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OPTIMIZATION OF CORROSION RESISTANCE AND MACHINABILITY OF PM 316L STAINLESS STEEL

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ABSTRACT

Austenitic stainless steels offer significantly superior corrosion resistance, when compared to ferritic and martensitic stainless steels. Austenitic stainless steels are however difficult to machine. Austenitic alloy 303L is formulated with a small sulfur addition, which leads to the formation of MnS precipitates in the matrix. Presence of MnS in the alloy does lead to improved machinability. Alternately, it is possible to add a machinability enhancing additive, such as MnS or MoS_2 to a standard grade of stainless steel in the powder form in order to improve its machinability. Unfortunately, the presence of a sulfide in an austenitic stainless steel significantly lowers its corrosion resistance. Hence, neither of these options makes it possible to combine good corrosion resistance with good machinability.

This study evaluates a sulfur free additive for enhancing machinability of PM 316L, along with its effect on the corrosion resistance of the alloy. Two currently popular additives, namely MnSE and MoS_2, are also included in the study for comparison. The new additive is found to offer enhanced machinability without any adverse effect on the alloy's corrosion resistance. All sintering was carried out under conditions that maximize corrosion resistance. Machinability was determined by drilling.

INTRODUCTION

Pressed and sintered PM alloys are more difficult to machine in comparison to their wrought counterparts due to the presence of porosity. Porosity not only lowers the rate of heat transfer, but also leads to interrupted cuts, thus imposing a cyclic form of loading on the tool tip. Most often PM alloys are machined without a liquid lubricant, with a view to avoid the cumbersome task of removing such liquids from the pores, without which the parts can develop staining. Resin impregnation of sintered parts offers a reasonable solution with respect to avoidance of interrupted cuts, as well as with prevention of cutting fluid entrapment in the pores. Significant improvements in the machinability of PM stainless steels have been reported as a result of resin impregnation [1]. However, it does not remedy any metallurgical defects formed in alloy during processing which are primarily responsible for the loss of corrosion resistance.

Austenitic stainless steels, both wrought and PM, exhibit significantly lower machinability, when compared to ferritic stainless steels and low alloy steels. This stems from a number of material properties inherent to this family of alloys, such as: a large spread between their yield and tensile strengths, high ductility and toughness, high rate of work hardening, and low thermal conductivity [2]. Austenitic stainless steels become gummy during machining and lead to non-uniform cuts and a high rate of tool wear. The machining swarf tends to be long and stringy leading to frequent interruption of the machining operation, thus reducing process efficiency.

Grades 303L in PM and 303 in wrought are formulated with a small addition of sulfur, in order to enhance machinability. During melting of the alloy, sulfur combines with manganese (and chromium) present in the alloy to form fine globules of manganese-rich sulfides in the alloy matrix. When machining, these sulfides coat and lubricate the tool tip and also act as chip breakers; both of which contribute to ease of machining. PM process is amenable to introduction of manganese sulfide or any other suitable machining additive to a base alloy powder via the admix approach. Hence, if an application requires both good machinability and good corrosion resistance, it is a common practice for parts makers to select the 316L grade of alloy powder for its superior corrosion resistance, and blend in a machinability enhancing additive to improve its machinability. Unfortunately, the presence of sulfides in the alloy matrix, whether admixed or in-situ formed, does lead to a significant loss of corrosion resistance. This effect is well documented for both wrought and PM stainless steels [3, 4, 5]. Since the PM stainless steels, even when processed carefully, do exhibit a markedly reduced corrosion resistance in comparison to their wrought counterparts, any additional loss of corrosion resistance due to the presence of sulfides is highly undesirable.

The goal of the present study was to identify one or more sulfur-free additives that would be effective as machinability enhancing agents, while not having an adverse effect on the corrosion resistance of the sintered alloy. Alloy 316L was employed here as the base alloy. Several new additives were included in the study. Additive-free 316L and two commercially known additives, MnSE (manganese sulfide) and molybdenum disulfide, were included in the study for comparison.

It may be noted here that both corrosion resistance and machinability of PM stainless steels are strongly influenced by the processing parameters, most important among them being the composition and the dew point of the sintering atmosphere, sintering temperature, and the sintered density. As a result, there can be significant variance in the outcomes of studies carried out under different sets of processing parameters. In this study, process parameters that are known to be ‘optimal’ from the corrosion resistance point of view were employed [6]. Machinability was determined by the use of a drilling test, since drilling is fairly commonly practiced with PM stainless steels, and also because the test is relatively simple.

MATERIALS

A commercially available, compacting grade of 316L stainless steel powders was used in the study. The powder was produced by water atomization and had a nominal particle size of – 100 mesh (<149μm). Table 1 lists its chemical composition, apparent density (A. D.), and the fines (<45μm) content.

Copper Sulfate Test was conducted to confirm freedom from contamination with less noble metal powders (e.g., iron, low alloy steel, and ferritic stainless steel powders). This was essential in order to ensure that the results of the corrosion tests are not influenced by the presence of such contaminants in the test material.

Table 1: Properties of the base alloy powder (316L), wt %

Cr	Ni	Mo	Si	Mn	S	P	C	O	Fe	A. D. g/cm^3	-325 mesh
16.88	12.92	2.20	0.83	0.18	0.007	0.014	0.016	0.21	Bal.	2.66	40.2

Three different additives were included in the study. These were: MnSE, MnX, and MoS_2. Including the additive-free material, there were four different powder blends in the study. All powders were admixed with 1.0% Acrawax C to aid in compaction. MnSE is a stabilized version of manganese sulfide with a purity of 99.0% and a D_{50} of 5µm. MnX is proprietary products of Hoganas A.B. and it has a D_{50} of 20µm. Molybdenum disulfide employed here was a commercially available lubricant grade product with a purity of 98.0%, and a D_{50} of 35µm. In the case of MoS_2 the amount added was 2.0% by weight, which is the most popular level in the PM industry. In the case of the other two additives the amount used was 0.5% by weight. The addition levels selected here for MoS_2 and MnSE have also been demonstrated as the optimum levels for machinability enhancement in an earlier study [4].

PROCESSING

Three types of specimens were prepared from each of the four powder blends:

1. Round discs having a diameter of 80 mm (3.15 in) and a thickness of 25 mm (1.0 in) - for machinability testing.

2. Standard 'dog bone' tensile test specimens with a gage length of 25 mm (1.0 in) - for determination of room temperature tensile strength, yield strength, and elongation.

3. Transverse rupture strength (TRS) specimens measuring 31.75 mm (1.25 in) x 12.7 mm (0.5 in) x 6.35 mm (0.25 in) - for determination of compacting properties, sintered properties, and corrosion resistance.

Specimens of the above three types were prepared from the four powder blends, utilizing a hydraulic press, under a compaction pressure of 560 Mpa (40.6 TSI). Specimens were delubricated under an atmosphere of dissociated ammonia at 593^{0}C (1100^{0}F) using a laboratory belt furnace. Delubrication time period was 30 minutes for the round discs, and 20 minutes for the other two types of samples. Sintering was carried out in a dry, 100% hydrogen atmosphere at a temperature of 1316^{0}C (2400^{0}F), for 30 minutes. The dew point of the sintering atmosphere was – 46^{0}C (-55^{0}F). Sintering was conducted in a laboratory batch furnace.

TESTING

COMPACTING AND SINTERED PROPERTIES:

The powders were tested for apparent density and flow rate, green strength, and green density in accordance with MPIF Standards 04, 15 and 45, respectively. Sintered TRS specimens were used for measurement of apparent hardness, dimensional change, and sintered density in accordance with MPIF Standards 43, 44, and 42, respectively. Sintered TRS specimens were also utilized for determination of oxygen, nitrogen, carbon and sulfur contents. Oxygen and nitrogen analyses were made using a LECO Model TC-436 analyzer, and the carbon and sulfur analyses were made using a LECO Model CS-244 analyzer.

Sintered "dog bone" tensile test specimens were tested using an Instron constant displacement hydraulic test machine for determination of yield strength, tensile strength and percent elongation, as per MPIF Standard 10.

CORROSION RESISTANCE

As-sintered transverse rupture strength (TRS) specimens were utilized for corrosion tests. From each of the four grades of material, six replicate specimens were subjected to the test. The tests were performed by immersion in a neutral, 5% sodium chloride solution, in accordance with ASTM Test Method B 895-05. Test specimens were placed in individual glass jars (closed top) containing the test solution. A layer of 3 mm (0.1 in) diameter glass beads was placed at the bottom the jars in order to help minimize crevice corrosion from contact with the flat surface of the jar bottom. Specimens were examined periodically for evidence of corrosion (stain or rust). Observations were recorded in accordance with the following scale:

Rating	Criteria
"A"	Until any sign of rust or stain
"B"	Up to 1% of specimen surface covered with rust or stain
"C"	Up to 25% of specimen surface covered with rust or stain

For each specimen, the elapsed time from the beginning of the test until a rating change was determined

MACHINABILITY

A drilling test was employed to determine relative machinability of the four test materials. From each of these materials five round discs (test blocks) were available for the drilling test. All drills used in the test were taken from the same production lot. The test parameters were as follows:

Drill size:	3.5 mm (0.138 in) in diameter
Drill type:	HSS M-2, DORMER A108 Jobber drill for stainless steel, DIN 388
Drill speed:	700 rpm
Feed rate:	25 mm (1.0 in) per rotation
Lubrication:	None
Depth of hole:	12 mm (0.5 in)
Spacing:	7.0 mm (0.28 in), center-to-center

A new drill was used for each test, and the test criterion was set as the number of holes drilled until the drill was worn out sufficiently to stop drilling. Each material was tested six times, and the average number of holes drilled per test was reported.

RESULTS AND DISCUSSION

COMPACTING AND SINTERED PROPERTIES

Table 2 shows the compacting properties of the four powders. Addition of MnSE, in the amount shown, y had no real effect on the compacting properties of the base alloy powder 316L + 1.0% Acrawax C. MnX addition appears to have had a small negative effect on the A. D. and the green density of the powder. Addition of MoS_2, by 2.0 wt.%, had a marked influence on the A.D., green density, and green strength of the base powder. It appears that MoS_2 provides additional lubrication to the powder blend, which led to an increase in A. D. and green density, along with a small reduction in green strength.

For all practical purposes none of the three modifications would be a cause for any concern from the point of view of powder compactibility.

More remarkable differences are noted in the sintered properties of these materials, as shown in Table 3. The sintered densities and the sintered strengths of the MnSE and MnX blended powders are very close to those of the additive-free alloy.

Table2: Compacting properties of the test blends

Property	316L - No additive	316L + 0.5% MnSE	316L + 0.5% MnX	316L + 2.0% MoS_2
Apparent density, g/cm^3	2.67	2.67	2.65	2.79
Flow rate, sec/50g Hall	42	39	42	40
Green density, g/cm^3 @ 560 MPa *(40.6 TSI)*	6.60	6.60	6.56	6.68
Green strength, MPa, *(psi)* @ 560 MPa *(40.6 TSI)*	8.3 *(1204)*	8.5 *(1232)*	8.2 *(1190)*	7.5 *(1088)*

Note: All powders were lubricated with 1.0% Acrawax C.

Table 3: Sintered properties

Property	316L - No additive	316L + 0.5% MnSE	316L + 0.5% MnX	316L + 2.0% MoS_2
Sintered density, g/cm^3	7.03	7.00	6.95	7.18
Tensile strength, MPa *(x 10^3 psi)*	369 *(53.5)*	357 *(51.8)*	360 *(52.2)*	403 *(58.4)*
Yield strength MPa *(x 10^3 psi)*	165 *(23.9)*	165 *(23.9)*	168 *(24.4)*	206 *(29.9)*
Elongation, %	30.5	29.0	27.0	24.0
Hardness, HRB	37	36	39	56
Dimensional change, % from die size	-2.24	-2.14	-2.05	-2.39

Table 4: Oxygen, nitrogen, carbon and sulfur analyses of sintered samples

Property	316L - No additive	316L + 0.5% MnSE	316L + 0.5% MnX	316L + 2.0% MoS_2
Oxygen, ppm	1858	1877	2158	1814
Nitrogen, ppm	64	81	78	103
Carbon, wt. %	0.007	0.005	0.023	0.028
Sulfur, wt. %	0.001	0.112	0.005	1.008

The MoS_2 blended alloy exhibited significantly higher sintered density, sintered strength, and apparent hardness in comparison to the other three alloys. The increase in sintered density may be in part due to the higher green density and partly due to a higher rate of shrinkage, in comparison to those of the additive free alloy. The increase in the strength and apparent hardness are disproportionably greater than what might be expected from the increase in sintered density. It appears that there has been some enrichment of the matrix with molybdenum from the additive which may have contributed to the increased strength and hardness (with concomitant reduction in ductility). This is discussed in more detail in the next section.

For all practical purposes the two molybdenum-free additives had no measurable influence on the sintered density, sintered strength, hardness or the dimensional change of the base alloy. Molybdenum disulfide addition, on the other hand did result in higher strength and hardness, along with a moderate decrease in ductility.

The oxygen, nitrogen, and carbon contents of all three additive containing alloys were found to be in the acceptable ranges for these interstitials. Sulfur containing additives showed high residual sulfur contents as expected.

MICROSTRUCTURES

Sintered samples were examined by metallography in the as-polished condition, as well as after etching with Glyceregia. It was easier to identify the residues of the various additives in the as-polished specimens, especially under a scanning electron microscope (SEM). These residues are expected to act as chip breakers, and in some instances may also provide lubrication for the tool tip. Hence, their particle size distribution and uniformity of dispersion would influence the machining behavior of the alloy.

Figure 1 is a scanning electron micrograph of the as-polished MnSE containing alloy. The manganese-rich sulfide inclusions are present both within the pores and in the matrix of the alloy. It is not surprising to find some of the inclusions in the matrix (both at grain boundaries and within the grains) due to the high rates of shrinkage and grain growth which occur during high temperature sintering. Most of the small and medium sized inclusions have a well rounded morphology, which indicates that the inclusions were at or near their melting point during sintering. It is difficult to estimate the actual melting point of these inclusions, since during sintering the pure form of MnS that was introduced may have combined with some Cr and/or Fe via diffusion, and this could have altered its melting behavior.

Figures 2 and 3 are scanning electron micrographs of the as-polished MnX containing alloy, taken at two different magnifications. Residues of MnX are seen here as irregular sized particles, residing mostly in the pores. The largest particles are around 25μm in size.

Figures 4 and 5 are scanning electron micrographs of the as-polished MoS_2 containing alloy, taken at two different magnifications. Here, the residues are seen mostly as fine globules within the matrix. The size distribution of these residues is significantly different from that of the additive used. SEM/EDX (energy dispersive x-ray) analysis of these inclusions showed these to be free of Mo, and rich in Mn, Cr, and S. It appears that at the temperature employed for sintering MoS_2 dissociated into Mo and S; and the sulfur atoms diffused in the matrix to combine primarily with Mn present in the alloy and formed Mn (Cr) sulfides. Using SEM/EDX technique it is not feasible to determine the precise composition of these fine precipitates in a matrix of 316L. Nevertheless, it is likely that these sulfides may comprise some amount of Fe in addition to Mn and Cr. The total absence of Mo in the sulfide precipitates leads us to believe that all molybdenum from the additive did diffuse into the alloy matrix, and this may have led to solid solution strengthening of the alloy matrix.

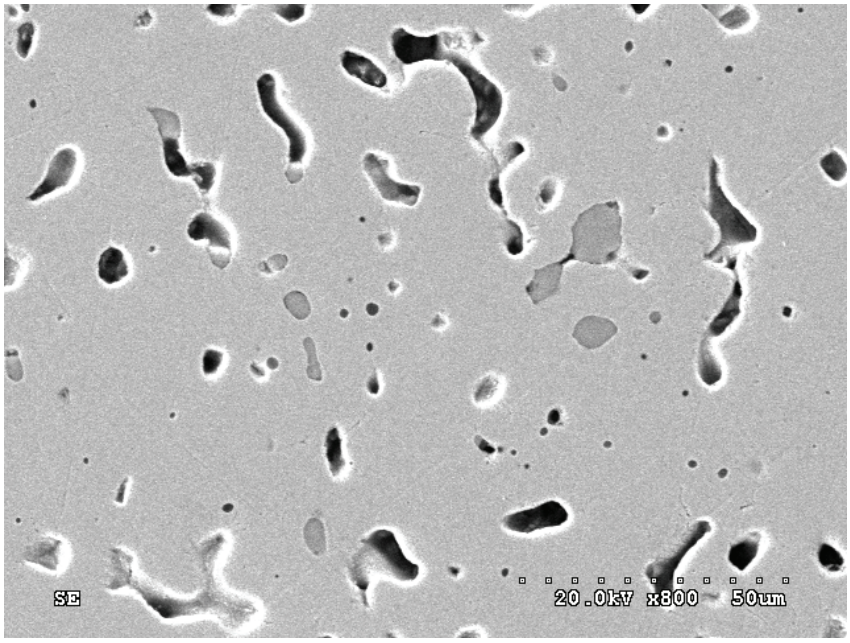


Figure 1: SEM of MnSE containing alloy

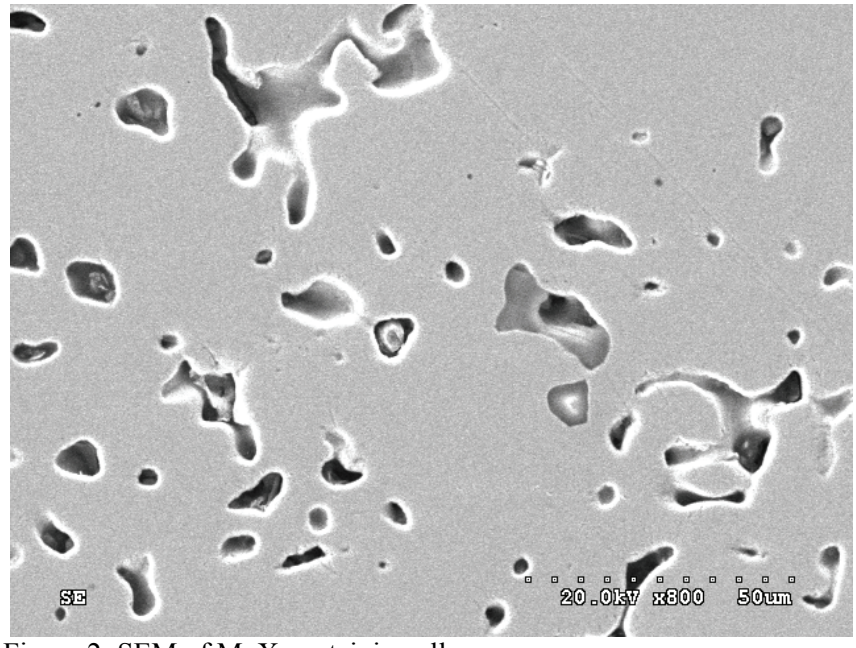


Figure 2: SEM of MnX containing alloy

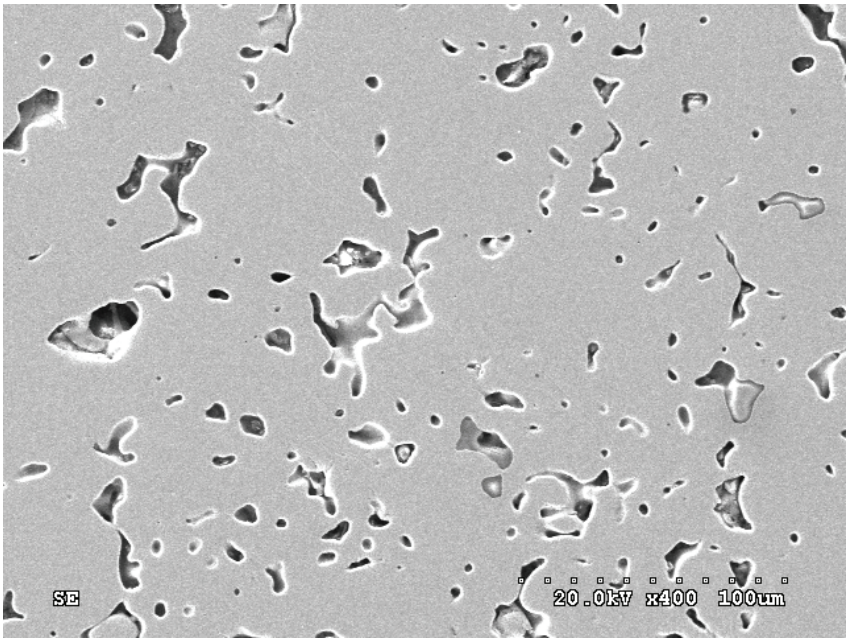


Figure 3: SEM of MnX containing alloy

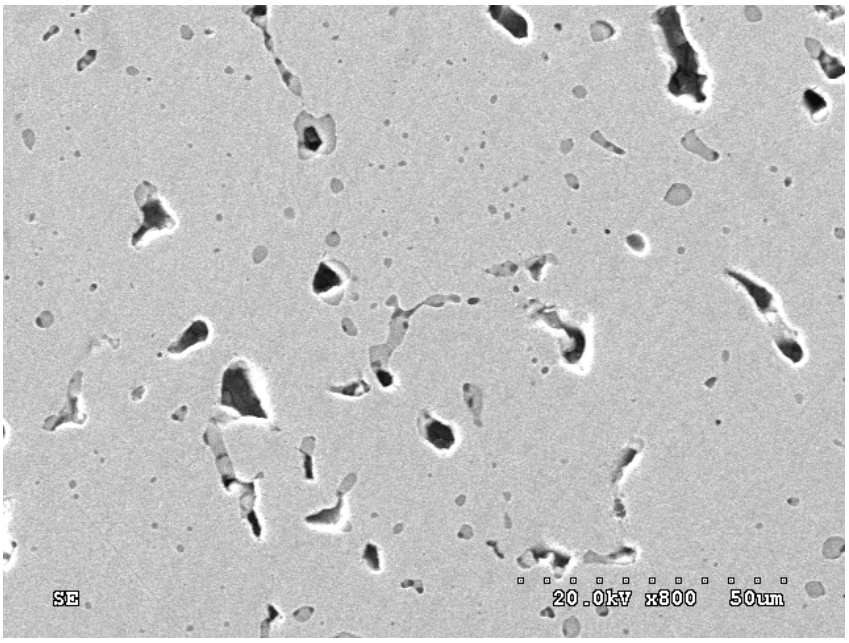


Figure 4: SEM of MoS_2 containing alloy

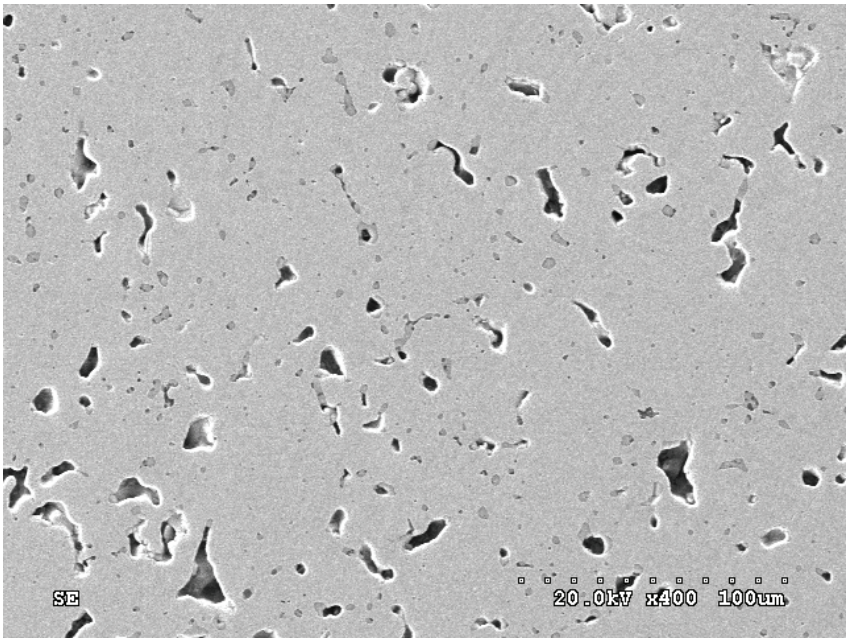


Figure 5: SEM of MoS_2 containing alloy

CORROSION RESISTANCE

Table 5 lists the corrosion resistance and machinability of the four alloys. Corrosion resistance is shown here as A rating hours, based on immersion in 5% aqueous sodium chloride solution. Optimally sintered 316L is expected to yield approximately 850 A rating hours, and approximately 1660 B rating hours. Based on this, the tests were terminated after 900 hours. Until the termination of the test all specimens from the group with MnX addition and the group with 'No Addition' remained entirely free of rust.

The low corrosion resistance performance of 17 A rating hours for the 0.5% MnSE added samples is similar to those reported in literature for 303L, and for 0.5wt.% manganese sulfide modified 316L alloy [4,7]. Similarly, the moderate corrosion resistance of the order of 240 A rating hours seen for the MoS_2 added alloy is nearly equivalent to a 720 B rating hours reported for this material in the literature [4].

It is interesting to note that while both the MnSE added alloy and the MoS_2 added alloy consisted of manganese sulfide inclusions in the sintered matrix, there is a substantial difference in their corrosion behavior. This variance in their corrosion behavior may be attributed to possible differences in the composition of the sulfides present in these two alloys. It is presumed that the type of sulfide present in the MnSE added alloy is very close to the pure form of MnS, while the type of manganese sulfide present in the in the MoS_2 added alloy could be combined with some chromium and/or iron. Working with wrought stainless steels, Kovach and Moskowitz have determined that the type of sulfide that forms in a re-sulfurized steel is determined by the Mn:S ratio in the alloy [8]. At low Mn:S ratios of less than 0.4, only a chromium sulfide forms, which has a hexagonal structure. At intermediate Mn:S ratios, ranging from 0.4 to 1.8, a cubic, chromium rich, manganese sulfide forms in the steel. At Mn:S ratios greater than 1.8, pure MnS forms in the matrix. From the corrosion resistance point of view, the pure form of MnS is highly undesirable, although it has the highest beneficial effect from the machinability point of view.

Table 5: Results of the corrosion tests

Powder blend	No Additive	With 0.5wt% MnSE	With 0.5wt% MnX	With 2.0wt% MoS_2
Corrosion Resistance, in "A" rating hours	900+	17	900+	240
Machinability rating, in no of holes drilled	15	41	42	33

MACHINABILITY

Table 5 also lists the results of the machinability (drilling) test. As expected, additive-free 316L showed the lowest machinability. This represents the typical degree of difficulty encountered with machining a standard austenitic stainless steel. Addition of MoS_2 led to approximately 100% improvement in machinability. Both MnSE and MnX are found to be highly effective in enhancing machinability, with nearly three fold increase in the number of holes drilled. Figure 6 compares the four alloys in terms of both corrosion resistance and machinability.

As discussed earlier, the inclusions seen in the MoS_2 added material are sulfides of manganese and chromium. The relatively lower performance of the MoS_2 added alloy in comparison with the MnSE added alloy in the machinability test may be attributed to two possible factors. The type of sulfides present in the MoS_2 added alloy, as discussed above, could be rich in chromium, and hence is not as effective as the pure form of manganese sulfide from the machinability enhancement point of view. The second possible factor could be the finer particle size of the inclusions in the MoS_2 added alloy, in comparison to those in the MnSE added alloy. The size distribution of these fine precipitates may be less than optimum from the machinability point of view.

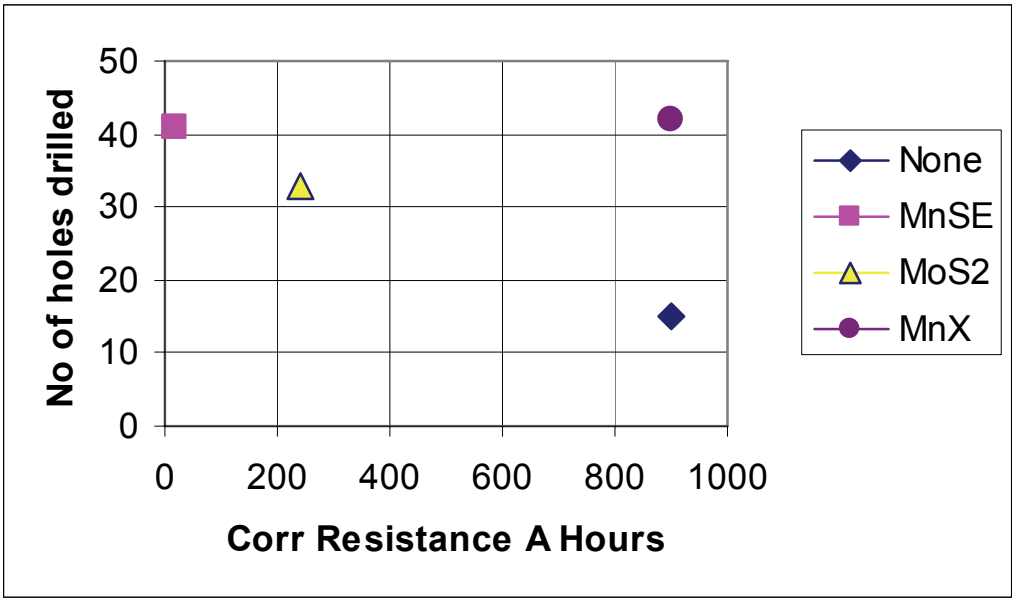


Figure 6: Relative corrosion resistance and machinability of the five materials

FUTURE DEVELOMENT

A newly developed machinability enhancing additive called SM1 has shown excellent performance in a number of low alloy steels. Addition of SM1 to 316L at 0.5wt% level is determined to have no adverse

effect on the alloy's corrosion resistance. Tests are under way to determine the effect of SM1 addition on the machining behavior of PM 316L.

CONCLUSIONS

Manganese sulfide and molybdenum disulfide are effective machinability enhancing additives for austenitic stainless steels. These additives however, adversely impact the corrosion resistance of the alloy. While the loss in corrosion resistance is rather drastic with the manganese sulfide addition, it is somewhat less severe with the molybdenum sulfide addition.

A sulfur-free additive, known as MnX, is found to have no adverse effect on the corrosion resistance of 316L austenitic stainless steel. Addition of 0.5wt.% MnX provides same level of machinability enhancement as is achieved with the highly popular machinability enhancing additive MnSE.

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