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Abstract. Low temperature thermochemical surface hardening of the precipitation hardening austenitic stainless steel A286 in solution treated state was investigated. A286 contains, besides high amounts of Cr, also substantial amounts of strong nitride formers as Ti, Al and V. It is shown that simultaneous surface hardening and bulk hardening is possible and that high treatment temperatures can be applied, provided that the nitrogen activity in the imposed gas phase is low. Expanded austenite is shown to be stable even at temperatures as high as 500°C; this is ascribed to the presence of Ti.

Introduction

Steel A286 (AISI 660) is a fully austenitic precipitation hardening (PH) stainless steel, specially designed for high temperatures applications. The material can also be used at low temperatures where it possesses non-magnetic properties and a good ductility and toughness compared to the PH martensitic stainless steels. The high strength of the material derives from the precipitation hardening treatment where γ'-Ni_3(Ti,Al) forms. The precipitation hardening or ageing treatment is typically performed at 720°C for 16 hours. The more widely used martensitic and semi-martensitic PH stainless steel are typically aged hardened at temperatures below, say, 480°C which coincides with typical time/temperature conditions for low temperature surface hardening (see ref. [1] in this respect). The significantly higher ageing temperature required for the A286 can be attributed to its austenitic structure and hence slower growth kinetics. The A286 is comparable to the 'traditional' and widely used austenitic stainless steels in terms of chromium content and corrosion resistance in aqueous media, but contains a substantial amount of very strong nitride formers, viz. Ti, V and Al. In that sense the material serves as an excellent model system for investigating the influence of strong nitride formers on low temperature nitriding of (austenitic) stainless steel.

To the authors' knowledge only one paper can be found about low temperature nitriding of A286 alloy [2]. In this work the material was aged prior to plasma nitriding which means that the alloying elements, namely Ti and Al, were bound as γ'-Ni_3(Ti,Al) and not 'available' in solid solution. Plasma nitriding of the aged A286 resulted in formation of expanded austenite. For temperatures higher than 420°C also Cr_2N was observed [2]. The typical upper limit for expanded austenite in the standard austenitic stainless steel grades, e.g. AISI 304 and AISI 316 is around 450°C depending on process conditions. Typically the formation of CrN and not Cr_2N is observed in these alloys.

Materials largely identical to the A286 (20Cr/25Ni base composition with varying amounts of strong nitride formers - namely Ti) have previously been investigated by gaseous nitriding at intermediate to high temperatures [3,4] These alloys were gaseously nitrided in a solution treated state, i.e. with Ti in solid solution. Nitriding conditions could be established such as mainly Ti (rich) nitrides were formed and essentially no precipitation of CrN or Cr_2N occurred. Alternatively, hydrogen reduction of the nitrided material was performed at high temperatures (1000°C or higher), which retracted nitrogen bound by Cr(CrN/Cr_2N) but not nitrogen bound by Ti (TiN). Reportedly, this restored the corrosion resistance [4].

One of the major problems in low temperature surface engineering of stainless steel is the limited layer thickness that can be produced without forming chromium nitrides. Normally, low temperature surface hardening is associated with temperatures below, say, 450°C, where expanded austenite is formed without the formation of CrN. In this contribution we have deliberately chosen to extend this 'definition' of the upper limit to significantly higher temperatures, as the material has a distinctively different behavior than the normal austenitic stainless steel. In this work the nitriding response of *solution heat treated* A286 is investigated at temperatures lower than hitherto applied for gaseous nitriding.

Experimental

Squared samples of A286 (AISI 660) were cut from the supplied plate and solution heat treated at 900ºC for 2 hours in argon as a protective atmosphere. The nominal chemical composition of the steel in wt-% is presented in Table 1. Subsequently, the specimens were ground and polished to a mirror like surface finish for thermochemical treatments.

Table 1 - Nominal chemical composition in wt-% of the studied alloy.

	C	Mn	Si	Cr	Ni	Mo	Ti	V	Al	Fe
A286	0.08	2.00	1.00	13.5-16.0	24.0-27.0	1.0-1.5	1.9-2.3	0.1-0.5	0.35	bal.

Gaseous themochemical treatments were conducted in a Netzsch STA 449 thermal analyzer at different temperatures and gas compositions according to Table 2. Nitriding was performed in ammonia (NH_3) or nitrogen gas (N_2) and hydrogen (H_2) was added to regulate the nitrogen activity. For nitrocarburising propene (C_3H_6) was applied in addition to NH_3 and H_2. Activation of the samples to remove the protective oxide layer was carried out in-situ prior to nitriding or nitrocarburising; details of this treatment are proprietary.

Table 2 presents the composition of the gas mixtures employed in each experiment together with the treatment temperature and duration.

Table 2 - Experimental conditions utilized in the thermochemical gaseous treatments.

Gas composition	T (ºC)	t (h)
100%NH₃	440	16
96%H₂+4%NH₃	500	60
83%H₂+17%NH₃	500	14
50%H₂+50%NH₃	500	16
50%H₂+40%NH₃+10%C₃H₆	500	12
90%H₂+10%NH₃	720	16
96%H₂+4%NH₃	720	16
80%H₂+20%N₂	720	16

Cross sections of the thermochemically treated samples were prepared by conventional metallographic techniques. Optical microscopy was performed on the cross sections using a Leica optical microscope after etching the samples with Kalling's reagent no. 1.

The microhardness profiles were obtained using a Future Tech model FM-700 hardness tester on the mounted cross sections applying a load of 5 g and dwell time of 5s.

For phase analysis X-ray diffraction was performed on the surface of the samples using a Bruker D8 Discover diffractometer with Cr-Kα radiation. The diffractograms were obtained with a step size of 0.025º and step time of 3s.

Results and discussion

Optical microscopy. Figure 1 presents light optical micrographs from the cross sections of A286 samples treated under different conditions at 440 and 500°C. The temperature of 440°C is somewhat a standard condition frequently applied for other types of austenitic alloys such as AISI 316 and AISI 304. In this sense the specimen serves as a reference for comparison purposes. By using 100% of NH_3 at 440°C for 16h (Fig. 1a) a thick case is obtained although visible cracks are seen throughout the layer. The presence of cracks in the surface adjacent zone can be attributed to a high concentration of nitrogen, which induces high compressive stresses in the layer eventually leading to stress relaxation. Nitriding in 100% NH_3 (infinitively high nitriding potential) represents the maximum growth rate of the nitrided case. Precipitates are not observed in the nitrided case, which indicates that higher temperatures are applicable.

Nitriding at 500°C for 60 hours in a very lean atmosphere of only 4% of NH_3 (Fig. 1b) results in a thin homogeneous layer of nitrogen expanded austenite (γ_N). For the specimen nitrided at 500°C for 14 hours in 17% of NH_3 (Fig. 1c) a very similar layer is produced. Both layers were largely unaffected by the chemical reagent employed to reveal the microstructure which indicates a satisfactory corrosion resistance. Interestingly, the gas composition plays a major role for the growth kinetics of the nitrogen case in this material. It should also be emphasized that a temperature of 500°C (and 60 hours!) is unprecedented for thermochemical treatment of austenitic stainless steels; the applied conditions would normally result in massive formation of dark-etched chromium nitrides in the surface.
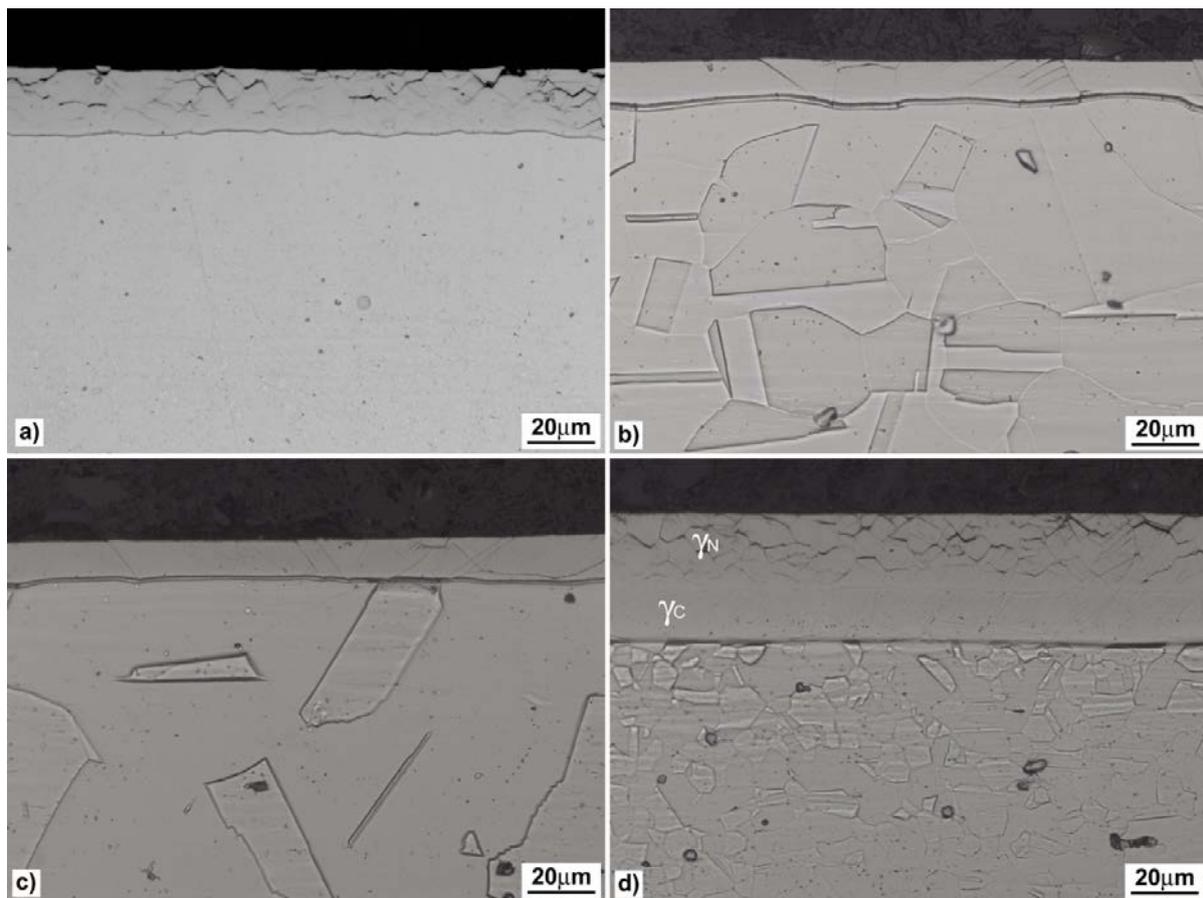

Figure 1 - Light optical micrographs from cross sections of A286 samples gas treated at: (a) 440°C for 16h - 100% NH_3, (b) 500°C for 60h - 96% H_2+4% NH_3, (c) 500°C for 14h - 83% H_2+17% NH_3 and (d) 500°C for 12h - 50% H_2+40% NH_3+10% C_3H_6.

The introduction of propene (C_3H_6) with a slightly higher percentage of ammonia markedly changes the kinetics of the process (Fig. 1d). After nitrocarburizing at 500°C in an atmosphere of

50%H$_2$+40%NH$_3$+10%C$_3$H$_6$ for 12h (Fig. 1d) a significant increase in layer thickness is observed. The surface adjacent part of the layer is characterised by grain boundary cracks indicating too high nitrogen content in the expanded austenite. Below the nitrogen rich and cracked nitrogen expanded austenite, carbon-rich expanded austenite (γ_C) with no visible cracks can be observed. Again, the temperature is very high compared to 'normal' austenitic stainless steels. The observance of cracks can also be attributed to the stress relaxation as stated before for Fig. 1a.

Optical micrographs of solution heat treated A286 samples gas nitrided at 720ºC for 16hours using 20% of N$_2$, 4% of NH$_3$ and 10% of NH$_3$ are shown in Figure 2. Changing the nitrogen source from ammonia to 20% of nitrogen gas (N$_2$) and also increasing the treatment temperature to 720ºC changes the growth kinetics. The reason for raising the temperature 720ºC is that this is the usual ageing temperature for A286. Hence, at this temperature bulk hardening and surface hardening can in principle be performed simultaneously in one treatment. The produced layer is relatively thin (Fig. 2a) and appears to have more pronounced grain boundaries as compared to the substrate, suggesting the presence of another phase along the grain boundaries. The nitrided case appears featureless, which indicates that the corrosion resistance is largely maintained. The reason for the relatively shallow thickness at this (high) temperature is attributed to a lower nitrogen activity in the gas, because ammonia was replaced by nitrogen gas.

The specimen treated with 4% of NH$_3$ at 720ºC (Fig. 2b) reveals a thick layer containing darkened areas near the surface and at grain boundaries. Increasing the ammonia content to 10% (Fig. 2b) produces an even thicker layer but also yields substantial precipitation of dark compounds on the surface and grain boundaries. The dark precipitated phases are most likely chromium nitrides.
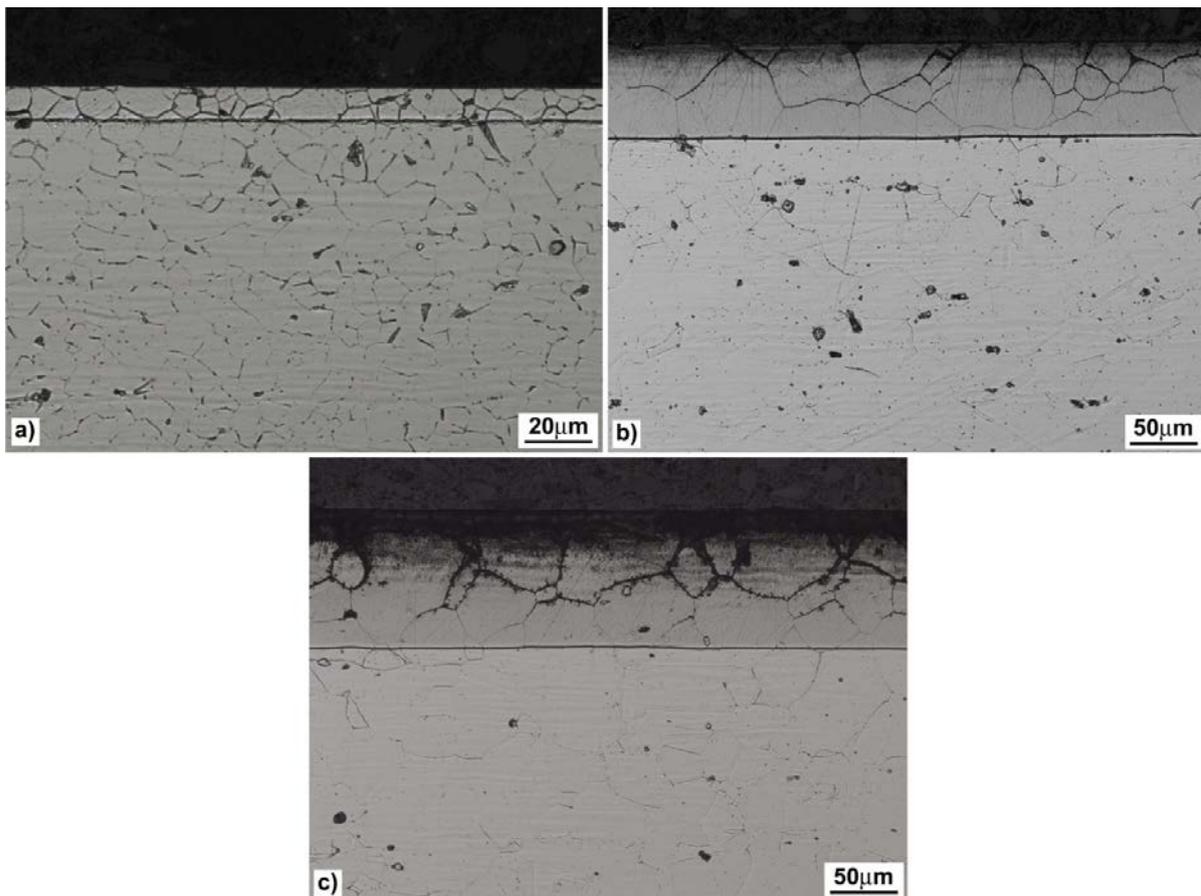

Figure 2 - Light optical micrographs from cross sections of A286 samples gas nitrided at 720ºC for 16h in a atmosphere containing: (a) 20% of N$_2$, (b) 4% of NH$_3$ and (c) 10% of NH$_3$.

Apparently the temperature and the ammonia content in the atmosphere are too high to prevent precipitation, presumably of detrimental chromium nitrides. Most abundant precipitation throughout

the grains is observed close to the surface. Apparently, homogeneous precipitation is possible in this oldest part of the nitrided case, which has experienced the longest ageing time. Also dark regions along the grain boundaries are observed. These are interpreted as developed by discontinuous precipitation, where precipitation starts at the grain boundary and grows into the grain under the partitioning of nitride forming and non-nitride forming elements. Obviously, provided that the precipitates contain high amounts of Cr, raising the ammonia content in the gas mixture has a detrimental influence on the corrosion properties.

X-ray diffraction analysis. Figure 3 depicts the X-ray diffraction patterns after gaseous nitriding at 500ºC for 14hours (17% of NH_3) and 60 h (4% of NH_3) and also the sample nitrided in 100% NH_3 at 440ºC - (see micrographs above). The reference pattern obtained from an un-treated A286 (solution treated) is also shown at the bottom of Fig. 3. Clearly, the material is textured with a strong (220) reflection; this texture appears to be retained after nitriding.
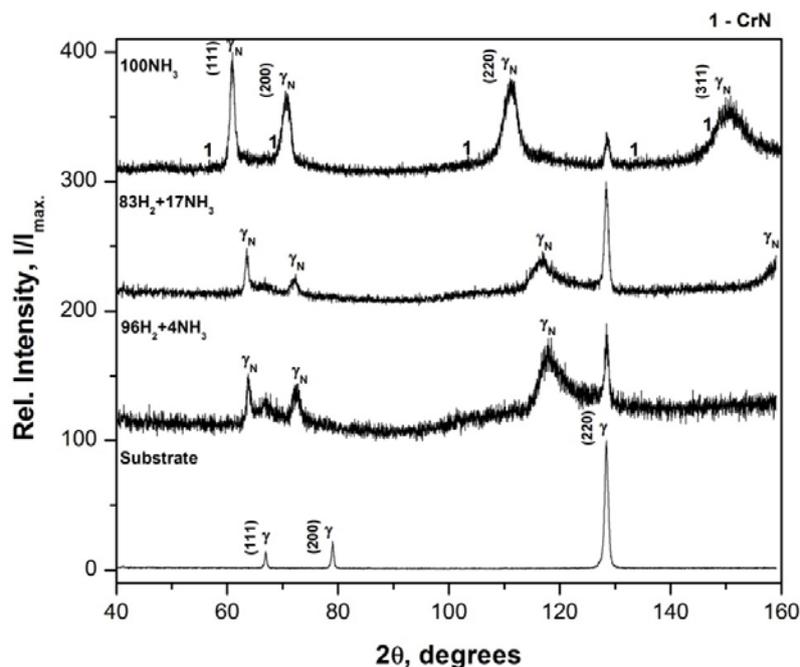

Figure 3 - X ray diffraction patterns of A286 samples gas nitrided at 440 and 500ºC in different nitriding potentials (positions of CrN reflections are marked by 1).

The formation of expanded austenite is observed after nitriding for all process conditions at 440 and 500ºC. This is evidenced by the shift of the austenite peaks to lower diffraction angles. Furthermore, the peaks are significantly broadened which is attributed to depth gradients of composition and stress within the volume probed with the X-rays. The larger peak shift for samples nitride at high nitrogen activity shows that a higher nitrogen content is obtained in the sample nitrided with the highest nitriding potential. The expected peak positions of CrN are indicated in the figure, but this phase could not be identified, indicating that its fraction is very low (or the precipitates are very small). The absence of CrN strongly hints at a positive effect of the strong nitride formers, which appear to suppress the formation of (unwanted) CrN. Nither is TiN observed, as such reflections would be found close to those of crystallographically identical CrN.

Figure 4 depicts the X-ray diffraction patterns of the A286 samples treated at 720ºC for 16h in different gas compositions. The diffractograms for the 720°C treatment are distinctively different from those for the 500°C treatments. Again, the (220) reflection is the most dominant peak and this is significantly broadened which is likely to be a consequence of formation of small MN-type precipitates in the austenite.

A sligth shift of the austenite peaks can be observed; a high content of NH_3 in the gas gives the largest shift. The presence of MN nitrides are unambiguously identified in all the diffractograms; the precipitates are likely to be TiN or (Ti,Cr)N. It is hypothesised that the main reason for the broadening of the austenite peaks are the presence of very small (stable) TiN nitrides, which induce local strain gradients in the austenite matrix. The sample nitrided in a gas mixture of N_2 and H_2, i.e. at low nitrogen activity, contains almost no observable nitride phase (cf. Fig.4).
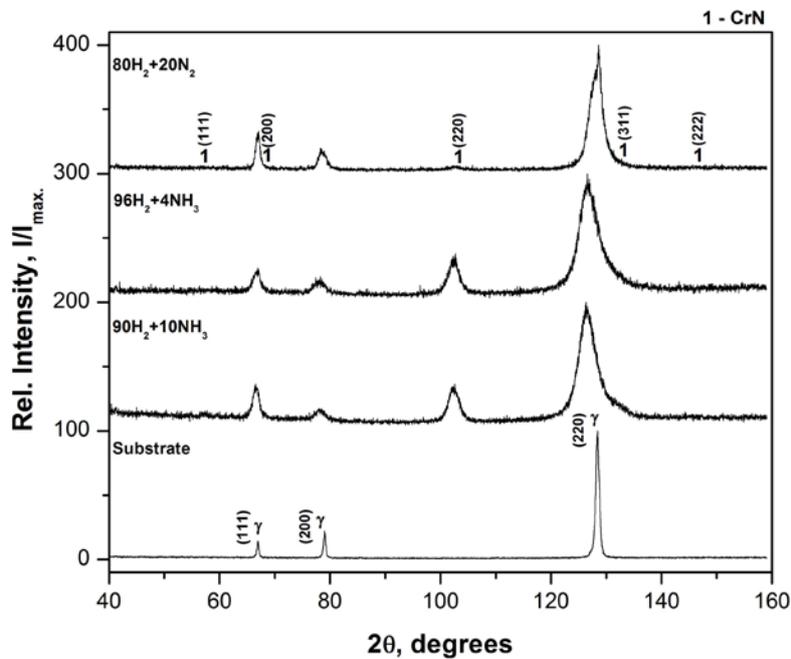

Figure 4- X ray diffraction patterns of A286 samples solution heat treated and gas nitrided at the ageing temperature (720ºC) for 16h in different atmospheres.

Case depth and hardness. In Table 3 the average layer thickness (l, µm) of the A286 samples thermochemically treated at different temperatures and in different gas compositions are shown. Nitriding at 440ºC in pure ammonia (infinite nitriding potential) produces a thicker layer than those obtained at 500ºC, applying a nitrogen lean atmosphere. Samples nitrided with 4 and 17% of NH_3 at 500ºC, but for different durations, resulted in very similar thickness and case morphology.

Table 3 - Average layer thickness from A286 specimens gaseously treated in different conditions.

Gas composition	t (h)	T (ºC)	l (µm)
100%NH_3	16	440	19.1±0.7
96%H_2+4%NH_3	60	500	12.2±0.4
83%H_2+17%NH_3	14	500	12.2±0.9
50%H_2+50%NH_3	16	500	33.5±0.8
50%H_2+40%NH_3+10%C_3H_6	12	500	37.7±0.7
80%H_2+20%N_2	16	720	9.4±0.3
96%H_2+4%NH_3	16	720	70±2
90%H_2+10%NH_3	16	720	103±2

At 500ºC nitrocarburizing in 40%NH_3+10%C_3H_6 for 12hours produces a layer thickness comparable with nitriding at the same temperature using 50%NH_3 but for 16h. This confirms that introducing carbon results in faster case growth. For the treatments performed at 720ºC it is clear from Table 3 that raising the nitriding potential markedly increases the layer thickness.

Figure 5 shows the hardness profiles for selected A286 samples after gaseous thermochemical treatment at 500ºC (Fig. 5a) and 720ºC (Fig. 5b) for different treatment times and gas compositions. All samples treated at 500ºC yield hardness values in the treated case of approximately 1100HV.

Samples treated at 500ºC with 4 and 17% of NH_3 yield very similar hardness profiles both showing an abrupt drop on the hardness reaching the substrate hardness.

Nitriding and nitrocarburizing at 500ºC in 50%NH_3 and 40%NH_3+10%C_3H_6, respectively, produced similar layer thickness (Table 3), but with different hardness profiles. The nitrocarburized specimen yielded a smooth drop on hardness close to the substrate interface, which is related to the presence of a carbon expanded austenite. Carbon expanded austenite has intrinsically lower hardness and can act as a load bearing support layer for the nitrogen expanded austenite zone located at the surface [5,6]. The bulk hardness has slightly increased to around 220-240 HV after treatment; this can for many applications be sufficient.
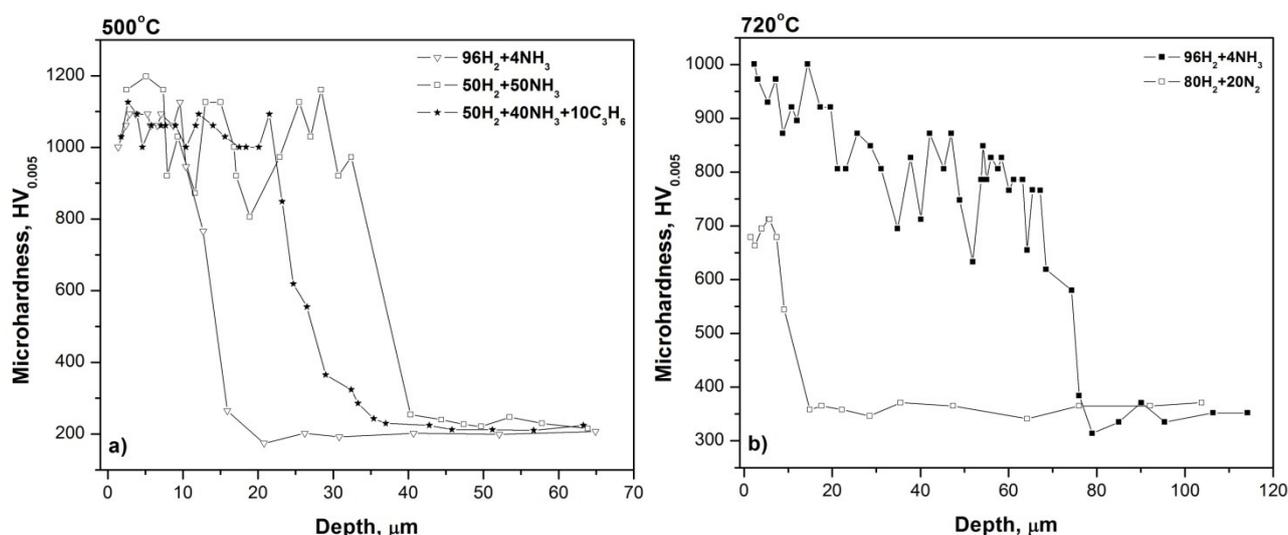

Figure 5 - Microhardness profiles of A286 samples thermochemically treated at (a) 500ºC and (b) 720ºC, for different treatment times and gas compositions.

At 720ºC using 4 or 10% of NH_3 as nitrogen source the shape of the hardness profile is similar apart from the different case depth. Both treatments result in a surface hardness of 1000HV and the values decrease with depth. The hardness profile for the sample nitrided in 10% of NH_3 is not shown due to the presence of a dark ecthed layer on the surface (see Fig. 2c) which impeded the measurements close to the surface. However the values are similar along the inner part of the layer.

Using 20% of N_2 as nitrogen source decreases the nitrogen activity which results in a thinner layer with a hardness of around 700 HV. The 720°C / 16 hours surface hardening treatment yields a substrate hardness of more than 350HV. The average hardness of the substrate after thermochemical treatments performed at 500 and 720ºC were found to be 218±13HV and 359±14HV, respectively. Hence, surface hardening and bulk hardening have occurred simultaneously. It is expected that at 720ºC for 16hours, which is the standard ageing condition, fine precipitates of γ'-Ni_3(Ti,Al) are formed in the bulk which provide the observed hardening. Clearly, surface hardening and ageing can be performed simultaneously.

General discussion. Solution annealed A286 can be treated at much higher temperatures- up to several hundred degrees- than traditional austenitic stainless steels without developing chromium nitrides and compromising the corrosion properties. This behavior can be attributed to the presence of the strong nitride formers, viz. Ti (Al and Nb), which have a stronger affinity to N than Cr. It is contemplated that Ti will function as a nitrogen getter, that prevents (or at least postpones) chromium to react with the available nitrogen atoms. Thus, the nitride to form first should be based

on Ti, i.e. TiN or mixed nitrides of the type (Ti,Cr)N, depending of the Ti:Cr ratio. It is expected that lean nitriding conditions should result in the formation of primarily TiN rather than CrN; such conditions will keep Cr in solid solution. For the temperature interval below 500°C it is not clear whether TiN forms as a chemical compound or whether Ti atoms (in solid solution) act as trap sites for nitrogen in (expanded) austenite.

The temperature stability of expanded austenite in solution annealed A286 is significantly higher than for, say, austenitic stainless steel AISI 316. Nitriding AISI 316 at 500°C would result in massive formation of CrN, which is obviously not the case for A286. The formation of CrN is clearly impeded in this material. This behavior has to be ascribed to the presence of Ti. It can be hypothesized that the strong interaction between Ti and nitrogen, either as actual TiN precipitates or by short range ordering could impede the diffusion of Cr and thus make nucleation of CrN more difficult. Alternatively, formation of CrN could be impeded if stable TiN/Ti-N occupies available nucleation sites for CrN, i.e. diffusion of Ti-N 'pairs' is required.

Summary

Precipitation hardening austenitic stainless steel A286 in a solution heat treated condition can be successfully surface hardened by thermochemical treatment over a large range of temperatures. Surface hardening can be carried out simultaneously with bulk hardening. The presence of strong nitride formers, viz. Ti, in the material has a strong influence on the nitriding response. It has been shown that expanded austenite in this material is fully stable even at prolonged exposure at 500°C.

Acknowledgements

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