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Structure of 310S steel-based Fe–Cr–Ni coatings

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Parameters have been presented of fabrication and characterisation of microcrystalline coatings applied by the magnetron sputtering method in a pure Ar atmosphere at the pressure of 0.03 Pa and the table voltage of –50 V. Coatings of the AISI 310S steel were applied on an AISI 310S steel substrate for 1 h. The characterization of the coatings in terms of phase composition was made by the XRD, GXRD and TEM techniques. It was found that the coatings have a columnar bcc-type structure, different from that of steel being sputtered. In the coating structure, an fcc phase has also been found by the TEM technique. The bcc structure is metastable, and as early as after 15 min of annealing at 600 °C it transforms into the fcc phase but a certain amount of unconverted bcc phase remains in the structure. The texture of the bcc structure varies along the coating thickness starting from (211) at the substrate to (110) in near-surfacial part. The transformation of the metastable bcc phase into the fcc phase as a result of 30 min annealing at 600 °C does not remove the texture but changes the crystallographic texturing plane $(211)_{bcc}$ to $(220)_{fcc}$.

Key words: *microcrystalline coating; magnetron sputtering; columnar structure*

1. Introduction

The magnetron sputtering deposition (MSD) method is one of the basic and most important methods of vacuum deposition (PVD). It is successfully used to deposit thin coatings for a wide range of applications, such as electronic equipment and magnetic recording media, as well as for improving the wear resistance, corrosion resistance and heat resistance of elements. The MSD technique parameters include Ar pressure in the magnetron chamber, substrate temperature, the distance between the targets and the surface being coated, and the magnitude of voltage applied to the substrate [1, 2]. In an investigation into the optimization of the MSD process, a correlation between the process parameters and the properties and microstructure of coatings has been found. The process parameters define the coating deposition rate which, in turn, determines the size of grains in the coatings and their hardness.

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Coatings of corrosion resistant steels, widely used in industrial conditions, exhibit increased resistance to oxidation, corrosion and erosion compared to steels of the same composition. The most modern grades of austenitic steels, including 310S steel, are also used for coatings [3–6]. Under normal conditions (including sub-zero treatment), these steels have an austenitic structure resulting from the stabilizing effect of Ni. However, during the deposition of coatings of these steels by the PVD methods such as magnetron sputtering, metastable phases of the bcc structure may form in the coatings, despite the amount of nickel being as high as 25% [7]. It was found that more Ni was necessary to stabilize the fcc phase in sputtered Fe–Cr–Ni steels. The fcc single phase can be formed at room temperature in as-sputtered 330S steel coatings (36 wt. % of Ni) [8].

The paper presents results of the X-ray examination of the phase composition of AISI 310S steel coatings deposited by the magnetron method on an AISI 310S steel substrate. The phase structure on the coating cross-section was examined immediately after deposition and after a short-duration annealing at 600 °C.

2. Material

Coatings of 310S heat-resisting steel, deposited on a substrate of the same steel by the magnetron sputtering method, were examined. The starting steel had an austenitic structure with numerous precipitates of chromium carbide. The magnetron targets were two discs, each of the dimensions of 63×49×2 mm^3, and those of the coating substrate were 10×10×1 mm^3 commercial sheet cut-outs of the same steel grade. Prior to the deposition of coatings, the steel surface was cloth buffed and washed with acetone in an ultrasonic washer. After suspending the cut-outs in the magnetron vacuum chamber, both the coating substrate surfaces and the targets were additionally cleaned for several minutes by a glow-discharge method under an argon pressure of approx. 3 Pa. During coating deposition, the temperature of the cut-outs was ca. 150 °C. Other parameters of the magnetron deposition process were as follows: argon flow pressure 0.03 Pa, table polarization potential –50V, and the distance between the targets and the substrate 200 mm. Two targets situated opposite to one another, each of a power of 3 kW, were used. The time of coating deposition was 1 h.

Table 1. Chemical composition of the substrate/targets (standard) and the coating (EDX analysis), wt. %

Steel	C max	Si max	Mn max	S max	Cr	Ni	Fe
310S	0.1	1.5	2.0	0.015	24–26	19–22	rest
coating	–	0.7	1.3	–	25.8	18.6	53.7

In the previous investigation, a uniform dispersion of constituent elements in coatings of this composition and deposited with this method was shown. EDX measurements showed that the chemical composition of coatings corresponded to the contents of alloying elements in the 310S steel used for the targets. The Ni content was at the level of 19 wt. % (Table 1). An analysis on the coating cross-section also showed a uniform distribution of constituent element over the coating thickness [9]. The coating thickness, as determined microscopically, was 8.5 μm.

3. Experimental

The coatings were subject to observations using an electron transmission microscope Philips CM 20 and examined on a Seifert 3003TT polycrystalline diffractometer. The coating cross-sections were subject to examination by TEM. The XRD examination was performed directly on the coating surfaces using filtered $K_\alpha Co$ (0.17902 nm) radiation. The X-ray examination was carried out by the classical method in the diffraction angle range 2θ of 40–110° and by the constant-angle exposure method in the angular range of occurring reflections (111) from the fcc phase and (110) from the bcc phase [9]. In X-ray measurements on a diffracted beam, long Soller slits were used, which limited the diffusion of the diffracted beam to 0.4°. The intensity of diffraction reflections was measured with a stepwise counter shift of 4 s/step. The Bragg angles were read out from the reflection maxima. Coatings as magnetron-deposited (after 2 months of storage at room temperature) and coatings subject to one-time and two-time annealing at 600 °C for 15 min were examined. The annealing was carried out in ambient atmosphere.

3. Results

The coatings examined had a globular surface morphology, typical of magnetron-deposited coatings. On their cross-sections, the coatings had a columnar structure. Due to a local insufficiently tight adhesion of columns to one another, discontinuities occured within the coating. A separation of columns appeared on substrate irregularities (Fig. 1).

The XRD analysis, performed in the symmetric diffraction geometry, showed that, in spite of the fact that the austenitic steel targets had been sputtered, the coating had a ferritic bcc structure (Fig. 2). In the angular range applied, the diffraction pattern obtained from the 310S steel contains reflections typical of the fcc austenitic structure (111), (200) and (220). In the diffraction pattern obtained from the coating, weak reflections from the fcc phase occur, similar as in the substrate steel, but reflections from the bcc phase are dominant. The bcc phase is characterized by a strong texture of (211) planes and an abnormally weak (110) reflection. Due to the coating thickness (8.5 μm) being smaller than the depth of $K_\alpha Co$ radiation penetration into the coating material, the reflections from the austenitic phase originate from the substrate.

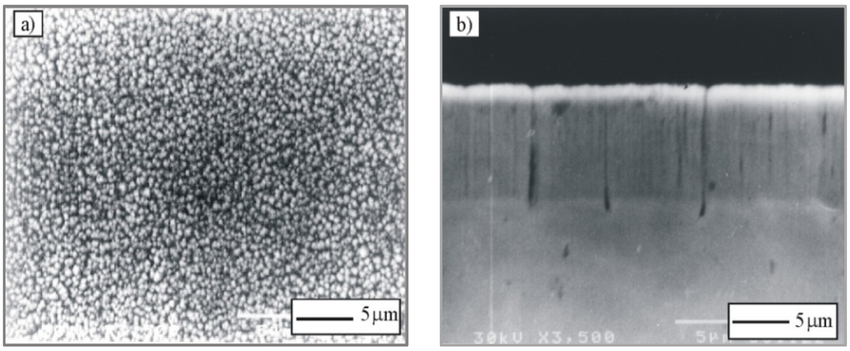

Fig. 1. Globular morphology of the coating surface (a) and the coating cross-section with a visible column separation on substrate surface irregularities

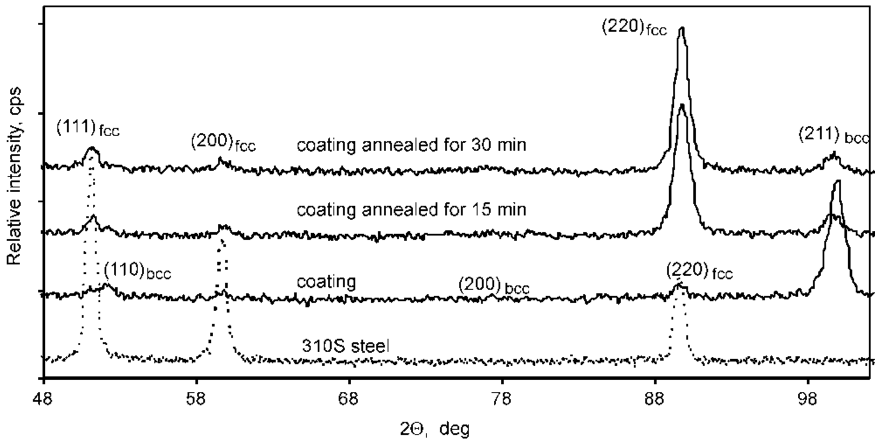

Fig. 2. Diffraction patterns of 310S steel and coating before and after annealing at 600 °C in air atmosphere (the intensities of reflections from the steel has been decreased respectively); the details are given in Table 2

Table 2. Details of the diffraction patterns shown in Fig. 2

d, nm	0.207	0.203	0.180	0.143	0.126	0.117
Structure	fcc	bcc	fcc	bcc	fcc	bcc
Relative intensity, %						
310S steel	100	–	61	–	42	–
Coating	10	19	9	7	14	100
Coating, 15 min	21	–	12	9	100	19
Coating, 30 min	19	–	12	6	100	15

Diffractions from the coating cross-sections, obtained using the electron transmission microscopy, also indicated a predominance of the bcc phase in the coating structure. In the electron diffraction image, beside the strong reflections from the bcc phase, weak reflections from the fcc phase also appear. This means that small amounts of the fcc phase are present in the coating structure (Fig. 3b).

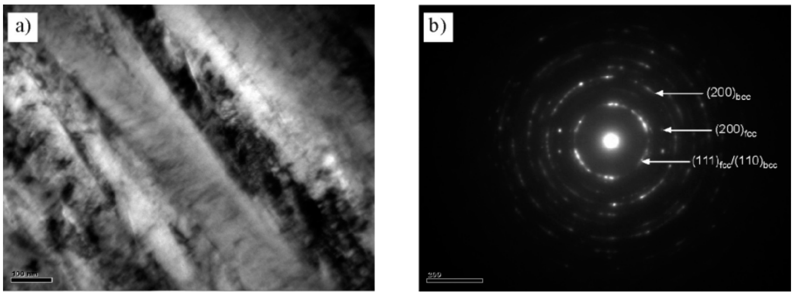

Fig. 3. Highly defected bcc phase columns in the coating (a) and the electron diffraction from the coating at its mid-thickness (b)

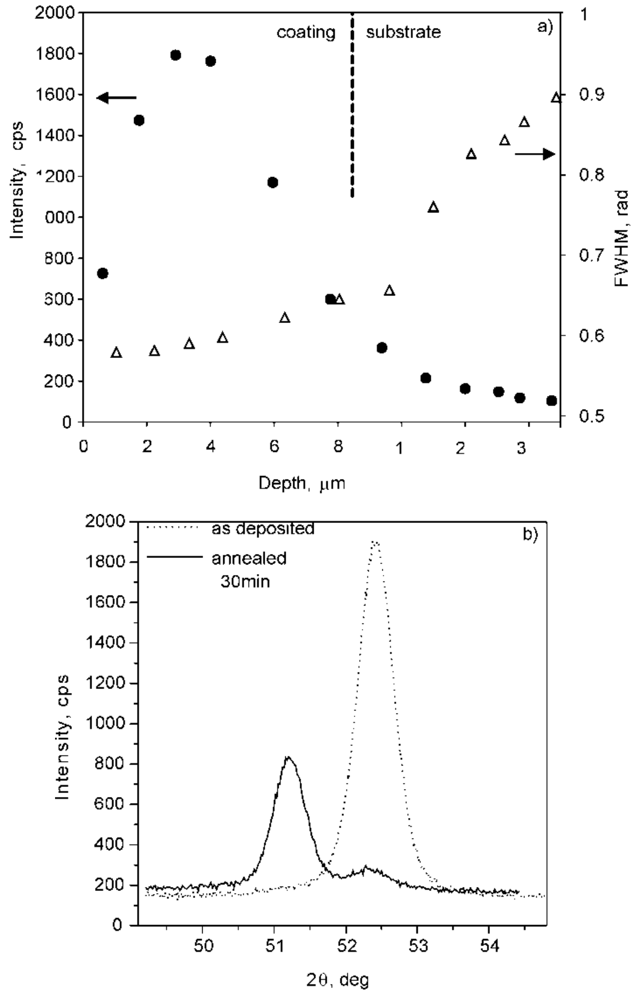

Fig. 4. Intensity of reflection 110 as a function of measurement depth (a) and comparison of main reflections of as deposited or annealed at 600 °C/30 min 310S steel determined for the coating at the depth ca. 3 μm (b)

The TEM observations indicate that the bcc phase columns have diameters ranging from 0.2 μm to 0.5 μm and exhibit features of highly defected structures (Fig. 3a). The degree of structure defecting (and the associated size of subcrystallites) increases from the coating surface towards the substrate. The electron diffractions from the outer part of the coating are typical of polycrystalline structures. The diffractions from the coating near the substrate exhibit more continuous rings typical of amorphous structures. Figure 3 shows an intermediate diffraction image, obtained in the area of the coating mid-thickness. The defecting of the coating structure was also reflected in the profile of diffraction peaks obtained in GXRD examinations and originating from deeper coating layers, through decreasing their intensity and increasing their half-intensity width (Fig. 4a). The highest intensity of reflection (110) from the bcc phase was determined for the measurement depth in the range of 3–3.5 μm (Fig. 4a).

After short annealing, the diffraction image of the coatings totally changed. As early as after 15 min of annealing at 600 °C, the bcc and the fcc phases coexist in the coating. Intensities of the (110) reflections from the bcc phase decreased, and the fcc phase was predominant in the coating. The transformation of the metastable phase bcc into the fcc phase did not remove the coating texture. As a result of the change in crystallographic structure, the texture of (211) planes in the bcc phase was taken over by planes of the (220) type in fcc phase. Re-annealing of the coating under the identical conditions did not result in any changes in the coating structure. A summary of the relative intensities of reflections recorded after annealing of the coating is given in Table 2. In the diffraction image of the annealed coatings, similarly as for the non-annealed coating, the reflections from the fcc phase can be partially summed with the reflections from the coating substrate, since in the classical measurement the beam of radiation penetrated into a depth greater than the coating thickness, whereas the reflections from the bcc originate solely from the bulk of coating. In Figure 4b diffraction patterns obtained by the GXRD methods for measurement depth corresponding to intensity maximum read from Fig. 4a are compared. It results from these diffractogramms that after 30 min of annealing at 600 °C certain amount of bcc phase in the coating structure remained which did not undergo transformation. Because of texturization, a direct evolution of phases concentration is hard to accomplish. The set of diffractions determined for various depths of X-ray penetration into as deposited 310S coating has been demonstrated elsewhere [10].

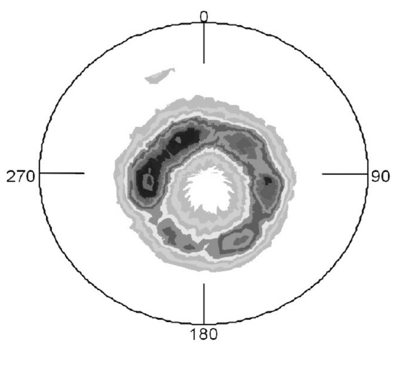

Fig. 5. Polar figure of {111} planes; coating annealed at 600 °C for 15 min

5. Discussion

Chemical composition of coatings (EDX analysis performed from the coating cross-section) was contained within the quantitative limits specified for 310S steel. The amount of austenite-stabilizing Ni corresponded to the lower limit of content specified for 310S steel. Thus, during the magnetron deposition of coatings, the Cr/Ni quantitative ratio, which would have changed the steel structure to bcc, did not change. This indicates that in the process of magnetron deposition of the coatings under investigation, factors determining phase compositions of the coatings are the deposition process parameters. Two-phase composition of the tested coatings which has been obtained in the process conditions is in good agreement with the "substrate temperature-Ni contents" for sputtered austenitic steels diagram presented by Zhang et al. [6]. As results from this diagram, monophase austenitic structure in sputtered 310S steel is formed upon substrate temperature exceeding 200 °C. The structure of 310S steel-based coatings on 310S substrate has also been tested by Liu et al. [4], however, the thickness of the coatings was much lower than those examined in the present paper. The authors found monophase bcc structure of the coatings although they did not mention the substrate temperature. As results from the empirical diagram [6], formation a pure bcc phase at temperatures higher than 0 °C is impossible. One can assume that the coating thickness and rate of its deposition may affect phase composition of the final coating. The coatings thickness certainly influences its texturization. Based on diffractogramms of as sputtered 310S steel (Figs. 2 and 4b) one may conclude that the bcc phase shows a strong texturization of (211) planes at the substrate whereas in near-surfacial parts the (110) planes texture predominates.

It was also found that the bcc phase transformation into fcc phase takes place just after annealing of sputtered 310S steel at 600 °C during 15 mins. This temperature is clearly lower than that reported in literature (700 °C/1 h and 800 °C/20 min) [6]. Malavasi et al. [11] reported a constant disorientation of planes in the bcc phase around the axis perpendicular to the coating substrate. The same disorientation in a converted fcc phase was additionally demonstrated in this paper.

6. Conclusions

310S austenitic steel-based Fe–Cr–Ni coatings magnetron-deposited on a substrate of the same steel exhibited (with the process parameters applied) a structure of a bcc type with slight amounts of fcc phase detectable by TEM technique. The bcc columnar structure exhibits a texture which varies along the coating thickness from (211) at the substrate to (110) in near-surfacial parts of the coating.

The bcc structure is metastable, and as early as after 15 min of annealing at 600 °C it transforms into the fcc phase. A certain amount of unconverted bcc-phase remains in the structure.The transformation of the metastable bcc phase into the fcc phase during

30 min annealing at 600 °C does not remove the texture, but it changes the texturing planes from $(211)_{bcc}$ to $(220)_{fcc}$.

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