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Numerical simulation on phase stability between austenite and ferrite in steel films sputter-deposited from austenitic stainless steel targets

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ABSTRACT

This contribution presents a theoretical discussion on phase hierarchy stability between face-centered cubic (FCC), austenite, and body-centered cubic (BCC), ferrite, lattice structures of stainless steel (SS) films that are sputter-deposited from austenitic targets under non-reactive atmospheres. Data published in literature on both phase characterization and chemical composition of diverse SS films are interpreted anew in this contribution in the light of lattice stability thermodynamic simulations. For films obtained from 304 and 316 steel targets, thermodynamic simulations predict that the ferrite phase is more stable than the austenite phase at low thermal energies. In contrast, simulations forecast thermodynamic stability at low thermal energies of the austenite phase in films that are sputtered from 330 steel targets. The criterion of lattice stability reveals that structures observed in the experiments cannot be described comprehensively by thermodynamic states where either full atomic partitioning among phases is established or zero atomic partitioning takes place. Thereby, a description of an equilibrium with incomplete atomic partitioning is proposed here, with the aim of depicting the structures reported in the literature. Such an equilibrium with incomplete atomic partitioning adequately describes the gradual destabilization of ferrite and the increased fraction of austenite (up to fully austenitic structures), when either the substrate heating is intensified, or the Ni content of the alloy is increased, with an 73Fe18Cr9Ni, wt%, initial alloy as a basis.

1. Introduction

Current research stresses the multipurpose character of stainless steel (SS) films [1–3] which are being developed in pursuit of superior electrochemical corrosion resistance, oxidation resistance, tribological performance and mechanical strength [1–3]. Functional interlayers of SS in optoelectronic applications are being studied [4–6].

The face-centered cubic (FCC), austenite, and body-centered cubic (BCC), ferrite, phases are prevalent in steel films obtained by magnetron sputtering from austenitic SS targets under non-reactive atmospheres [7–9]. Ferritic-austenitic phase fractions are tunable through variations in either the target chemical composition or the substrate heating [9–11]. Table 1 lists the typical chemical compositions of austenitic SS grades used most frequently as targets.

Formation of intermetallic sigma (σ) [12], intermetallic epsilon (ε) [9] and amorphous [12,13] phases have been reported in sputtered SS films. In films alloyed with either carbon or nitrogen, the formation of carbides or nitrides has also been reported [14,15]. Stabilization of the amorphous phase has been achieved by cryogenic substrate cooling or by alloying the film with glass forming elements, namely carbon, nitrogen, and silicon [14–16].

Films that are sputtered from 304 SS and similar targets exhibit prevalence of ferrite when the substrate is not heated externally. At mild substrate heating (around 600 to 800 K), duplex ferritic-austenitic structures are reported, while at high substrate heating (higher than around 1000 K), prevalence of austenite is reported [9].

Prevalence of the ferrite, in as-deposited film structures alloyed with rather moderated Ni-content (around 10 wt%), has been the focus of several studies [17–19]. It has been pointed out that the assumed “more stable” austenite phase is absent in such films and, consequently, the ferrite phase observed experimentally has been classified as metastable [16,19,20]. While trying to explain the absence of the presumed more stable FCC phase, instead of the BCC one, Malavasi et al. pointed out that, “It is then likely that the α/vapor interfacial energy is lower than the γ/vapor one,” where α and γ stand for ferrite and austenite, respectively [12].

As a rule of thumb, the elemental composition of the SS target is successfully transferred to the SS film without drastic variations in the

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Table 1
Typical chemical composition of main atomic species in austenitic stainless steels referenced in this work, wt%.

Steel specification	Cr	Ni	Mn	Si	N	C	Others	Fe
UNS S30400[a]	17.5–20.0	8.0–11.0	2.0 max	0.75 max	0.1 max	0.08 max	–	Bal.
UNS S31600[b]	16.0–18.0	10.0–14.0	2.0 max	0.75 max	0.1 max	0.08 max	Mo, 2.0–3.0	Bal.
UNS S32100	17.0–19.0	9.0–12.0	2.0 max	0.75 max	0.1 max	0.08 max	Ti = 5(N + C); Mo, 0.75 max; Cu, 0.75 max	Bal.
UNS N08330	18.0–22.0	34.0 37.0	2.0 max	1.0–1.5	–	0.08 max	Cu, 1.0 max	Bal.
UNS S31000[c]	24.0–26.0	19.0–22.0	2.0 max	1.5 max	–	0.25 max	Cu, 0.5 max	Bal.

[a] There exists a similar specification, namely UNS S30403.
[b] There exists a similar specification, namely UNS S31603.
[c] There exists a similar specification, namely UNS S31003.

chemical composition [15]. However, differences in either Ni or Cr content between the target and film have been reported (differences in chemical composition lower than around 6% of nominal Ni or Cr content) [12]. Zhang et al. proposed that the decreased stability of the austenite phase in SS films sputter-deposited from a Fe18Cr8Ni (wt%) target is a partial consequence of the low levels of Ni in the film with respect to the target [20].

Stabilization of austenite, instead of ferrite, has been observed when (i) the targets were rich in Ni, (ii) the deposition experiments were carried out under sputtering gases rich in N_2, or (iii) the substrates were heated at rather high temperatures [9,20,21]. Stabilization of austenite, through the addition of alloying elements, could lead to either ferritic-austenitic duplex structures or fully austenitic structures [16,20,22]. Fig. 1 presents a diagram, proposed by Zhang et al. [20], for demonstrating the effects of both target chemical composition and substrate heating temperature on actual phases in as-deposited samples of SS films sputter-grown from austenitic targets (permission to reprint this figure was granted by Cambridge University Press). Zhang et al. [20] prepared this plot in Fig. 1 following an empirical approach, from data in their own work, as well as published data [9,12,15,20,23]. The high level of either Ni alloying or substrate heating needed to fully stabilize the austenite is emphasized in the original work [20].

Formation of crystalline phases in coatings magnetron sputtered from metallic targets is a far from equilibrium metallurgical phase formation. Advanced experimental researches correlating the deposition conditions with the phase structure of metallurgical sputtered coatings have been undertaken. One remarkable example in the realm of SS coatings is the work by Zhang et al. [20], where a comprehensive diagram (Fig. 1) relates the external substrate heating and SS chemical composition with coating phase structure. Zhang et al. [20] affirmed that “this plot is by no means a regular phase diagram. Instead, given the composition of sputtering target and substrate temperature during deposition, this plot can serve as a guide to what phases, single or mixture, will be formed” [20].

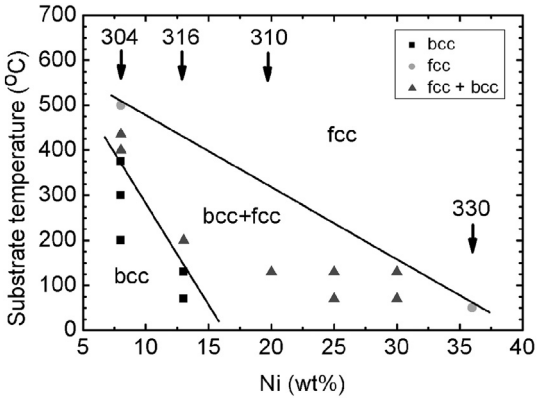

Fig. 1. Stability phase scheme proposed by Zhang et al. [20] for depicting the dependence of SS film structure with target chemical composition and substrate heating temperature. Permission to reprint this figure was granted by Cambridge University Press under license number 4414290227017. The diagram was constructed empirically for Zhang et al. [20] from their own results and additional data from the literature [9,12,15,23].

No research has been conducted to correlate the thermodynamic equilibrium conditions with observed phase fractions in metallurgical coatings magnetron sputtered. No work has been published on the role of either diffusion or atomic ordering in controlling the kinetics of phase formation in magnetron sputtering of metallic alloys.

This work presents an insight into the conditions of equilibria appropriate to depict the phase structure of metallurgical coatings magnetron sputtered. In this work, results available in the literature on both phase characterization and chemical composition of diverse SS films are analyzed aiming at stablishing what theoretical conditions of equilibria have a straightforward correspondence with the experimental evidence.

The aim of this work is to assess the lattice stability hierarchy between FCC and BCC phases in SS films that are grown by magnetron sputtering from austenitic targets under non-reactive atmospheres. Thermochemical phase stability of the lattice structures in diverse typical FeCrNi alloys is studied at different temperatures. This work presents a theoretical simulation of lattice stability hierarchy and not experiments were carried out.

Next section depicts the simulation methods used. Next, a section comparing diverse predictions of classical equilibria with experimental results on volumetric metallurgical alloys is presented. This section aims at stablishing the predictive capacity of the numerical model used and the associated database (TCFE5). Then, it is presented a section where it is predicted the ferrite to austenite relative phase stability under diverse equilibria states (both conventional equilibrium and diverse metastable equilibria). Those predictions are compared to actual ferrite to austenite phase fractions reported elsewhere for diverse SS sputtered coating. Finally, a discussion on the challenges for correlating actual phase fractions in SS sputtered coatings with thermodynamic simulations is presented.

2. Simulation methods

The thermochemical stability of lattice structures in diverse FeCrNi alloys was assessed by using the thermodynamic framework referred to as “Computer Coupling of Phase Diagrams and Thermochemistry” - Calphad. The commercial software Thermocalc and database TCFE5 were used. Full descriptions of the Calphad method and the Thermocalc interface are presented elsewhere [24,25].

The Thermocalc software was used to predict values of the Gibbs free energy, equilibrium phase fractions, and the equilibrium chemical compositions of different lattices as a function of temperature and Cr and Ni contents.

Simulations were carried out in systems with 1 mol of atoms at 1 atm (101,325 Pa) absolute pressure. Temperatures between 300 and 1300 K were assessed. Solid uncompressible phases were simulated. Thus, no meaningful changes in the equilibria predicted are induced by changes of around 1 atm of the absolute pressure.

At first, the Gibbs free energy as a function of temperature was