Structural and phase transformations in austenitic chromium-nickel steels during nanostructuring frictional treatment

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Abstract. The parameters of the structure and phase composition of austenitic structural steels subjected to frictional treatment with a sliding indenter were studied by X-ray diffraction and transmission electron microscopy. It has been found that the strengthening of deformation-stable austenitic steel was due to the formation of finely divided austenite, with the intensification of the grain-boundary and dislocation strengthening mechanisms. Additional strengthening of metastable austenitic steel was due to the formation in the surface layer of about 70% of the volume fraction of nanocrystalline strain-induced martensite. It is proposed to use nanostructuring frictional pretreatment as a promising method for hardening austenitic structural steels before the subsequent application of superhard, dead-hard, and heat-resistant nanocomposite coatings.

1. Introduction

Austenitic chromium-nickel steels are popular structural materials in the chemical, oil and gas producing, and medical industries, in thermal and nuclear power engineering. To increase the lifetime of stainless steels and to use them under special conditions (high temperatures, corrosive and abrasive environments, high mechanical loads), special processing of the surface layer is required. One of the effective state-of-the-art techniques for increasing operationally important characteristics of metal products is the formation of nanocomposite coatings on their surfaces by physical vapor deposition (PVD) [1, 2]. Such coatings are highly strong, wear-resistant, and thermally stable [3]. However, an essential disadvantage of nanocomposite coatings is their high brittleness, which manifests itself under significant deformation of the base during operation of coated products [4]. Therefore, dead-hard, (HV ~40 GPa), superhard (HV ~60 GPa), and heat-resistant thin-film coatings are mainly applied onto a high-strength structural steel substrate. The strengthening of the surface layer of relatively low-strength structural steels before applying nanocomposite thin-film coatings onto their surfaces considerably expands the area of application of such coatings. This is particularly relevant for soft ductile austenitic steels.

Frictional treatment with a sliding indenter is an effective technique for strengthening thermally nonhardenable chromium-nickel austenitic steels with different contents of nickel (~10 and 14 wt%), which stabilizes austenite to strain-induced γ→α' transformation [5-7]. Besides, the frictional
treatment of austenitic steels prone to contact seizure produces high-quality surfaces with low roughness and without material discontinuities [6, 8]. When coatings are applied, an important role is played by the strength characteristics and the quality of the substrate surface [9, 10]; therefore, frictional treatment can be considered a promising method of surface preparation of chromium-nickel austenitic steels for subsequent deposition of nanocomposite coatings. The structural-phase state of the surface layer of the substrate material is known to be able to affect significantly the mechanical and adhesive properties of coatings [10]. Therefore, it is relevant to study the features of the phase transformations and structural changes that may occur in the surface layers of austenitic steels during frictional treatment [11], i.e. at the stage of preparation for coating application.

Thus, the aim of this paper is to study the effect of frictional treatment on the structure and phase composition of austenitic chromium-nickel steels with different stabilities of austenite to strain-induced transformation. This will create a scientific basis for the formation of thin-film heat-resistant, superhard, and dead-hard nanocomposite coatings on friction-hardened austenitic steel surfaces.

2. Material and experimental procedure

The corrosion-resistant austenitic steels 12Cr18Ni10Ti (0.10 C, 17.72 Cr, 10.04 Ni, 0.63 Ti, 1.33 Mn, 0.57 Si, 0.227 Mo, 0.064 Co, 0.014 Nb, 0.057 Cu, 0.031 P, 0.014 S, the rest Fe, wt%) and 03Cr16Ni14Mo3Ti (0.03 C, 15.69 Cr, 14.17 Ni, 1.17 Ti, 0.25 Mn, 0.64 Si, 2.67 Mo, 0.03 Co, 0.004 Nb, 0.11 Cu, 0.030 P, 0.008 S, 0.043 V, the rest Fe, wt%) were studied. Samples of the 12Cr18Ni10Ti steel sized 98×38×8.6 mm were cut from a rolled sheet and water-quenched from 1050 °C. Samples of the 03Cr16Ni14Mo3Ti steel sized 36×36×6.5 mm were cut from round stock and water-quenched from 1100 °C.

The frictional treatment of austenitic steels was performed with a hemispherical synthetic diamond indenter, with the hemisphere radius \( R = 3.0 \) mm, sliding in a noncorrosive argon environment. The 12Cr18Ni10Ti steel was processed with the number of scans \( n = 11 \) and the load on the indenter \( P = 392 \) N; the 03Cr16Ni14Mo3Ti steel was friction loaded at \( n = 7 \) and \( P = 294 \) N. The smaller load and number of scans in the frictional treatment of the 03Cr16Ni14Mo3Ti steel are explained by the development of seizure on its surface when the load on the indenter is \( P = 392 \) N.

All the samples were cut on a Fanuc Robocut α-0iE electroerosion wire cutting machine. The structure was examined on a JEOL JEM-200CX transmission electron microscope with the use of unilateral mechanical and electrolytic thinning of the workpieces (foils). The phase composition and the integral breadth \( B \) of the line (111)\( _{γ} \) was determined on a Shimadzu XRD-7000 X-ray diffractometer in CrKα radiation.

3. Experimental results and discussion

X-ray diffraction phase analysis has shown that, during frictional treatment, strain-induced \( γ \rightarrow α' \) transformation actively develops in the surface layer of the 12Cr18Ni10Ti steel (figure 1 a, b). In the diffraction pattern, side by side with the austenite line (111)\( _{γ} \), there is the line (110)\( _{α} \), which corresponds to strain-induced \( α' \)-martensite (figure 1 b). The intensity of the peaks of martensite X-ray lines is higher than that of austenite ones, this being indicative of the predominance of the martensitic phase in the structure of the 12Cr18Ni10Ti austenitic steel after frictional treatment. The quantity of \( α' \)-martensite that has formed in the surface layer of the steel reaches 70 vol\%, and this testifies to the high metastability of the 12Cr18Ni10Ti austenitic steel to strain-induced martensitic phase transformation.

According to the data of X-ray analysis (figure 1 c, d), after frictional treatment, in the severely deformed thin layer of the 03Cr16Ni14Mo3Ti steel, the austenitic structure remains practically intact. In the diffraction pattern shown in figure 1 d there are X-ray line peaks of austenite (111)\( _{γ} \) and (200)\( _{γ} \) and a very low intensity peak of the (110)\( _{α} \) line, which corresponds to strain-induced \( α' \)-martensite. The low intensity of the peak of the martensite lines testifies to a low martensite content in the surface layer of the friction-treated 03Cr16Ni14Mo3Ti steel. The calculation has shown that the fraction of strain-induced martensite is at most 2 vol\%. Thus, the 03Cr16Ni14Mo3Ti steel has a very
high deformation stability, even under conditions of extremely severe plastic deformation implemented during frictional treatment.

As is known, the presence of strain-induced martensite may reduce the corrosive characteristics of austenitic steels [12]. However, the application of a nanocomposite coating onto a friction-treated 12Cr18Ni10Ti steel substrate can enhance the corrosion-resistance of the surface layer [13]. The decrease in corrosion resistance can be avoided if the 03Cr16Ni14Mo3Ti steel is used as the substrate material, which was shown above to be highly stable to strain-induced transformation.

The analysis of X-ray diffraction patterns shows that the frictional treatment of the austenitic steels under study increases the integral breadth $B$ of the $(111)_\gamma$ austenite line. For the metastable 12Cr18Ni10Ti steel, this increase amounts to 73 min (from $B=13$ min for the as-quenched state to $B=86$ min for the friction-hardened one). For the deformation-stable 03Cr16Ni14Mo3Ti steel, the increase in the austenite X-ray line breadth is 43 min (from $B=27$ min for the as-quenched state to $B=70$ min after frictional treatment). This increase in the breadth of the $(111)_\gamma$ X-ray lines is caused, first of all, by increased dislocation density in the austenite and increased microdistortions of the fcc austenite lattice [14].

In the initial as-quenched state, the structure of the 12Cr18Ni10Ti and 03Cr16Ni14Mo3Ti steels is represented by coarse (~2 μm) polyhedral austenite grains with a developed dislocation substructure [6, 7]. In the structure of the 12Cr18Ni10Ti steel there also are individual inclusions of titanium carbide TiC [6]. Transmission electron microscopy on unilaterally thinned thin foils demonstrates (figure 2) that frictional treatment causes intensive dispersion of the structure of the thin (~5 μm) surface layer of the austenitic steels under study. In the electron microdiffraction pattern for the 12Cr18Ni10Ti steel structure (figure 2 a) annular reflections of austenite $(111)_\gamma$ and martensite $(110)_\alpha$ are visible, this being consistent with the data of the X-ray diffraction phase analysis of this steel (figure 1 a, b). The dark-field images in the reflections under study indicate the formation of predominantly nanocrystalline (with crystallites sized below 100 nm), and submicrocrystalline structures of austenite and strain-induced martensite (figure 2 b, c) in the surface layer of the metastable steel under frictional treatment. In the surface layer of the deformation-stable 03Cr16Ni14Mo3Ti austenitic steel, frictional treatment results only in fragmented submicrocrystalline and nanocrystalline austenitic structures, as evidenced by the presence of annular reflections of austenite$(111)_\gamma$ and $(200)_\gamma$ in the electron microdiffraction pattern (figure 2 d).

**Figure 1.** X-ray diffraction patterns of the surfaces of the 12Cr18Ni10Ti (a, b) and 03Cr16Ni14Mo3Ti (c, d) steels, as-quenched (a, c) and friction-treated (b, d).
Figure 2. The structure of the surface layer of the friction-treated 12Cr18Ni10Ti (a–c) and 03Cr16Ni14Mo3Ti (d) austenitic steel samples: bright-field images and microdiffractions (a, d), dark-field images in the (110)\(\alpha\) (b) and (200)\(\gamma\) reflections (c).

It was reported in [6, 7, 15] that nanostructuring frictional treatment increases the microhardness of quenched austenitic steels from 220 to 710 HV 0.025 (by a factor of 3.2) for the 12Cr18Ni10Ti steel and from 270 to 720 HV 0.025 (by a factor of 2.7) for the 03Cr16Ni14Mo3Ti steel. Consequently, after frictional treatment, the surface microhardness values of these steels are about the same for the two steels (710-720 HV 0.025) despite a lower load applied to the indenter and a lower number of scans in the frictional treatment of the deformation-stable steel than in the treatment of the 12Cr18Ni10Ti steel. Thus, nanostructuring frictional treatment provides intensive strain-hardening of both austenitic steels, independently of the different phase compositions formed on their surfaces (figures 1, 2), and it can be recommended as a preparatory strengthening technique for subsequent application of high-strength nanocomposite coatings onto relatively soft austenitic steels.

The more than 3-fold hardening of the 12Cr18Ni10Ti steel after frictional treatment is due to the formation of a severely dispersed (up to the nano- and submicrocrystalline state) martensite/austenite structure and the appearance of 70 vol% of strain-induced martensite as a result of strain-induced phase transformation. This is evidenced by experimental data presented in figure 1 a, b and figure 2 a, b, c. It follows from figure 1 c, d and figure 2 d that the increase in the microhardness of the 03Cr16Ni14Mo3Ti steel under frictional treatment stems from the severe refinement of austenite grains and the corresponding intensification of the grain-boundary strengthening mechanism. The above-mentioned severe increase in the integral breadth of the austenite X-ray line in both steels under frictional treatment testifies to a sharp increase in the dislocation density during the formation of the nano- and submicrocrystalline structures of the surface layer.

Thus, the main contribution to the hardening of the 03Cr16Ni14Mo3Ti steel under frictional treatment is made by the dislocation and grain-boundary strengthening mechanisms, which become more active during the formation of nano- and submicrocrystalline austenite. In the case of the
frictional treatment of the 12Cr18Ni10Ti steel, side by side with the above-mentioned strengthening mechanisms, an additional contribution to strengthening is made by the formation of finely divided strain-induced martensite in the structure of the thin surface layer.

The effectiveness of the formation of heat-resistant, superhard, and dead-hard coatings on an austenitic steel substrate and the service properties of thin-film coatings can be largely determined by the structural-phase state of the surface layer, which has been formed by strengthening frictional pretreatment. Particularly, the studies have shown that, depending on the chemical composition of austenitic steels, frictional treatment can form a substrate with both austenitic and mixed martensite/austenite structures. This will enable one to study the effect the type of the lattice of the nanostructured steel substrate has on the adhesion of deposited thin-film coatings.

4. Conclusion
Frictional treatment has been proposed to be used as a preparatory strengthening technique for subsequent application of high-strength thin-film coatings. The development of structural and phase transformations in chromium-nickel austenitic steels under frictional treatment has been comparatively analyzed. It has been shown that, depending on the chemical composition of austenitic steels, frictional treatment can form a nanostructured substrate both with mixed martensite/austenite structures (in the metastable 12Cr18Ni10Ti steel) and with a single-phase austenitic structure (in the deformation-stable 03Cr16Ni14Mo3Ti steel). Effective surface hardening by frictional treatment (from 220-270 to 710-720 HV 0.025) is implemented in the 03Cr16Ni14Mo3Ti steel due to the grain-boundary and dislocation strengthening of austenite; in the 12Cr18Ni10Ti steel, an additional contribution is made by the progress of the strain-induced γ→α' transformation. The intensification of the studied mechanisms of strengthening promotes the formation nano- and submicrocrystalline structures of austenite and strain-induced α'-martensite in the thin surface layers of austenitic steels under frictional treatment.

The results obtained will serve as an important scientific basis for substantiating the new comprehensive technique for strengthening structural austenitic steels, which consists in frictional treatment followed by deposition of heat-resistant, superhard, and dead-hard nanocomposite coatings.

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