A micro-combinatorial TEM method for phase mapping of thin two-component films

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DOI: 10.1002/9783527808465.EMC2016.6952
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Keywords: binary thin films, phase analysis, combinatorial TEM

The aim is to introduce a new method to transmission electron microscopy (TEM) for the preparation and investigation of combinatorial samples. TEM is a very efficient analytical technique in materials science and technology in structural characterization of bulk and thin films that are determined by their composition. The equilibrium phase diagrams of the bulk are well explored (Binary Alloy Phase Diagrams), however, phases of thin films may remarkably differ and due to difficulties they are hardly studied. The common procedure to reveal the properties of concentration dependent phases is the preparation of numerous two-component samples, one for each $C_A/C_{B=1-A}$ composition, and the investigation of these individuals. This is a low efficiency procedure, that costs enormous time of man and machine. For a study of high number of samples combinatorial methods are preferred i.e. instead of carrying out numerous individual experiments samples of varying composition are prepared in a single process. In materials science and especially, electron microscopy, however, due to technical difficulties, combinatorial methods are not widespread.
The first examples for combinatorial TEM investigations are published from the 90-ies. P. Schultz et al [1] and K.E. Roskov [2] These were partly efficient solutions since only the preparation of discrete samples was combinatorial the investigation was not. P. B. Barna, and later G. Radnóczi and F. Misják implemented an experimental arrangement [3] that was already micro-combinatorial, since samples with various compositions were both deposited and investigated in a single TEM grid: Two sources were facing the substrate through an aperture at inclined angles so that the thin film was deposited at two overlapping areas, where two-component film of Ag-Cu was grown. The drawback of that method [3] is that the region of changing concentration is very short (100-150 µm), due to the concentration gradient the phases are accumulated and the sample does not contain the entire (0-100%) composition range.
The idea for developing a really efficient micro-combinatorial method that eliminates the incompleteness of the above solutions means that the preparation and investigation have to be carried out in a single TEM grid within the whole 0-100% composition range (micro-combinatory) so that the formed binary phases and variants may be well separated. The method and device was patented by G. Sáfrán [4]. The present method is typically for the preparation of two-component combinatorial samples with a constant concentration gradient that are deposited on electron transparent film on microgrid suitable for TEM investigations, as well as SEM, EDS and Auger analysis, or nanoindentation. The micro-combinatorial device incorporates a cover plate with a narrow slit that is moved in fine steps above the substrate e.g. TEM grid, meanwhile the fluences of the magnetron sources "A" and "B" are regulated as synchronized to the path of the slit [4]. This new solution provides micro-combinatorial preparation and investigation, so that the length of the concentration transition region, compared to the former solution [3], increases with one order of magnitude to 1500 microns.
For a demonstration MnAl micro-combinatorial samples were DC magnetron sputter deposited on TEM grids covered with amorphous C and SiOx films at various temperatures. The results of the phase analysis of the combinatorial samples are not discussed here.
A photo of a TEM grid with a deposited Mn-Al micro-combinatorial sample is shown in Fig. 1. Fig 2.(b) represents energy dispersive X-ray spectrometer (EDS) data that, aside from the edges, shows linear concentration distribution along the 1500 micrometer stripe. The gradient of a limited concentration range can be adjusted to arbitrarily low values for an enhanced separation of the formed thin film phases. In addition, the device is suitable for the study of the effects of parameters (residual gas pressure, temperature, etc.) changing with time.

References:
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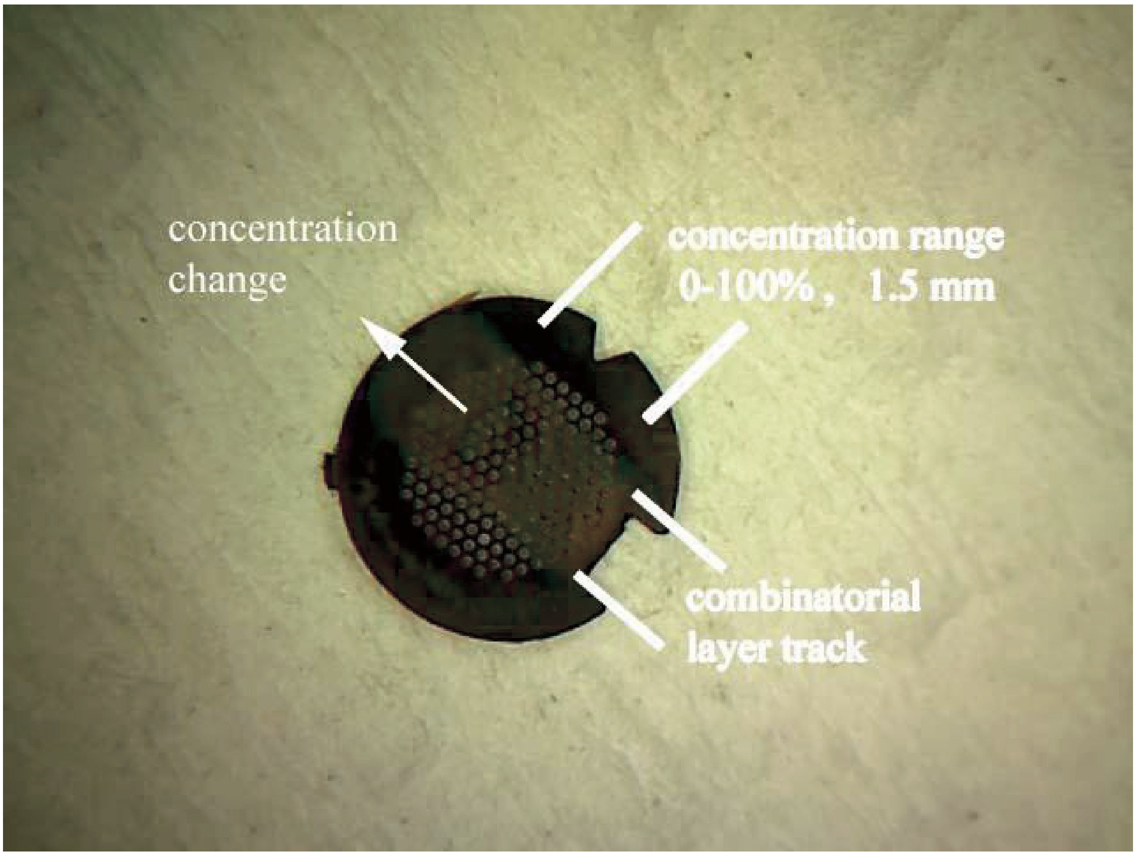

Fig. 1 Two component micro-combinatorial Mn-Al sample DC sputter-deposited on a TEM grid. The length of the 0-100% concentration range is 1.5mm that enables detailed TEM characterization of the formed binary phases.

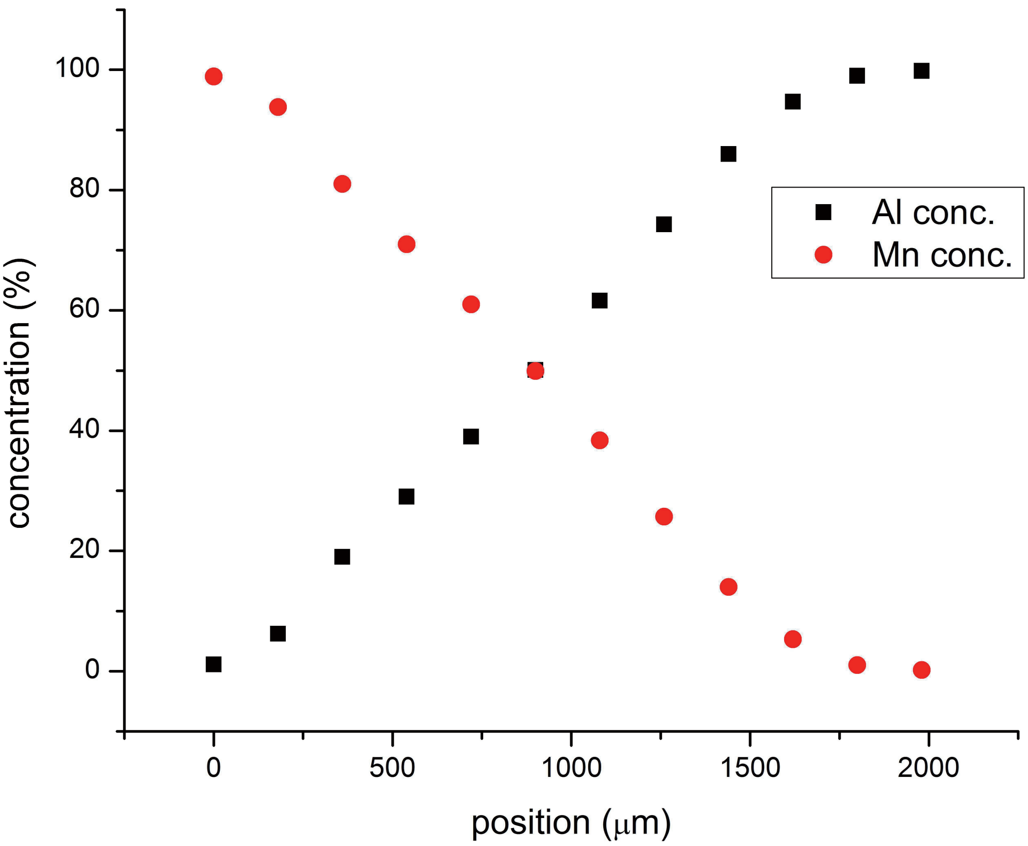

Fig. 2 Mn-Al micro-combinatorial sample on TEM grid; concentration distribution measured by EDS