similar length.

Figure 1d) shows the analysis of atomic orbitals in real space, a unique feature of MLWFs; this allows qualitatively describing the nature of Al-θ'-Al bonds. The valence bands have the d orbital character in the metallic bond, with positive and negative contributions at the symmetry positions. This system shows the qualitative information of the atomic orbitals in real space, making a significant difference concerning the standard DFT, which is solved in reciprocal space.

Turning to our system with θ' phase within the Al matrix, three features can be concluded: I) the p-character orbitals are an explicit feature of the interaction of the needle with the matrix. II) The hybridization of p-d orbitals is a consequence of lattice modification in the Al layers immediately adjacent to the copper needles. III) The p and d orbitals are the ones driving the Cu/Matrix interaction possessing lower total energy than other proposed orientations for the θ'-Al system, explaining the existence of a single orientation observed by HR-STEM [5].

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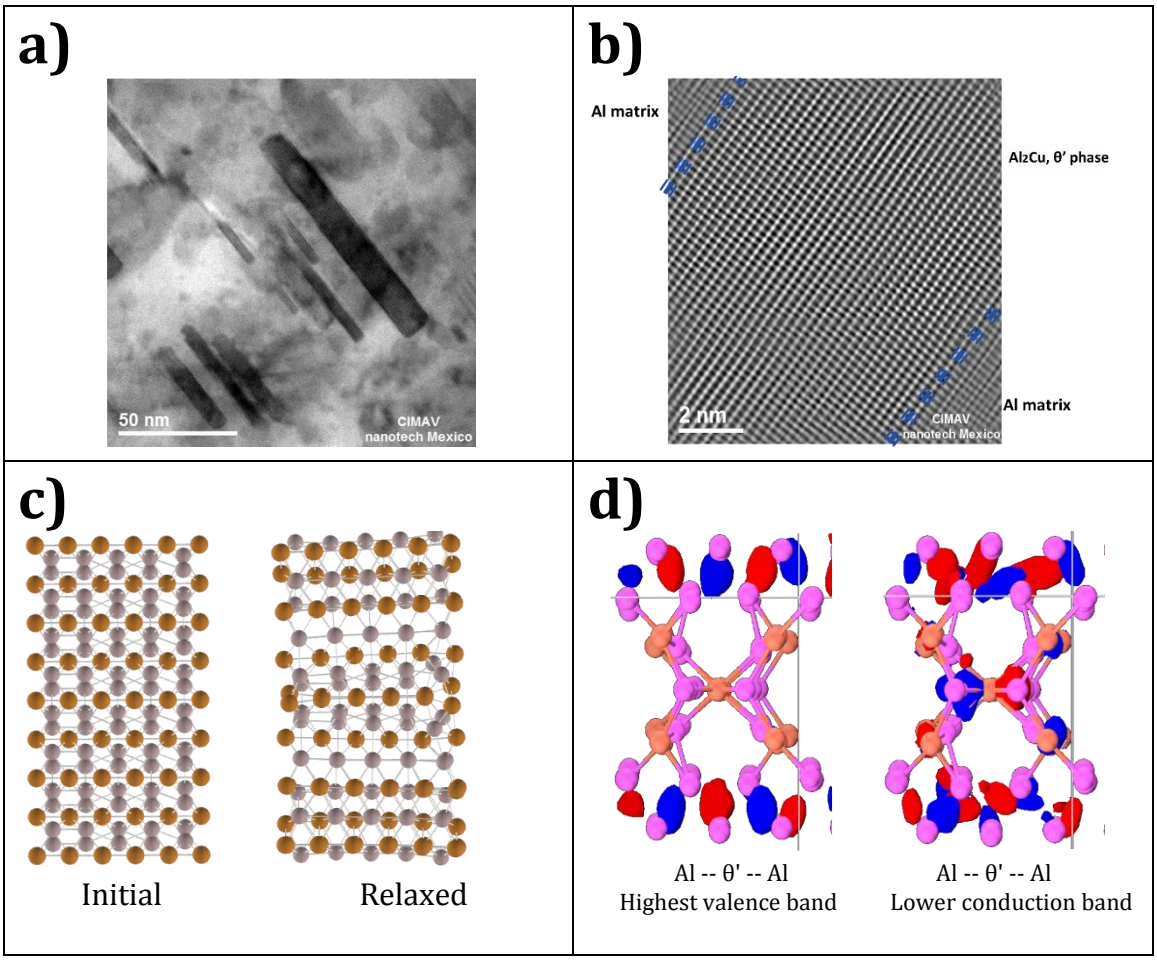

Figure 1. Al_2Cu needles, a) Micrography obtained by HR-STEM, b) Micrography with atomic resolution and filtered by Fourier transform, c) Initial and relaxed structure of the Al_2Cu precipitate (the atoms of the Al matrix are hidden for better clarity), d) Relaxed structure and showing the Highest valence band and the Lower conduction band calculated by MLWF.

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