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# Formation of hard surface layer on austenitic stainless steels via simultaneous chromising and nitriding by pack cementation process

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ABSTRACT

This study aims to increase surface hardness of austenitic stainless steels via simultaneous chromising and nitriding by the pack cementation process. The pack powder mixtures used for the process consisted of $Cr_2N$ as a source of both N and Cr for the simultaneous process, $NH_4Cl$ as activator and $Al_2O_3$ as inert filler; in some cases, Cr powder was added as an additional source for depositing Cr. The AISI204 austenitic stainless steel is studied as a substrate. It is demonstrated that a top $Cr_2N$ layer with a Cr enriched layer underneath can be formed on the steel surface at 1100 °C. Hardness values of more than 1800 HV are obtained at the outermost surface of the treated specimen. It has been shown that the hardness profile at the cross-section of the surface depends on the pack chemistry.

## 1. Introduction

The austenitic stainless steels are corrosion resistant but have insufficient tribological properties due to their low hardness, which hinders their wider applications under corrosion-wear conditions [1]. Thus, many studies have been made to increase their surface hardness using various physical and thermochemical surface treatment processes [2–5]. Among these processes, the low temperature plasma and solution nitriding processes are the most notable ones in terms of commercial importance [6–11]. In the former process, the precipitation of chromium nitrides is suppressed and hence the corrosion resistance of the treated steels is preserved by keeping the nitriding temperature sufficiently low (normally below 450 °C) [5–8]. In the latter process, the nitriding process is normally carried out at temperatures higher than 1050 °C and the suppression of chromium nitride precipitations is achieved by rapid cooling to temperatures below 420 °C [9,10]. With the low temperature plasma nitriding process, an extremely hard surface layer, which is termed S-phase layer with hardness values over 1300 HV, can be synthesised on the surface of various austenitic stainless steels [6]. But the surface hardness obtainable with the solution nitriding process is usually moderate, reaching only about 350 HV depending on the grades of the steels treated [8,9]. However, with the low temperature plasma nitriding process, the growth rate of the S-phase layer on the surface is undesirably slow due to the low treatment temperatures used. Thus, only a thin S-phase layer can be produced with a thickness of normally less than 20 μm. Furthermore, because the S-phase is metastable, the prolonged nitriding treatment can lead to precipitation of chromium nitrides even at 400 °C [8,12] unless even lower nitriding temperatures down to 300 °C are used, in which case long nitriding times lasting up to 8000 h are needed to form a S-phase case with a thickness suitable for practical applications [13]. It is thus highly desirable to have a process by which hardness of the surface layer formed is comparable to those obtainable with the low temperature plasma nitriding process and the growth kinetics of the hard surface layer is as high as those achievable with the solution nitriding process.

One of the thermochemical surface treatment techniques that may be used to achieve the objective stated above is the pack cementation process, which is a thermally activated process commonly used to form diffusion coatings on metal surfaces [14,15]. The process is capable of simultaneously depositing more than one element to form diffusion coatings with properties tailored for different application conditions [16–20]. And also in comparison with other physical or chemical vapour deposition processes, the pack cement process is easier to apply to coat components of complex surface geometry without the so-called line-of-sight restrictions [14,15]. The present study is an attempt to simultaneously chromise and nitride the surface of austenitic stainless steels by pack cementation process at 1100 °C. It aims to form a hard surface layer on austenitic stainless steels with hardness values comparable to those achievable with the low temperature plasma nitriding process but with much faster surface layer growth kinetics.

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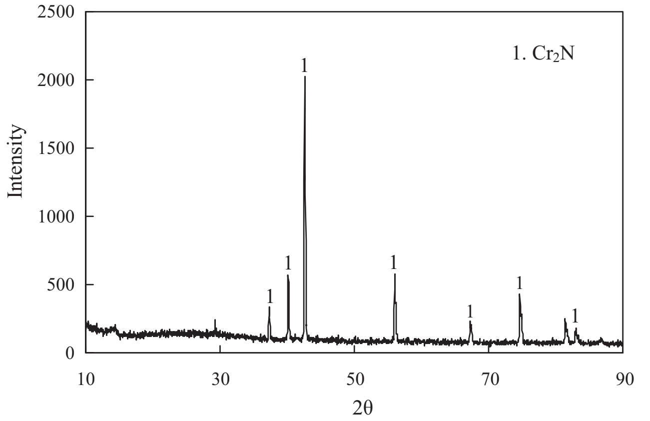

**Fig. 1.** XRD pattern from the surface of the specimen treated in $15Cr_2N–83Al_2O_3–2NH_4Cl$ (wt%) pack at 1100 °C for 8 h.

## 2. Experimental procedures

The material used for this study was cold-rolled thin sheets of austenitic stainless steel AISI 204 with a thickness of 1 mm; the nominal chemical composition of the steel was Fe–15Cr–9Mn–2Ni–3Cu (wt.%). The pack powder mixture for the pack cementation process consisted of $Cr_2N$ as a source of both N and Cr for the simultaneous chromising and nitriding purpose, Cr as an additional source for depositing Cr, $NH_4Cl$ as an activator and $Al_2O_3$ (calcined) as inert filler. Both $Cr_2N$ and Cr powders used were of purity of over 99.8 wt%. The particle sizes of $Cr_2N$, Cr, $Al_2O_3$ powders were all below 40 μm. $NH_4Cl$ was ground but not sieved before it was added into the pack powders. The specimens were cleaned with organic solvent and then buried in the pack powder mixture contained in an alumina retort of 30 mm diameter and 40 mm length. Only one specimen was packed into the alumina retort at a time. The retort was sealed with alumina lid and alumina cement. When the cement was fully dried, the retort was loaded into a horizontal tube furnace and then heated to the treatment temperature used under the protection of flowing Ar gas. The treatment temperature used in all cases was 1100 °C, but the treatment duration varied. The Ar gas flow was maintained until the treatment process was completed and the furnace was cooled to room temperature.

The cross-sections of the treated specimens were analysed using scanning electron microscopy (SEM) (Nova nano-SEM400). The phases formed in the surface layer of treated specimens were analysed by X-ray diffraction (XRD) (PHILIPS X'Pert PRO MPD diffractometer with Cu-Kα source radiation operated at 40 kV and 40 mA). Microhardness was measured from the cross-section using a microhardness indenter; the indent load used was 25 g.

## 3. Results and discussion

### 3.1. Conditions for the formation of the surface layer by simultaneous chromising and nitriding

The initial series of pack powder compositions studied was $xCr_2N–(100-x)Al_2O_3$ (wt%) ($x = 8, 15, 25, 50$), into which 2 wt% $NH_4Cl$ was added as activator. It was observed that when the $Cr_2N$ content in the pack powders was higher than 15 wt%, the pack powders were partially sintered after treatment at the temperature used and only when the $Cr_2N$ content was at or below 15 wt%, can the partial sintering of the pack powders be prevented.

The XRD pattern measured from the surface of the specimen treated for 8 h in the pack containing 15 wt% $Cr_2N$ is shown in Fig. 1, which indicates that a top $Cr_2N$ layer was formed on the specimen surface. The nitrided specimen surface looked smoother than the original as-cold-rolled surface with a bright-grey metallic luster appearance containing no entrapped pack powder particles, indicating that the surface $Cr_2N$ layer formed was deposited from the vapour phase species generated at the treatment temperature within the $NH_4Cl$ activated pack. No such a continuous $Cr_2N$ layer was formed on the surface in un-activated $Cr_2N$ packs [4].

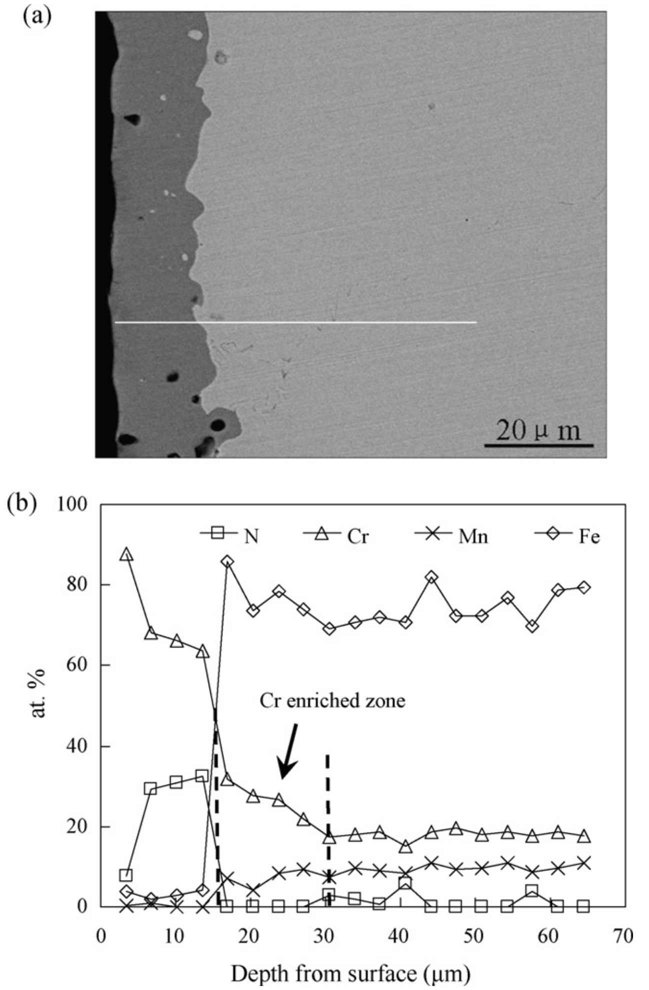

**Fig. 2.** Cross sectional SEM image and depth profiles of elements in the surface layer of the specimen nitrided in 2 wt% $NH_4Cl$ activated $15Cr_2N–85Al_2O_3$ (wt%) pack at 1100 °C for 8 h.

To find out whether or not Cr and N had diffused into the inner surface layers of the steel substrate, the specimen was cross-sectioned, polished and analysed using SEM and EDS. The results are presented in Fig. 2, where depth profiles of elements in the surface layer shown in Fig. 2b were analysed along the straight line vertical to the surface as shown in Fig. 2a. It can be seen that a continuous deposit formed on the surface in which the atomic ratio of Cr to N was approximately 2. This was consistent with the result of surface XRD analysis, which showed that the phase formed on the surface was $Cr_2N$ (Fig. 1). Micropores with diameters in the range of 1–2 μm were also present in the $Cr_2N$ deposit in isolated locations. The presence of such isolated micropores may affect the tribological properties of the surface layer formed. It can also be noted that the treated surface was of a corrugated feature (Fig. 1a); the degree of corrugation will certainly depend on that of the untreated surface. How this feature and the presence of the isolated micropores may modify the tribological properties of the treated surface will depend on the application conditions in which the