Diffusion profiles after nitrocarburizing austenitic stainless steel

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ABSTRACT

The mutual effects of nitrogen and carbon interstitials on diffusion profiles resulting from low temperature interstitial hardening were examined in AISI 316L austenitic stainless steel. Samples were nitrided, carburized, or nitrocarburized at low temperatures (703 to 723 K), and the resulting concentration-depth profiles of nitrogen and carbon were determined by Auger electron spectroscopy. The presence of carbon does not affect the nitrogen diffusion profiles. The presence of nitrogen does not affect the carbon diffusion depths, but it does reduce the near-surface carbon concentrations. Processing parameters, such as the order of treatment, gas species, gas flow, time, and temperature, are examined to reveal their relative importance and the potential to tailor diffusion profiles for specific applications.

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1. Introduction

Significant surface hardening of austenitic stainless steels results from very high (non-equilibrium) near-surface concentrations of interstitially dissolved carbon or nitrogen that arises from low temperature carburizing or nitriding. In this technique, carbide and nitride formation is inhibited kinetically, since the low processing temperatures effectively immobilize the substitutional elements, and a "colossal" supersaturation – several orders of magnitude times the equilibrium solubility at the treatment temperatures – of interstitially dissolved carbon or nitrogen is achieved [1]. Treatments that combine dissolution of both carbon and nitrogen, here denoted as "nitrocarburizing", can also be applied to the same material — successively or simultaneously. Unusual composition profiles have been obtained in this way [2–11]. In particular, when simultaneously nitrocarburizing (with a gas containing both nitrogen- and carbon-bearing molecular species), two distinct regions are formed at the alloy surface: a nitrogen-rich layer at the outer surface and a carbon-rich layer beneath it. When previously carburized samples are subsequently nitrided a similar two-layer structure is formed, with the nitrogen remaining near the surface and the carbon diffusing deeper into the sample. Surprisingly, when previously nitrided samples are subsequently carburized, the same two-layer structure results, as the carbon atoms diffuse through the nitrogen-rich layer to form the carbon-rich layer beneath [9].

Nitriding austenitic stainless steels generally produces a greater surface hardness than does carburizing, while carburizing produces a thicker hardened surface layer ("case") for equivalent treatment times. Therefore, simultaneous nitrocarburizing may achieve maximum benefits in the shortest amount of time. In fact, simultaneous nitrocarburizing has been reported to achieve a thicker case than carburizing alone [4,8], possibly due to nitrogen causing the carbon to diffuse more rapidly [4]. If case depths can be increased with no increase in processing time, this would have important industrial applications.

Two explanations have been proposed for the peculiar diffusion profiles: the trapping model [4,7] and a thermodynamic model with concentration-dependent diffusivity [1]. In the trapping model [12–14], also called the trapping–detrapping model, each Cr atom in the stainless steel is associated with a trap site for one interstitial, i.e., it can arrest one diffusing interstitial atom. In this model, since Cr has a higher affinity for nitrogen than for carbon, the trap sites near the surface are preferentially filled with nitrogen atoms, while the carbon atoms will diffuse deeper into the material to locate unfilled trap sites.

The thermodynamic model [1], in contrast, explains the observed diffusion profiles as a result of an interaction between nitrogen and carbon. The activity coefficient of carbon and nitrogen in the steel is determined by the interaction between the interstitial solutes and the matrix elements. In addition, the presence of either interstitial solute changes the activity coefficient of the other, i.e., there are changes in the "apparent" concentration, relative to the actual concentration. This effect can be quantitatively modeled using parameters from the CALPHAD literature to describe the mutual variation in the chemical potentials of nitrogen and carbon interstitials within the specific alloy matrix. The results of such modeling show that carbon and nitrogen mutually increase their activity coefficients. The observed diffusion profiles then follow directly from concentration-dependent diffusion [15,16] – without trapping – in response to the physical driving force for diffusion, namely gradients in chemical potential (rather than gradients in concentration).

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In this work, we have carried out gas-phase nitriding, carburizing, and nitrocarburizing on AISI 316L austenitic stainless steel, along with careful measurements of the resulting diffusion profiles by Auger electron spectroscopy. This has allowed us to accurately determine the mutual effects of the two interstitial species on diffusivities and case depths.

1.1. Background — dilute carbon and nitrogen diffusivities in austenite

Fig. 1a and b shows literature data for carbon [17–24] and nitrogen [25–31] diffusivities in dilute (<5 at.%) interstitial solid solutions for both Cr-free and Cr-rich (≥12 wt.%), austenite. The diffusivities of both interstitial species decrease when Cr is added to austenite. Fig. 1c compares the diffusivities of carbon and nitrogen in Cr-free austenite. Within the experimental scatter, the diffusivities are equal. Fig. 1d compares the diffusivities of carbon and nitrogen in Cr-rich austenite. The diffusivity of carbon is significantly higher than that of nitrogen — about two orders of magnitude higher at temperatures below ≈ 800 °C.

These results are counterintuitive when considering only the elemental atomic radii. Cr is larger than Fe (166 pm compared to 156 pm), and its addition to the alloy increases the lattice parameter. This would be expected to enlarge the spacings between metal atoms

and make interstitial diffusion easier. Carbon is a larger atom than nitrogen (67 pm compared to 56 pm). Therefore, it would be expected to diffuse more slowly through the alloy, and its diffusivity might be enhanced more by the expansive effect of Cr additions. However, none of these simple-minded predictions are correct.

The reported dilute diffusivities are consistent with the trapping model. For Cr-rich stainless steels, the interstitial concentration is considerably lower than the Cr content, and most of the interstitials will be contained in trap sites. The trap energy must then be overcome before the trapped atom can diffuse. Therefore, the measured diffusivity for Cr-rich austenitic stainless steels is lower than for Cr-free austenite. The difference is greater for nitrogen than for carbon, because the Cr–nitrogen affinity is greater than the Cr–carbon affinity [1], and therefore the trap energy is greater for nitrogen.

However, the decrease in interstitial diffusivity in Cr-rich austenite does not necessarily confirm the trapping model. The addition of Cr may generally slow down interstitial diffusion in the alloy, with all the interstitial sites remaining equivalent. For example, the presence of Cr may have a non-local effect on interstitial diffusion, by modification of the conduction band electron density. Rather than Cr preferentially trapping nitrogen, the observed concentration profiles of nitrogen and carbon could be explained by the large differences in carbon and
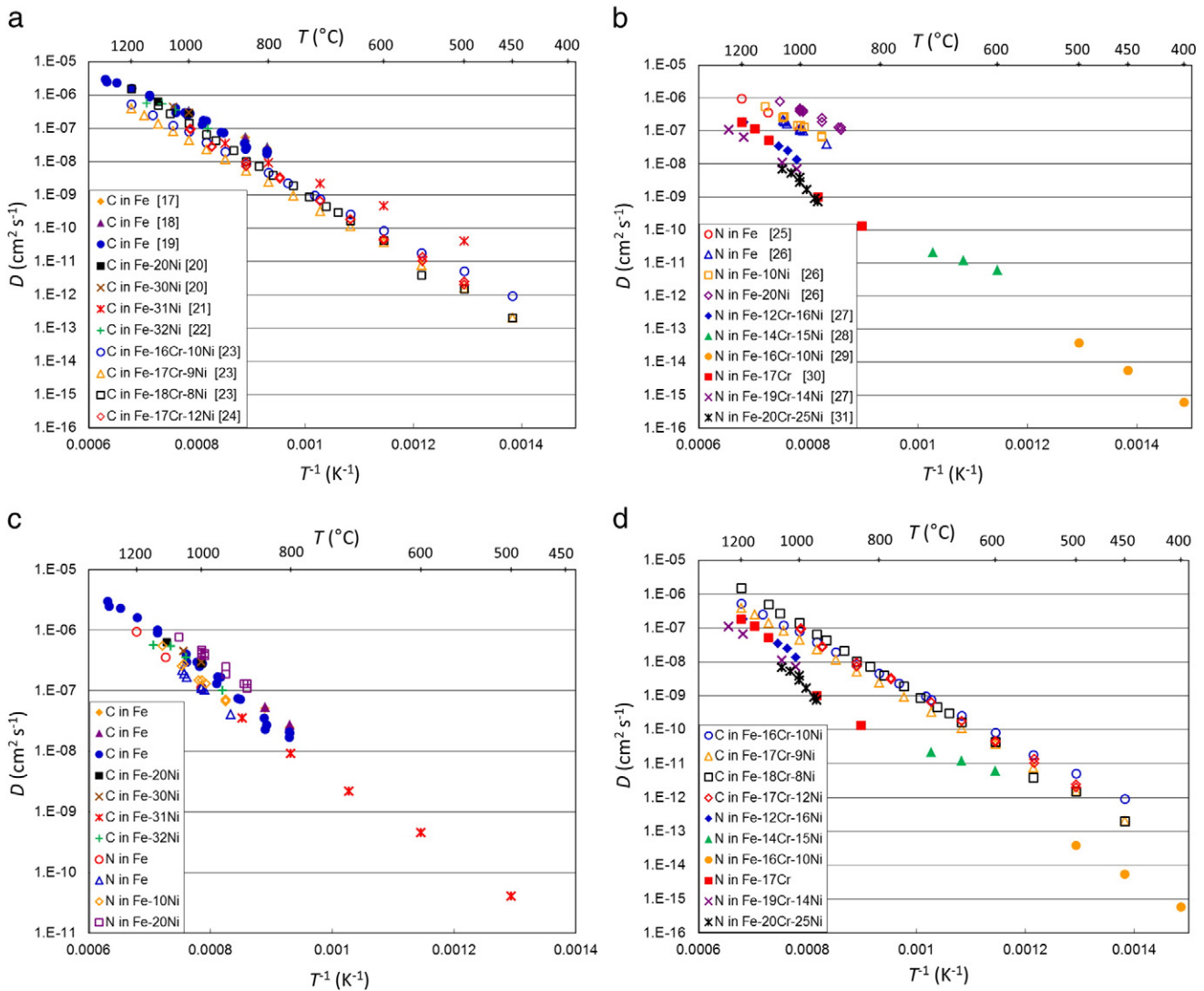

Fig. 1. Dilute (<5 at.%) diffusivities, *D*, of carbon and nitrogen in austenite as a function of inverse temperature. (a) Diffusivity of carbon in Cr-rich austenite (open symbols) and Cr-free austenite (solid symbols). (b) Diffusivity of nitrogen in Cr-rich austenite (solid symbols) and Cr-free austenite (open symbols). (c) Diffusivity of carbon (solid symbols) and nitrogen (open symbols) in Cr-free austenite. (d) Diffusivity of carbon (open symbols) and nitrogen (solid symbols) in Cr-rich austenite.