FORMATION OF A QUASICRYSTALLINE AL-NI-CO STRUCTURE BY SOLID STATE REACTION OF MULTILAYERS PREPARED BY PLD

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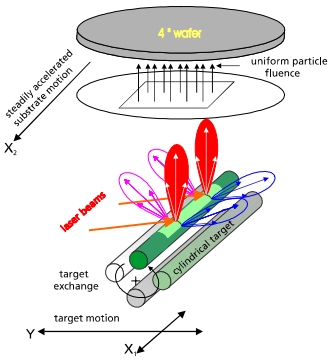
Abstract

Thin layers of the decagonal phase of the Al-Ni-Co system were synthesized by Pulsed Laser Deposition (PLD). The short range order of these layers was characterized by Extended X-Ray Absorption Fine Structure (EXAFS) measurements.
It is shown that single-phased decagonal structures can be formed by solid state reactions of PLD prepared multilayers. A 10-period Co/Al/Ni multilayer has been fabricated under UHV conditions (low 10^{-8}mbar), using the first harmonic of a Nd:YAG pulsed laser (τ=7...9ns, λ=1064nm). After determination of deposition rates of each material, the element composition of the layer stack can be adjusted very exactly, because of the high precision of the PLD process. Finally, the formation of the decagonal phase was reached by post-annealing of the multilayer at 700°C for 5 hours. The five-fold symmetry of the structure is shown in a TEM micrograph cross-section. Specular X-ray diffraction investigations indicate that the periodic direction of the decagonal structure is aligned perpendicularly to the substrate surface. This is in correspondence with known results of the isotypic structure of decagonal Al-Cu-Co [1]. The comparison of the EXAFS measurements of the quasicrystalline thin layers with a quasicrystalline reference sample shows a very high level of similarity. Therefore both the short range order and the long range order (responsible for the X-ray diffraction pattern) of the produced quasicrystalline samples were found to be equivalent to the short and long range order in a quasicrystalline reference sample.

Multilayer Preparation

Looking at the ternary phase diagram of Al, Ni and Co [2] it can be seen that the formation of the decagonal phase d-Al-Ni-Co is possible just in a narrow existence area. Inside this area different structure modifacations are found [3]. Therefore the exact adjustment of the atom ratio Al:Ni:Co plays a decisive role.
The large area Pulsed Laser Deposition (PLD) method [4] enables us to deposit thin films with a very good reproductibility. A schema of the PLD principle is shown in figure 1.

Fig. 1: Principle of thin film depositition by large area PLD method.



Depositing single thin films of the three constituents Al, Ni and Co and measuring the layer thicknesses and the mass densities by X-ray reflectometry the deposition rate for each element can be determined and the nominal composition in the multilayer stack can be choosen very precisely. After that the multilayer with 10 periods of the sequence Co/Al/Ni, whereby the first Co layer was deposited on a (012) sapphire substrate, was prepared. From the layer thicknesses and the mass densities of each element the overall composition was determined to $Al_{73}Co_{16}Ni_{11}$ [5].

Finally, the formation of the quasicrystalline phase was reached by post-annealing of the multilayer at 700°C for 5 hours with a heating rate of 1K/min and at a pressure less then $2x10^{-7}$mbar.

Phase Analysis

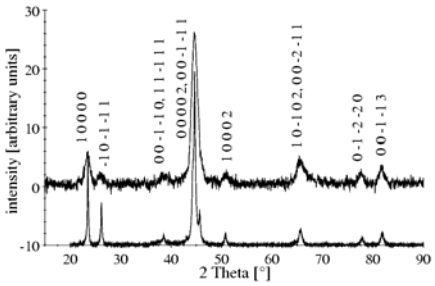


Fig. 2: Comparison of diffraction patterns of the thin film (above) and a quasicrystelline reference sample* (below). Indexing according to Kek [2].

As can be seen in figure 2 the thin film only contains the d-Al-Co-Ni phase and in addition at least amorphous components. All reflections of the x-ray diffraction pattern can be indexed on base of the decagonal quasicrystalline phase [2]. Moreover, comparison with a pattern of decagonal reference sample shows good agreement.
However, a strong preferred orientation with periodic direction aligned perpendicular to the substrate surface can be stated (Fig. 3, right). The 00002 reflection, representing the periodic direction, is very sharp having high intensity compared to all other decagonal reflections. The rocking scan of the 00002 reflection confirms the strong alignment of the periodic direction perpendicular to the substrate surface.
Finally an electron diffraction pattern was taken (Fig3, left). The electron beam direction is parallel to the periodic direction of the decagonal structure.

* *The powder reference sample with the composition $Al_{72}Ni_{15.5}Co_{12.5}$ was kindly put to our disposal by B. Grushko (Institut für Festkörperforschung, Forschungszentrum Jülich)*

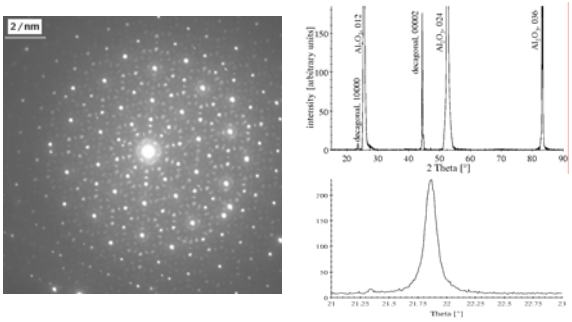


Fig. 3: left: TEM micrograph cross-section of the annealed thin layer (taken from H. Banzhof, Institute of Applied Physics and Didactics, TU Dresden). The beam direction corresponds with the periodic direction of the decagonal structure.
right above: X-ray diffraction pattern of the Θ–2Θ-scan of the thin film.
right below: Rocking scan of the 00002 reflection which represents the periodic direction.

EXAFS Measurements: Information about the short-range order

EXAFS measurements were carried out at the "Hamburger Synchrotron Strahlungslabor" (HASYLAB). (For set-up cf. [6]). Because of the substrate (sapphire wafer with thickness of 500µm), the usual way to measure the absorption coefficient at Co and Ni K absorption edges by transmission was not applicable. Therefore the fluorescence intensity was measured to obtain the absorption coefficient $\mu(E)=\mu_0(E)(1+\chi(E))$ for EXAFS. E is the energy of incident X-ray photons, $\mu_0(E)$ is the absorption coefficient of free atoms without contributions of neighbours. $\chi(E)$ is the characteristic EXAFS function. This function was compared with results obtained from measurements at the quasicrystalline reference powder sample. Both functions χ agree well (Fig 4).

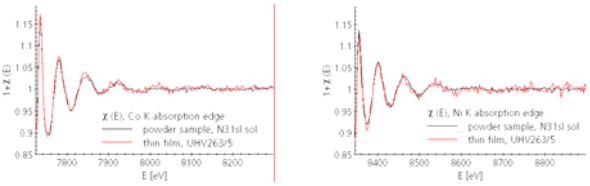


Fig. 4: Comparison of the EXAFS functions of the thin film and the quasicrystalline reference sample at Co and Ni K absorption edge. High frequency oscillations of the red curve are probably due to the statistics of the small diffraction volume.

On the basis of five-dimensional structure models the next neighbourhood (sort, number and distance of atoms around the absorbing central atom) of the transition metal atoms was calculated and the adaptation of the calculated EXAFS function χ to the measured one was carried out. The detailed analysis of the measured curves and the description of the underlying structure model is performed elsewhere [7].

References

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