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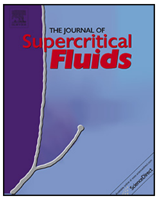

Different corrosion behaviour of autoclaves made of nickel base alloy 718 in ammonobasic and ammonoacidic environments

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ABSTRACT

The ammonothermal process is a promising technique for cost-effective growth of nitride based bulk-semiconductors. Degeneration of growth reactors made of a Ni—Fe—Cr alloy is a limiting factor of the growth process. Corrosion is initiated by supercritical ammonia and acidic as well as basic mineralizer up to 600 °C and 300 MPa. We investigated the corrosion processes with microscopic (optical and scanning electron microscopy) and spectroscopic (energy dispersive X-ray and auger electron spectroscopy) methods. It showed that ammonobasic environments lead to the formation of a nitrited layer. Composition and thickness changes depending on the number of loads. The corrosion layer does not reach a steady state and therefore degenerates as consequence of cyclic ammonothermal loads. For ammonoacidic conditions on the other hand significant general corrosion occurred which is connected to the dissolution of the metal phase in the supercritical. Moreover, a high tendency to stress corrosion cracking was observed.

1. Introduction

The ammonothermal method is a promising way for low-cost production of nitride bulk crystals like Gallium nitride (GaN) and ternary or higher nitrides [1]. From a technical point of view the growth of Gallium nitride is most interesting due to the wide range of industrial applications such as devices for high power electronics and optoelectronics [2]. GaN is mainly grown via vapour phase techniques like HVPE (Hydride vapour phase epitaxy) where main limitations are a restricted film height and high defect density. However, the ammonothermal technique allows the growth of bulk materials [3–5]. The process takes place in supercritical ammonia at up to 600 °C and 300 MPa with acid or basic additives to enhance important growth parameters like solubility or transport properties. Finally this results in high tensions in the reactor walls. To reach the high temperatures we use an outside heating system as shown in Fig. 1 and therefore a material with high temperature strength is required. Nickel base alloys like Inconel Alloy 718 (DIN ISO EN 2.4668) offer compulsory mechanical properties at elevated temperatures ($T_{\text{max strengh}} = 650\,^{\circ}\text{C}$). This is a consequence of its microscopic strengthening mechanisms like order hardening of γ''-phase, precipitation hardening of γ'-particles in a γ-matrix as well as Chrome or Molybdenum carbides populating grain boundaries [6,7]. Alloy 718 also shows high corrosion resistance due to its high chrome content [8].

Despite its chemical resistance, significant amounts of metal from the alloy can be found in crystals grown under ammonoacidic as well as ammonobasic conditions (compare Table 1) [1,9]. The main source of these impurities is found in the autoclave wall. Furthermore some groups work with autoclaves lined with shrunken platinum crucibles. This technology is limited because lining the sealing parts is not possible. In this way the interaction of the corrosive fluid with the alloy is just minimized but not prevented [9]. Regardless of the corrosive environment and the associated high concentration of impurities ammonoacidic growth processes show a high potential regarding growth rates for industrial applications. For ammonium chloride growth rates up to 170 μm/day are postulated theoretically. Nonetheless, experimentally only growth rates of 80 μm/day are realized [9]. Using ammonium iodide mineralizer growth rates up to 105 μm/day [10] are shown. Recently Bao et al. realized growth rates up to 300 μm/day [11] using NH_4F. Typical values for the ammonobasic growth are in the range of 20–80 μm/day [12].

Wang and Callahan found different growth rates depending on the size of the autoclave and hence the interaction surface [1]. Furthermore, Zhang et al. identified Ni-containing intermediates

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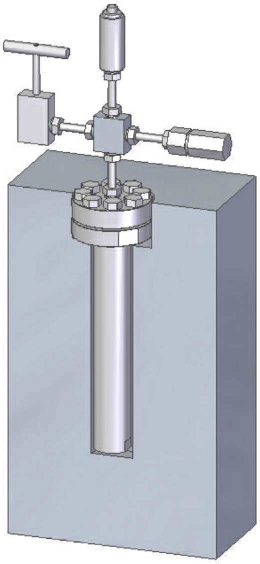

Fig. 1. Ammonothermal autoclave positioned in a heater. Total length of the autoclave is approximately 300 mm, outer diameter is 50 mm and inner diameter is 21 mm. A high pressure valve, a rupture disk and a pressure transducer are placed on the top of the autoclave.

investigating the ammonoacidic growth of GaN [13]. As a possible consequence the growth rate is also determinated by those primary corrosion products. In this way, understanding corrosive interaction for ammonoacidic and ammonobasic conditions delivers fundamentals for developing suitable and cost-effective liner technologies. Consequently, the growth of crystals with improved purity and enhanced growth rates can be enabled. Additionally autoclave lifetime can be increased.

Although there are several studies dealing with corrosion of reactors made of nickel base alloys for the hydrothermal crystal growth [14], there is still a lack of knowledge regarding the mechanism of corrosion for supercritical ammonia [15,16].

In this study we choose a phenomenological, metallographic approach to examine the impact of corrosion, because no reliable data regarding the physiochemical properties of the supercritical fluid are obtainable. First, there are no experimental data regarding the decomposition of ammonia under ammonothermal conditions [1,15,17]. Second, simulations describing the molecular structure of ammonia at pressures and temperatures of 300 MPa and 600 °C in presence of a nickel based alloy surface are not available. However, the decomposition in presence of Ni or Fe surfaces was described in several studies [18]. To obtain more information regarding the fluid structure, more experimental studies are nessesary.

Table 1
Literature evaluation: metallic impurities from the autoclave wall found in ammonothermally grown crystals [1,9]. Ammonoacidic conditions lead to concentrations several magnitudes higher than for ammonobasic environment.

Element	Impurities in grown crystals [atoms/cm^{-3}]	
	Ammonobasic	Ammonoacidic
Ni	$\leq 8 \times 10^{15}$	10^{17}–10^{20}
Fe	$\leq 2 \times 10^{17}$	10^{17}–10^{20}
Cr	Not reported	10^{15}–10^{18}
Pt	$\leq 5 \times 10^{16}$	$\leq 10^{16}$

Table 2
Composition (mass fraction in %) of semi-finished products for fabrication of our reactors. Elements in lowest quantities (<0.2%) are not shown here (C, S, Mn, Si, Cu, Pb, Co).

Ni	Cr	Fe	Nb	Mo	Ti	Al
52.9	18.5	18.3	5.3	3.0	1.0	0.5

We investigated the microstructure of autoclaves, used for ammonobasic and ammonoacidic experiments with different numbers of loads. To complement these results, material samples made of the Alloy 718 were tested in special ammonothermal environments to prove influencing factors. Furthermore we are able to evaluate lifetime limiting factors like stress corrosion cracking. The results represented here are based on the method described in a preliminarily study [19].

2. Materials and methods

The autoclaves used for investigations were fabricated from semi-finished material (Thyssen Krupp) with a composition described in Table 2. The material is hot rolled and aged. The samples are taken from several ammonothermal autoclaves with different numbers of loads.

Fig. 2 shows how the samples were taken from the autoclave. This sampling enables to evaluate pressure effects on general corrosion behaviour and stress corrosion cracking. To determine if there are preferred positions of corrosive attack regarding the total length, the samples were located at different positions at the autoclaves. To obtain appropriate surfaces for investigating the microstructure samples have been grinded and polished as described in [19].

For sub-surface microhardness profiling a Vickers hardness tester (KP30; KP Prüftechnik) in combination with a multipurpose microscope were used. Optical microscopy (DM2500M; Leica Microsystems) and Scanning Electron Microscopy (Gemini Ultra 55; Carl Zeiss) allow a precise representation of metallic microstructure. Chemical information regarding the composition of the corroded layer was delivered by Energy Dispersive X-Ray Spectroscopy (NORAN System SIX; ThermoScientific).

3. Results und discussion

3.1. Corrosion of alloy 718 under ammonobasic conditions

3.1.1. Formation of corrosion layer

As shown in Fig. 3, comparing SEM pictures of a new autoclave after honing and an autoclave, which was used in approx. 30 ammonobasic growth experiments, delivers two characteristics of corrosion. First, surface quality is degenerated. Second, we observed the formation of a corrosion layer.

For detailed understanding of the time dependent behaviour of the layer formation, we extend our investigations on three autoclaves with a strongly different number of loads. In all cases optical microscopy of etched samples showed a corrosion layer while the same general composition and same appearance of the interface

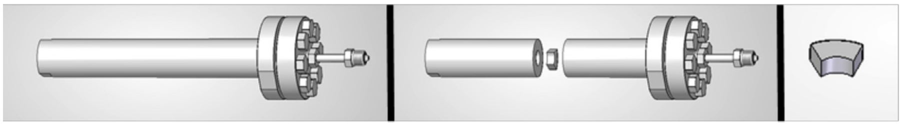

Fig. 2. Preparation and position of corrosion samples delivered from investigated autoclaves.