Optimised Sintering and Heat Treatment of the Nickel-free High-Nitrogen MIM-Steel X15CrMnMoN17-11-3

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ABSTRACT

Metal Injection Moulding has emerged as an attractive route for obtaining high-nitrogen stainless steels. Since the solubility of nitrogen in Fe-Cr austenite is much higher than in the liquid phase, the required amount of nitrogen can be added to the alloy without application of high pressures. Motivated by concerns regarding allergic reactions to nickel containing alloys, BASF has developed a polyacetal based MIM feedstock with the product name Catamold® PANACEA. This feedstock contains a prealloyed ferritic steel powder, which is nitrided either simultaneously during sintering or during a post sintering solution annealing process. In this paper several cost effective industrial sintering and solid state nitriding processes for the high-nitrogen and Ni-free stainless MIM steel X15CrMnMoN17-11-3 are presented and discussed from the view point of a toll heat treating company.

INTRODUCTION

Nickel is the most frequent cause of contact allergy in industrialised countries. About 10-15% of the women and 2-5% of the men are liable to suffer from nickel allergy, if submitted to repeated or continuous contact with this element. The nickel is transferred from Ni coatings like on spectacle frames, from Ni alloys like coins and bracelets or from stainless austenitic CrNi steels used e.g. for wrist watches. Although the latter are regarded as corrosion resistant, enough Ni ions may be dissolved by sweat or body fluid to cause inflammation of the skin or tissue [1]. Prevention of nickel allergy is of great concern. The EU Nickel Directive aims at the prevention of sensitization and elicitation of nickel dermatitis. The Nickel Directive limits nickel release (limit: 0.5 $\mu g/cm^2$/week) from certain items intended to come into direct and prolonged contact with the skin and it limits nickel content (limit: 0.05%) of inserts for pierced parts of the body [2]. This directive has already been shown to have an impact. For instance in 2004, compared to the situation in 1999, a significant decrease was recorded in the proportion of items (jewellery, watches, spectacles, clothes and shoes) on the Swedish market that would not fulfil the requirements of the Nickel Directive [3]. The delays in enacting this Directive have allowed considerable time for manufacturers to commence addressing the materials used to produce their products and find suitable alternatives [4]. Although some austenitic CrNiMo stainless steels, such as the AISI 316L type, are reported to have a very low Ni release rate and did not cause dermatitis in Ni-sensitive subjects [5], the development of Ni-free stainless steels was spurred. Of the Ni-free stainless body-centered cubic (bcc) steels the standard martensitic ones lack corrosion resistance, which is a prerequisite in most body friendly applications. The ferritic as well as the martensitic ones may not offer a sufficient toughness. In addition a non-magnetic material is preferred in some applications. If the steel is to be austenitic (face centered cubic, fcc) and nickel free, according to the Schaeffler diagramm (Fig. 1), the total nickel equivalent needs to be provided by appropriate amounts of cobalt, manganese, nitrogen and carbon [6].

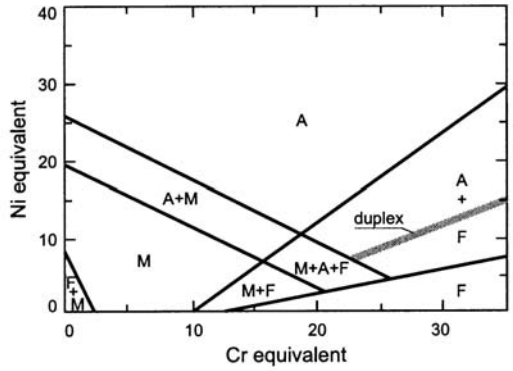


Figure 1: Schaefler diagram, revised after Speidel and Uggowitzer (1993) with (mass%):

Cr_{eq} = Cr+1.5Mo+1.5W+0.48Si+2.3V+1.75Nb +2.5Al

Ni_{eq} = Ni+Co+0.1Mn-0.01Mn^2+18N+30C

A = austenite M = martensite F = ferrite

Cobalt however is undesirable in such steels because it can cause allergic reactions similar to nickel and carbon tends to form carbides and therefore reduces the corrosion resistance. Therefore CrMn(Mo)N austenites were adopted to body friendly applications along the following lines: Nitrogen is used as the major substitute of Ni but is limited to 1 mass% to avoid cleavage-like, brittle failures. Since Cr raises the N solubility more than Mo, high Cr levels are encountered in steels melted under normal pressure, while high Mo contents prevail in steels produced by the pressurized electro-slag-remelting process (PESR). Manganese is added to promote the N solubility and to retard the precipitation of M_2N. Two examples for pressure melted austenitic CrMnMo-steels are P558 (X20CrMnMoN17-11-3) and P2000 (X13CrMnMoN18-14-3) from Böhler Edelstahl GmbH and Energietechnik Essen GmbH respectively [7, 8]. P2000 bone fixtures were successfully tested on rabbits, which makes this alloy a potential candidate for medical applications in the human body [9]. Promising results were also achieved with P558 during in vitro studies [10].

Instead of adding nitrogen to a melt, it may be introduced into a steel powder or powder skeleton with open pore channels through solid state nitriding. The high-nitrogen and Ni-free stainless steel Catamold® PANACEA (X15CrMnMoN17-11-3) was developed by BASF for Metal Injection Moulding MIM [11]. PANACEA contains a prealloyed ferritic steel powder which picks up nitrogen during sintering (one-step process) or is solution nitrided after sintering (two-step process). As can be seen from Figure 2, the solubility for nitrogen decreases with increasing temperature and decreasing N_2-partial pressure. The advantage of the two-step process is that sintering and nitriding temperature and atmosphere can be set independently. However, since diffusion distances are significantly longer, extended processing times are required and the process is therefore thought to be too expensive to be applied to thick parts [12]. During normal furnace cooling after sintering Cr_2N-precipitates tend to be formed. Therefore a post sintering solution annealing in the austenite regime followed by rapid cooling is necessary. As can be concluded from the CCT-diagram in Figure 3, cooling rates of >150°C/min should be ensured.

Figure 2: Influence of temperature and atmosphere on the nitrogen content

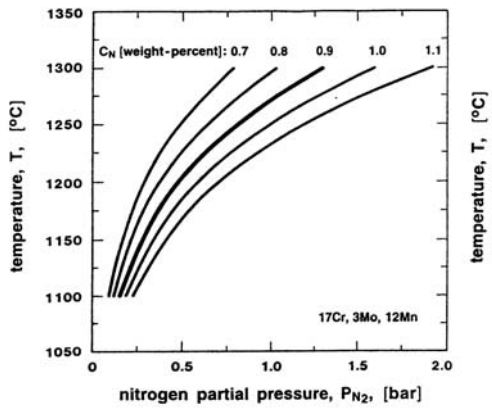
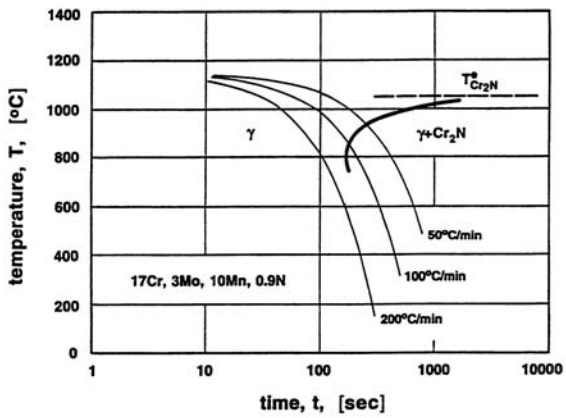


Figure 3: continuous Cooling Transformation (CCT) diagram for PANACEA material



In the present work several industrial sintering and solid state nitriding processes for the high-nitrogen and Ni-free stainless MIM steel X15CrMnMoN17-11-3 are presented and discussed from the view point of a toll heat treating company. Specimens were catalytically debinded, pre-sintered, solid state nitrided, sintered, solution annealed and quenched. The development of the microstructure was investigated and the microstructure and chemical composition of the samples characterised.

EXPERIMENTAL PROCEDURE

Sintered specimens for the present investigation were produced with BASF's commercial Catamold® product PANACEA. The chemical composition of the alloy is given in Table 1.

Table 1: chemical composition of Catamold® product PANACEA (X15CrMnMoN17-11-3)

% C	% N	% Cr	% Ni	% Mo	% Mn	% Si	Fe
≤ 0.2	0.75-0.90	16.5-17.5	≤ 0.1	3.0-3.5	10.0-12.0	≤ 1.0	balance

Sample parts of different geometry comprising wall sizes up to 5mm were injection moulded and catalytically debinded using the BASF process [13]. Secondary thermal debinding and pre-sintering were done in a bell type hot wall furnace. To facilitate binder burnout a dry hydrogen protective atmosphere was used in this process. During pre-sintering a soak temperature of 800°C was held for 1 hour. At the end of the process cycle, the samples were furnace cooled under protective atmosphere to a temperature below 60°C. After pre-sintering the part strength proved to be suitable for further handling purposes while the still remaining open porosity enabled rapid nitriding during the following sintering step. Solid state nitriding, sintering, solution annealing and rapid cooling were done in a cold wall vacuum furnace (CWVF) designed to allow high temperature cycles with high partial pressure nitrogen and high pressure gas-quenching. The furnace features a well sealed graphite chamber and an effective water-cooling system. For comparison purposes samples were sintered in a muffle atmosphere furnace (MF) at 1 bar atmospheric pressure. The solution annealing was also preformed in a conventional hot wall furnace (HWF), followed by water quenching. Metallographic samples were polished and etched using aqua regina (2 parts HCl, 1 part HNO_3 and 3 parts Glycerine) at room temperature for 1 to 2 minutes. The density of the samples after sintering was evaluated by pycnometric measurement. Nitrogen elemental analysis was done by the combustion method.

RESULTS AND DISCUSSION

An overview of the sintering tests and the results obtained is given in Table 2. The first test was accomplished in a muffle furnace at 1250°C with a protective atmosphere of 100% H_2. Following this, two sinter cycles were done at 1200°C and 1250°C respectively with a protective atmosphere of 75% N_2 and 25% H_2. Two further sinter tests were done at 700mbar partial pressure N_2 in the cold wall vacuum furnace. The first one of these with a continuous heat-up ramp up to sintering temperature (1250°C), the second one with an intermediate holding step at 1050°C to enable solid state nitriding throughout the porous MIM parts. A final sinter run was done at 1270°C with 900mbar partial pressure N_2. After sintering the parts were air cooled in protective atmosphere. The metallographic evaluation of the samples sintered in hydrogen atmosphere identifies austenite, ferrite and Cr_2N (Fig. 4). Both samples sintered in 75% N_2 and 25% N_2 on the other hand show a 100% austenitic structure in the core (Fig 5). The samples sintered at 1250°C contain less nitrogen than the samples sintered at 1200°C. These results were expected considering the solubility of nitrogen at sintering temperature and the phase diagram for the PANACEA alloy (Fig. 6).

Table 2: overview of the sintering tests and results

run No	furnace	atm.	ramp (°C/min)	soak temp.	soak time	ρ (g/cm^3)	% N	phases in core	phases at surface
1	MF	100% H_2	2.5	1250°C	2hrs	7.66	< 0.05	α, γ, Cr_2N	α, γ, Cr_2N
2	MF	75% N_2, 25% H_2	2.5	1200°C	2hrs	7.48	0.90	γ	γ, Cr_2N
3	MF	75% N_2, 25% H_2	2.5	1250°C	2hrs	7.59	0.79	γ	γ, Cr_2N
4	CWVF	700mbar N_2	5	1250°C	2hrs	7.69	-	α, γ	γ, Cr_2N
5	CWVF	700mbar N_2	5	1050°C 1250°C	2hrs 2hrs	7.40	0.86	γ	γ, Cr_2N
6	CWVF	900mbar N_2	5	1050°C 1270°C	2hrs 2hrs	7.55	0.89	γ	γ, Cr_2N

Figure 4: etched core microstructure of PANACEA sample after sintering at 1250°C in H_2 (run No 1): austenite, ferrite and Cr_2N

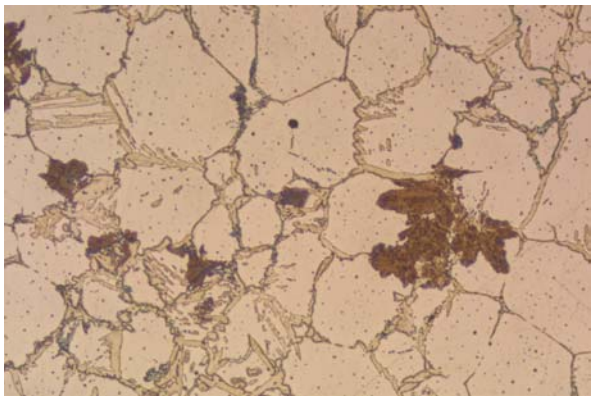


Figure 5: etched core microstructure of PANACEA sample after sintering at 1250°C in 75% N_2 and 25% H_2 (run No 2): austenite

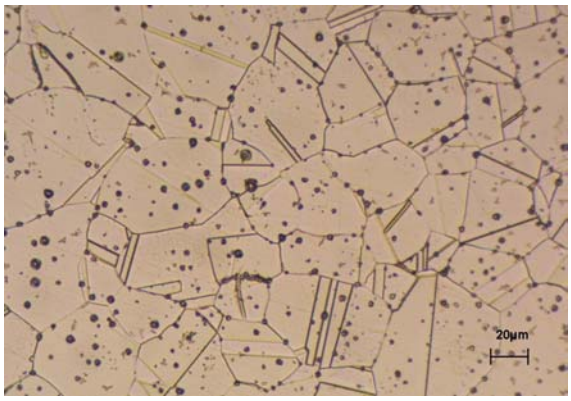


Figure 6: computer generated phase diagram for iron base alloys with 17% Cr, 10% Mn, 3% Mo and nitrogen

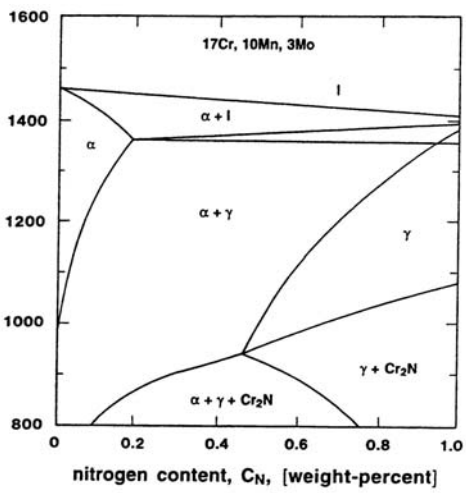
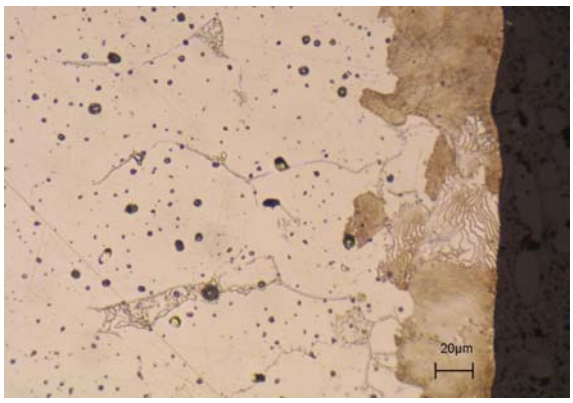


Figure 7: etched surface microstructure of PANACEA sample after sintering at 1250°C in 700mbar N_2 (run No 5): austenite and Cr_2N



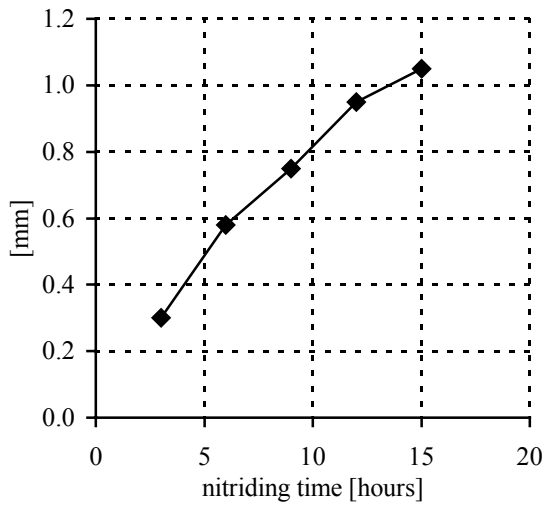
The microstructures observed in the samples sintered at partial pressure nitrogen in the cold wall vacuum furnace correspond also well with the nitrogen solubility and equilibrium diagrams. The microstructure was austenitic, although samples from run No 4 with wall sizes above 3mm showed a considerable amount of ferrite in the core. This could be explained by the more rapid heat up cycle in comparison to the sintering performed in the muffle furnace. It was assumed, that during heat up the open porosity was closed prior to achieving a sufficient nitrogen content in the core of the samples. Since the diffusion distances then became significantly longer, a ferrite containing core remained after sintering. It was indeed possible to eliminate this undesirable two phase core structure by adding a nitriding soak at 1050°C for two hours during ramp up (run No 5).

Generally at a given sintering temperature higher densities were achieved with parts containing ferrite. This can be explained by the diffusion coefficient, which for the bcc phase is about two orders of magnitude above that of the fcc phase. In order to improve the density after sintering of fully austenitic parts, the soak temperature was eventually increased to 1270°C. To maintain the required nitrogen content, the partial pressure N_2 at soak temperature was set to 900mbar. With these parameters fully austenitic parts with wall sizes up to 5mm, a density of 7.55g/cm^3, a nitrogen content of 0.89% and a hardness of 330HV$_{30}$ were produced (run No 6).

In all samples a precipitation of Cr-nitrides occurred during slow cooling from sintering temperature at the surface (Fig. 7). Since the nitrogen solubility increases during cooling, precipitation tends to start in the near surface part of sintered PANACEA parts, especially if the surface nitrogen content is close to the solubility limit. As the nucleation is promoted by grain boundaries, an intercrystalline net of hard particles is formed followed by a discontinuous pearlite-like precipitation within the grains [14]. For the sake of toughness and corrosion resistance these Cr_2N phases have to be removed by post sintering solution annealing in the austenite region followed by quenching. Solution annealing at atmospheric pressure nitrogen for 1 hour at 1150°C in a hot wall furnace, followed by water quenching as well as solution annealing in a cold wall vacuum furnace at 800mbar nitrogen at 1150°C for 1 hour, followed by overpressure inert gas cooling proved to be successful. A main disadvantage although of the water quenching is the formation of scale on the surface of the parts. This has to be removed either mechanically or by pickling. Quenching with high pressure inert gas on the other hand leaves the parts completely free of any discoloration.

Since at a given sintering temperature higher densities were achieved with the presence of a bcc phase, the post sintering solid state nitriding of such parts was investigated. Hydrogen sintered samples from run No 1 were solution annealed, followed by overpressure inert gas quenching. Uptake of nitrogen lead to a fully austenitic case, the depth of which obviously depended on the soak time. Starting with a nitrogen content below 0.05%, after 3 to 15 hours soak at 1150°C in 800mbar N_2 a nitrogen concentration of at least 0.62% was achieved within cases of 0.3 to 1.05mm depth (Fig. 8). It is concluded that the solid state nitriding of PANACEA MIM parts with wall sizes up to 3mm, sintered to high density in H_2 atmosphere, seems to be a promising option.

Figure 8: depth of fully austenitic case after solid state nitriding of H_2 sintered PANACEA sample



CONCLUSIONS

In this work the results obtained during sintering and solid state nitriding of the high-nitrogen and Ni-free stainless MIM steel X15CrMnMoN17-11-3 were presented. Simultaneous nitriding to a fully austenitic microstructure and sintering to densities above 97% of the theoretical value were achieved with a muffle atmosphere furnace and with a specially designed cold wall vacuum furnace. Unwanted Cr_2N phases were removed by post sintering solution annealing in the austenite region followed by quenching. Water quenching after annealing in a hot wall furnace proved to be successful, although the corresponding processing in the cold wall vacuum furnace with overpressure inert gas quenching delivered a much superior surface quality. Sintering in the ferritic region to achieve densities above 99% of the theoretical value could be a promising route for obtaining parts with excellent suitability for a mirror like polish. Processing times required for the post sintering solution nitriding of these parts were presented. If the wall thickness stays below 3mm - which is very often the case for MIM parts - fully austenitic microstructures are achievable within reasonable processing time.

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