Ultrastrong nanocrystalline binary alloys discovered via high-throughput screening of the CoCr system

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Nanocrystalline (nc) alloys are stronger than their coarse-grained versions. Here, we report ultrastrong alloys, discovered via high-throughput screening of the nc CoCr system. The nc materials library was fabricated using magnetron co-sputtering. The alloys consist of textured, columnar structures with grain size in the nanometric regime. We found that the texture and phase composition can be tailored by changing the Cr concentration. In the investigated region of the nc CoCr system, a relatively broad spectrum of yield strength, determined via micropillar compression tests, was found ranging from 1.41 GPa up to 3.64 GPa. The remarkable strength increment was caused by a chemically- and thermally-driven phase and microstructure evolution of the system. The strongest alloys were found in the regions containing the 6CoCr phase, which was considered previously as metastable. Density functional calculations revealed that the 6CoCr phase is more energetically favourable in Cr-rich regions compared to single-phase simple solid solutions (HCP, BCC). Experimental results showed that the range of its occurrence is wider than previously thought, i.e. after annealing the 6CoCr phase was found above 44 at. % of Cr. We demonstrate that systematic screening of materials libraries can boost the discovery of new materials with outstanding properties.

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1. Introduction

The interest in understanding the nature and properties of nanocrystalline (nc) systems is motivated mainly by the opinion “smaller is stronger”, which is firmly rooted in the materials science community [1–4]. With decreasing grain size, enhanced mechanical properties can be attained, such as strength, wear resistance and toughness, which are attributed to a large volume of atoms located at the grain boundaries [5–7]. Due to the superior mechanical properties of nc materials compared with their coarse-grained versions, tremendous efforts have been dedicated for their analysis. The in-depth studies of nc pure metals, such as Cu, Ni, Al, Mo, Ta, W, Fe and Cr [8–15], binary alloys, e.g. PtAu [7], NiCo [16], and multicomponent alloys, including high entropy systems, e.g. NbTaMoW [17,18] and CoNiFeAlCu [19], were performed. Researchers, despite obtaining very attractive properties, were mostly focused on investigating the mechanical properties of materials with specific chemical compositions. As the universe of nc materials with outstanding properties is extensive, their probing requires the use of highly efficient experimental methods. The search for new materials can be accelerated through the use of combinatorial deposition techniques such as co-sputtering [20,21], and high-throughput characterization techniques, e.g. automatic chemical analysis and phase analysis with programmable sample-positioning stages, as well as high-speed nanoindentation [22,23]. In contrast to conventional methods, such approaches allow for the fast screening of a wide range of compositions and correlation with searched properties, e.g. mechanical, optical, magnetic, etc. [24].

The main goal of this study is to evaluate the efficacy of gradient libraries for identifying the optimal composition in nc systems from the point of view of mechanical properties. As an example, we selected the CoCr system, synthesized via magnetron co-sputtering, in a wide compositional range. The alloys based on the CoCr system exhibit interesting properties, like good wear and corrosion resistance, high tensile strength, good biocompatibility, high magnetization, and high coercive force. Consequently, they find applications as surgical implants [25,26], in the aerospace industry [27] and also as thin films used for the production of mag-

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netic recording media [28,29]. Studies on CoCr thin films were performed mainly up to 22% of Cr (all compositions in this work are given in at. %), due to their magnetic properties [30]. However, phase and orientation-dependent mechanical properties of the high-chromium nc CoCr system remain poorly understood, leaving ambiguous puzzles. They concern the influence of the synthesis via magnetron sputtering on the formation of metastable phases, their stability and decomposition paths, and finally their effect on mechanical properties [31,32]. The strength of the high-chromium nc CoCr alloys has not yet been reported, so it is not clear in what range of chemical composition the strongest alloys are located. Furthermore, the most significant scientific question that remains unanswered is which factors influencing the strength of the nc CoCr system are dominant?

The first stage of our work is devoted to structural characterization in order to understand the influence of the synthesis method on the formation of metastable phases and their thermal stability. The experimental results are discussed with respect to the equilibrium phase diagram and density functional theory (DFT) calculations. Next, we analyzed the effect of the chemical composition on thin film texture. The mechanical properties of the material library were investigated via nanoindentation and micropillar compression tests. Finally, the chemical composition, structure, and mechanical properties were correlated, which allowed determining dominant factors influencing the strength of the investigated alloys from the nc CoCr system. The findings of this study are transferable to different systems and can be used to optimize the strategy of high-throughput searching for materials with exceptional properties.

2. Experimental

2.1. Material

The CoCr thin film, with a gradient chemical composition, was deposited at room temperature (RT) onto an oriented (100) silicon wafer by magnetron co-sputtering. The silicon wafer had a 200 nm thick diffusion barrier composed of amorphous silicon nitride, which is characterized by a high melting point and low reactivity. The presence of the diffusion barrier was essential for the annealing experiment. For the deposition, high purity Co (99.99%+) and Cr (99.95%) targets with diameters of 3 in. were used. Deposition was performed at a base pressure of less than 9.0 × 10⁻⁷ mBar and working pressure of approx. 6.1 × 10⁻³ mBar. A schematic diagram of the magnetron co-sputtering is shown in Fig. 1a.

To investigate the stability of the microstructure, annealing was performed. Region A, presented in Fig. 1b, was cut out and annealed at 670 °C for 24 h. The process was carried out under vacuum at 7.0 × 10⁻⁶ mBar.

2.2. Chemical composition and thickness of the film

The chemical composition and thickness of the deposited thin film was determined using the X-ray fluorescence (XRF) spectrometer X-Ray XDV-SSD by Fischerscope. A measurement array of 30 × 30 (total 900) of equally spaced measurements was made. A beam energy of 50 kV with a spot size of 0.3 mm were selected for the analysis.

2.3. Phase analysis

Phase identification along the chemical gradient of the thin film was performed using X-ray diffraction (XRD). The XRD measurements were done with CuKα₁ and CuKα₂ radiations (λ = 1.5406 and 1.54439 Å, respectively) by means of the Bruker D8 Discover diffractometer, equipped with programmable sample-positioning stage. The phase composition of the CoCr thin film was identified using XRD data in the 2θ range from 20 to 110° obtained under the conditions: voltage of 40 kV, current of 40 mA, step size of 0.02° and the collection time at each step of 2 s. The exact same 17 areas, located in the central part of the sample (Fig. 1b), were examined both before and after annealing. The 0/2θ-scans were performed with an offset of 2° from the symmetrical diffraction geometry to avoid a too high intensity from the (000) reflection of the oriented (100) single crystal Si substrate. To determine the lattice parameters of the identified phases, the XRD data were analyzed using the profile-fitting software TOPAS 5 [33], based on the Rietveld method [34].

2.4. Theoretical methods

The density functional theory calculations were performed to predict an equilibrium phase for selected compositions in the CoCr system and to estimate trends in lattice parameters changes as a function of chromium concentration. The calculations were carried out using the full-potential (linearized) augmented plane-wave plus local orbital (FP-(L)APW + lo) method implemented in
WIEN2k code [35]. For the exchange–correlation functional, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE-GGA) scheme was used [36]. The calculations were done for a systematic series of CoCr supercells and have been converged with respect to the number of k points in the Brillouin zone and the \( K_{\text{max}} \) value of 8. Due to the high concentration of Cr in the investigated alloys, which lowers the Curie temperature [37], only non-magnetic states were taken into account in the calculations. The lattice constants of the hexagonal structures were determined via 2D-optimize package [38]. The equilibrium lattice constants at \( T = 0 \text{K} \) have been extracted by fitting the energy vs volume using a Birch-Murnaghan fit [39,40].

2.5. Microstructure investigations

Microstructural observations of the top and cross-section views of the thin film in selected regions were carried out using the SEM Hitachi S-4800 scanning electron microscope (SEM). Additionally, the microstructure of the selected alloys was studied by transmission electron microscopy (TEM) using the JEOL JEM2200fs, equipped with a field emission electron gun (FEG) operated at 200 kV. The TEM studies were performed on TEM lamellae, prepared via focused ion-milling (FIB technique) using the FIB-SEM Tescan Lyra FEG system.

2.6. Nanoindentation tests

Nanoindentation experiments were performed using a Hysitron Ubi nanoindenter, equipped with a diamond Berkovich tip. The loading and unloading segments of indentation took 5 s per segment and the holding time at the maximum load was 2 s. The hardness and the elastic modulus were determined using the Oliver-Pharr method [41]. Before measurements, the tip area function had been calibrated for the relevant measurement range. During the first experiment, a line scan of measurements spaced at an interval of 1 mm along the chemical gradient of the CoCr thin film was made. The load of 6 mN was selected to ensure a penetration depth of approx. 200 nm, i.e. 10% of the film thickness. The second experiment was carried out to estimate the size effect of three selected regions with different phase composition and/or texture containing 36, 50 and 66% of Cr, respectively. The 49 measurements were made on each region with the applied load in the range between 0.4 and 10 mN. Both experiments were performed in region A (Fig. 1b) before and after annealing.

2.7. Fabrication of micropillars and flat punch compression test

The nc CoCr micropillars with diameters of \( \sim 1.2 \mu m \) were fabricated from the 2.2 \( \mu m \)-thick film using the FIB-SEM Tescan Lyra FEG system. The micropillars were fabricated in CoCr regions containing 36, 50 and 66% of Cr, respectively, in two states, i.e. in as-deposited state and after annealing at 670 °C for 24 h. The dimensions of the micropillars and the taper were determined from SEM images. The small aspect ratios of the micropillars, varied between 1.8 and 2, were selected to reduce the possibility of micropillars buckling [42]. The taper angles of the micropillars were between 3.5° and 5.5°. At least six micropillars were compressed to estimate the strength of the investigated region. The microcompression test was performed using an Alemnis in situ nanoindenter with a 5 \( \mu m \) side-flat diamond indenter. The experiments were performed in the SEM chamber of the Philips XL30 ESEM FEG. The micropillars were compressed under the displacement-controlled mode at strain rate \( (\dot{e}) \) of \( 10^{-3} \text{s}^{-1} \). The load–displacement curves were corrected for instrument and compliances [43] before converting them into engineering stress–strain curves. Stress values at 0.2% strain offsets of the engineering stress–strain curves were considered as the yield strengths of the respective films.

3. Results

3.1. Compositional and thickness distribution

The XRF analysis of the as-deposited CoCr thin film is presented in Fig. 2. The materials library covers a wide compositional range, i.e. from 33 to 69% of Cr. The thickness of the thin film mostly exceeds 2 \( \mu m \). Fig. 3 shows the effect of annealing at 670 °C for 24 h on lateral diffusion. It is visible that the lateral changes in composition are marginal and are below 1%.

3.2. Structural characterization

Fig. 4 shows results obtained from XRD analysis of the CoCr material library. The XRD data were correlated with chemical composition, determined via XRF (Figs. 2 and 3). Fig. 5 shows representative Rietveld refinements of the X-ray diffraction patterns collected at 36, 50 and 66% of Cr in as-deposited and annealed at 670 °C for 24 h states, with appropriate phase indexing. From Fig. 4, it is visible how the reflections’ intensities and positions change as a function of Cr concentration in the range between 36 and 67%. Fig. 4a presents results for the as-deposited states. Three characteristic regions, marked as 1, 2 and 3, can be distinguished. Macroscopically, these regions exhibit differences in color, visible with the naked eye (Fig. 1b). Regions 1 and 2 correspond to the \( \varepsilon \)CoCr phase with the hexagonal symmetry (space group P6_3/mmc). However, between the regions, there is a clear difference in texture. In region 1, intensity of (011), and (112) Bragg reflections dominate. With increasing Cr contents, the intensity of both reflections gradually decreases and below \( \sim 46\% \) of Cr (region 2, Fig. 4a) the (010)_e and (002)_e reflections exhibit higher intensities. From \( \sim 52\% \) of Cr, the (002)_e and second order (004)_e reflections of the \( \delta \)CoCr phase with the cubic symmetry (space group Pm\text{3}n) appeared.

The effect of annealing at 670 °C for 24 h on phase and texture evolution is shown in Fig. 4b. The intensity of reflections corresponding to both \( \varepsilon \)CoCr and \( \delta \)CoCr phases significantly increased, while their broadening decreased, suggesting microstructural changes, i.e. growth and/or strain reduction of the crystallographically coherent domains. The difference in the reflections’ intensity is more clearly visible in Fig. 5. The range of phase occurrence, identified in as-deposited state, is significantly expanded. Consequently, the region containing \( \varepsilon \)CoCr and \( \delta \)CoCr phases is broader compared to the as-deposited state and is located between 44 and 65% of Cr. In the case of the \( \varepsilon \)CoCr phase, additional reflections, such as (012)_e and (113)_e were found. Furthermore, in the annealed state, additional reflections are visible, which correspond to neither the \( \varepsilon \)CoCr nor \( \delta \)CoCr phase. The number of reflections available raises some uncertainty in identifying the phases. Nevertheless, considering all known phases based on the CoCr system [37], the new reflections most likely correspond to the (Cr, Co)\text{2}O\text{3} (space group R\text{3}c) and \( \gamma \) phase (space group P4\text{2}2\text{m}2\text{m}2\text{m}). Interestingly, in the case of the \( \varepsilon \)CoCr phase, anisotropy of the (002)_e reflection was observed, which is clearly visible in the inset of the Fig. 5c. The (002)_e reflection was fitted using two unit cells of \( \delta \)CoCr phase with slightly different lattice constants.

3.3. Ground-state structures

In this section, we focus on the phase stability at \( T = 0 \text{K} \) for the selected CoCr system compositions. Fig. 6 presents the total energy per atom vs volume per atom for CoCr alloys containing 50, 62.5 and 75 at. % of Cr in BCC, HCP and \( \delta \)CoCr-based crystal structures.
From Fig. 6 it can be found that with increasing chromium contents the total energy of the considered structures increases. In the CoCr50 alloy (Fig. 6a) the equilibrium structure with the lowest total energy as a function of the volume is the HCP. Interestingly, the δCoCr structure has a slightly greater energy, however, still clearly lower than the BCC structure. For the CoCr62.5 alloy (Fig. 6b), we found that the most energetically favourable structure is the δCoCr and the BCC structure has the highest energy. In the CoCr75 alloy, the equilibrium structure is the δCoCr, however, the BCC structure has lower energy than the HCP structure.

3.4. Microstructural evolution

The grain morphology of the selected regions, presented in Fig. 7, suggests that the film grows via the mechanisms typical for “zone I” and “zone T” according to Thornton classification [45]. Surface morphology of thin films for alloys containing 36, 50 and 66% of chromium is clearly different (top view, Fig. 7a). The CoCr50 and CoCr62.5 alloys exhibit very fine fibre-like morphology (zone I), while the CoCr75 alloy presents much coarser grains (zone T). In zone I, the film contains small diameter fibres, which is determined by the nucleation density and statistical fluctuation [46]. However, it is visible that the grain morphology in the top view of the CoCr50 alloy resembles a fine plate-like structure, while in the case of the CoCr62.5 alloy grains exhibit equiaxed shapes. The grain morphology of the CoCr50 alloy is also equiaxed, however, the tops of the grains consist of a sloped surface, with fourfold mirror symmetry. Such morphology and grain size, which is most likely a result of the growth via mechanism of zone T, suggests higher self-surface diffusion compared to the CoCr52.5 and CoCr62.5 alloys. After annealing (Fig. 7b), more cracks in the thin film were found, which is related to thermal stress and structure evolution. Nevertheless, based on cross-sections, the columnar structure was maintained. The width of columns was determined to be 37 ± 12 nm, 118 ± 64 nm and 65 ± 17 nm for the CoCr36, CoCr50 and CoCr66 alloys, respectively. After annealing the width of the columns slightly increased to 53 ± 12 nm, 126 ± 67 nm and 79 ± 19 nm for CoCr36, CoCr50 and CoCr66 alloys, respectively.

Fig. 8 shows the effect of chromium concentration and annealing at 670 °C for 24 h on the microstructural evolution in the nanocrystalline Co-Cr alloys. In the cross-sectional view, revealed via TEM, it is visible that columnar structures contain many nano-subgrains. The nanocrystalline structure is also confirmed by selected area electron diffraction (SAED) patterns, shown in insets to the corresponding TEM images. In the as-deposited state, the reflections are significantly broadened compared to the annealed state and form clear Debye-Scherrer rings. In the CoCr36 alloy, grains and/or subgrains sizes are limited by the width of the columns. During annealing, the coarsening of grains and/or subgrains took place, which is manifested by an increase in the intensity of the dominant reflections in the SAED pattern in Fig. 8b. In the CoCr50 alloy, the blurred rings in the SAED pattern indicate very fine nanocrystalline or even a partially amorphous structure (Fig. 8c). The crystalline regions are significantly smaller than the width of the columns (Fig. 7). Annealing at 670 °C for 24 h caused recrystallization and significant coarsening of the grains (Fig. 8d). Similarly, in the CoCr66 alloy after annealing, much coarser grains were revealed. Simultaneously, the strong texture, found in the as-deposited state, was strengthened, which can be concluded based on sharper reflections in the SAED pattern in Fig. 8f. Moreover, in each of the alloys after annealing, the presence of additional rings was found, which indicate the appearance of new phases in the structure, most likely (Cr,Co)2O3 and σ phase.
Fig. 4. X-ray diffractograms collected along the chemical gradient of CoCr materials library, following the scheme presented in Fig. 1b. (a) As-deposited state. (b) Annealed at 670 °C for 24 h state. X-ray diffractograms were correlated with compositional data, obtained using XRF. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Representative Rietveld refinements of X-ray diffractograms collected at 36, 50 and 66% of Cr in as-deposited (D) and annealed at 670 °C for 24 h states, with appropriate phase indexing. $I_{obs}$ – measured XRD data, $I_{calc}$ – modelled X-ray diffractograms in Rietveld refinement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
3.5. Hardness and Young’s modulus vs composition

The effect of Cr concentration on hardness and Young’s modulus of the CoCr materials library is shown in Fig. 9. The data were divided into three regions with different texture and/or phase composition based on XRD analysis (Section 3.2.). In region 1D (D refers to as-deposited state), hardness seems to be chemical composition independent. Only a very small negative slope of the fit line was found. With increasing chromium contents in the range between 46 and 52% of Cr in region 2D, it is visible that the hardness increases from 2.69 to 3.58 GPa (the hardness values found on the fit lines were taken into account). Concurrently, in region 2D the largest spread of hardness values was observed, which is most likely associated with the highest roughness found in this region (Fig. 7, region containing 50% of Cr). In region 3D, the highest hardness values were obtained, which increased with increasing chromium contents up to 3.82 GPa at 69% of Cr. After annealing at 670 °C for 24 h, the hardness of the whole library increased. It is visible that hardness increases with increasing chromium contents, however, the slope of the fit lines strongly depends on texture and/or phase composition of the investigated material. In addition to the hardness, Young’s modulus was also determined based on the contact stiffness. Interestingly, the lowest Young’s modulus at the level of ~132 GPa was recorded for region 3D with (002), oriented phase. After annealing, the Young’s modulus increased significantly, especially in regions 2A and 3A (A refers to annealed state). The lack of a clear trend was found in region 1A due to high data spread. In general, data spread was significantly greater in the annealed state, most likely due to the larger amount of surface cracks.

Fig. 10 presents the effect of nanoindentation depth on mechanical properties of the CoCr materials library, estimated in the load range between 0.4 and 10 mN and in selected regions containing 36, 50 and 66% of Cr. An overall tendency of increasing hardness and Young’s modulus with decreasing nanoindentation depth can be found. Thus, the average values and standard deviations were determined in the plateau region, i.e. between 150 and 200 nm of nanoindentation depth. Probably the main factors influencing the observed increase in the Young’s modulus along with a decrease in the nanoindentation depth are the surface roughness, which depends on the texture and phase composition (Fig. 7), the presence of oxides on the surface (Fig. 4), and microcracks (Fig. 7) around which the stress fields are rapidly changing. It seems that at shallow indentation depth the load–displacement characteristic is dominated by surface effects. This can be indirectly concluded based on nanoindentation data obtained after annealing, where surface oxides and greater density of microcracks were observed. The effect of nanoindentation depth on the hardness and Young’s modulus is clearly greater after annealing than before. Considering the region between 150 and 200 nm of the nanoindentation depth, it can be seen that the influence of annealing on the mechanical properties in the alloy containing 36% Cr was relatively small. Hardness increased by 13% from 3.1 to 3.5 GPa, while Young’s modulus remained almost on the same level of 148 GPa. Changes in mechanical properties after annealing were more clearly visible in regions containing 50 and 66% of Cr (Fig. 10b and c, respectively). In the alloy containing 50% of Cr, the hardness increased by 30% from 3.3 to 4.3 GPa and Young’s modulus increased from 145 to 172 GPa. The biggest changes in mechanical properties were noticed for the alloy composed of the (002), oriented δ phase in the as-deposited state and containing 66% of Cr, i.e. hardness increased by 44%, from 4.1 to 5.9 GPa, while Young’s modulus increased by 25%, from 132 to 165 GPa. It seems, therefore, that the mechanical properties are significantly influenced by temperature-driven structural evolution.

3.6. In situ micropillars compression

Fig. 11 shows results of micropillars compression in selected regions of the CoCr materials library containing 36, 50 and 66% of Cr, as well as SEM images of the micropillars after deformation. When comparing the mechanical properties of different alloys, surface micro-cracks should be taken into account. We observed that
crack density depends on chemical composition and it increased significantly after annealing. The highest micro-crack density was observed in chromium-rich regions (Fig. 7). The presence of micro-cracks in the micropillar might cause its destruction at a lower stress level. In order to determine compressive yield strength with statistical importance, we compressed at least six micropillars per state. We noticed that micropillars from the same series behaved similarly under load which is manifested in the relatively low standard deviation of compressive yield strength. Nevertheless, as the chromium content and micro-crack density increase, a greater underestimation of the investigated alloy mechanical properties should be expected. Engineering stress–strain curves (Fig. 11) display very high compressive yield strength. The lowest compressive yield strength of 1.41 ± 0.05 GPa was noted for the CoCr36 alloy in as-deposited state (Fig. 11a). A monotonic increment of the flow stress was observed up to 0.08 of engineering stress. Above this value, a mild decrease in the flow stress was observed, which is related to the splitting and buckling of the columnar grains. The exemplary micropillar compression tests were recorded as movie files (see videos V1 and V2). In as-deposited state, with increasing chromium contents, the compressive yield strength increased to 2.04 ± 0.21 GPa and 2.78 ± 0.25 GPa for CoCr50 and CoCr66 alloys, respectively (Fig. 11b and c). Despite the larger grain size in the CoCr50 alloy, compared to the CoCr36 alloy, similar behaviour of the flow stress and mechanisms of micropillars plastic deformation were observed. In the highly deformed micropillars, columns underwent a high degree of grain bending. Simultaneously, at the top part of micropillars, grain coarsening was found (Fig. 11a and b). However, in the CoCr66 alloy, the columns seemed to be more brittle compared to the other alloys (Fig. 11c). After annealing, a significant increment in the compressive yield strength was noted, i.e. 1.62 ± 0.03 GPa for the CoCr36 alloy, 2.48 ± 0.30 GPa for the CoCr50 alloy and 3.64 ± 0.22 GPa for the CoCr66 alloy, which compared to the as-deposited state corresponds to an increase of 15, 22 and 31%, respectively. In post-mortem SEM analysis of the micropillars, no changes in deformation mechanisms were found. Due to splitting and bending of columns in the investigated alloys during compression the elastic properties were not analyzed.

4. Discussion

4.1. Phase composition of nanocrystalline CoCr system

The equilibrium CoCr system contains five phases, i.e. the liquid, the FCC solid solution (αCo-based), the HCP solid solution (εCo-based), the BCC solid solution (Cr-based) and the intermetallic σ
phase [37]. Fig. 12 shows the calculated phase diagram of the CoCr binary system. The composition range, investigated in this study, is marked with the blue rectangle. The equilibrium phases at RT are HCP (εCoCr) and BCC phases. However, at the temperature of the annealing experiment (670 °C), four regions can be distinguished depending on Cr concentration, i.e. HCP, HCP + γ phase, γ phase, BCC + γ phase. In the investigated case in as-deposited state, the εCoCr and the δCoCr phases were identified (Figs. 4 and 5).

In the past, the δCoCr phase, in contrast to the εCoCr, was considered as metastable, as it was observed only under special circumstances [31,32]. Yukawa et al. [32] studied CoCr particles, synthesized by evaporation and condensation in argon, and found that the δCoCr phase exists in the range between 55 and 100% of Cr. Their results are in good agreement with our observations of CoCr thin film, synthesized via magnetron co-sputtering. In our case, in the as-deposited state, the δCoCr phase was already visible above 52% of Cr (Fig. 4). It is intriguing that the δCoCr phase, belonging to the Frank-Kasper phases family [47] and having a complex structure, forms during sputtering instead of simple solid solutions, such as FCC, HCP or BCC, which are present in the equilibrium CoCr system (Fig. 12). However, based on our ab initio DFT calculations, shown in Fig. 6, the appearance of the δCoCr phase in Cr-rich region during deposition at RT can be expected. The DFT results indicate that the δCoCr phase in the CoCr62.5 and CoCr75 alloys has lower energy per volume compared to single-phase simple solid solutions (HCP, BCC) and thus its formation is more energetically favourable, at least in the low-temperature regime.

The presence of δCoCr phase reflections from the same crystallographic plane family and their high intensity suggests strong preferential growth during deposition. It should be noted that the σ phase belongs to the same family of phases, however, it was not formed during sputtering. Pundt and Michaelsen [48] suggested that the formation of the σ phase in thin films is due to its complex tetragonal structure containing 30 atoms. After annealing at 670 °C for 24 h, partial reactions of δ → σ in the range between 65 and 67% of Cr, δ → σ + ε in the range between 52 and 65% of Cr and ε → δ + σ in the range between 44 and 52% of Cr, were observed. Consequently, a three-phase region containing εCoCr, δCoCr and σ phases, between 44 and 65% of Cr was formed. These results show that the compositional range of the δCoCr phase occurrence is much broader than previously thought [32]. Despite the long annealing time of 24 h, the δCoCr phase did not fully decompose, which proves its high thermal stability. The anisotropy of the (002), reflection, observed after annealing, is related to the chemical modulation on the interfacial regions, driven by partial phase transformation of the δCoCr phase into (Cr,Co)2O3 and σ phase. The local chemical modulation is coupled with the structural modulation, which is reflected in broader range of unit cell lattice parameters and anisotropic shape of the (002), reflection. It can be expected that the formation of (Cr,Co)2O3 is a surface event, however, it might have resulted in local depletion of grains in Cr and Co and additional broadening of Bragg reflections, observed on X-ray diffractograms.

4.2. Lattice parameters vs Cr concentration

Fig. 13 presents changes in εCoCr phase’s lattice parameters and c/a ratio, while Fig. 14 shows changes in δCoCr phase’s lattice parameter as a function of Cr concentration. For comparison,
annealing, changes in lattice parameters of vs Cr concentration, calculated via DFT. Interestingly, after Fig. 13 it is visible that the lattice parameter of the as-deposited state was observed. From theoretical lattice parameters, determined via DFT method, were to the web version of this article.)

Furthermore, the lattice parameter of the CoCr phase vs Cr concentration, after annealing, is very similar to results of Yukawa et al. [32], despite the fact that they reported the CoCr phase with greater lattice parameters. The differences in lattice parameters can be a result of different in-plane stress and crystallite size obtained by Yukawa et al. [32].

These findings indirectly suggest that lattice parameters of phases in the nc CoCr system are strongly crystallite size-dependent. Experimental results of other authors showed that lattice parameters of nc materials can contract, e.g. Cu [51], Au [52], Sn and Bi [53], or expand, e.g. Pd [54], Nb [55] and Ge [56]. Furthermore, lattice contraction up to critical grain size (~40 nm) and expansion below this value was reported in Ni [57]. Therefore, it seems clear that crystallite coarsening in the CoCr thin film after annealing at 670 °C (~0.56 of the melting point) resulted not only in higher intensity of the Bragg reflections (Figs. 4 and 5) but also in changes in the phases’ lattice parameters, identified in this study (Figs. 13 and 14). To understand the crystallite-size dependence of the lattice parameters, several models considering the roles of different factors have been proposed. Among them are approaches that take into account intracrystalline pressure [58], interface stress [59], interfacial excess volume [60], grain boundary enthalpy [61], excess grain-boundary volume [62], a supersaturation of vacancies [63] and effective negative pressure corresponding to the electrostatic energy of the interatomic interaction (also referred to as Madelung pressure) [64]. Significant changes in the energetic state of the interfaces and most likely in-plane stress in the nc CoCr system after annealing plays an important role in the mechanical behaviour, which is manifested in hardness (Figs. 4 and 5) and strength (Fig. 11) increment.

4.3. Preferred orientation

In this study, the substrate was coated with an amorphous diffusion barrier (silicon nitride). Consequently, the formation of randomly oriented islands at the early stage for low-temperature thin film deposition should be facilitated [65]. The interface energy γi for a given substrate surface is in general strongly related with the crystallographic orientation of the particle, formed during deposition. In the case of an amorphous substrate, γi can change with rotation through two axes parallel to the substrate, however, not for rotations through the axis perpendicular to the substrate. In such case, γi minimization can lead to texture uniformity, i.e. all grains will have the same planes parallel to the plane of the film [65]. A columnar morphology of grains is related to deposition at a relatively low temperature, at which significant grain boundary motion did not occur during coalescence or thickening. For materials with high growth velocity anisotropies, low atomic surface self-diffusivities and low grain boundary mobilities, the increase in columnar grain width with increasing thin film thickness can be expected, which was observed, e.g. in region containing 50% Cr (Fig. 6). It is possible that the occlusion of slow-growing grains by faster-growing grains occurred, in directions out of the plane and in the plane of the film [45,66]. The lack of clear widening of the columnar grains with increasing distance from the film/substrate interface suggests limited surface diffusion of the deposited atoms. Therefore, during film growth the orientation of initial nuclei might be preserved [45]. This behaviour can be assigned to regions containing 36 and 66% Cr (Fig. 7).

To study the preferred orientation of a certain crystal plane (hkl) in nc CoCr film the texture coefficient TC(hkl) was employed [67]:

![Image](image-url)
Fig. 10. Results of hardness and Young's modulus analysis in as-deposited and annealed at 670 °C for 24 h states. Measurements were performed in selected regions of the CoCr materials library containing (a) 36, (b) 50 and (c) 66% of Cr in the load range between 0.4 and 10 mN. The average values and standard deviations were determined based on data points in the range of nanoindentation depth between 150 and 200 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 11. In situ compression experiments. Exemplary compressive engineering stress–strain curves with SEM images of micropillars in the as-deposited state before and after deformation in selected regions of the CoCr materials library containing (a) 36, (b) 50 and (c) 66% of Cr. D refers to as-deposited state and A refers to annealed state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
\[ T_{C(hkl)} = \frac{I_{hkl}}{\sum_{hkl} I_{hkl}} \]  

where \( T_{C(hkl)} \) is the texture coefficient of the \((hkl)\) plane, \( I \) is the measured intensity, \( I_0 \) is the intensity for randomly oriented sample and \( N \) is the number of reflections. The \( I_0 \) intensities were modelled for \( \varepsilon \text{Co} \) and \( \delta \text{Cr}_3\text{Co} \) unit cells using VESTA software [68]. Fig. 15 shows the effect of Cr on texture in nc CoCr system. Equation (2) shows that for a fully aligned sample the \( T_{C(hkl)} \) is equal to \( N \), while for a randomly oriented sample the \( T_{C(hkl)} \) of each crystal plane is equal to unity (1). As the number of Bragg reflections, observed on X-ray diffractograms, differs depending on Cr concentration (Fig. 4), we decided to normalize \( T_{C(hkl)} \) and apply the same \( N \) number to each X-ray diffractogram. We used \( N = 7 \), which is the highest number of reflections found on single X-ray diffractogram in the investigated CoCr system. As a result, the effect of Cr on texture evolution in different regions can be directly compared. The consequence of using \( N = 7 \) in the equation (2) is that for a randomly oriented sample \( T_{C(hkl)} \) of each crystal plane will be equal to \( N/n \) instead of unity, where \( n \) is the number of observed reflections in the analyzed X-ray diffractogram. The \( N/n \) values were plotted in Fig. 15a and b for reference. The \( T_{C(hkl)} \) was calculated separately for each crystal plane \((hkl)\) of \( \varepsilon \text{CoCr} \) and \( \delta \text{CoCr} \) phases. The greater the difference between \( T_{C(hkl)} \) Crystal planes and \( N/n \), the more the sample is textured. To describe the globally preferred orientation, we additionally plotted the standard deviation \( \sigma_{SD} \) of all \( T_{C(hkl)} \) values of each diffracting crystal plane (Fig. 15c). The \( \sigma_{SD} \) values allow to compare the degree of orientation between different samples. The lower \( \sigma_{SD} \) values indicate more randomly oriented phases. The \( \sigma_{SD} \) of \( T_{C(hkl)} \) values is defined as [69]:

\[
\sigma_{SD} = \sqrt{\frac{1}{N} \left( T_{C(hkl)} - 1 \right)^2}
\]

The results indicate that the preferential orientation of the \( \varepsilon \text{CoCr} \) phase in the investigated film is the strongest in the CoCr36 alloy with dominating \((112)\varepsilon \) plane (Fig. 15a). With increasing Cr contents up to ~46%, the difference between \( T_{C(hkl)} \) and \( N/n \) values decreases and above this value slightly increases. The weakest texture was observed in the region between 42 and 47% of Cr. The same trend is also clearly visible for \( \sigma_{SD} \) values in Fig. 15c. Such observations suggest a chromium-dependent change in growth mechanism during deposition. Indirectly, it can be concluded that, depending on the chromium concentration, crystal growth speeds will change for specific crystallographic directions. Faster-growing crystals will grow over the slower-growing ones leading to the
so-called competitive growth texture [70]. After annealing at 670 °C for 24 h, the texture seems to be weaker compared to the as-deposited state. Furthermore, the region with the weakest texture is broadened and it is located between 42 and 53% of Cr. The decrease in $T_C(hkl)$ and $\sigma_{SD}$ is caused by nucleation and/or growth of grains with orientations, which were not observed in as-deposited state. The $d$-CoCr phase in as-deposited and annealed states has only two Bragg reflections, which belong to the same family of planes, thus the $T_C(hkl)$ is equal to 7 ($N$) and $\sigma_{SD}$ has maximum value, which means that the phase exhibits out-of-plane orientation alignment.

4.4. Mechanical properties

The nanoindentation results (Fig. 9) revealed a general trend of hardness increment with increasing chromium contents, which is in agreement with findings reported by Mahdavi et al. [71], who investigated electrodeposited CoCr alloys. We noticed that hardness is sensitive to chromium-driven texture and phase composition changes. Simultaneously, we found that temperature-driven microstructure evolution including grain size growth, changes in texture and formation of the secondary phases, have a significant effect on hardness increment. Of course, when analysing materials libraries, solid solution strengthening cannot be neglected. However, based on hardness trends in regions with different phase composition and/or texture (Figs. 4 and 9), it seems clear that the solid solution effect alone is insufficient to explain remarkable strengthening of the CoCr alloys with increasing chromium contents.

Grain refinement is known to induce significant strengthening in metallic systems. Nonetheless, at grain sizes in the nanometric regime, the breakdown of classical Hall-Petch behaviour can be found, typically resulting in less strengthening than would be expected through the Hall-Petch type response [5]. The reason of this is that the nanometric grains can support a very small number of dislocations, thus their internal interactions result in limited strengthening of the material. Concurrently, other aspects of the material, such as grain boundary volume fractions, triple junction volume fractions, grain boundary sliding, and grain boundary diffusion become important in terms of deformation and strengthening mechanisms [5,60,72]. This can explain why CoCr alloys in as-deposited state exhibit lower strength compared to the annealed state (see Section 3.6). Annealing caused grain coarsening and reduction of grain boundary volume fraction (Fig. 8), which was reflected in higher strength. The grain coarsening effect explains the strength increment in CoCr$_{36}$ alloy, in which no changes in
phase composition and texture were observed. However, in the case of the CoCr50 alloy, the effect of secondary δCoCr, σ phases and (Cr,Co)2O3, formed during annealing (Figs. 5 and 8), on the mechanical properties should be additionally taken into account. Secondary phases typically nucleate at the grain boundaries and act as additional barriers for dislocation motion. Interestingly, temperature-driven microstructural evolution with the partial transformation of the δCoCr to the σ phase in the CoCr66 alloy and most likely formation of the (Cr,Co)2O3 on the grain boundaries caused the largest increments in hardness and strength. A clear correlation between nanoindentation and micropillar compression results was found, which is in agreement with the generally accepted knowledge that strength is proportional to hardness [73,74]. Fig. 16 shows the yield strength of the alloys, investigated in this study, as a function of hardness. It is visible that yield strength is higher for alloys with larger hardness. For most metals and alloys in this hardness to yield strength (H/σy) ratio is around 3 [73,74]. The H/σy ratios for alloys, investigated in this study, are significantly lower than 3 and fall between 1.6 and 2.2. Typically, low H/σy values can be found in alloy systems with high defect density, such as highly-deformed or nanocrystalline materials [75–77]. Fig. 17 shows the strength-density Ashby chart for metals and alloys. The nc CoCr alloys, investigated in this work, are compared to commercial bulk alloys and nc metals and alloys. It is visible that nc metal and alloys clearly exhibit greater strength compared with their coarse-grained (conventional) versions. Readers should be aware that the data presented for the nc materials were obtained using micropillar compression tests. In these tests, the authors often examined the effect of micropillar size on the mechanical properties. Micropillar compression studies revealed an increase in strength for single-crystal pillars with diameters below 10 μm [78–80]. In small volumes of material, the free path of dislocations is reduced, therefore during plastic deformation at large strain, the dislocations relatively early begin to interact with each other and self-organize, forming crystallographic substructures. Such microstructural changes are reflected in the flow stress increment [81]. Taking into account the small size of the micropillar and nanocrystalline structure, much greater mechanical properties compared to single crystals or coarse-grained materials should be expected. The strength data for nc materials, presented in Fig. 17, refer to the maximum values obtained for a given material at room temperature. Additionally, in the case of compression of micropillars, in which the grain size is much smaller than the pillar size, as in the tested case, it should be expected to obtain the same strength both in the micro- and macro-scale [82,83]. Therefore, a materials library produced by magnetron co-sputtering can be used to determine the macro-scale strengths of bulk materials if a comparable nc microstructure is produced.

In the investigated part of the nc CoCr system, a relatively broad spectrum of compressive yield strength was found i.e. from 1.41 GPa for the as-deposited CoCr50 alloy up to 3.64 GPa for the annealed CoCr66 alloy and they partially go beyond the box of regular alloy properties for the given density class. The compressive yield strength of regions with different composition depends on solid solution strengthening, grain size, texture and presence of secondary phases. The highest compressive yield strength of 3.64 GPa was reported in the annealed CoCr66 alloy consisted of highly textured δCoCr phase, additionally strengthened by the σ phase and most likely by the (Cr,Co)2O3.

Fig. 16. Yield strength as a function of the hardness. The values next to the data points represent the hardness to yield strength (H/σy) ratio. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 17. Strength-density Ashby chart for metals and alloys. This chart compares properties of the nc CoCr alloys, investigated in this study, with commercial alloys [90] and nc metals and alloys [18,84–89,91–95]. The strength of nc alloys was obtained via compression tests (mainly using micropillar compression) except the strength of the cold-drawn pearlitic nc FeC alloy, which was obtained via tensile test [89].

5. Conclusions

In summary, the nc CoCr materials library was fabricated via magnetron co-sputtering. The high-throughput approach of this study allowed for efficient screening of a broad range of alloys from the investigated system and to draw the following conclusions:

1. The DFT calculations revealed that the cubic δCoCr phase in Cr-rich region has lower energy per volume compared to single-phase simple solid solutions (HCP, BCC) and thus its formation is more energetically favourable, at least in the low-temperature regime. Furthermore, the experimental results showed that the range of the δCoCr phase occurrence is wider than previously thought, i.e. in the as-deposited state, the δCoCr was detected above 52% Cr, and after heat treatment above 44% Cr. Long-term annealing for 24 h at 670 °C proved the high thermal stability of the phase. Only partial reactions of δ → σ in the range of 65 and 67% of Cr, δ → ε in the range between 52 and 65% of Cr and ε → δ + σ in the range between 44 and 52% of Cr were observed.
2. Lattice parameters of phases in the nc CoCr system strongly depend on crystallite size and compositional separation between primary and secondary phases, formed during annealing by partial phase transformation. A change in the...
energetic state of the interfaces in the nc CoCr system after annealing plays an important role in mechanical behaviour, which is manifested in hardness and compressive yield strength increment.

3). The texture and phase composition can be tailored by changing the Cr concentration. Highly textured regions in contrast to weakly textured regions tend to maintain an initial grain orientation during heat treatment.

4). In the investigated region of the nc CoCr system, a relatively broad spectrum of compressive yield strength was found ranging from 1.41 GPa up to 3.64 GPa. The remarkable strength increment was caused by chemically- and thermally-driven phase and microstructure evolution of the system. It is important to note that synthesized alloys have the grain size much smaller than the tested pillar size, thus the same strength both in the micro- and macro-scale can be expected if a comparable nc microstructure is produced. Consequently, the alloys reported in this study can act as lead materials for scale-up.

The results herein reported demonstrate that high-throughput screening of materials libraries can significantly boost the discovery of new materials with outstanding properties. We have achieved ultrastrong materials in a binary system, so it can be expected that by increasing complexity of the system, the area of metallic alloys’ mechanical properties can be significantly expanded. Thus, it seems natural to focus efforts on multicomponent alloys to improve mechanical properties by solid solution strengthening, grain boundary engineering and precipitation of strengthening phases.

CRediT authorship contribution statement

K. Wieczerczak: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. O. Nowicka: Investigation, Visualization. S. Michalski: Investigation, Visualization. T.E.J. Edwards: Investigation, Writing - review & editing. M. Jain: Investigation, Writing - review & editing. T. Xie: Investigation, Writing - review & editing. L. Petró: Investigation, Writing - review & editing. X. Maeder: Investigation, Writing - review & editing. J. Michler: Investigation, Writing - review & editing. Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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