Available online at www.sciencedirect.com
SCIENCE DIRECT®
Acta Materialia 53 (2005) 2563–2579
Acta MATERIALIA
www.actamat-journals.com

Plasma nitridation of aluminized high purity iron

Koji Murakami [a,*], Norihide Nishida [a], Kozo Osamura [b], Yo Tomota [c], Tetsuya Suzuki [d]

[a] Industrial Technology Center of Okayama Prefecture, Department of Materials Engineering, 5301 Haga, Okayama City Okayama Prefecture 701-1296, Japan
[b] Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
[c] Institute of Applied Beam Science, Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan
[d] Research Center for Superplasticity, Faculty of Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

Received 31 October 2004; received in revised form 3 February 2005; accepted 7 February 2005
Available online 2 April 2005

Abstract

Surface treatment of high-purity iron by powder liquid coating aluminization and plasma nitridation is investigated with respect to the mechanism of hardening and nitrogen diffusion. Grain boundaries in the aluminized layer are found to be preferentially nitrided in the early stage of nitridation, accompanied by the formation of γ'-Fe_4N platelets in the substrate. Aluminization and nitridation increase the hardness from HV110–120 for the original α-Fe(Al) to HV1200–1500 for the modified specimen, which consists of an α-Fe(Al) matrix with γ'-Fe_4N and rocksalt AlN. Transmission electron microscopy observation reveals the AlN to be present in the form of platelets of 2–3 nm in thickness with an orientational relationship of $(0\,0\,1)_\alpha // (0\,0\,1)_{AlN}$ and $[1\,1\,0]_\alpha // [1\,0\,0]_{AlN}$ (Baker–Nutting relationship). The kinetics of plasma nitridation is formulated, and good agreement with the experimental results is obtained when first- or second-order reactions are assumed for the formation of AlN under constant N flux at the surface.

Keywords: Plasma nitridation; Aluminization; Iron; Kinetics

1. Introduction

The powder liquid coating aluminization technique recently reported by Murakami et al. [1–4], in combination with plasma nitridation, is expected to be a useful surface treatment for die casting machines as protection against severe erosion by molten Al or other liquid metals. The major benefit of such a treatment technique is the ability to treat the internal surfaces that are exposed to these severe environments; in contrast, other protective coatings such as CrN, TiN, and TiAlN films are deposited by physical vapor deposition, a technique that is restricted to external surfaces. The combination of aluminization and nitridation has already been proposed by Tsuji [5,6] and Bindumadhavan [7] for tool steel and carbon steel, and hardnesses of HV1000–1500 have been achieved for the modified layer. Hardening by steel nitridation is thought to occur through the formation of hard nitrides, resulting in higher internal stress in the matrix, or Guinier–Preston zones. However, the detailed hardening mechanism has yet to be studied in detail for this aluminization and nitridation technique.

In this study, high-purity iron is treated by powder liquid coating aluminization and subsequent plasma nitridation, and the hardened layer is characterized. A diffusion equation for nitrogen is formulated taking

* Corresponding author. Tel.: +81 862 869 600; fax: +81 862 869 630.
E-mail addresses: kouji_murakami@pref.okayama.jp (K. Murakami), norihide_nishida@pref.okayama.jp (N. Nishida), kozo.osamura@materials.mbox.media.kyoto-u.ac.jp (K. Osamura), tomota@ mx.ibaraki.ac.jp (Y. Tomota), tetsuya@mx.ibaraki.ac.jp (T. Suzuki).

1359-6454/$30.00
doi:10.1016/j.actamat.2005.02.014

the formation of nitrides in the aluminized layer into consideration.

2. Experimental

High-purity Fe (99.9%) disks were used as substrates. The substrate was polished with abrasive paper to #600 and washed twice with acetone in an ultrasonic cleaning bath for 0.3 ks each time. For powder liquid coating aluminization [4], a slurry was prepared by stirring a mixture of atomized Al powder (under 3 μm in diameter), crushed Al_2O_3 (levigated to 1 μm) and ethanol (12.0×10^3 mm^3 for mixed powders of 1.0×10^{-2} kg) with an impeller at 50 revolutions per second for 0.6 ks. The slurry was pasted onto the disks to a coverage of 0.50 mg/mm^2, and the specimens were heated in an oven at 333 K for 1.8 ks to remove ethanol. Each of the prepared disks was then heated in a quartz cylinder by infrared radiation in a vacuum of 1.3×10^{-3} Pa. The temperature was raised at 1.33 K/s, held at 1273 K for 3.6 ks, and then the samples were cooled under N_2 gas flow at about −2 K/s to room temperature.

After the residual powder had been removed with acetone in an ultrasonic cleaning bath, the aluminized substrates were placed in the plasma nitriding chamber. The chamber was evacuated to 1.3 Pa and mixture of Ar and H_2 gas (Ar:H_2 = 1:1 by volume) was introduced at an inflow rate controlled by massflow controllers so as to maintain a total chamber pressure of 1.3×10^2 Pa. The aluminized substrates were heated to 873 K under direct current (dc) glow discharge to remove the passive oxide surface layer, which prevents effective nitridation. After sputtering for 3.6 ks, gas supply was changed to N_2:H_2 = 7:3, and the total pressure was maintained at 3.9×10^2 Pa. The nitriding temperature was varied from 773 to 873 K, and nitriding was conducted for 3.6–32.4 ks. The specimens were furnace cooled after nitridation. The nitriding conditions are hereafter denoted by *T*K-*t*ks, and this expression implicitly means that the

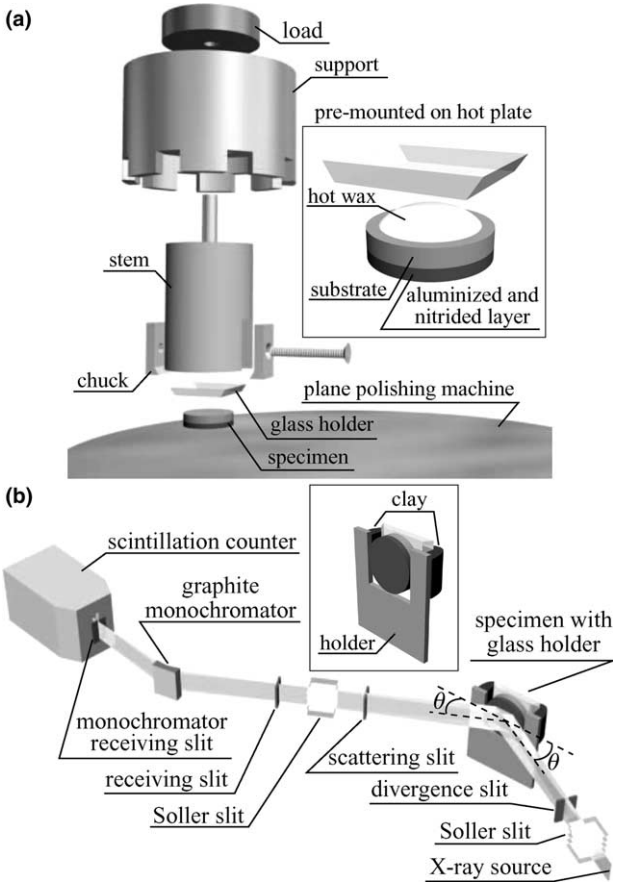

Fig. 1. Schematic illustration of (a) plane-polishing and (b) XRD measurement.

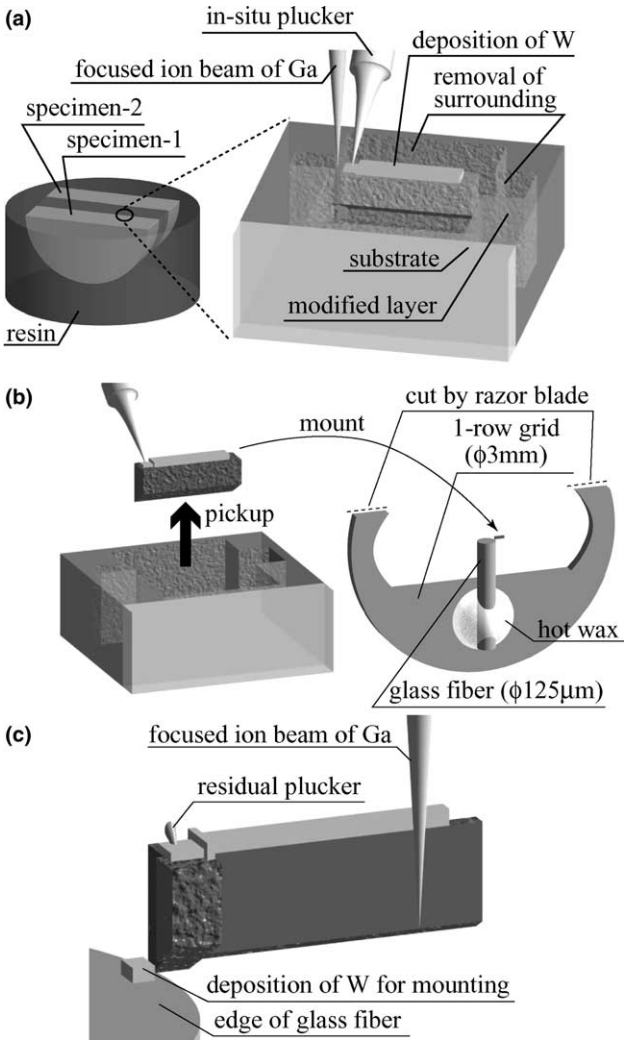

Fig. 2. Schematic illustration of specimen preparation for TEM observation: (a) polished and chemically etched plane showing cross-sectional microstructure (left) and the FIB configuration (right); (b) picking of a thin fragment from the molded specimen and mounting on a grid; (c) final thinning.