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Nitriding of iron-based ternary Fe–V–Si alloy: The precipitation process of separate nitrides

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Abstract

Iron-based ternary Fe–V–Si and binary Fe–Si alloy specimens were nitrided in a NH_3/H_2 gas mixture at 580 °C (853 K) with a nitriding potential of $r_N = 0.1$ atm$^{-1/2}$ until nitrogen saturation in the specimens was achieved. In contrast to previously investigated iron-based ternary Fe–Al–Cr and Fe–Ti–Cr alloys, no so-called “mixed” nitrides developed in the Fe–V–Si alloy. Instead, in the first stage, all vanadium precipitated as crystalline VN and, subsequently, all silicon precipitated as amorphous Si_3N_4. Moreover, the precipitation rate of Si_3N_4 in the nitrided ternary Fe–V–Si alloy was much lower than in the binary Fe–Si alloy nitrided under identical conditions. This much lower Si_3N_4-precipitation rate is attributed to the presence of first precipitated VN: coherency strains caused by the (semi-) coherent VN precipitates interact with the strain fields surrounding the Si_3N_4 precipitates and are obstacles to the movement of dislocations necessarily introduced in the ferrite matrix by growing Si_3N_4 precipitates. This interpretation is supported by additional experiments, in which the first precipitated VN platelets were coarsened by annealing before subsequent nitriding led to, now much faster, Si_3N_4 precipitation.

Keywords: Nitriding; Ternary alloys; Precipitation kinetics; Microstructure

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1. Introduction

Nitriding is a widely used thermochemical surface treatment for components made of ferritic iron-based alloys. Nitriding can greatly improve mechanical properties such as the wear and the fatigue resistance, as well as chemical properties such as the corrosion resistance [1–3]. Different nitriding methods exist: gas nitriding, plasma nitriding and salt-bath nitriding. In contrast to the other nitriding methods, gas nitriding offers the advantage of being able to precisely adjust the chemical potential of nitrogen in the nitriding medium. Thereby, it is in principle possible to control the developing phases and microstructures upon gas nitriding [4].

Gas nitriding is performed with a flowing NH_3/H_2 gas mixture. During nitriding, NH_3 molecules dissociate catalytically on the iron surface, leading to atomic nitrogen adsorbed at the surface [5,6]. The adsorbed nitrogen atoms can be dissolved in the solid of the surface and subsequently diffuse to larger depths in the substrate. By choosing appropriate nitriding parameters (temperature and nitriding potential; for details see Ref. [4]) the formation of iron nitrides can be avoided, so that only a nitrogen-diffusion zone develops.

If the iron is alloyed with elements, *Me*, with an affinity for nitrogen (e.g. *Me* = Al, Ti, V, Cr or Si), alloying-element nitrides can develop in the diffusion zone upon nitriding. These precipitated (semi-)coherent nitrides can

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induce pronounced improvement in the fatigue resistance of nitrided work-pieces [7].

Most studies on nitriding response have dealt with ferritic iron-based binary Fe–*Me* alloys [8–12]. In contrast, commercial nitriding steels contain multiple alloying elements, each of specific interaction with nitrogen. Until now, few studies have been devoted to the nitriding behavior of ternary iron-based Fe–Me_a–Me_b alloys (Fe–Mn–Si [13], Fe–Cr–Al [14–16], Fe–Cr–Ti [17,18], Fe–Al–Si [19]). In the case of nitrided Fe–Cr–Al [14–16] and Fe–Cr–Ti [17,18] alloys, it was found recently that metastable, mixed ternary nitrides, $Me_{a(1-x)}Me_{b(x)}N$, develop, instead of the stable, binary nitrides, Me_aN and Me_bN. Strikingly, these mixed ternary nitrides develop in systems for which the separate binary nitrides are of the same stoichiometry (i.e. same *Me*/N atomic ratio) and of the same crystal structure (cubic rock-salt type of crystal structure).

With respect to the above discussion, the question arises what happens on nitriding if in one (iron-based) alloy, two alloying elements, both with a strong chemical affinity for nitrogen (as in the above cases), are dissolved, but which show, on nitriding of the corresponding binary alloys, rather different nitriding behaviors, such as those exhibited by different *Me*–N stoichiometries for the binary nitrides. During nitriding binary Fe–V alloys, V precipitates rapidly as stoichiometric VN of a rock-salt type of crystal structure [20]. During nitriding binary Fe–Si alloys, Si precipitates relatively slowly as stoichiometric Si_3N_4, which is of an amorphous nature [21–23]. The investigation of the nitriding responses of V and Si jointly present in a ternary Fe–V–Si alloy is the subject of the present research project.

It will be shown that, although no mixed ternary nitride precipitates but separate binary nitrides develop, the kinetics of nitride precipitation in the ternary alloy differs remarkably from what is observed for the corresponding binary alloys. A corresponding explanation is offered on the basis of additional, dedicated experiments.

2. Experimental procedures

2.1. Specimen preparation

The iron-based binary Fe–Si alloy and the iron-based ternary Fe–V–Si alloy casts were produced by melting elemental granules of Fe (purity 99.98 wt.%), V (purity 99.9 wt.%) and Si (purity 99.999 wt.%) in an induction furnace under a protective Ar atmosphere. The melts were cast to rods with length 100 mm and diameter 10 mm. These casts were ground to remove surface oxides and cold-rolled to sheets with a thickness of ~1 mm. Rectangular prism-shaped specimens with dimensions 15 × 10 × 1 mm were cut from these sheets. The specimens were ground, polished (the last step was 1 μm diamond paste) and, finally, ultrasonically cleaned in ethanol. Next, the specimens were encapsulated in quartz tubes under a protective Ar atmosphere and recrystallized at 800 °C for 20 min. Subsequently, the specimens were again polished (1 μm diamond paste) and cleaned ultrasonically in ethanol.

Inductively coupled plasma optical emission spectroscopy was used to determine the actual amounts of V and Si in the casts, carrier gas hot extraction was used to determine the amounts of oxygen and nitrogen, and the combustion method was applied to determine the amounts of carbon and sulfur. The results of the chemical analysis of the different alloys are gathered in Table 1.

2.2. Nitriding

Gas nitriding treatments were performed in a vertical multi-zone quartz-tube furnace (inner diameter 28 mm) equipped with gas mass-flow (flow variation ±2.5 ml min^{-1}) and temperature (temperature variation ±1 K) controllers (see Ref. [24] for a detailed description of the nitriding facility). Nitriding was performed at a temperature of 580 °C using a nitriding potential of $r_N = 0.1\ atm^{-1/2}$ (45 ml min^{-1} NH_3 and 455 ml min^{-1} H_2; nitriding potential is defined as $r_N = p(NH_3)/p(H_2)^{3/2}$, where p denotes partial pressure [1]). For the nitriding treatment, high-purity NH_3 (purity 99.998 vol.%) and H_2 (purity 99.999 vol.%) gases were used. Note that, on applying this nitriding condition, no iron nitrides (ε-Fe_3N_{1+x} or γ′-Fe_4N_{1-y}) can develop upon nitriding pure iron [25] and did not develop in the case of nitriding the iron-based alloys investigated in this study. The nitriding treatments were interrupted at certain times by quenching the specimens in water that was purged with N_2 gas to minimize the amount of oxygen dissolved in the water. The first set of specimens were nitrided for 1, 4, 8 and 24 h. The second set of specimens were nitrided in steps of 72 h to a total time of 1656 h.

2.3. Weighing

The specimens were weighed with a comparator balance (Mettler XP56) before and after each nitriding treatment. For each weighing, five measurements were carried out,

Table 1
Alloying element and light element impurity contents in the pure iron, the binary iron-based Fe–Si alloy and the ternary Fe–V–Si alloy casts prepared and employed in the present work.

Alloy	V (at.%)	Si (at.%)	O (μg g^{-1})	N (μg g^{-1})	C (μg g^{-1})	S (μg g^{-1})
Fe	–	–	70	<10	<10	<10
Fe–2.0Si	–	1.99 ± 0.02	30	<20	<10	<20
Fe–0.3V–2.0Si	0.29 ± 0.01	1.97 ± 0.01	60	<20	<10	<20