

# A long-lasting exploration journey through classic, new and rediscovered approaches for studying Mg-containing intermetallics

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The *R-T*-Mg systems are widely studied not only due to the beneficial effects of rare earth (*R*) and transition metals (*T*) addition in Mg-based alloys for structural applications but also for their interest in different fields, including hydrogen storage, glassy alloys and magnetic materials [1, 2]. Moreover, these systems are very rich in ternary intermetallics with a variety of stoichiometries and crystal structures, making them attractive also for fundamental structural and chemical bonding studies. Several of such systems and compounds have been the object of long-lasting investigations by our research group [3-5], focused to highlighting trends and regularities, possibly evolving into rational classifications and generalizations.

Common strategies to discover new intermetallics include exploratory syntheses based on already known compounds or (more recently) on theoretical predictions and phase equilibria investigations. The classic experimental methods include preparation by direct reaction and characterization via SEM/EDXS and XRD both on powders and single crystals. A good number of compounds has been elucidated by these routes, nevertheless in some cases problems arose, due to the intrinsic features of certain systems, such as structural complexity, multiphase microstructures, difficulties in growing or selecting suitable crystals, etc. These issues were then addressed for example applying the “old”, underrated diffusion couple method and the relatively new 3D-ED technique for structural analysis for nanosized crystals. In this contribution, some illustrative results obtained by different approaches on selected families of the intermetallics of interest will be presented.

The *R*-rich *R-T*-Mg compounds form a huge group, containing recurrent stoichiometries, like  $R_9TMg_4$ ,  $R_4TMg$ ,  $R_{23}T_7Mg_4$  and  $R_{15}T_5Mg_2$ , the structures of which are all characterized by the presence of *T*-centered trigonal prisms and Mg-centered core-shell polyicosahedral clusters with *R* at vertices. All of them have been rationalized in terms of linear intergrowth of common slabs corresponding to existing parent types, *i.e.*  $R_{9+x}TMg_{4-x}$  and  $R_7T_3$  (for trivalent *R*) or  $R_{13}T_6Mg$  (for divalent *R*). The structural affinity between these compounds, often coexisting in the same system, stays at the origin of the formation of agglomerates of crystals with coherent interfaces, hampering smooth structure solutions. Nevertheless, focused strategies generally permit to overcome these difficulties.

The Y-Ni-Mg system, exemplifying many of the abovementioned difficulties, contains numerous compounds clustered in compositionally and structurally similar groups. In this case, the realization and characterization of diffusion couples helped to obtain and undoubtedly identify ternary phases, the nanocrystals of some of which were elucidated by 3D electron diffraction measurements. Particularly, the structures of some Mg-based LPSO phases were solved, turning out to be complex compounds, modulated due to the aperiodic distribution of Mg@Y<sub>8</sub>Ni<sub>6</sub> clusters in a close-packed Mg matrix [6]. Their structural analysis allowed to generalize an entire family of challenging compounds.

As a conclusion, our long experience in this field shows that new horizons continuously appear in the intermetallics research, bringing together the development of classical approaches and the application of recent and emerging techniques.

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