Spatially Optimized Diffusion Alloys: A Novel Multi-Layered Steel Material for Exhaust Applications

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Abstract

A novel Spatially Optimized Diffusion Alloy (SODA) material has been developed and applied to exhaust systems, which are an aggressive environment subject to high temperatures and loads, as well as excessive corrosion. Traditional stainless steels disperse chromium homogeneously throughout the material, with varying amounts ranging from 10% to 20% dependent upon its grade (e.g. 409, 436, 439, 441, and 304). SODA steels, however, offer layered concentrations of chromium, enabling an increased amount along the outer surface for much needed corrosion resistance and aesthetics. This outer layer, typically about 70μm thick, exceeds 20% of chromium concentration locally, but is less than 3% in bulk, offering selective placement of chromium to minimize its overall usage. Since this layer is metallurgically bonded, it cannot delaminate or separate from its core, enabling durable protection throughout manufacturing processes and full useful life. The core material may be comprised of various grades, however, this study employs interstitial free steel (low carbon), which eases manufacturing operations, as it is more formable than stainless steel grades. The material and its manufacturing process are described, including characterization measurements comparing its forming and corrosion resistance response to baseline exhaust materials. Rolled mufflers are manufactured with high-volume manufacturing equipment and processes without incident, demonstrating the ease of material substitution versus aluminized 409 stainless steel (409AL). Each application is exposed to various test conditions, including fatigue, corrosion, and thermal cycling and compared against baseline materials. Results overall demonstrate favorable performance, even along exposed and welded edges, which may be further protected locally with cold spray. SODA offers unique value in performance versus baseline materials, enabling a competitive alternative with much less chromium.

Introduction

Steel has been made in a consistent manner for generations, leveraging significant capital investments for decades, and is a significant material source for many industries, including automotive [1, 2]. The introduction of stainless steels has been one of its few evolutionary changes, increasing chromium content to reduce corrosion [3, 4]. Chromium is a key ingredient in the varying grades of stainless steel, as low as 10% in 409 and as high as 20% in 304. Although it offers significant improvements in corrosion, the material becomes much less formable due to an increase in work hardening as chromium content increases, having limits and requiring more iterative force to form into shape [5, 6]. Stainless steel has been adopted by the mobile exhaust market once regulations demanded warranty coverage for emissions controls systems [7]. Since then its use was extended from the emissions-demanding hot end, or front half of the exhaust with the catalyst and much higher temperatures, to downstream, the cooler cold end with acoustic components of the exhaust, such as mufflers, resonators, and tailpipes [8]. Aluminized stainless steel has offered additional corrosion protection, providing both structural and visual performance benefits, with a coating of aluminum on its surface by a hot dip process [9]. Material gauge across most exhaust applications is between 0.5 - 2mm, and often is provided as a coil which is fed into various manufacturing forming processes, such as stamping, slitting and rolling.

Stainless steels have surcharges to account for the varying market price of specialty metals, such as chromium and nickel [10]. As a result, swings in the price of stainless steel occur over time, causing fluctuations in costs, often resulting in uncertainty across the supply chain [11]. It is of interest to minimize the amount of such specialty metals applied, providing better price stability. Furthermore, it is always helpful to introduce alternative competitive materials into the supply chain, providing advantage with market supply options.

Spatially optimized diffusion alloy (SODA) steel technology significantly reduces the amount of chromium applied, enabled by the steel composition spatially varied, localizing chromium at the substrate surface where is most beneficial rather than evenly distributed throughout. Figure 1 shows a schematic representation of the normal Cr distribution in a monolithic stainless steel (1A) as well as an etched cross section (1B) to demonstrate the grain structure of a standard
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In Figure 1C, a schematic of chromium bearing SODA steel composite and an etched cross section with Nital (1D) optically reveals the substrate grain structure and the location of high Cr regions. Total chromium content is significantly reduced in the SODA composite, as its core is low-carbon or interstitial-free (IF) steel. This unique material technology is described in the following sections and characterized, comparing its properties with various baseline materials. Successful exhaust applications are demonstrated, including builds from plant operations running at rate, as well as their various typical validation tests.

Description and Material Characterization

SODAs are produced with standard operating equipment already employed by the steel industry, including coating lines, batch annealing ovens, and cleaning lines [12]. Coils of steel are coated with a proprietary slurry then subjected to a deposition and diffusion heat treatment. The generated chromium layer thickness can be varied based on application need, ranging from 20 - 200 μm, which does have an influence on its performance attributes; about 70 μm was chosen for this study. The core material used in this study was an interstitial-free carbon steel, of gauges between 0.9 and 1.4 mm, covering the thicknesses needed for external muffler components.

Table 1 describes the effective average concentration of chromium across a variety of core thicknesses and chromium layer concentrations. The chromium layer assumed is 70 μm, and the results are geometrically dependent. For instance, based on a 1.5 mm thickness that has a 0.14 mm chromium layer applied on both surfaces (70 μm each), such that 9% of its volume is high chromium concentration while the remaining has none (IF steel, low carbon core), resulting in an average chromium concentration of 1.9%. The results demonstrate significantly lower chromium content when compared with common grades between 10% and 20% chromium.

Chromium bearing SODA steel composites do not delaminate or flake off, as the chromium is deposited via chemical vapor deposition (CVD), and diffuses into the substrate, resulting in an integral, metallurgically bonded alloy layer. Figure 2 demonstrates a cross-section of the material after it is bent 180°, illustrating its ability to stretch with the core material without separation or cracking. Its adherence has been demonstrated across numerous manufacturing processes, including stamping, as well as more aggressive cold spinning in which the end cone is spun down from the parent shell material (see Figure 3). Adherence is proven across a range of validation tests, including fatigue, corrosion and thermal shock.

This material’s formability benefits are measured through the Olsen cup test, which demonstrates a material’s ability to stretch as it is being pressed by a sphere in its center while its edges are retained. The resulting dome height prior to rupture is measured and compared with various stainless steel grades (see Figure 4A). SODA material stretches the most when compared with stainless steel options, demonstrating its softness and enhanced forming capability. This benefit is demonstrated in simulating stamping performance, particularly thinning effects of a given design. Figure 4B illustrates the maximum thinning results from a 3D finite element analysis (FEA) stamping assessment, resulting in nearly half
of the thinning with the SODA material versus various stainless grades, which has a favorable effect improving structural fatigue life. Table 2 describes the basic tensile and forming properties as measured for SODA (IF-Cr) in comparison with baseline grades of 409 and 439 stainless steels. The SODA material is softer, however its work hardening rate (n) is similar. The r-value, the plastic strain ratio, is a measure of the resistance of a sheet metal to change in thickness, and SODA exhibits higher values than the baseline grades, indicating better drawing properties.

Corrosion resistance is characterized with pitting potential measurements, which are the least positive currents and voltages for pits to develop on its surface [13, 14, 15]. Results are measured in millivolts and are often in reference to a saturated calomel electrode (SCE) or saturated silver-silver chloride (SSC) electrode. The more positive the necessary voltage is in reference to a standard half-cell necessary to induce pits, typically the more corrosion-resistant a given material will be [16]. Figure 5 highlights that a range of performance is possible for SODAs depending upon the surface Cr concentration, as tested in conditions outlined by the g61 ASTM polarization method [17], comparing performance with several standard stainless materials. It is important to note that the referenced chromium content in each IF-Cr sample is that only in the external layer, i.e. not across the bulk material which has none. It is apparent that the lowest Cr bearing SODA concentrations perform better than 409 and are comparable to 439, and as the surface chromium concentration increases, the pitting resistance increases. At the highest concentration, the SODA composite performs significantly better than all other materials, including 304, an austenitic stainless.

Welding is also an important manufacturing requirement of the material, as exhaust systems most often apply welds to join various components. Numerous welds were applied across samples and system components, including TIG, MIG, ERW, plasma and laser, none of which demonstrated any physical integrity concerns. Figure 6 illustrates weld cross-sections from two- and three-ply lap welds, demonstrating appropriate quality with sufficient heat penetration. It is realized, though, that welds result in chromium-diluted regions, which could expose the welded regions to corrosion, which is necessary to evaluate. Additionally, it is realized that this technology does not envelop the entire surface of the applied materials, resulting in exposed edges. Corrosion response of exposed edges are also of concern, for both structural influence, as well as visual aesthetics and must be considered in application.
Exhaust Application Requirements

Stainless steel is by far the most abundant material used within exhaust systems, applying a variety of grades in both austenitic and ferritic, depending upon application, customer and region. Exhaust systems are often categorized into hot and cold ends, separated by layout positioning, such that the hot end is attached to the engine while the cold end is downstream in a relatively cooler environment. The hot end often contains the catalysts, particulate filter and any other emissions controls device, as they are temperature-dependent and positioned closer to the engine to accelerate catalyst light-off to enable effectiveness. Gas temperatures in this region may exceed 1000°C at times, resulting in significant material temperatures, often under stress also from engine and road load vibrations. SODA material temperatures are limited by the migration of chromium into the base substrate, which begins above 800°C [18]. Cold-end material temperatures, however, are much less aggressive, especially the muffler’s externals since they distribute heat across larger surface areas, yielding more ambient cooling. For these reasons, muffler heads and shells are considered to be of less risk to apply such new materials, as its interstitial-free steel core also has thermal limits resulting in structural softening. Furthermore, muffler shells are large surface areas per part, which offers a means to achieve volumes necessary for process optimization, a critical element in scaling of any new technology introduction.

Muffler materials are highly application and customer dependent, but aluminized 409 (409AL) is common across many, as the aluminized coating offers measureable corrosion resistance. But, the aluminized coating also leaves residuals throughout the manufacturing process, causing tools and welding equipment to undergo more maintenance for cleaning, expected to be eliminated with SODA. Rolled mufflers are often more tubular in shape and are produced by forming an oval shell and stuffing it with internal components, such as baffles, connecting pipes, and possibly roving. Afterwards, the stamped heads are spun onto its ends, sealing its edges by forming the metal at each seam to wrap it inward, folding the head and shell edges together as opposed to welding. This keeps that edge from open environmental exposure, reducing the likelihood of excessive corrosion and poor visuals. Mufflers include one or more inlets and outlets, which are welded to adjoining pipes. Hanger rods are also often welded to the muffler shell, heads, or adjoining pipes to retain the system appropriately under the vehicle as it thermally grows and vibrates. All of these points of interface must be tested for adequate performance, including qualification measurements before and after.

Mufflers undergo significant thermal cycles, corrosion and vibrations, as they are attached directly to the engine and hang along the underbody of the car, exposing them fully to the environment with high temperatures and structural loads. Bushing and hanger fatigue, thermal shock and corrosion tests are typical, stressing performance under thermal and structural loads, as well as accelerating corrosion measured visually and with leak qualifications. Fatigue tests involve mounting the body of the muffler while oscillating loads on the pipes and hanger rods, simulating loads anticipated from the field. These tests are done cold (ambient, not heated) across established loads and samples and verify durability performance with pass/fail criteria, supported with historical data. Thermal shock tests simply cycle temperatures hundreds of times up and down with extreme ramps through the use of a blower and natural gas burner to assess effects of thermal stress. Corrosion not only occurs externally, but also throughout the exhaust internals, with sensitivity dependent upon the fuel and its quality, such as sulfur content.

Builds and Testing

Three production applications are manufactured from three different customer platforms, extending across five plants contributing various portions of the muffler systems. Applications include two pick-up trucks, as well as a sport utility vehicle, of which each muffler product is illustrated in Figure 7. Plant operations start with steel coils and end with final assemblies that are then shipped for storage and testing. Bodies for muffler shells are slit and then rolled, and the muffler heads are stamped. Muffler bodies are assembled, which ultimately become muffler systems with attaching accessories and pipes. Each manufacturing step is performed at rate, however, since less than 50 parts are targeted, run times are quick and much shorter than that needed for setup. Operators had no issues in applying the material, as it was successful across all operations.

![Figure 7](Image) Examples of various muffler designs produced with SODA.
Bushing and hanger rod fatigue testing is completed, successfully passing the required number of cycles at each load for the necessary number of samples. Values for each application vary based on customer requirements and the application’s road-load test data, but none of the applications had premature failures. Figure 8 illustrates results of one example, comparing load and cycle data from SODA to the minimum application requirement (90% reliability and confidence, green line), demonstrating acceptable performance with significant safety margin. Similar results occurred for all applications, inlet and outlet bushings, as well on any attaching hanger rods. Each application is tested under two loads across five samples, providing appropriate confidence.

Thermal shock testing was completed, successfully passing one thousand cycles without concerns of any kind, cycling between 100°C and 800°C gas temperatures at approximately 100kg/hr mass flow rate. Leak tests are performed before and after testing, applying 30kPa while measuring its flow rate if losing pressure.

Corrosion testing is completed over a 10-week protocol in a corrosion chamber bench with internal and external corrosion applied, equivalent to 10 years (full useful life). Figure 9 illustrates the results of one of the rolled mufflers, comparing the SODA composite (A) with baseline material 409AL (B). SODA visually performs better, and leak tests were completed for each sample before and after testing. No leaks were found in any of the samples at the start of test, acknowledging the drain holes are traditionally plugged. The only sample that leaked after corrosion testing was the 409AL rolled muffler, although it was small and still within acceptable limits. No concerns of edge corrosion occurred, illustrated with close-up of the SODA rolled muffler edge in Figure 10.

**Conclusions**

Overall, in cold-end exhaust applications, the SODA material performs as well, if not better than 409AL. Its unique multi-layer structure significantly reduces chromium content, applying it only at its outer surface, reducing surcharge dependencies and improving formability versus stainless grades. Its softness provides material forming advantages, enabling complex shapes without significant material thinning. Manufacturing processes are demonstrated at rate with SODA, acknowledging it can be substituted easily without necessary process change investments. Assembled mufflers are tested across a range of inputs, including structural fatigue, thermal shock, and corrosion, comparing results with those from baseline materials. Edge exposure is controlled within the system design and does not reveal structural concerns after a representative ten years of corrosion. However, neither of the corrosion tests qualified visual appearance within the ten years, only at the end, making it difficult to judge how it looks in its early life, which is when such aesthetics are more critical.

**Recommendations**

It is recommended to assess SODA’s performance sensitivity to a varying chromium layer thicknesses, particularly regarding aesthetic corrosion, better understanding visual impacts, especially within the first year or two of life when customer expectations are at their peak. Aesthetic corrosion response needs to be compared with baseline materials even well within year one, especially if there are any risks during early transport and time spent soaking at dealer lots.

Visual appearance as well as leak testing qualify corrosion effects, but it may be of interest to evaluate fatigue response
after corrosion testing to compare with fresh build results to verify no structural integrity losses. Although, this is not traditionally done and would require comparative results from baseline materials, especially if performance degradation occurs.

It is also suggested to investigate options to help protect exposed and welded edges if needed. Cold spray technologies, for instance, offer means to apply a thin protective layer of material, such as aluminum, in areas necessary, such as weld perimeters or lock-seam joints.

Formability benefits may also lead to thinner gauges since it is less likely to thin during processing, maintaining its strength and resulting in an overall lighter system. It is recommended to investigate this further to assess its potential to lightweight via gauge thinning.

Finally, additional exhaust components may be of interest to manufacture with this material, particularly components not exposed to excessive temperatures and structural loads. Exhaust pipes, for instance, offer additional content potential, including upstream interconnecting pipes as well as downstream tailpipes. Converter shells are another potential example, insulated from the converter heat with support mats. Converter shells also have relatively low structural loads distributed around its perimeter edge, not often a system stress point compared with smaller diameter adjoining pipes and end cones.

References


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Definitions/Abbreviations

CVD - Chemical Vapor Deposition
Cr - Chromium
ERW - Electric Resistance Welding
FEA - Finite Element Analysis
IF - Interstitial Free
MIG - Metal Inert Gas
SCE - Saturated Calomel Electrode
SSC - Saturated Silver-Silver Chloride Electrode
SODA - Spatially Optimized Diffusion Alloy
TIG - Tungsten Inert Gas