The Pathology of PM HIP Duplex Stainless Steels

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Abstract. Tests were conducted to simulate possible issues in manufacturing of Powder Metallurgical HIPed Duplex Stainless Steels. Root causes, and consequences are analyzed and discussed from a manufacturing, metallurgical and properties point of view. The results highlight the importance of material understanding and good process control when manufacturing these alloys. While some issues are unique to PM HIP material, many of them can also be found in conventional wrought materials e.g., sigma phase and nitride precipitation. In addition, the findings in this study puts into question limitations stated in some specifications for this process and alloys. The findings show the importance of staying within these limitations but also show that some aspects are not as critical. The majority of these specifications are based on forging specifications that might result in unnecessary limitations on the PM HIP process and materials. This while not necessarily ensuring material quality or possibly limiting material use.

Introduction

Duplex Stainless Steels are characterized by high mechanical strength combined with excellent resistance to stress corrosion cracking, pitting and crevice corrosion and general corrosion. In applications for the Subsea Oil & Gas Industry and chemical industry the demands on the material are getting tougher as operating pressures and temperatures are increasing combined with an increasing demand for material integrity. This is pushing the limits on the manufacturability of conventional forged materials and the industry is moving more and more to PM HIP materials as conventional forging cannot meet the tougher requirements.

Duplex Stainless Steels contain an approximate 50/50 mixture of ferrite (α) and austenite (γ) and has a fairly complex metallurgy that if not processed properly can cause a number of issues. Many of these issues can be eliminated by the use of PM HIP, e.g., segregation caused by insufficient hot working and other microstructural defects associated with forgings. The major limiting factor for PM HIP DSS is shared with the conventional materials, the precipitation of unwanted phases during heat treatment, i.e., the formation of embrittling intermetallic and nitride phases during water quenching following the solution annealing. Even small amounts of intermetallic and/or nitride phase may affect the impact toughness and/or corrosion resistance adversely for DSS and SDSS components, although this is not always the case, especially for intermetallic phase. The formation of unwanted phases is most often a consequence of poor heat treatment process, possibly in combination with a large wall thickness. It can also be a consequence of poor chemistry caused by an overly wide alloy composition range. To find the detrimental precipitates, Light Optical Microscopy is used as the standard test method in manufacturing testing according to most customer specifications. Sometimes LOM might prove insufficient as some

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detrimental precipitates are so small that they require more sophisticated analysis methods in order to be found.

One of the major benefits of PM HIP DSS is the fine isotropic microstructure in the material. The γ-spacing of PM HIP DSS is normally in the range of 10-15 µm and it is essentially the same throughout the component whether it is a 1kg part or a 10-ton part. If we should compare this point to large forgings, they are rarely below 30µm without very special processing. In the Oil & Gas industry the small γ-spacing provides a major benefit with an increased resistance to Hydrogen Induced Stress Cracking [1]. In the Urea industry the fine γ-spacing improves the corrosion resistance to ammonium carbamate as the negative effects of the preferential corrosion of the γ-phase can be limited [2].

Unlike conventional materials the level of oxygen content in PM HIPed components is extremely important as it has a significant influence on properties, especially impact toughness [3, 4, 5]. In this study the effect of oxygen has been compensated for to examine other factors when the measured oxygen content cannot explain a deviation from the expected properties.

Experimental

The test material in this study has been manufactured to simulate issues that can and do appear in the manufacturing of PM HIP SDSS components. All the tested material is in a thickness range that in normal manufacturing does not result in issues with properties and/or microstructure. The alloys used in this study is APM2327 (UNS S32505) and APM2329 grade (UNS S32906). The nominal chemistry for each alloy can be seen Table 1.

Table 1. Nominal chemical composition of alloys in this study.

	C	Cr	Mo	Ni	Cu	N	Fe
APM2327	<0,03	26	3	7	2	0,27	Bal.
APM2329	<0,03	29	2,3	7	<0,8	0,35	Bal.

Powders used in this study was manufactured using nitrogen gas atomization. The particle size is -500µm with a d_{50} of 100-120 µm. The materials have been HIPed at 1150ºC, 1000 bar with 1-3 hours dwell time. APM2327 (UNS S32505) solution annealed at 1070ºC and APM2329 (UNS S32906) at 1060ºC, both followed by quenching in cold water. The material thickness and quench rate has been varied to simulate process variations that can be seen in regular manufacturing.

Mechanical testing has been performed according to ASTM A370. Microstructural analysis has been performed using LOM on specimens etched with 10% oxalic acid in a first step to reveal precipitates like carbide and nitrides. In a second step the sample is electrolytically etched in 20% NaOH to reveal intermetallic phases like Sigma and Chi. Ferrite content has been measured according to ASTM E 562-11 and γ-spacing has been measured according to DNV-RP-F112.

SEM/EDS has been used for more in depth-analysis of precipitates. EBSD has been used for evaluating phase distribution, phase identification and to measure the amount of sigma phase.

Results

<u>*Intermetallic precipitation*</u>. There are a number of intermetallic phases that can form in DSS e.g., Sigma (σ-phase), Chi, and R phase. In general, it is only the σ-phase that has been found to be the limiting for the more common PM HIP SDSS. All these intermetallic phases affect the properties, but σ-phase is the dominating phase, at least after longer aging times. σ-phase is a Mo and Cr rich, hard embrittling precipitate that nucleate and grow primarily in α/α and α/γ phase boundaries in the approximate temperature interval of 600 - 1000°C [6, 7]. At 900ºC it can take as little as 2 minutes for the α in a 25Cr SDSS to transform to σ-phase. Due to the rapid precipitation this is also the main limiting factor as to how thick section can be manufactured as the cooling rate after

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HT must be fast enough to avoid the precipitation. Table 2 shows the typical thickness range for a selection of DSS manufactured by PM HIP, limited by precipitation of σ-phase.

Table 2. Typical maximum thickness of common PM HIP DSS.

APM2377	**APM2328**	**APM2327**	**27Cr**	**APM2329**
UNS S31803	UNS S32750	UNS S32505	UNS S32707	UNS S32906
300-350mm	100-150mm	175-225mm	50-100mm	250-300mm

Any σ-phase in the microstructure will affect the material negatively. Studies performed have shown that even small amounts, less than 0.1% of σ phase can cause a large drop in impact toughness [8]. However, for it to affect the corrosion resistance there needs to be a substantial amount of σ-phase in the microstructure, typically above 0,5% [9, 10]. Even at low amounts, the precipitates are usually clearly visible, even at moderate magnifications during microstructural investigation using SEM or LOM on etched specimens. Fig. 1 shows typical LOM micrograph of σ-phase in APM2327 SDSS. The σ phase is indicated with red arrows.

The presence of σ-phase in the material does not immediately disqualify the material as it may still have good mechanical and corrosion properties. The micrograph in Fig. 1 is from T/2 (mid-section) on a APM2327 test piece with 191 mm thickness, i.e., close to the limit for what is practically feasible with APM2327. The test piece was positioned poorly in the quench tank so water flow around it was low during quenching and consequently the cooling rate was lower than ideal. Measurements in LOM indicates the volume of σ-phase is 0,1-0,17%. Analysis with EBSD confirmed 0.1%. Despite this the material had an impact toughness of 83J at -46ºC, well above the acceptance criteria of 40J. Furthermore, corrosion testing using ASTM G48 method A at 50ºC showed no weight loss. Another example, a large production part with 178mm section thickness with a design causing significant restrictions to water flow in and around the part during quenching. Most of these parts had σ-phase at T/2. The impact toughenss was 65-70J at -46ºC and corrosion test showed no weight loss. Tests performed at T/4 showed only 10J higher impact toughness despite containing no σ-phase at all. In all cases the tensile properties far exceeded the minimum requirements.

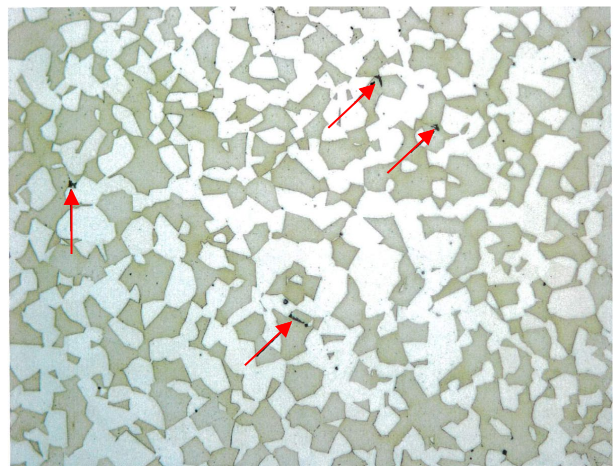

Figure 1. Typical microstructure of APM2327 containing a small amount of sigma phase.

Tight control of the powder chemistry in combination with a well-controlled and executed heat treatment is paramount for manufacturing a material without σ-phase. If there is σ-phase in the material, it may have many causes, but the driving factor is low quench rate in the critical temperature interval. Low quench rate can be caused by many things e.g., too large part thickness, too low agitation in tank, poor part design, poor part placement HT lot, etc. In rare cases it can also be connected to poor chemistry control and wrong HT-temperature.

*<u>Other detrimental precipitates</u>***.** Most HIP DSS materials specifications are derivatives of forging specifications and only dictate LOM for investigating the microstructure. While this in most cases is sufficient to confirm that the microstructure is sound, the resolution limit of LOM can mean some things may be overlooked e.g., nitrides. Nitrides not only reduces toughness, but unlike σ-phase, also corrosion resistance already at very low amounts [10]. There are two main types of

nitrides found in Duplex stainless steel, equilibrium and non-equilibrium nitrides. Non-equilibrium nitrides, or quenched nitrides form when there is insufficient time for nitrogen to diffuse from α as the solubility gets lower with reducing temperature during quenching. The nitrides are usually found as clouds of precipitates inside larger α-grains where nitrogen has a further distance to diffuse. These nitrides are less likely to form in the more common HIPed DSS grades due to the very fine microstructure which means that nitrogen has a shorter distance to diffuse out of the α. The grain size dependence has been identified by others [11] and confirmed in experiments [12].

Equilibrium nitrides can be found in the grades of PM HIP SDSS found in Table 2. Fig. 2. shows an example of APM2329 test material that in standard testing using only LOM was reported to have a very small amount of intermetallic phase (<0,1%) and no other precipitates of any kind. Despite this, the impact toughness was only 28J at -35ºC at T/4 (quarter thickness) which is surprisingly low for this material at 223mm thickness. Normally the toughness for 250mm thick material is in the range of 50-90J at -35ºC at T/4. When the material was studied in SEM it became evident that there were significant amounts of nitrides in the γ-α grain boundaries across the section thickness. Using ThermoCalc software it was concluded that an elevated Cu-content of the alloy increases the stability of the Cr-nitride phase. The Cu-content was within specification but the deviation in combination with large section thickness and unfavorable geometry for quenching meant the cooling rate was not sufficient to suppress the formation of nitrides.

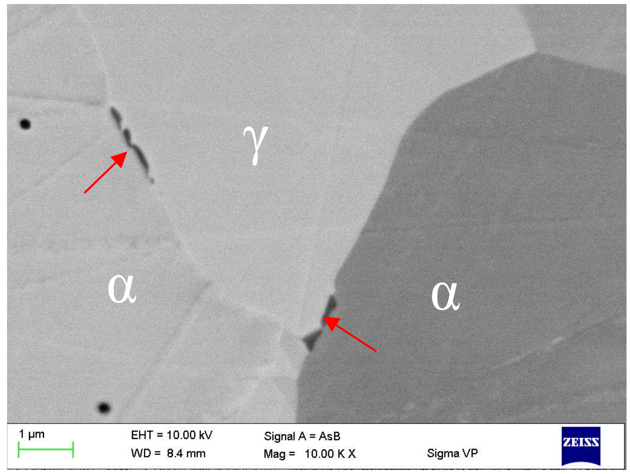

Figure 2. Micrograph of 29Cr alloy with grain boundary nitrides

Figure 3 shows another example of a APM2327 material that had lower than expected impact toughness despite only a very small amount of σ phase, <0,1% measured with EBSD. Basic LOM and SEM investigation did not provide any explanation to the low impact toughness. Only after careful sample preparation and very high magnification SEM a possible explanation came into light. 20-50 nm Cu-rich precipitates was found on γ-α grain boundaries as well as inside the α-grains, see Fig. 3. The Cu-rich precipitates have been found in several other test materials and are only found when σ is present in the material. Other studies have found that the cooling rate influences the precipitation of the Cu-rich phase and have found that Cu-precipitates could in fact also be found in materials without intermetallic phase, at least in other alloys than APM2327 [13]. Materials investigated in this study always contains a significant amount of these precipitates only when σ-phase is present in the APM2327 material. The exact mechanism of the formation is yet to be fully understood but is clear they can contribute to lowering the impact toughness of the material.

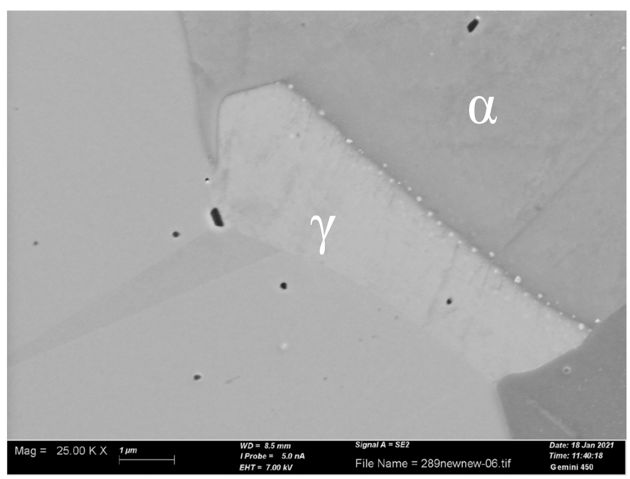

Figure 3. SEM micrographs on APM2327 showing Cu-rich precipitates in ferrite and austenite-ferrite grain boundaries.

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Phase balance and austenite spacing. As mentioned earlier, the fine austenite spacing of PM HIP DSS is often a major advantage in many applications. However, if too small the γ-spacing may have a negative effect on the impact toughness. One example of this is a production part in APM2329 that had surprisingly low impact toughness (CVN), 35J at -35ºC. This despite having a good microstructure without intermetallic or any other detrimental precipitates. The reported α-content was of 49% (SD=5%) with a γ-spacing of 7,2µm (SD=0,1µm). When studying the fracture surface from the impact testing it is evident that the fracture contains, except for the initiation zone, dominantly a brittle fracture with small islands of ductile fracture between, see Fig. 4a. Figure 4b shows a EBSD mapping on a cross section of the fracture surface, just under the initiation zone. It is evident that the crack propagates through a combination of fracture of the α (red) and in the α-γ grain boundaries. The small areas of ductile fractures in the γ (blue) can also be seen. Note that severely distorted regions in the EBSD map are not mapped in Fig. 4b and appear black.

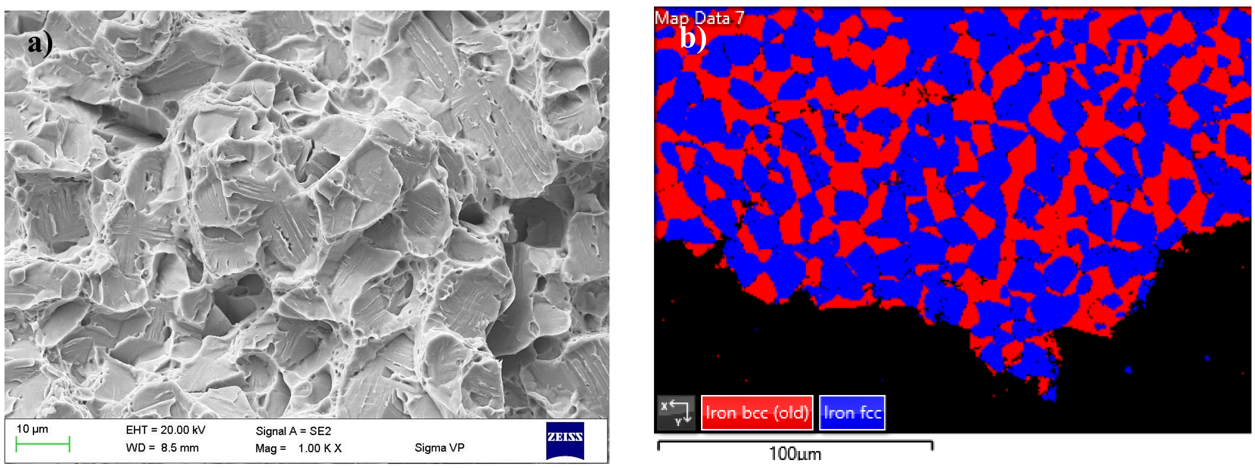

Figure 4. Micrograph of CVN specimen fracture surface (a) and EBSD mapping of fracture surface (b).

Without any obvious explanation to the poor toughness, we would propose that it is a consequence of the fine γ-spacing. With the very fine γ-spacing cracks can easily propagate as less energy is adsorbed when cracks are forced to change direction at phase boundaries. The issue can be worsened further by high α-content in the material which can essentially create a material with a α matrix further simplifying the crack propagation. Especially at lower temperature where the ferrite behaves brittle.

Conclusions

- Even if there is σ-phase present in the material, the mechanical properties can still be good
- Corrosion resistance may still be good even if 0,5% σ-phase is exceeded
- Even small amounts of σ-phase will affect impact toughness while the corrosion resistance is less sensitive to σ-phase
- In some cases, standard LOM might not be sufficient to resolve all detrimental phases that can have a negative effect on material properties
- Poor chemistry control may result in the formation of detrimental phases not seen in LOM
- Very low austenite spacing may have a negative effect on impact toughness

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