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Formation of metastable diffusion layers in Cr-containing iron, cobalt and nickel alloys after nitrogen insertion

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ABSTRACT

The formation of expanded austenite after nitrogen insertion into austenitic stainless steel and related CoCr and NiCr alloys is reviewed focusing on selected topics using existing literature and additional new experimental results: there is clear evidence for the exceptional behaviour of nitrogen in (Fe,Co,Ni)CrN alloys with fast diffusion. At the present, limiting the compositional field is not possible due to restrictions in accessible alloys. The expanded phase is characterized by a thermally activated interstitial diffusion with an activation energy of 0.8–1.0 eV. Surface oxides acting as barriers or insufficient nitrogen supply can lead to the reporting of false, lower diffusivities or apparent time dependent diffusivities. Furthermore, the decay of the metastable phase during the nitrogen insertion process will introduce additional artefacts in the diffusion rate. At the same time, a dynamic transition from a low expansion to the high expansion "expanded austenite" is identified.

1. Introduction

Transition metals nitrides and carbides are ceramics with technologically interesting properties as high chemical inertness, high melting point, high hardness and decorative appearance [1]. At the same time, their formation using straightforward physical vapour deposition (PVD) processes has been established in research and applied for more than a quarter of a century. Initially, commercial applications focused on TiN and CrN [2], followed by ternary compounds or multilayers [3,4].

The early transition metal nitrides and carbides are exceptionally stable due to the relatively low number of valence electrons [5]; subsequent transition metal groups and periods exhibit a decreasing stability as more electrons are occupying the outer orbitals [6]. There are reports in literature on formation of cubic FeN with either zincblende or sodium chloride structure as this phase is metastable only up to 400 °C in vacuum or even at reducing hydrogen atmosphere [7,8]. Ordered Co-N and Ni-N compounds are even more unstable [9–11]. To account for the common behaviour, these three metallic elements Fe, Co and Ni are commonly referred to as the group VIIIB, 4th period in the nomenclature of the Chemical Abstracts Service (CAS).

In the case of iron and low alloy steel, nitrogen insertion using different methods such as gas nitriding, plasma nitriding, or energetic methods like low energy ion implantation (LEII), or plasma immersion ion implantation (PIII) results in the formation of a closed compound layer (mixture of Fe_3N and Fe_4N nitrides) followed by a diffusion layer with nitrogen in solid solution [12]. This nitriding process is a standard industrial hardening process for >50 years with outstanding results for industrial applications [13,14].

However, high alloy steels including stainless steel do not exhibit this behaviour. There, a completely different situation is observed after nitrogen insertion, where three classes of fcc alloys are showing a predisposition for similar behaviour: iron, cobalt and nickel based alloys. Due to alloying fundamentals (Cr is necessary in addition to Ni to stabilize the fcc phase in iron, respective steel), chromium is nearly always present in technologically interesting or commercially available alloys [15]. Here, a nitrogen supersaturated phase – so called expanded austenite – with nitrogen in solid solution and surface concentration up to 38 at.% is formed [16,17]. This phase does not fit into the simple picture for conventional metal-nitrogen phases for several reasons: i) this phase exists in a very large compositional range instead of an ordered compound with fixed stoichiometry and additional restricted range for vacancies and interstitials; ii) the lattice structure is directly derived from the (fcc) host matrix, growing coherently without any additional nucleation and Ostwald ripening; iii) This phase in these alloys is metastable with a fast decay – respective phase separation – into CrN/Cr_2N precipitates and a Cr- and N-depleted matrix left behind starting around 400 °C [18].

Historically, expanded austenitic steel was discovered in the mid-1980s by Kolster [19] after attempting to carburize austenitic stainless steel due to its ubiquitous utilization in corrosion prone environments at a very large scale while presenting simultaneously a very soft surface with poor tribological properties. Normally, the discovery of expanded austenite is also attributed to Zhang and Bell after plasma nitriding of austenitic stainless steel [20]. This expanded phase formed in austenitic

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stainless steel is characterized by significantly higher hardness up to a factor of 5 harder than the base material. The wear resistance is >4 orders of magnitude higher after nitriding, with the absolute values similar to nitrided low alloy martensitic steels [21]. No cold welding is observed (in contrast to the untreated stainless steel where two clean, flat surfaces will strongly adhere if brought in contact) after nitriding. All these properties are present while still maintaining the excellent corrosion resistance after controlled processing (i.e. avoiding CrN precipitation). Furthermore, a direct implantation of carbon leads also to the formation of an expanded austenitic phase with similar tribological properties [22,23]. The diffusion of carbon is even faster than that of nitrogen, however coupled with lower atomic concentrations [24].

Formation of expanded phase in CoCr alloys and NiCr alloys is less well investigated; nevertheless CoCr alloys exhibit very similar performance after nitrogen insertion. For formation of this phase, only PVD methods and related processes have been successfully used while the standard path of production from the melt is not possible even using modern metallurgy. High nitrogen steel alloys, despite gaining prominence in applications, are still about one order of nitrogen content lower than expanded austenite. As an aside, the notation of the composition in wt.% for engineering and in at.% for physics does not really help in bringing the disparate communities into contact and information exchange.

Among the works focused on nitriding of certain groups of alloys there are only a limited number of reviews and comparative studies on the formation of expanded phase in different fcc alloys [25–27]. At the same time, there are several open questions, unresolved discrepancies, diverging results and competing models for phase formation proposed by different groups. The purpose of this review article is to present the current status of nitrogen insertion into austenitic stainless steel, CoCr and Ni base alloys using information available in the literature and recent, selected experiments. The focus is (i) to explore the common aspects for nitrogen in (Fe,Co,Ni)Cr alloys with an fcc structure (with expanded phase formation and nitrogen diffusion shown in Fig. 1 for typical examples from these three classes of alloys), (ii) to assess apparent discrepancies in the literature and (iii) to point towards open questions. After concentrating on the nitrogen transport and the influence of surface barriers, the initial phase formation will be investigated. There is supposedly enough literature agreeing on the decay process of the metastable phase [18,17,28], thus this regime will be mentioned only briefly.

Before starting with experimental methods employed to obtain expanded austenite, some comments about what is not covered in this manuscript. The expanded austenite phase or layer is assumed to be different from the substrate and to form a sharp interface with the substrate (as suggested by the literature) and the formation and growth of this layer is investigated. It is acknowledge that there is a large and detailed literature on the concentration dependent diffusion coefficient for nitrogen and carbon in expanded austenite describing the microscopic nitrogen/carbon transport. At the same time stress and plastic flow and stress gradients are known to influence the XRD data (with peaks from the expanded phase normally much broader and highly asymmetric compared to the substrate) and the diffusion. While these points and their detailed influence on the nitrogen transport and phase formation are interesting and worthy of clarification, their inclusion into this manuscript is omitted for space and clarity.

2. Experiment

While a plethora of austenitic stainless alloys has been investigated, the focus here will be on two common kinds of austenitic stainless steel – AISI 304 (corresponding to DIN 1.4301/X5CrNi18.10, composition in wt.%: 18 Cr, 10 Ni, balance Fe) and AISI 316Ti (corresponding to 1.4571/X6CrNiMoTi17.12.2, composition in wt.%: 17 Cr, 12 Ni, 2 Mo, balance Fe). For CoCr, the focus will be on the alloy HS188 (22 Ni, 22 Cr, 14 W, 3 Fe, balance Co), and a commercial Ni80Cr20 alloy (Nichrome – with a chemical composition of 20 wt.% Cr and 80 wt.% Ni) will be investigated as a representative Ni-base alloy. For the experiments present here, disc-shaped samples with thickness of 2.5 mm were cut from rods, grinded and polished to mirror finish before implantation.

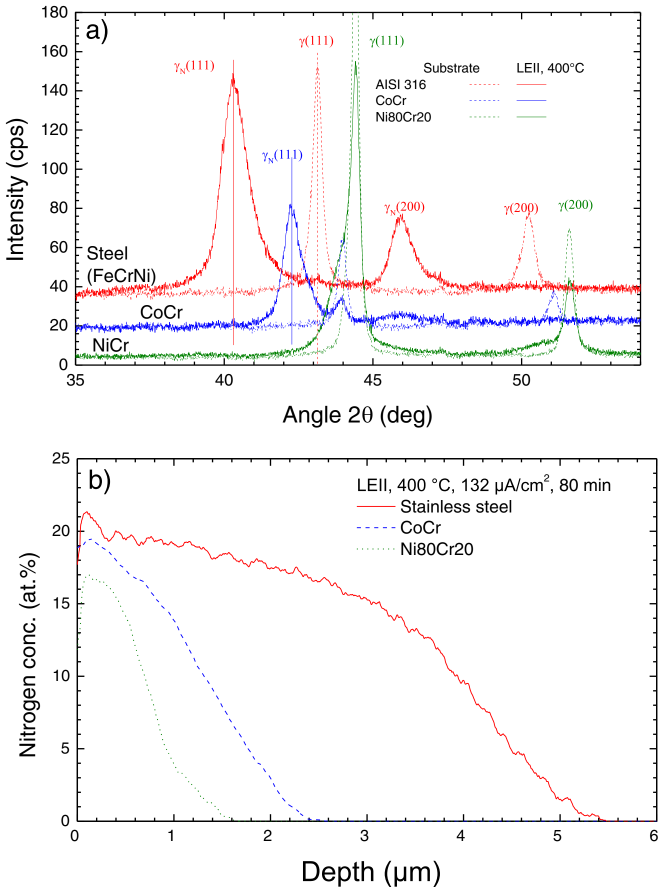

Fig. 1. a) XRD spectra of austenitic stainless steel, CoCr and NiCr alloy after nitriding by LEII at 400 °C for 80 min. The positions of the base material peak and expanded phase peak for two different orientations are marked with γ and γ_N, respectively. The spectra are vertically shifted for clarity; b) corresponding nitrogen depth profiles as obtained from GDOES measurements.

The nitriding experiments were carried out using two methods – LEII and (PIII). Using LEII, the positive ions are extracted and accelerated from a plasma forming a directed, broad ion beam (which is not mass separated) impinging on the substrate at energies between typically 200 and 2000 eV. Collisions with the background gas during the transport may lead to charge exchange collisions. In PIII, the substrate is immersed within the plasma and the negative high voltages pulses lead to a receding plasma sheath and the acceleration of the ions towards the substrate. While the whole surface is implanted simultaneously, the emission of secondary electrons and local ion flux variations do not allow a control of the local ion current density. At the same time, electrons and low energy ions may impinge on the surface between the pulses. Details on further experimental designs and active plasma processes relevant to steel nitriding can be found e.g. in Ref. 13.

For LEII experiments a system equipped with Kaufman ion source, an auxiliary heating stage and allowing in-situ XRD measurements during the implantation process was employed. More details about the equipment can be found in a previously published paper [29]. The system is outfitted with an electronic beam switch allowing pulsed mode and thus permitting the adjustment of the average ion current density without changing either the plasma conditions or the extraction optic [30]. The combination of external heating system and the electron beam switch gives possibility for ion current variation in a broad range encompassing more than one order of magnitude difference.

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