Multilayer X-ray optics for energies E > 8keV and their application in X - ray analysis

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ABSTRACT

Performance of Ni/C, Ni/B_4C, Mo/B_4C and W/B_4C multilayers in the energy range E > 8keV is considered by simulation of X-ray reflectivity and resolution (FWHM) of 1st order Bragg reflection at three different photon energies. The results indicate, that Ni/C and Ni/B_4C multilayers show highest theoretical reflectivities of R > 80% for Cu Kα-radiation and also above the Mo K-edge (E= 20.04 keV) at 30 keV. For Mo Kα-radiation a reflectivity of R > 90% can be achieved by the use of Mo/B_4C multilayers. For applications, where period thicknesses d < 3 nm and high reflectivities are required W/B_4C multilayers can be used. Theoretical values are compared with X-ray reflectometry results, which were executed at 75 period Ni/C, Ni/B_4C and Mo/B_4C multilayers, fabricated by pulsed laser deposition (PLD) technology on Si substrates. Amorphous or nanocrystalline structures of single layers, smoothest interfaces and high reproducibility of single layer thickness across the entire layer stack are the results of this high precision PLD process.

Multilayer characterization is carried out by using HREM investigations and X-ray reflectometry.

A period thickness variation in the order of $\sigma_d \leq 0.1$ nm and an interface roughness $\sigma_R \leq 0.3$ nm are determined for Ni/C and Ni/B_4C multilayers. Reflectivities R> 75% for Ni/C and Ni/B_4C multilayers with 75 periods and period thicknesses d ≥ 3.5 nm are achieved as a matter of routine. For d> 3.8 nm reflectivities of both material systems exceed R = 80% . The 1st order BRAGG reflection widths (FWHM) of $\Delta(2\Theta) \leq 0.08°$ are typically observed.

First results, with peak half widths (FWHM) $\Delta(2\Theta) \leq 0.037°$ and R> 65% are achieved at E= 17.5 keV for Mo/B_4C multilayers with d= 3.5nm.

Therefore, these material combinations are especially suited as multilayer systems for Göbel Mirrors in X-ray reflectometry and diffractometry for Cu Kα- and Mo Kα- radiation or as flat monochromators in TXRF systems.

Key words: X-ray mirror, Göbel Mirror, parallel beam X-ray optics, PLD (Pulsed Laser Deposition), XRR (X-ray reflectometry), XRD (X-ray diffraction), HREM

1. INTRODUCTION

The application of Göbel Mirrors induced a decisive extension of possibilities in laboratory-based X-ray diffractometry and reflectometry. Released by a growing number of applications, X-ray optical multilayers are required which show an optimized performance in the used energy range. The performance of X-ray optical multilayers is mainly influenced by the optical design, the application and the X-ray source characteristics[1].

Ni and W absorbers are mainly used for Cu Kα-radiation while Mo absorbers are preferred for Mo Kα- radiation. Typical spacer materials are C and B_4C.

The advantageous characteristics of Ni/C multilayers for applications with Cu Kα- radiation – highly efficient reflectivity, Bragg-Brentano compatible resolution and brilliant Cu Kβ- suppression - were demonstrated by Holz et al.[2]. In the present paper peak reflectivity and resolution (FWHM) of 1st order Bragg reflection of Ni/C, Ni/B_4C, Mo/B_4C and W/B_4C multilayers are calculated in the period thickness range between 2 nm and 5 nm for Cu Kα- and Mo Kα- radiation and above the Mo K-edge (E= 20.04 keV) at E= 30 keV. To confirm the simulation results Ni/C, Ni/B_4C and Mo/B_4C multilayers, fabricated by PLD are characterized by means of HREM and X-ray reflectometry. Finally, selected applications of Ni/C multilayers as Göbel Mirrors for Cu Kα- and Mo Kα- radiation are discussed.

2. MULTILAYER DESIGN

The ratio of dispersion coefficient δ and absorption coefficient β often is an important parameter for the multilayer design beside the refractive index n ($n = 1 - \delta + i\beta$). The ratio δ/β increases proportionally to the photon energy between absorption edges. It can reach large values, especially for the light elements. The ratio decreases drastically at the absorption edges. The following δ/β ratios were calculated for the used absorber and spacer materials at three selected photon energies (table 1) by using Henke-data[3].

	8044 eV (Cu Kα)	17500 eV (Mo Kα)	30000 eV
Ni / Z=28	47,7	25,4	69
Mo / Z=42	15,3	57,6	22,2
W / Z=74	12	10,9	27,1
B / Z= 5	1230	7475	26585
C / Z= 6	627	3756	13558

Table 1: δ/β ratios for Ni, Mo, W, B and C, calculated at three different photon energies by using Henke data[3]

For applications with Cu Kα- and Mo Kα- radiation and for the energy at 30 keV reflectivities and resolution were simulated by means of IMD-software for modeling the optical properties of multilayers[4]. Simulations were executed by using the following parameters: number of periods N= 75, interface roughness σ_R= 0.3nm, variation of period thickness σ_D= 0.05nm, material densities ρ_{Ni}= 8.1g/cm³, ρ_{Mo}= 10.2g/cm³, ρ_W= 17.0g/cm³, ρ_C= 2.33g/cm³, ρ_{B4C}= 2.4g/cm³, ρ_{Si}= 2.32g/cm³. The simulation results are shown in fig. 1…3.

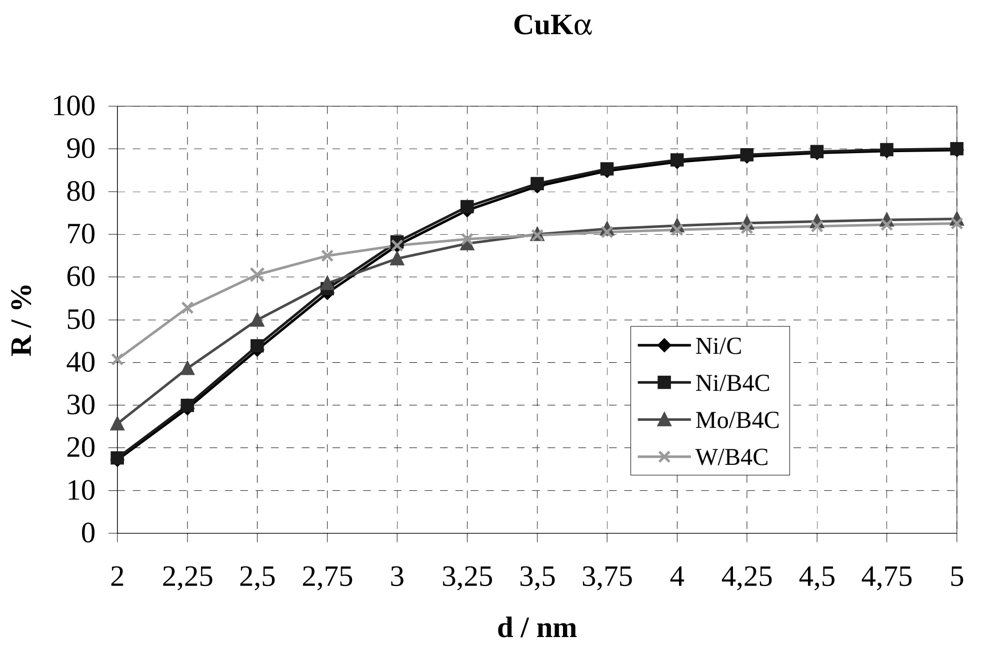


Fig. 1: Simulation of the attainable reflectivities of Ni/C, Ni/B_4C, W/B_4C and Mo/B_4C multilayers with 75 periods for Cu Kα-radiation as a function of the mean period thickness d

For Cu Kα-radiation the simulation of the attainable reflectivities of the different multilayer systems as a function of mean period thickness d shows that for Ni/C and Ni/B_4C multilayers with 75 periods highest values can be achieved for d> 3 nm (fig. 1). This is expected from the high value of the δ/β ratio valid for the Ni absorber (table 1). A minimum 1^{st} order Bragg reflection width (FWHM) of $\Delta(2\Theta)$= 0.054° is calculated for a multilayer with d= 3.5nm. Though tungsten has the lowest δ/β ratio high reflectivities are observed for minimum mean period thicknesses d< 3.0 nm due to the highest electron density contrast (i.e. δ- value contrast) between absorber and spacer material. Within the period thickness range of $d \geq 3.75$ nm reflectivities of more than 85% can be achieved for Ni/C- and Ni/B_4C- multilayers with 75 periods.

For Mo Kα- radiation the δ/β ratio of Mo becomes higher than the Ni ratio. Therefore highest reflectivities can be achieved with the Mo/B_4C multilayers (fig.2).

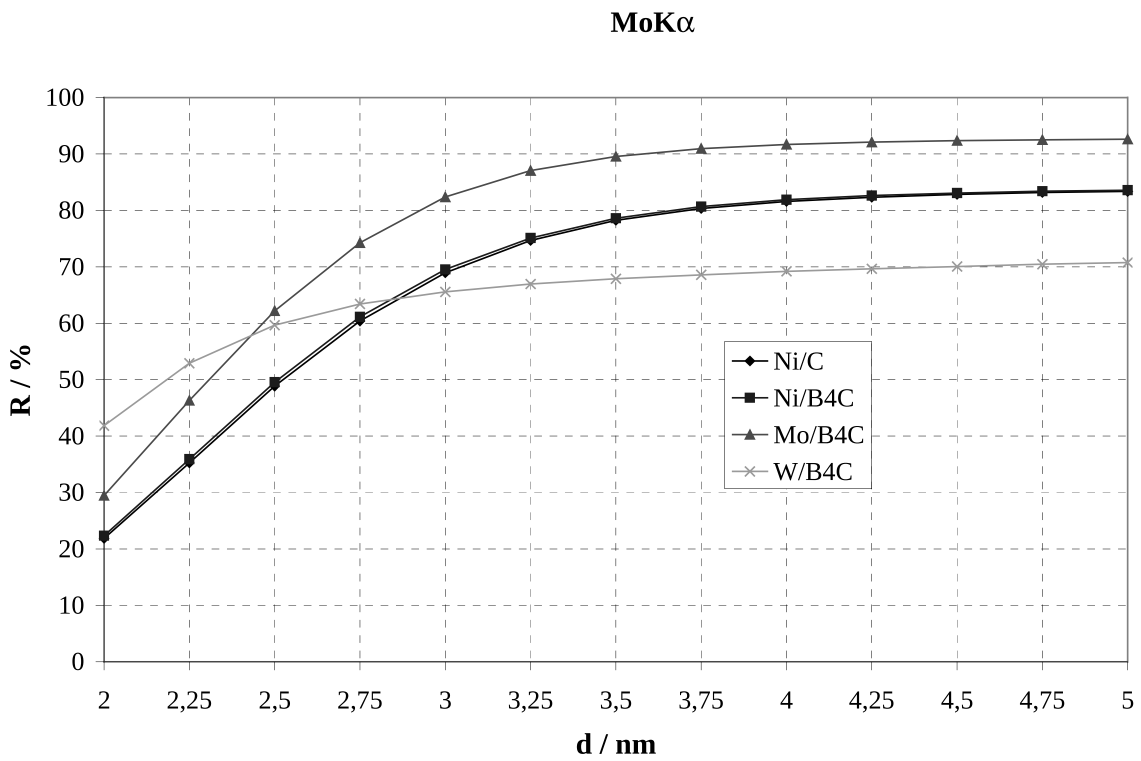


Fig. 2: Simulation of the attainable reflectivities of Ni/C, Ni/B_4C, W/B_4C and Mo/B_4C multilayer systems with 75 periods for Mo Kα-radiation as a function of the mean period thickness d

A comparison from the Mo Kα-reflectivities of the Mo/B_4C multilayers and from other layer stacks shows that the Mo/B_4C reflectivities are always significant higher than those of multilayers with Ni absorbers. The lowest width of the 1^{st} order Bragg reflection (FWHM) of $\Delta(2\Theta)$= 0.026° is calculated for a Ni/C multilayer (N=75) with d= 3.5nm. The width of the 1^{st} order Bragg reflection for a comparable Mo/B_4C multilayer is in the range of $\Delta(2\Theta)$= 0.032°. Within the period thickness range of d > 3.5 nm reflectivities of more than 90% can be achieved by the use Mo/B_4C multilayers with 75 periods.

In the energy range of 30 keV above the Mo K- edge (E= 20.04 keV) the Ni δ/β ratio is higher than the Mo δ/β ratio. Reflectivities of $R \geq 85\%$ and FWHM of $\Delta(2\Theta)$= 0.016° can be achieved by the use of Ni/C and Ni/B_4C multilayers with 75 periods. The optimum period thickness range is above d= 3.25 nm (fig.3).

The reflectivity of W/B_4C multilayers is higher for small periods $d \leq 3.25$ nm. For d= 2.0 nm a reflectivity of R= 55% is calculated.

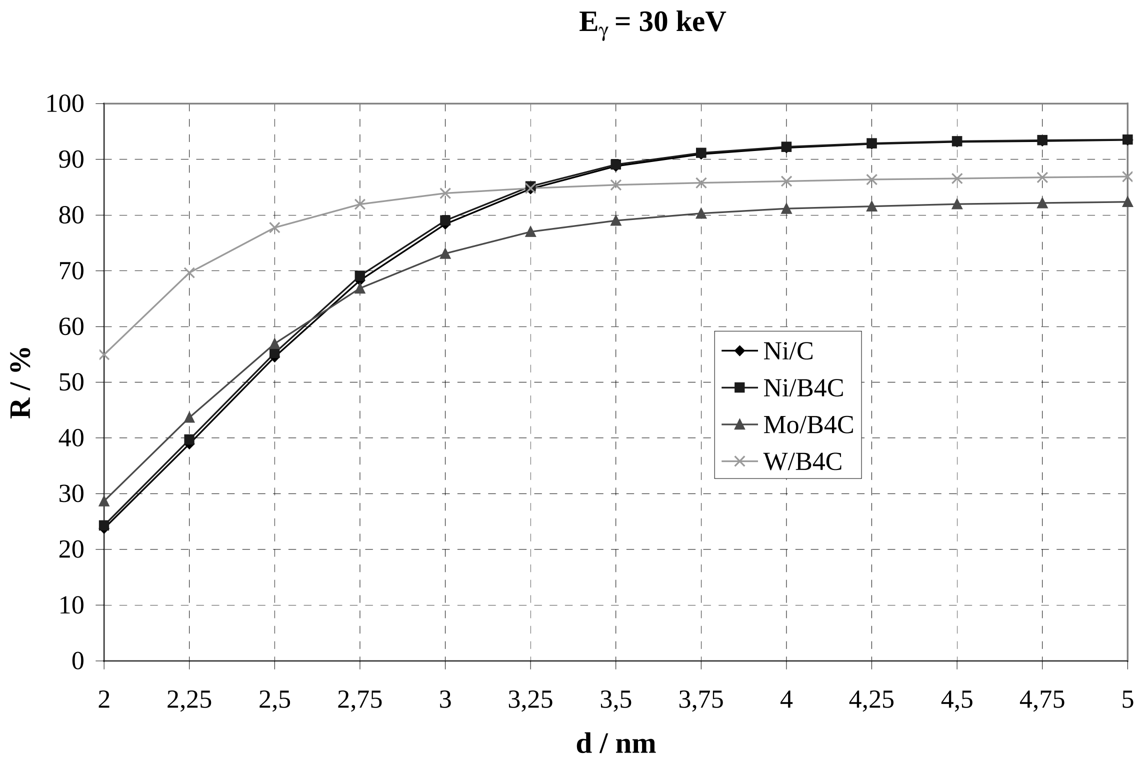


Fig. 3: Simulation of the attainable reflectivities of Ni/C, Ni/B_4C, W/B_4C and Mo/B_4C multilayer systems with 75 periods for 30 keV- radiation as a function of the mean period thickness d

The aim of these simulation processes is the multilayer optimization concerning reflectivity and resolution for a particular field of application. As a result the following parameters of Goebel Mirrors can be improved by the application of gradient multilayers with increased reflectivities:

- Increasing the parabola parameter p for given focal distances f (f – distance between parabola focus and center of a parabolic mirror) by reducing the mean period thickness d without a loss of reflectivity and thus an increase of parallel beam width b and of the collecting angle Θ for the radiation divergently emitted by the X-ray source.
- Increase of the mean reflectivity over the mirror length with retention of the given parabola parameter p.

3. MULTILAYER FABRICATION

Pulsed Laser Deposition (PLD) is used to synthesize Ni/C, Ni/B_4C and Mo/B_4C multilayers which the highest X-ray optical quality. The particular design of the dual-beam PLD source which was designed for high precision large area deposition and the particular features of the PLD process for multilayer synthesis are described in detail somewhere else[5,6].
The basic principle of the large area PLD target / substrate handling is shown in figure 5. The generation of a laterally homogenized integrated particle flux is achieved by an innovative control regime, utilizing the periodic change of spatial orientation of the plasma plume.

Typical features of PLD thin film growth are substantial kinetic particle energies in the range between 10 eV and 1 keV, high deposition rates per pulse of approx. 1nm/min. The vapor phase condensation far from thermal equilibrium creates vitreous amorphous or nanocrystalline[5] single layers. Results of this high precision PLD process are excellent thickness uniformity or tailored thickness gradients as well as smoothest interfaces between the amorphous or nanocrystalline single layers. No increase of interface roughness caused by the deposition process is observed. So values of interface roughness in the range of $\sigma_R \approx 0.3$ nm are reached in Ni/C multilayer stacks as a matter of routine. Usually the values of interface roughness correspond with the values of the substrate roughness.

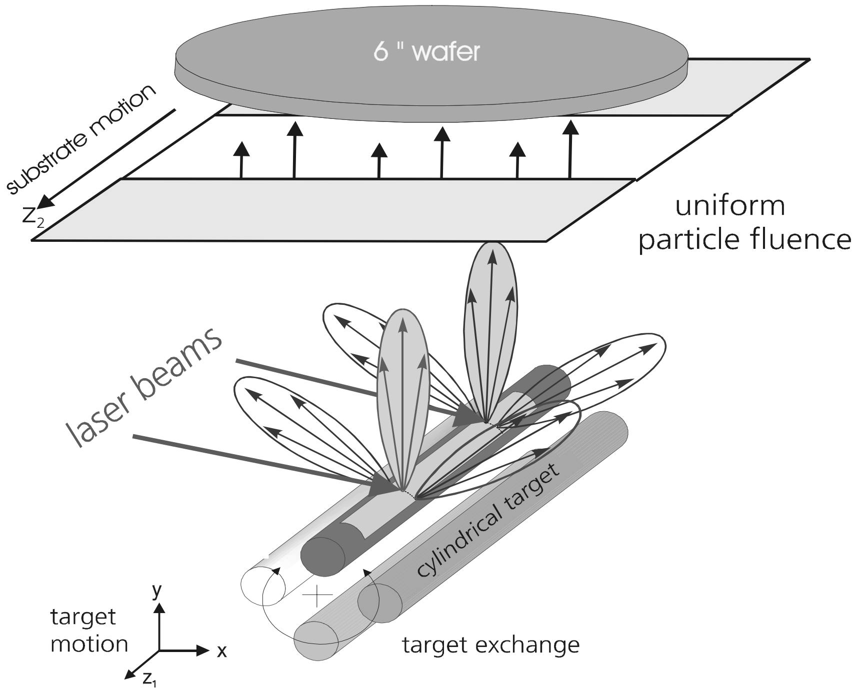


Fig. 4: Principle of large area PLD technology

4. CHARACTERIZATION

Ni/C, Ni/B_4C and Mo/B_4C multilayers are characterized by means of HREM investigations and X-ray reflectometry at selected photon energies in the spectral range above E = 8 keV.

To investigate morphology of layer stacks the structure of single layers as well as the interface roughness multilayers were imaged under high resolution conditions and in overview at medium resolution after preparation at cleavage edges as well as by ion beam milling.

In Ni/C multilayers with period thicknesses $d \leq 4.0$nm (thickness ratio $\Gamma \approx 0.5$) the C- and Ni- layers are always amorphous for X-rays. Very smooth symmetric interfaces without noticeable interdiffusion between Ni- and C- single layers are observed (fig. 5). For period thicknesses $d \geq 4$nm the C- layers are also amorphous while in the Ni- layers crystals with different orientations are observed[5]. There is no increase of roughness across layer stack during film deposition.

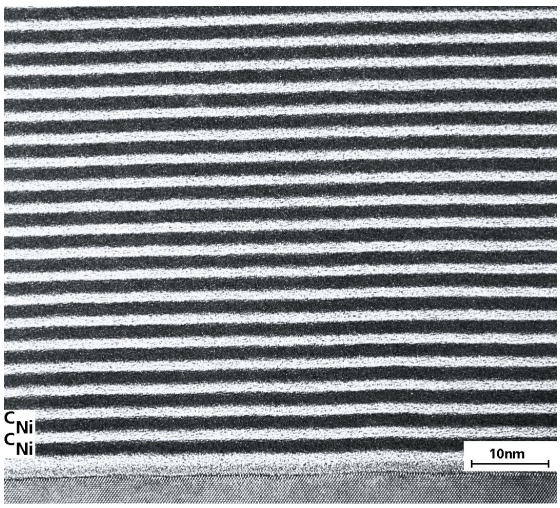


Fig. 5: Substrate near section of a Ni/C multilayer (V721-35), d ≈3.15nm, ion beam milling preparation (3D7110)

The structure of single layers in Ni/B_4C multilayers is amorphous for X-rays both for d ≤ 4 nm (fig. 6) and for d = 4,70 nm (fig. 7). No crystallites can be realized in the Ni layers with $d_{Ni} \approx 2.35$nm in fig.7. In contrast to Ni/C an asymmetric interface configuration is observed. As indicated in fig.6, interfaces B_4C on Ni are smoother than Ni on B_4C, which is also confirmed by density profile measurements across the layer stack. In fig. 6 the layer stack morphology appears as a three-layer system. Ni layers show a sharp interface to the adjacent small B_4C- layer which is followed by a more dense B_4C- Ni mixed layer with a rough interface to the next Ni layer. Asymmetric interfaces in the same way are also observed in other PLD systems like W/C[7].
Comparable to Ni/C multilayers there is no increase of interface roughness across the total Ni/B_4C layer stack (Fig. 8).

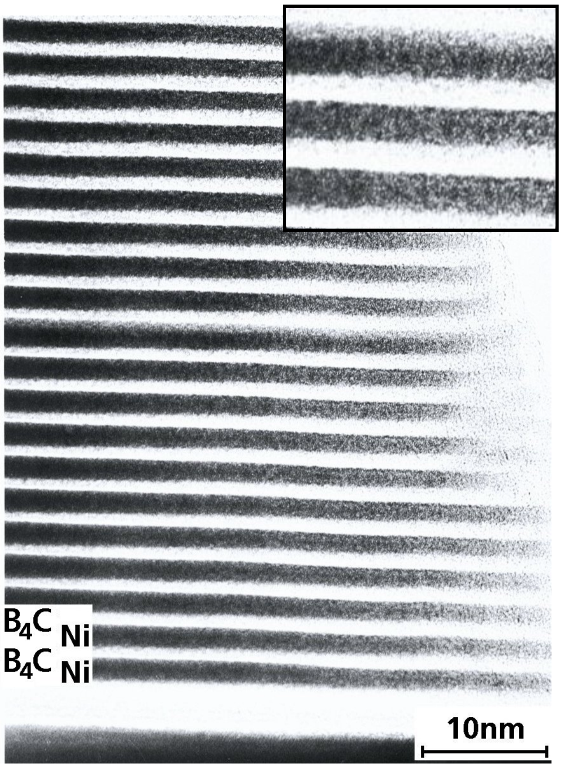
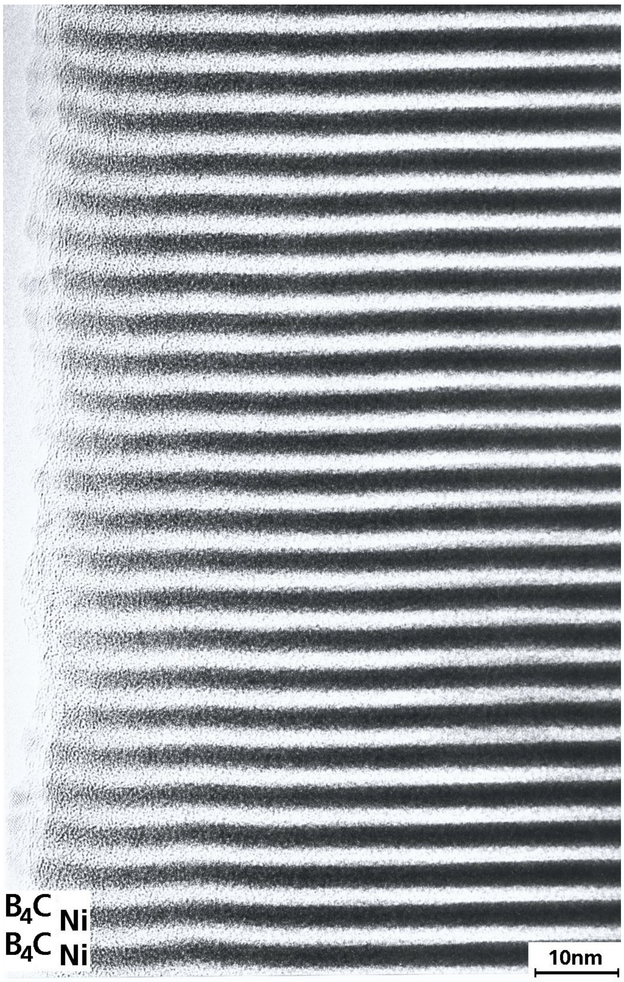


Fig. 6: Substrate near section of a Ni/B_4C multilayer (V764-20), d= 3.74nm, N= 75, prepared at cleavage edges (3D6777) / above

Fig. 7: section of a Ni/B_4C multilayer (V764+20), d= 4.70nm, N= 75, prepared at cleavage edges (3D 6876) / right



A period thickness variation in the order of $\sigma_d \leq 0.1$ nm and an interface roughness $\sigma_R \leq 0.3$ nm are confirmed for Ni/C and Ni/B_4C multilayers.

In Mo/B_4C multilayers asymmetric interface formation was not observed. Compared with Ni/B_4C the interface roughness increases. Highest values of interface roughness are observed in W/B_4C multilayers.
Results of HREM investigation are confirmed by X-ray reflectometry executed at E= 8.05 keV (Cu Kα), at E= 17.5 keV (Mo Kα) and at higher energies from E= 20 keV up to 70 keV.

For Cu Kα- radiation reflectivities R > 75% are observed for Ni/C and Ni/B_4C multilayers with 75 periods and period thicknesses d ≥ 3.5 nm. For d > 3.8 nm the reflectivities of both material systems increase to R > 80% (fig.9). The width of the 1st order BRAGG reflection (FWHM) of $\Delta 2\Theta \leq 0.08°$ is typically observed. These results, which are close to the simulation data, demonstrate the high quality of the Ni/C and Ni/B_4C multilayers.

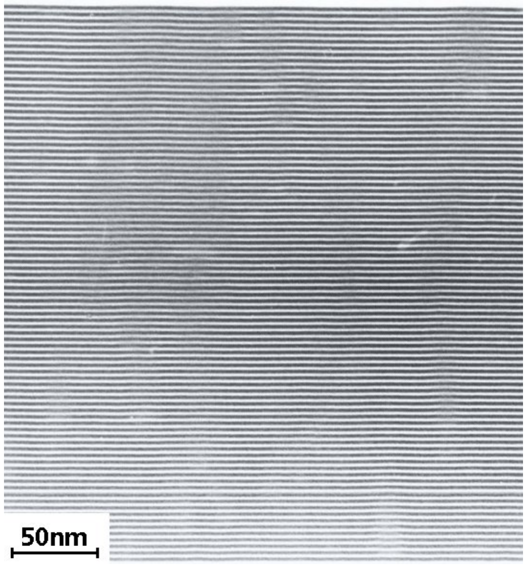


Fig. 8: Ni/B_4C multilayer (V764-20), d= 3.74nm, N= 75, ion beam milling preparation (3D 6822)

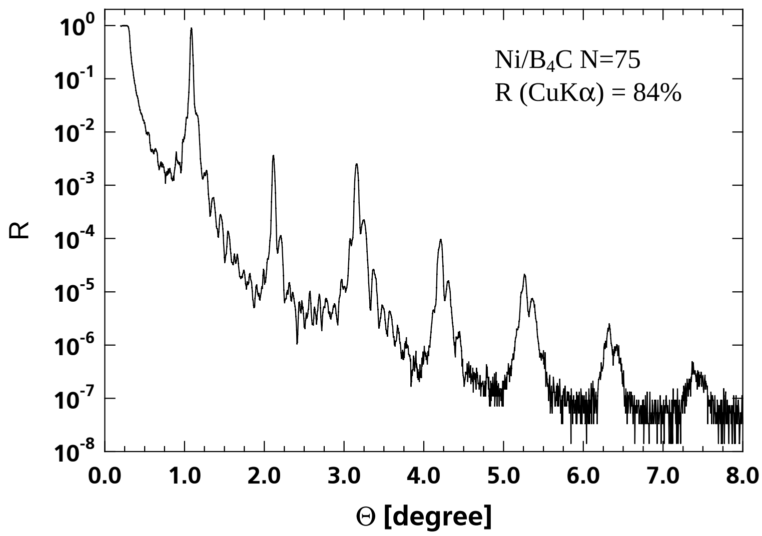


Fig. 9: Cu Kα- reflectivity of Ni/B_4C multilayer with 75 periods (V764-0), d=4.21 nm, R= 84%, measured across 7 decades using TGM arrangement

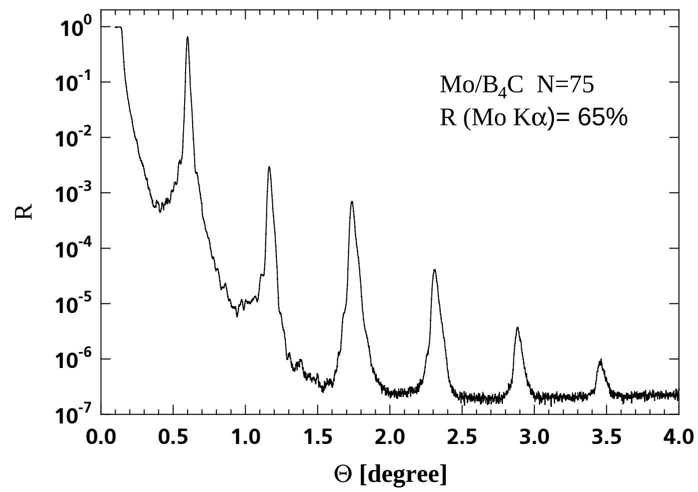


Fig. 10: Mo Kα- reflectivity of Mo/B_4C multilayer with 75 periods (PL042), d= 3.5 nm, R= 65%, measured across 6 decades using TGM arrangement

At E= 17.5 keV comparable results of R≥ 70% and peak widths (FWHM) $\Delta(2\Theta) \leq 0.05°$ are achieved for Ni/C and Ni/B_4C multilayers of 75 periods, typically. As expected from simulation Mo/B_4C multilayers show highest reflectivities at this energy. First reflectometry results, executed at a Mo/B_4C multilayer with 75 periods and d= 3.5 nm, show a Mo Kα-reflectivity of R= 65% and a width of the 1st order Bragg reflection (FWHM) $\Delta(2\Theta)$= 0.037° (fig.10).

In order to evaluate the performance of Ni/C multilayers at higher energies, X-ray reflectometry at several energies were performed in the range 8-70 keV by using a Ni/C multilayer with 100 periods and d = 3.9 nm ($\Gamma \approx 0.5$)[9]. Reflectivities of more than 80% are observed in the energy range between 20-40 keV. A decrease in peak reflectivity and an increase in bandwidth $\Delta\Theta/\Theta$, as shown in fig., 11 (filled circles) is found above 40 keV. The decrease in peak reflectivity reflects the finite roughness of the interfaces, which becomes more and more important for increasing photon energy and decreasing angle of incidence.
The peak reflectivity follows the same trend as the W/C reference multilayer does. For the Ni/C multilayer, the bandwidth is double but less dependent on the energy in this particular case. It is shown that Ni/C multilayers work satisfactorily in the hard X-ray range up to 70 keV and offers an alternative for W/C multilayers especially for low bandwidth applications.

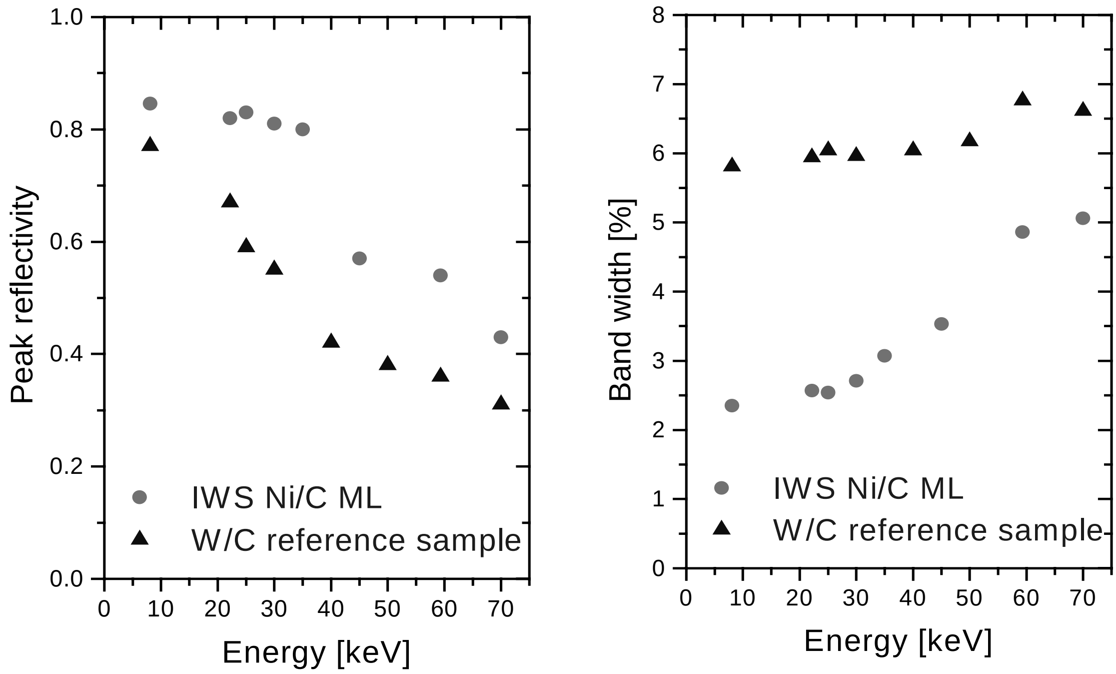


Fig. 11: Peak reflectivity (left) and bandwidth (right) of the 1. order Bragg reflection vs. photon energy for a Ni/C multilayer with 100 periods compared with a W/C reference multilayer with 100 periods (d = 4.7 nm, Γ= 0.37) The measured intensities were normalized to reflectivities by using measured intensities of the direct beam.

5. APPLICATION

Because of their striking X-ray optical properties, the above mentioned material combinations are very well suited for the fabrication of multiplayer systems for Göbel Mirrors used as parallel beam optics in X-ray reflectometry and diffractometry.
An advanced arrangement of Göbel Mirrors is demonstrated in fig. 12. A second Göbel Mirror is arranged at the diffracted beam side in this twin Göbel Mirror arrangement (TGM). With this face-to-face arrangement the parallel beam concept is realized on the diffracted beam side, too.

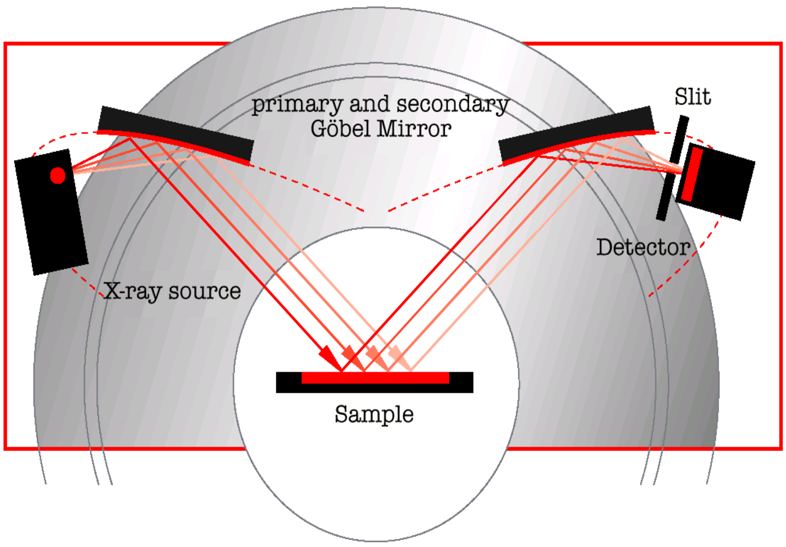


Fig. 12: Setup of twin Göbel Mirror arrangement in reflection geometry

Excellent beam parameters are achieved by first applications of Ni/C- Göbel Mirrors with Cu Kα- and Mo Kα- radiation[10].

For Cu Kα- radiation a high monochromized intensity of more than 10^9 cps is combined with low beam divergence ($\Delta\Phi <$ 0.02°) and superior suppression of Cu Kβ- radiation ($I(Cu\ K\alpha_1) / I(Cu\ K\beta) = 10^6$) (fig. 13).

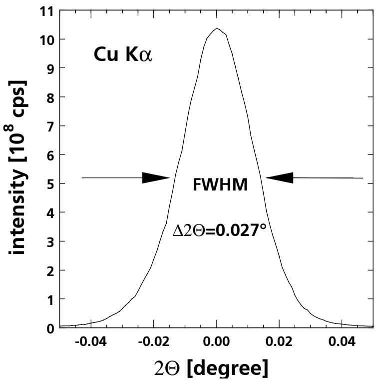


Fig. 13a: 2Θ-scan without sample: I > 1.000.000.000 cps

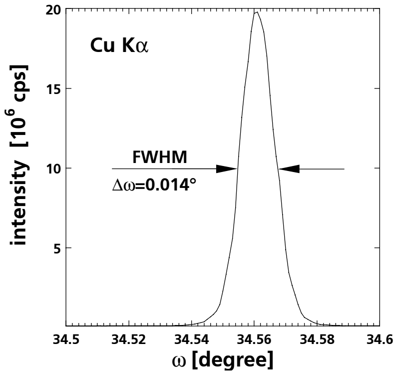


Fig. 13b: rocking scan Si (400) / silicon wafer: Δω< 0.02°

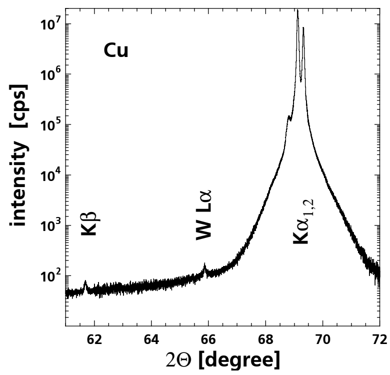


Fig. 13c: Θ-2Θ-scan Si(400) / silicon wafer: $I_{Cu\ K\alpha 1} / I_{Cu\ K\beta} >$ 1.000.000 : 1

For Mo Kα- radiation highest intensities of more than 200,000,000 cps are combined with low divergence, too (fig. 15). In the rocking curve of the silicon 004 reflection a FWHM of $\Delta\omega$= 0.012° was measured. The Mo Kβ- radiation is suppressed by an intensity ratio of ($I(Mo\ K\alpha_1) / I(Mo\ K\beta) = 90{,}000$).

By means of Twin Göbel Mirror Arrangement (TGM) a new quality of laboratory inhouse-reflectometry was created. There are some further advantages besides the demonstrated excellent beam parameters for Cu Kα- and Mo Kα- radiation. These are sample fluorescence suppression, no influence of sample surface position errors on peak position for reflectometry and diffractometry and easy and fast sample alignment for example offer new possibilities and fields of application in X-ray diffractometry and reflectometry.

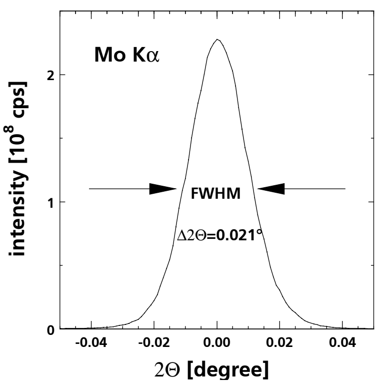


Fig. 14a: 2Θ-scan without sample: I > 200.000.000 cps

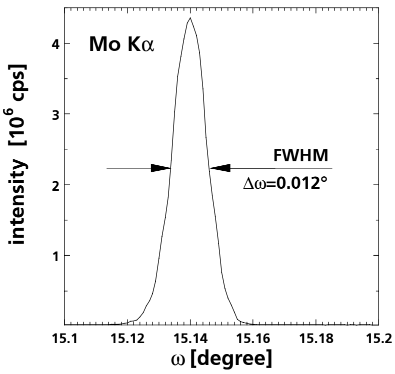


Fig. 14b: rocking scan Si (400) / silicon wafer: Δω< 0.02°

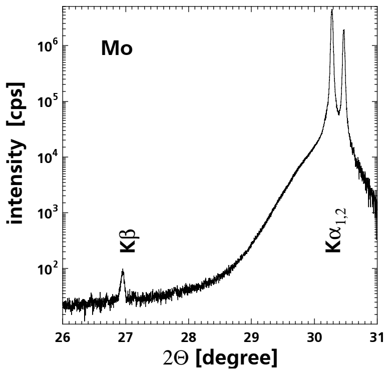


Fig. 14c: Θ-2Θ-scan Si(400) / silicon wafer: I $_{Mo K\alpha 1}$ / I $_{Mo K\beta}$ > 90.000 : 1

Measurements of retained austenite in steel with copper radiation can now be performed because of the suppression of the Kβ- and of the fluorescence radiation. Detection of contents of residual phases in the order of 1% in X-ray diffractometry can be realized with primary beam intensities of more than 10^9 cps (Cu Kα) (fig.15).

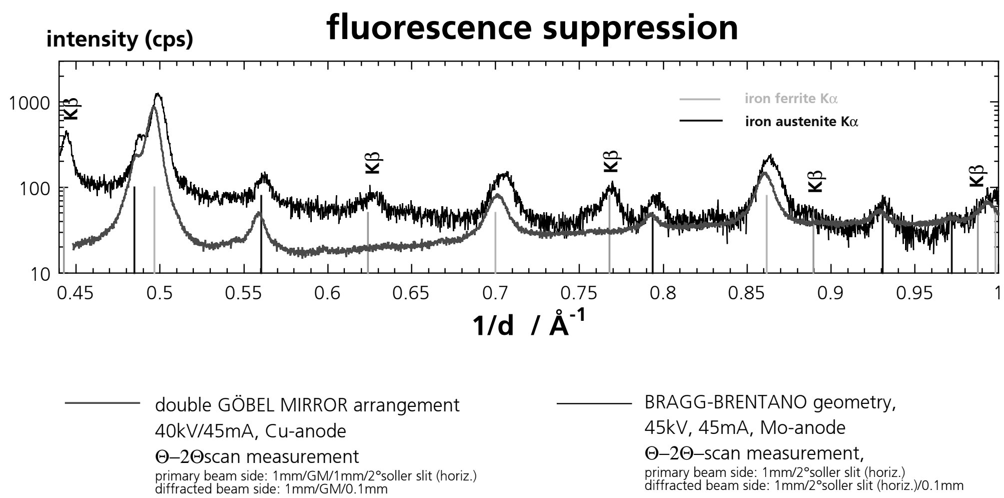


Fig. 15: Comparison of steel characterization by Cu Kα- radiation with TGM arrangement and by Mo Kα- radiation with Bragg-Brentano geometry

In TXRF (total reflection X-ray fluorescence) the background radiation can be reduced by means of flat Ni/C or Ni/B_4C X-ray mirrors. In this way the detection limit of mobile TXRF spectrometers becomes comparable with conventional 1.5 kW TXRF spectrometers[11].

6. SUMMARY

Ni/C, Ni/B_4C and Mo/B_4C are preferred material combinations for X-ray optics in the energy range above 8 keV. Except the energy range close to Ni K-edge (E= 8.3 keV) and preferred for Cu Kα- radiation and for energies E> 20 keV high reflectivities are achieved at multilayers with Ni- absorbers. For Mo Kα- radiation Mo/B_4C multilayers are preferred because of the highest theoretical and experimental reflectivities. Reflectivities of the 1st order Bragg reflection of more than R= 65% can be realized with period thicknesses d > 3 nm in the selected energy ranges by using the optimum material combination.

PLD is found as a wide usable multilayer deposition technique. PLD fabricated multilayers are characterized by smooth and sharp interfaces and high reproducibility of single layers across layer stack. In general, it is expected that the interface roughness is dominated by the roughness of the substrate surface.

Therefore the performance of the characterized multilayers consisting of Ni- or Mo- absorbers depending on the application energy is close to the simulation.

As a result optimized multilayers can be made available for designated applications.

In particular for Mo Kα- radiation an improvement of the Göbel Mirror performance can be expected by substitution of the currently used Ni/C multilayers by Mo/B_4C systems.

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