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Stability of nanosized alloy thin films: Faulting and phase separation in metastable Ni/Cu/Ag-W films

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ABSTRACT

A comparative study of Me(=Ni/Cu/Ag)-based, W-alloyed, nanocrystalline, heavily faulted thin films was carried out to identify parameters stabilizing the nanocrystalline nature upon thermal treatment. The three systems, initially of comparably, heavily twinned (twin boundaries at spacings of 1–5 nm) microstructures showed similarities but also strikingly different behaviours upon annealing, as observed by application of in particular X-ray diffraction (line-broadening) analysis and (high resolution) transmission electron microscopy. During annealing in the range of 30–600 °C, (i) segregation at the planar faults (for Me = Ni) and at grain boundaries (for Me = Ni,Cu,Ag), as well as nanoscale phase separation (for Me = Cu,Ag) take place, (ii) distinct grain growth does not occur and (iii) the twin boundaries either are largely preserved ((Ni(W) and Ag(W)) or disappear totally (Cu(W))), which was ascribed to an altered faulting energy, due to change of the amount of W segregated at the twin boundaries, and to the evolution of nano-precipitates. The nanosized films exhibit very large internal (macro)stresses parallel to the surface, which change during annealing in the range of 1 GPa (tensile) to −3 GPa (compressive) and thus are sensitive to the microstructural changes in the films (decomposition and relaxation) that happen on a nanoscale. The results are discussed in terms of thermodynamic and/or kinetic constraints controlling these processes and thus the thermal stability of the systems concerned.

1. Introduction

Nanocrystalline (NC) metals have received considerable attention owing to their unusual, often favourable properties as compared to their coarse-grained counterparts [1–12]: e.g. higher strength/hardness [13] or hard magnetic properties [8]. However, NC metals have two adverse properties: microstructural instability [14,15] and low ductility [16,17], which can be related to the large volume fraction of high-angle grain boundaries (GB) associated with excess energy [18]. At high homologous temperature, grain coarsening can occur, i.e. in the case of NC pure Ag, even at room temperature, so-called self-annealing [19,20]. To suppress the nano-grain growth and preserve the nano-scale microstructure, two approaches can be adopted [21,22]: (i) Thermodynamic approach: reduction of the driving force for grain growth, which in the GB-curvature driven growth models [23] is proportional to the GB energy per unit area of GB, by segregation of the solutes at the GBs [24], (ii) Kinetic approach: reduction of the grain-boundary mobility, by e.g. porosity, solute atoms and precipitates at the GBs, which impose drag forces [15,18,25].

Recent work on co-sputtered Ni-based solid solution films, with W as alloying element, has shown that these films possess an unusually high density of planar faults [26,27], which play a crucial role in stabilizing such metastable solid solution films at elevated temperatures [27]. Moreover, such nanotwinned metallic materials can exhibit unusual properties as compared not only to coarse-grained counterparts but even as compared to nanocrystalline metals [4,9,28,29]. Thus, very high tensile and fatigue strengths may be combined with good ductility and thermal stability [9,28]. Against the above background it appears worthwhile to investigate to what extent such nanotwinning can occur in related systems and also thereby to find out what the crucial parameters, determining the thermal (in)stability of such systems, are.

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The tendency to segregation of solute atoms may be described with simple thermodynamic rules (e.g. see Refs. [21,26,30]). However, results obtained for Ni-W [26,31], a system of weak segregation tendency, indicate that kinetic aspects, as the possible extent of diffusion, may dominate the whether or not occurrence of segregation and thus the stability against coarsening. Because of a possible high activation energy for diffusion, which holds for W in Cu or Ni, the (metastable) dissolved solute (W) atoms can diffuse only over (very) small distances. Thus, recognizing the high planar fault density in such films, development upon annealing of agglomerates of the alloying element at the closely-spaced planar faults is probable [26,31].

Ab initio calculations [27,32] suggest that in Ni(W) at low W solute content (less than 23 at.% of solute), the fcc-based crystal structures are the most stable crystallographic structures. The calculations also reveal that the fully relaxed, pure *hcp* and *bcc* Ni structures are found to be thermodynamically unstable, but a fully relaxed, *hcp* Ni(W) *superstructure* can be thermodynamically preferred. At nano-scale, by segregation of the solute W atoms, the closely spaced planar faults can be stabilized by a locally higher content of the solute W atoms at the faults. Therefore, the initial, stable and alloyed *hcp* superstructure can be maintained possibly even at, e.g., a higher temperature. Furthermore, these solute atoms exert significant drag forces on dislocations [33] in a deformation process, thereby enhancing the superior properties of such materials with respect to the strength and ductility in a de-twinned nanostructure [9].

In the current project, Ni-, Cu- and Ag-based thin films alloyed with similar W contents were rigorously investigated in the as-prepared, co-sputtered condition and with respect to their thermal stability, in particular applying X-ray diffraction and (high-resolution) transmission electron microscopy. A focus of the research was on the dissolved atom (re)distribution and the segregation behaviour as a function of time and temperature. Moreover, this paper provides the first direct evidence of solute segregation at the planar faults in nanotwinned metallic materials.

2. Experimental procedures

2.1. Layer deposition and chemical analysis

The (Ni, Cu, Ag)-W films were grown by magnetron co-sputtering at ambient temperature onto Si ⟨001⟩ -wafers covered with an amorphous Si_3 N_4/SiO_2 bilayer to a thickness of 500 nm, in an argon atmosphere of 5.6×10^{-3} mbar. The sputter power for the Ag, Cu and Ni targets was 100 W, 150 W and 200 W, respectively. The sputter power for the W target was adjusted to realize different compositions of the binary films. More deposition details have been given in Ref. [26]. The compositions were experimentally determined by inductively coupled plasma optical emission spectroscopy (ICP—OES). The results are shown in Table 1.

2.2. X-ray diffraction (XRD) measurements; in-situ annealing

X-ray diffractograms and pole figures were measured by the use of an X'Pert MRD Pro diffractometer (Panalytical, Almelo, The Netherlands) equipped with a Cu X-ray tube (45 kV, 40 mA) and an X-ray lens in the primary beam path and a parallel-plate collimator, a monochromator in the diffracted beam set to Kα radiation and a proportional counter. For the pole-figure measurements, employing the 111 reflection, the rotation angle varied between 0° and 360° and the tilting angle between 0° and 90°. Because all specimens investigated exhibited a {111} fiber-texture, pole-figure sections were constructed by summing up the intensities measured at a given value of the tilting angle for all rotation angles.

Table 1
Chemical composition of the Ni/Cu/Ag-W thin films determined by inductively coupled plasma optical emission spectroscopy. The Ni-W thin films used for the current project are identical to the ones already analysed and discussed in Ref. [31].

Alloy	c_{Ni}(at.%)	c_W(at.%)
Ni	100	0
Ni(W)-6	94.2	5.8
Ni(W)-7	92.6	7.4
Ni(W)-12	88.4	11.6
Ni(W)-17	83.5	16.5
Ni(W)-19	81.4	18.6
Ni(W)-21	79.1	20.9
Ni(W)-25	75.5	24.5
Alloy	c_{Cu}(at.%)	c_W(at.%)
Cu	100	0
Cu(W)-5	95.5	4.5
Cu(W)-9	90.7	9.3
Cu(W)-14	86.1	13.9
Cu(W)-19	81.4	18.6
Cu(W)-23	76.9	23.1
Alloy	c_{Ag}(at.%)	c_W(at.%)
Ag	100	0
Ag(W)-4	95.8	4.2
Ag(W)-13	86.7	13.3
Ag(W)-17	82.6	17.4

Stress and in-situ XRD measurements were performed with a D8 Discover diffractometer (Bruker AXS, Karlsruhe, Germany) which was equipped either with a Cu X-ray tube (40 kV, 30 mA), an X-ray lens and a Ni filter in the primary beam path and with a parallel-plate collimator and a scintillation counter in the secondary beam path, or without Ni filter but with an energy-dispersive detector to select Cu Kα radiation. For the in situ XRD stress measurements, on the basis of the crystallite-group method [34–37], the so-called unaffected reflections [38,39] (e.g. 111, $2\bar{2}0$, $3\bar{1}1$, etc.) were used to avoid the influence of the potentially present planar faults on the reflection positions (and shapes), recognizing the {111}-fiber texture of the films. A rotationally symmetric, planar state of stress was assumed. Then, the stress, parallel to the surface, can be determined from a plot of the lattice-plane spacing a_ψ versus $\sin^2\psi$, where ψ is the specimen-tilt angle. Additionally, the strain-free lattice parameter can also be determined by interpolation at the strain-free direction indicated by $\sin^2\psi_0$ [35]: $\sin^2\psi_0 = 2(-2S_{12} - 2/3(S_{11} - S_{12} - ½S_{44}))/S_{44}$, where S_{ij} are the single-crystal elastic compliance tensor components determined as the atomic concentration averaged single-crystal elastic compliances of Me = Ni/Cu/Ag and W.

The in-situ heating experiments were performed in a DHS 900 chamber (Anton Paar, Graz, Austria) under a reductive gas atmosphere (N_2/2 vol.% H_2) mounted on the D8 Discover diffractometer. In the case of the Cu(W) film, beginning at 32 °C the temperature was raised in steps of 25 °C, performing a stress measurement, requiring about 25 min measurement time, after each step, up to the maximum temperature of 577 °C. After a holding time of 6.5 h at 577 °C, the film was cooled down, measuring the stress after successive temperature steps of 50 °C, to 32 °C. In the case of the Ag(W) film, the same procedure was chosen but the start temperature was chosen to be 30 °C and the maximum temperature was 600 °C. In the case of the Ni(W) film, a slightly different procedure was chosen: the Ni(W) film was subjected to four successive thermal cycles, each beginning at 32 °C and in steps of 25 °C, performing a stress measurement, requiring about 20 min measurement time, after each step, to the successive maximum temperatures of 177 °C, 327 °C, 577 °C and 577 °C. After reaching each of the maximum temperatures, the Ni(W) film was cooled down in temperature steps of 25 °C to 32 °C. During the 3rd cycle,