Novel sample preparation technique for the study of multicomponent phase diagrams

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Abstract

A technique for alloy sample preparation, based on thin film deposition, has been developed for a study of binary and ternary compositions. Thin elemental wedge-shaped layers of the components were gradually sputtered in an alternating manner to form multilayered structure. The samples obtained had compositions which depended upon their location on the substrate. Such samples, containing differently composed Au–Ag–Cu alloys were heat treated to promote formation of stable phases. The alloys thus formed were studied by X-ray diffraction and various microscopic techniques. This article demonstrates the advantages of this method over conventional bulk-based methods.

1. Introduction

The goal of this study was to establish a method for the investigation of multicomponent phase diagrams based on thin multilayered samples. Conventional methods for the study of multicomponent phase diagrams, based on bulk samples, suffer from several drawbacks, including the need for a large number of single composition samples and the need for lengthy heat treatments to reach equilibrium. In the thin films method described here a moving shutter creates composition gradients by varying the thickness of the individual elemental layers which form a multilayered structure. The overall composition variations allow the formation of a large number of binary and ternary alloys in a single deposition experiment. In addition, the homogenization heat treatment periods are short thanks to the small thickness of the deposited films.

The composition of multilayers which form the ternary Au–Ag–Cu system has been studied by X-ray diffraction (XRD) and by energy dispersive spec-troscopy (EDS). The composition and structure of phases formed during heat treatments were examined by these techniques as well as by scanning transmission electron microscopy (STEM).

2. Experimental

2.1. Deposition procedure

Wedged multilayers were made by a magnetron sputtering system equipped with water-cooled, planetary rotated substrate table, ac/dc generators and a substrate shutter for wedge-shaped layer depositions. High-purity Ar was used for plasma sputtering off of 3 inch 99.99% Au, Ag and Cu targets. Prior to deposition, the sputtering chamber was evacuated to 1.3×10^{-5} Pa, 0.4 Pa of Ar was then introduced and the target pre-sputtered for 30 min with closed target shutters. The deposition was done with dynamic pressure of 0.4 Pa onto 3 mm, 100 mesh, Formvar-coated Mo grids. Fifty-five such grids, arranged in a

close-packed equilateral triangle (Fig. 1) were coated.

The sputtering power for each target was calibrated to produce identical thickness wedges rotated 120° relative to one another. The thickness of each component layer was gradually reduced from 12 nm at the apex of each triangle to zero at the triangle base. Thirty tri-layers of Ag–Au–Cu, each 12 nm thick, were deposited in this way. The complete triangular multilayered specimen consisted of 55 samples on individual grids, with composition variations that match the ternary phase diagram.

2.2. Characterization of the as-deposited samples

EDS and XRD were used to characterize the composition and the structure of the as-deposited samples. The composition of individual phases was determined by EDS in the TEM. Single-crystal Si was used as a reference standard, and pure bulk Au, Ag and Cu as the elemental standards. By using an accelerating voltage of 5 kV we prevented substrate contribution to the X-ray spectrum, since at this voltage, the excited depth does not exceed the thickness of our films [1]. Spectra obtained from different locations were compared several times, one with Mo grid bar underneath and the other at the center of the grid's opening, with no Mo below. Both spectra were identical and Mo lines could not be detected.

Moreover, the overvoltage for Au M, Ag L and Cu L lines is high enough for a simple ZAF correction. In order to assess the composition distribution, each sample was analyzed at five points, and two spectra were acquired at each point, i.e. a total of ten spectra
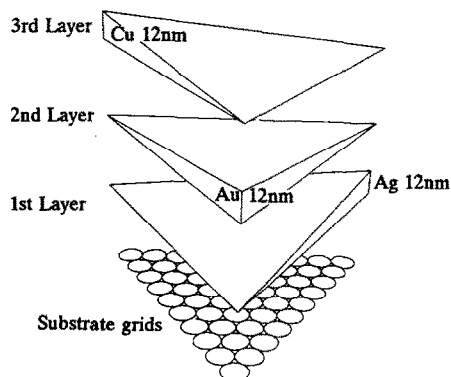
were taken from each sample. The correlation between the measured concentrations and those expected from geometrical considerations is plotted in Fig. 2.

The XRD patterns of all the as-deposited samples exhibited strong (111) preferred orientation (see Fig. 3a). Therefore, a modulation of the (111)-diffracted intensity is expected, provided that the superlattice is of good quality (with sharp interfaces between the subsequent layers and excellent repetition of these layers). Satellites around the (111) reflection were observed in all samples. In order to describe the resultant XRD patterns the kinematical diffraction approach [2] was applied to ternary superlattices [3], taking into account the imperfection of the superlattice expressed via the fluctuations, $\Delta H/H$, of the super-period H (the tri-layer thickness). The best fits for all samples (an example is shown in Fig. 3b) occurred at approximately $\Delta H/H = 1.5\%$ and $H = 12$
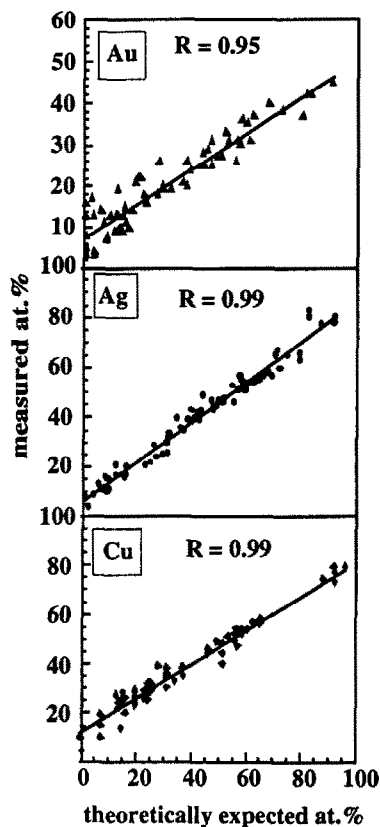

Fig. 2. Correlation between calculated average sample concentrations and measured ones.

Fig. 1. Schematic representation of the sequential gradual deposition of the wedged metallic layers onto coated grids.
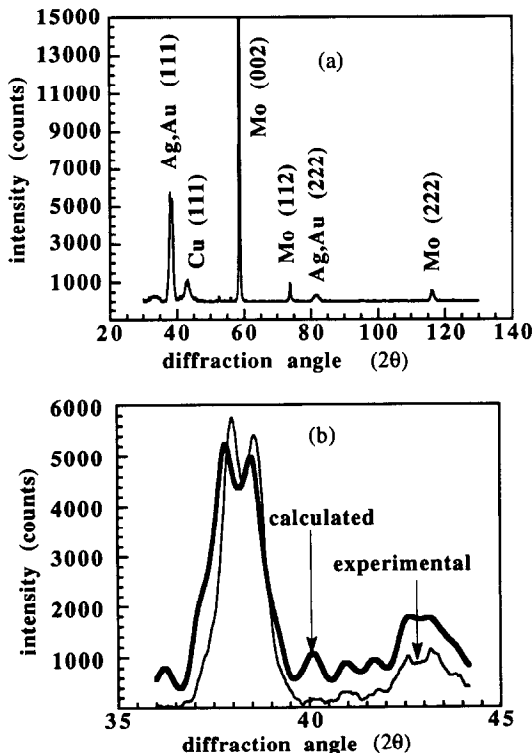
Fig. 3. (a) Typical XRD pattern of the as-deposited sample showing (111)-orientation. (b) Fitting of pattern (a) in the vicinity of the (111) reflection.

nm. This shows that the deposition technique produced a homogeneous multilayered structure.

2.3. Characterization of the heat-treated samples

An important step in establishing the sample preparation technique consists of characterization of the heat-treated samples in order to compare their phase content with known equilibrium phase diagrams. For example, an isothermal section of the Au–Ag–Cu phase diagram at 300°C [4] is shown in Fig. 4 together with some selected samples projected from the substrate triangle onto the section. These samples were heat treated at 300°C under vacuum for 2 h. As seen in Fig. 4, samples 1, 3, 6, 15 and 55 should contain a mixture of two solid solutions, α_1 (Ag-rich) + α_2 (Cu-rich), with increased α_2 content in the expense of α_1 content, when the sample number increases. XRD patterns of these samples, shown in Fig. 5a support the expected qualitative variations by the relative diffracted intensities from sample 1 to sample
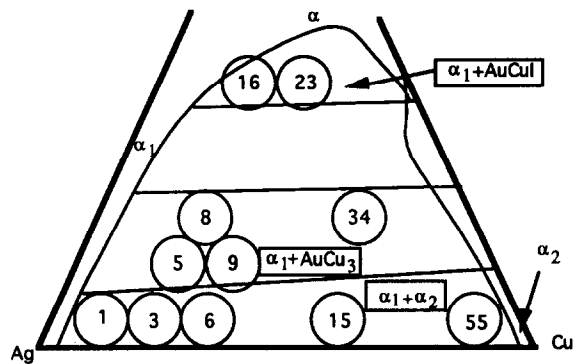

Fig. 4. Selected samples projection onto the 300°C-isothermal section of the Au–Ag–Cu ternary phase diagram.

55, comparing, for example, (111) α_1 and (111) α_2 lines. The same behavior in the 300°C-isothermal section is demonstrated in Fig. 5b, for the α_1 + AuCu$_3$ mixture (samples 5, 8, 9 and 34), and in Fig. 5c for the α_1 + AuCu I mixture (samples 16 and 23). On the basis of the XRD studies, it may thus be concluded that results from the thin film method correlate well with the established phase diagram.

In order to characterize the phase diagram obtained from these multilayered samples in more detail, the microstructure of the heat-treated samples was studied using a STEM equipped with EDS. The microstructural descriptions were reported elsewhere [5,6]. Only the phase composition of the samples containing the α_1 + AuCu$_3$ mixture will be reported here. Twinned α_1 and AuCu$_3$ grains together with the corresponding EDS spectra are shown in Fig. 6. The semi-quantitative data processing was performed using RTS-2/FLS software adopted for thin films. The silver-rich α_1 phase contained 11 at% of the dissolved gold and copper. The AuCu$_3$ phase was found stoichiometric, but with 5 at% gold replaced by silver. In both phases the elemental compositions, within the limit of the EDS experimental error, are in good agreement with the equilibrium solubilities expected from the bulk phase diagram [4]. Selected area electron diffraction (SAED) analysis of the ordered AuCu$_3$ phase revealed an unexpected microstructural feature: the [001] diffraction pattern, shown as an inset in Fig. 6c, exhibits splitting of the satellite (100), (010) and (110) spots. This splitting is characteristic of the long-period AuCu$_3$ II superlattice formation [7], which is not present in equilibrium structures in this composition range. Note that this
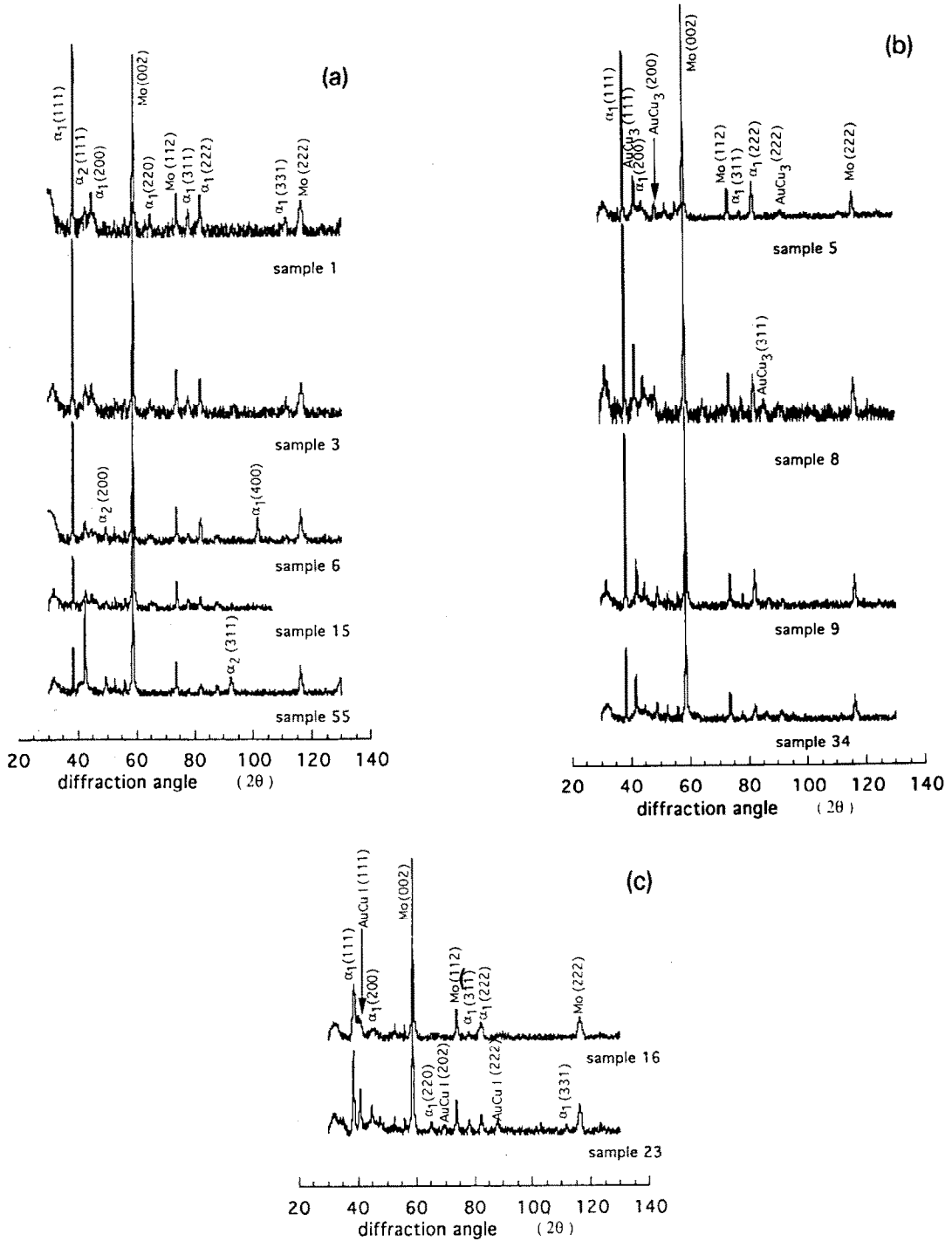
Fig. 5. (a) Superimposed XRD patterns of heat-treated samples containing $\alpha_1 + \alpha_2$ mixture. (b) Superimposed XRD patterns of heat-treated samples containing $\alpha_1 + AuCu_3$ mixture. (c) Superimposed XRD patterns of heat-treated samples containing $\alpha_1 + AuCu$ I mixture.
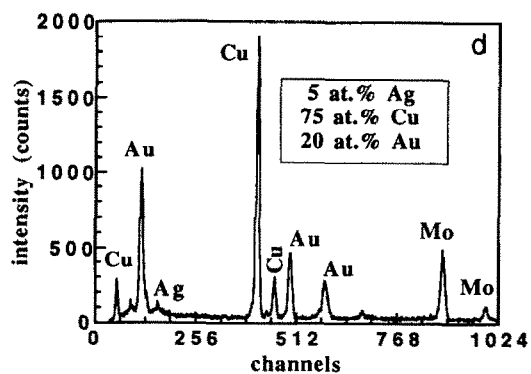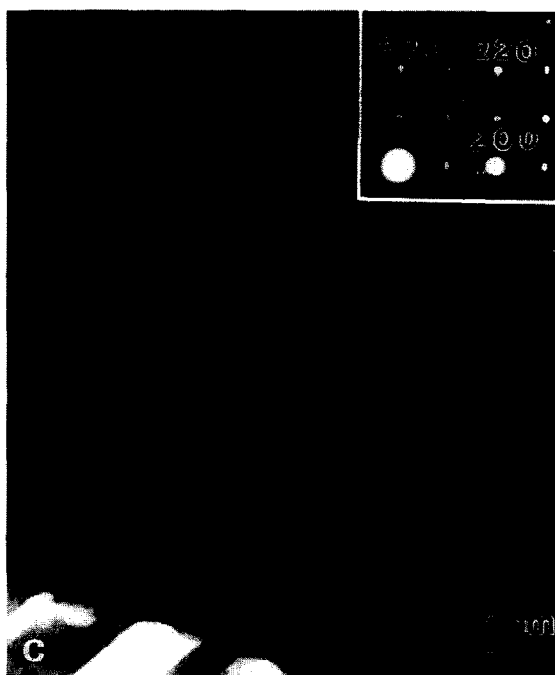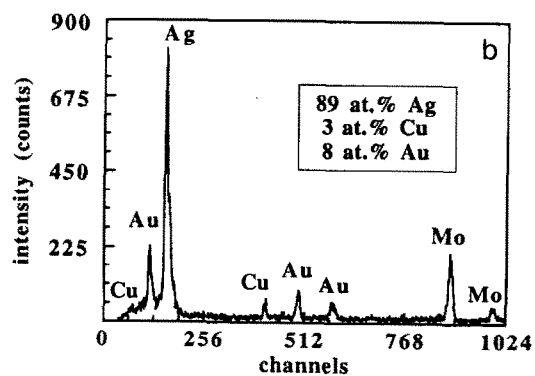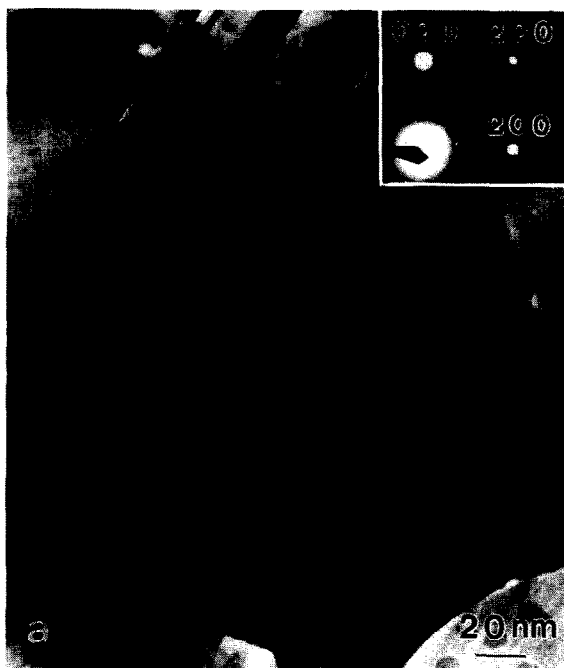
Fig. 6. Characteristic fcc twinned α_1 grain. [001]-SAED is shown in the inset. (b) EDS spectrum obtained from the grain in (a). (c) Typical dislocated $AuCu_3$ grain. [001]-SAED is shown in the inset. (d) EDS spectrum obtained from the grain in (c).

structure was not revealed by XRD, due to the similar interatomic spacings of the phases, nor by EDS, since it has the same composition.

4. Conclusions

Analyses of the as-deposited samples yielded good correlation with the equilibrium phase diagram. Studies of heat-treated samples correlate well with the known Au–Ag–Cu phase diagram, except in a small area of the isothermal section at 300°C, where additional higher ordering of AuCu$_3$ was observed to take place. The technique allows the rapid preparation of a complete set of ternary compositions and substantially shorter heat-treatment periods required to achieve equilibrium.

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