P/M STAINLESS STEELS FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

The performance of stainless steel powder metallurgy (P/M) materials at elevated temperature applications has become a subject of interest for automotive exhaust type applications. In this study a ferritic and a duplex sintered stainless steel has been evaluated for properties relevant for these applications, such as hot oxidation resistance, mechanical and corrosion properties. The performance of the stainless steels is reviewed and compared.

INTRODUCTION

The usage of sintered stainless steels is growing fast, primarily due to attractive high temperature and corrosion properties. Exhaust flanges and hot exhaust gas oxygen sensor bosses (HEGOS) are currently manufactured with powder metallurgy. Important properties for these applications are corrosion resistance, high temperature oxidation resistance, weldability, gas sealing quality and creep resistance[1].

This paper shows how the sintering temperature affects the properties of two different sintered stainless steels. The materials investigated are 444 L and a duplex material Cold DX[1]. The investigated properties are:

- corrosion resistance
- high temperature hardness
- high temperature oxidation resistance
- mechanical properties at room temperature

EXPERIMENTAL

Materials

In this investigation two powders were chosen, one ferritic 444 L and one duplex Cold DX. The chemical composition in the mixes, given in weight percent, was according to table 1 and the sieve distribution can

be found in table 2. As lubricant Kenolube™ was chosen for its good combination of compressibility, flowability and green strength.

Table 1. Chemical composition in weight percent of the materials used.

Material	%Cr	% Ni	% Mo	% Si	% Mn	% Kenolube™
444 L	18	0.1	2.3	0.89	0.08	1.0
Cold DX	17	6.5	1.7	0.75	0.11	1.0

Table 2. Sieve distribution in µm of the materials used.

Material	+ 150 µm	+ 125 µm	+ 106 µm	+75 µm	+53 µm	+ 45 µm	-45 µm
444 L	0.1	1.8	4.6	16.7	24.6	6.4	45.8
Cold DX	0.9	7.8	11.3	24.0	20.7	4.6	30.7

Compaction and sintering

Tensile test bars and impact energy test bars according to ISO 2740 and ISO 5754 were compacted at 600 MPa (43 tsi) in a 100 ton hydraulic press. The tensile test bars were used for tensile testing, corrosion and oxidation test. The impact energy bars were used for elevated temperature hardness testing and for impact energy measurements.

Dewaxing took place at 600°C (1112°F) in hydrogen. Three sintering runs were made at different temperatures; 1200, 1280 and 1350°C (2192, 2336 and 2462°F) for 45 minutes in 100 % hydrogen. The density, dimensional change, content of oxygen, carbon and nitrogen were measured. The values are presented in table 3.

Table 3. Physical and chemical data after sintering.

Material	Green density (g/cm^3)	Sintering temperature (°C / °F)	Sintered density (g/cm^3)	Dimensional change (%)	C (%)	O (%)	N (%)
444 L	6,31	1200 / 2192	6,85	-4.03	0.021	0.33	0.025
		1280 / 2336	7,02	-4.95	0.015	0.31	0.021
		1350 / 2462	7,18	-5,21	0.008	0.30	0.015
Cold DX	6,55	1200 / 2192	6,60	-1.09	0.049	0.32	0.010
		1280 / 2336	6,85	-2.24	0.030	0.26	0.012
		1350 / 2462	7,04	-3.66	0.007	0.20	0.021

Corrosion and high temperature oxidation properties

Three samples of each material were neutral salt spray tested according to standard test procedure ASTM B 117 over a period of 504 hours (3 weeks). This involves continuous exposure at 35 ± 1°C (95 ± 1,8 °F) to an atomised saltwater solution of 5 weight-% NaCl in deionized water. At each predetermined time the samples were investigated optically and photographed. The rating used agrees with ASTM 895-99, which is described in table 4. After the corrosion test the corrosion products were removed by shot peening in order to test the tensile strength after the salt spray test.

Table 4. ASTM 895-99 rating for corrosion test.

Rating	Appearance
A	The part is free from stain or rust
B	The first sign of stain or rust appears or up to 1% of the surface is covered by stain or rust
C	More than 1% and up to 25 % of the surface is covered by stain or rust
D	More than 25 % of the surface is covered by stain or rust

The high temperature oxidation properties were tested at 650°C in air for 865 hours (36 days). The weight was measured before testing and at predefined times at temperature. The increase in weight (%) was calculated, after the test the samples were tested in a tensile test machine.

Elevated temperature hardness test

The hot hardness tests were performed for all materials in a Bofors hot hardness tester. The samples were inserted in a special holder that can take three bars with dimensions described in the material section. The hardness HV5 was measured at room temperature before heating up the specimens. The materials were kept at test temperature for 20 minutes before making the indents. At each temperature five indents were made. The size of the indent was measured in a Leica microscope using Q600 image analyser.

RESULTS AND DISCUSSION

Mechanical properties and microstructure

Seven samples of each material were tensile tested. Table 5 shows the results.

Table 5. Mechanical properties after sintering.

Material	Sintering temperature (°C / °F)	Sintered density (g/cm^3)	Yield stress (MPa / ksi)	UTS (MPa / ksi)	Elongation (%)	Hardness (HV10)	Impact energy (J / ft-lb)
444 L	1200 / 2192	6.85	286 / 41.5	409 / 59.3	12	131	59 / 80
	1280 / 2336	7.02	292 / 42.3	433 / 62.8	12	145	119 / 161
	1350 / 2462	7.18	308 / 44.7	435 / 63.1	10	147	120 / 163
Cold DX	1200 / 2192	6.60	225 / 32.6	370 / 53.7	3.1	145	19 / 26
	1280 / 2336	6.85	255 / 37.0	525 / 76.1	7.8	146	37 / 50
	1350 / 2462	7.04	431 / 62.5	691 / 100	4.7	231	39 / 53

The ferritic 444 L shows very high densification during sintering as a result of ferritic microstructure at sintering temperature. Diagram 1 shows the phase composition at different temperatures based on a calculation in Thermo-calc. From this calculation it is obvious that the material is ferritic at all sintering temperatures.

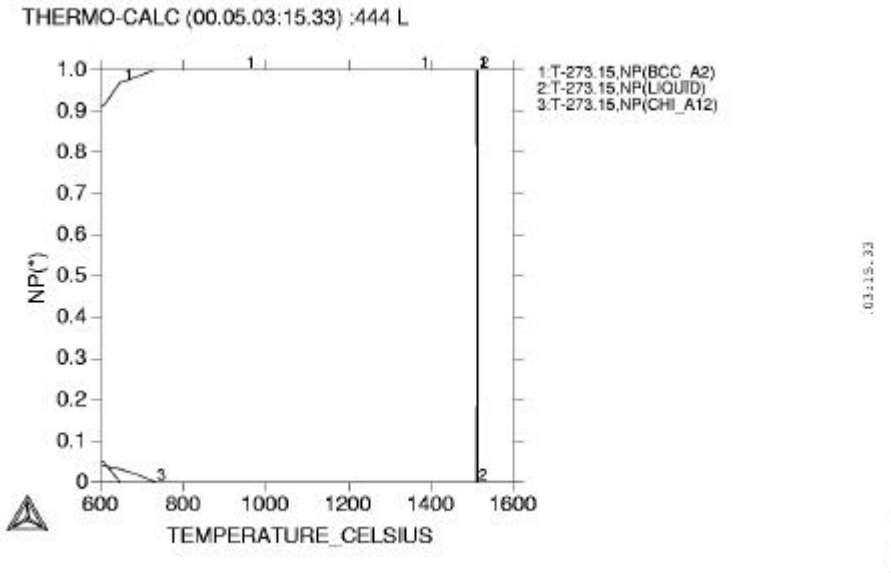
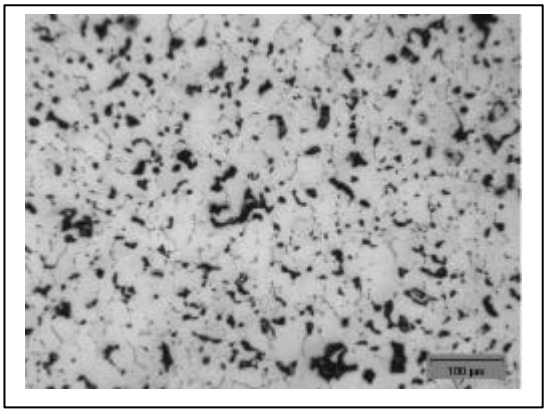
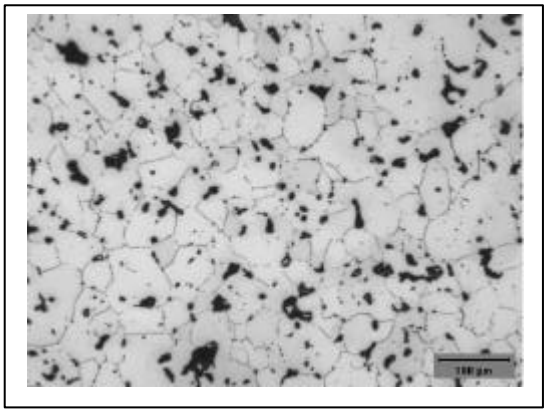


Diagram 1. Thermo-calc chart showing the percentage of ferrite (line 1), liquid (line 2) a chi-phase (line 3). At temperatures higher than 750 °C (1382 °F) the material is 100 % ferritic.

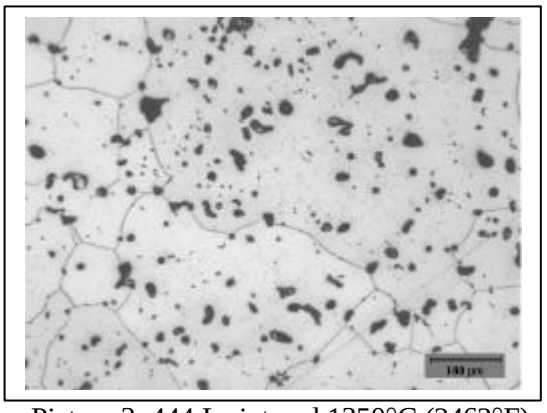
The tensile strength is above 400 MPa (58 ksi) at all density levels tested. The elongation drops at the highest sintering temperature, which is a result of grain growth (see pictures 1 –3). This explains why the properties doesn't increase with the density for 1350°C (2462°F) sintered material compared to 1280°C (2336°F). Interesting to note is the very high ductility with values of impact energy of 120 J (163 ft*lb).



Picture 1. 444 L sintered 1200°C (2192°F)



Picture 2. 444 L sintered 1280°C (2336°F)



Picture 3. 444 L sintered 1350°C (2462°F)

It is reported[2,3] that a minimum density of 7,2 g/cm³ is required for gas sealing and weldability for the exhaust flange application. In this investigation the density of the samples is lower, however the properties achieved indicate that the materials will have the properties required for the applications. To get higher sintered density with 444 L higher compaction pressure is needed since there can be grain growth at high sintering temperatures because of the fully ferritic microstructure at sintering temperature.

Cold DX is not as sensitive to grain growth. During cooling the about 80 % of the material will transform from ferrite to austenite. This transformation occurs between approximately 1270 to 950°C (2318 to 1742°F). Further cooling will transform part of the austenite to ferrite again (see diagram 2).

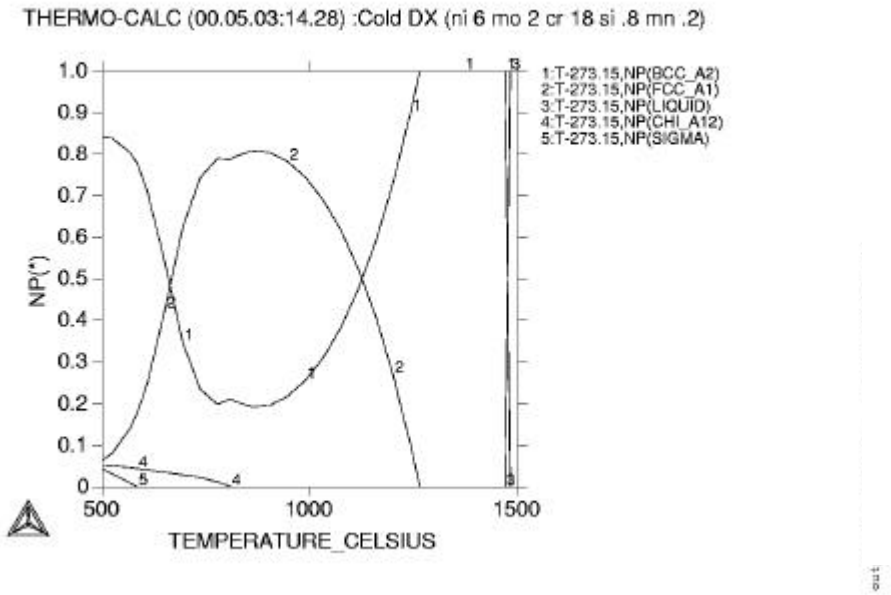
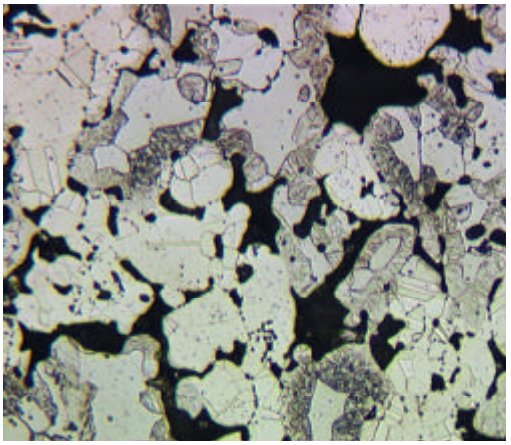
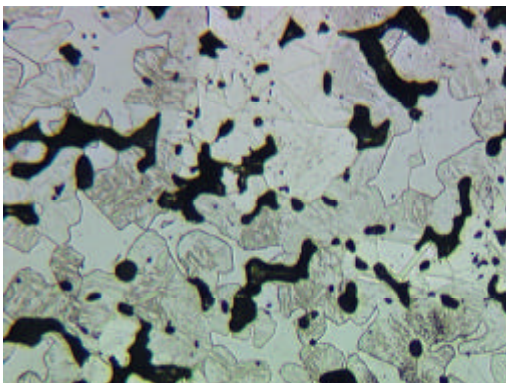


Diagram 1. Thermo-calc chart showing the percentage of ferrite (line 1), austenite (line 2), liquid (line 3), chi-phase (line 4) and sigma phase (line 5).

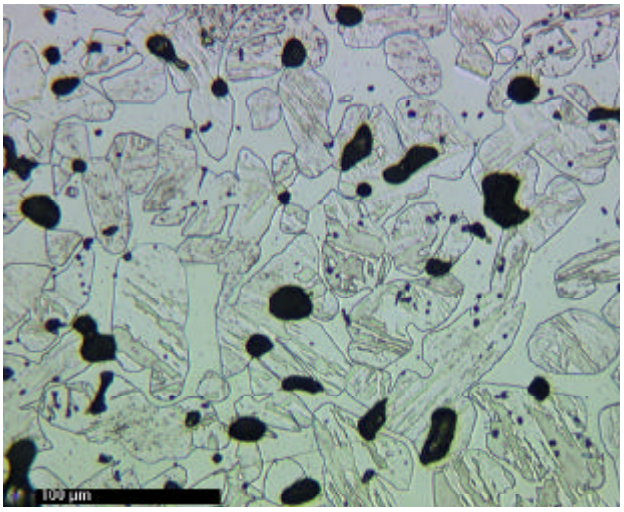
Because of this the microstructure will be normalised with regard to grain size (see pictures 4-6).. The final structure is duplex with approximately equal portions of austenite and ferrite. Between the austenitic and ferritic areas martensite is present, which explains the high strength and hardness of Cold DX.



Picture 1. Cold DX sintered 1200°C (2192°F)



Picture 2. Cold DX sintered 1280°C (2336°F)



Picture 3. Cold DX sintered 1350°C (2462°F)

Corrosion and high temperature oxidation resistance

The salt spray test (see table 6) shows that the lowest sintered density results in the best corrosion resistance in the salt spray test. This fact has been reported earlier[3] with the explanation that a build-up of the aggressive solution in the pores forms a crevice corrosion mechanism. However, there are some differences between the materials tested, 444 L shows good corrosion resistance also at the highest density level. This is probably connected to the fact, that there is a critical pore size when the crevice corrosion effect is most pronounced. At higher density levels this effect decreases.

Table 6. Results from salt spray test.

Material	Sintering temp. (°C/°F)	Time to rating B	Time to rating C	Time to rating D
444 L	1200 / 2192	1	6	336
	1280 / 2336	1	2	6
	1350 / 2462	24	96	240
Cold DX	1200 / 2192	6	24	>504
	1280 / 2336	6	24	96
	1350 / 2462	1	6	96

The results from the oxidation test can be seen in diagram 3 and 4. 444 L shows almost no oxidation when tested with density over 7.0 g/cm³ This fact indicates that the porosity is closed already at densities around 7.0 g/cm³. The oxidation behaviour of Cold DX is different, the oxidation is highest for the material sintered at 1280°C (2336°F) and lowest for the specimens sintered at 1350°C (2462°F). The reason for the oxidation rate being highest after 1280°C (2336°F) sintering is yet to be explained. As can be seen in the metallographic investigation the pore roundness is better for 444 L especially at the lower sintering temperatures (pictures 1-6). This is connected to the very high sintering activity for the completely ferritic structure in 444 L. The density for Cold DX needs to be higher than 7.04 g/cm³ in order to close the porosity completely. This explains why the overall oxidation behaviour is better for 444 L than for Cold DX.

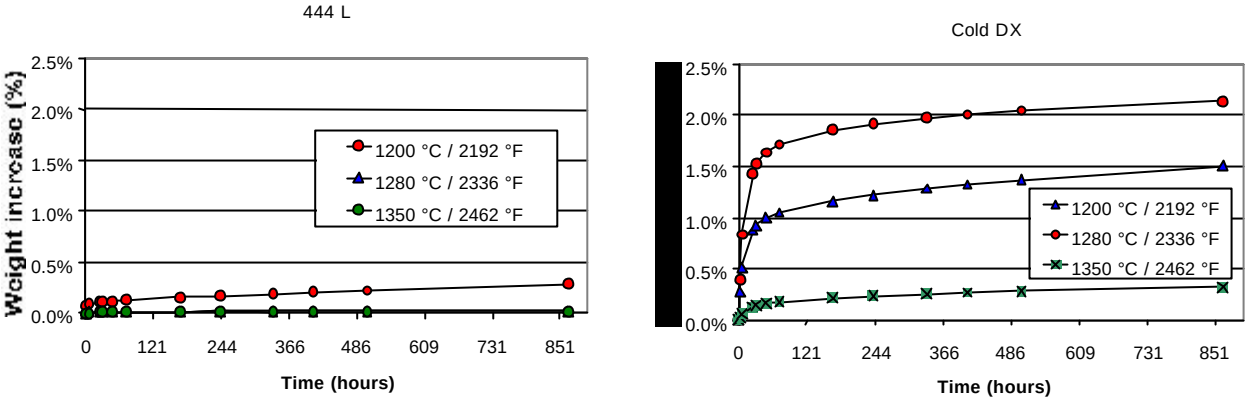


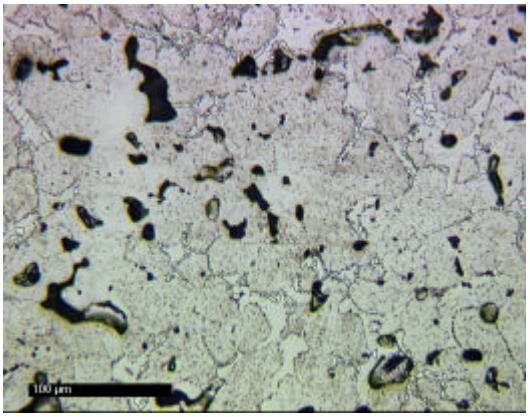
Diagram 3 and 4. Results from oxidation test.

Table 7. Mechanical properties after oxidation and corrosion tests.

Material	Sintering temperature (°C / °F)	After oxidation test			After corrosion test		
		UTS (MPa), Change (%)	Yield stress (MPa)	Elongation (%)	UTS (MPa) Change (%)	Yield stress (MPa)	Elongation (%)
444 L	1200 / 2192	403 (- 2%)	248	8.3	368 (-10 %)	267	6.9
	1280 / 2336	452 (+ 4 %)	261	13	296 (-32 %)	267	1.4
	1350 / 2462	459 (+ 5 %)	263	13	372 (-15 %)	299	3.7
Cold DX	1200 / 2192	296 (-20 %)	239	0.8	369 (0 %)	223	3.4
	1280 / 2336	406 (-23 %)	291	1.5	473 (-10 %)	249	7.9
	1350 / 2462	652 (- 6 %)	350	5.1	679 (- 2 %)	416	4.5

The mechanical properties after the oxidation test show that 444 L is practically unaffected by the test. The tensile strength is the same as before the test and the elongation is even better for the highest densities. It is of interest to investigate if any sigma phase is formed due to long time exposure to high temperature. No sigma phase has formed during this investigation in 444 L. The material is because of this suitable for high temperature applications as well as ambient temperature use.

Cold DX sintered at 1200 and 1280°C (2192 and 2336°F) has lost about 20 % of its tensile strength and quite a lot of its elongation. The explanation can be found in the microstructure. Picture 7 shows the microstructure for Cold DX sintered at 1350°C (2462°F) after the oxidation test. In this picture precipitates of sigma phase can be identified. This phase causes embrittlement of the material and because of this Cold DX is not suitable for high temperature applications. However, the material has a very attractive combination of mechanical and corrosion properties at ambient temperature.



Picture 7. Cold DX sintered at 1350°C (2462 °F) after oxidation test

Elevated temperature hardness

The hardness decreases with temperature as expected. At 550-600°C (1022-1112°F) the hardness drop is pronounced. Cold DX has overall higher hardness, especially at the highest test temperatures.

Table 8. Results from elevated temperature hardness test.

Material	Sintering temperature (°C / °F)	HV5 Room temp.	350 °C 662 °F	450 °C 842 °F	550 °C 1022 °F	650 °C 1202 °F	700 °C 1292 °F
444 L	1200 / 2192	161	114	111	99	59	45
	1280 / 2336	176	140	130	120	62	50
	1350 / 2462	226	146	144	135	88	55
Cold DX	1200 / 2192	143	108	95	71	56	53
	1280 / 2336	210	152	140	118	70	64
	1350 / 2462	253	191	169	146	90	69

CONCLUSIONS

- No significant oxidation occurs at 650°C for 444L with density over 7.0 g/cm³
- The strength of 444 L is not affected by the oxidation test
- The strength of Cold DX is almost not affected by the corrosion test
- Too high sintering temperature can lead to abnormal grain growth for 444 L
- Cold DX has very good combination of strength and corrosion resistance

To summarise the above it can be stated that 444 L is suitable for high temperature applications such as exhaust system flanges and HEGOS bosses. Furthermore it can be concluded that Cold DX has very good mechanical properties in combination with good corrosion resistance.

REFERENCES

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4. Troels Mathiesen, “Korrosionsegenskaber af sintret rustfrit stål”, Ph.D. Thesis, Technical University of Denmark, 1993