

Constraints Based Modeling for Innovative Product & Process Designs

K. Sampath

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An innovative, constraints based modeling (CBM) approach proved successful for product developments and process improvements. The product developments involved specifying the chemical composition range for a set of chromium-free, high-performance consumable electrodes intended for gas-metal arc welding (GMAW) of high-strength steels used in hull constructions while significantly reducing energy costs. The process improvements involved selecting appropriate non-carcinogenic chemicals for a non-chromate conversion coating bath used with corrosion protection of aluminum alloys. In both cases, successful application of the CBM approach also led to the award of U.S. Patents.

Keywords chromium-free, client needs, constraints based modeling, conversion coating process, energy savings, high-performance welding electrode, knowledge management, model validation, process design, product design, sustainability

1. Introduction

Constraints based modeling (CBM) is an innovative approach that is quite useful as a project management and knowledge management package for advancing designs for sustainable products and processes. Particularly, application of the CBM approach allows one to develop a sharp focus on client needs in advancing designs for sustainable products and processes, construct CBM to define experimental space relative to identified client needs, and design low-cost, low-risk rational experiments to validate the model while allowing one to offer unique and affordable solutions that meet or exceed specific client-centric metrics such as quality, quantity, schedule, and cost.

The construction of the CBM is founded on a critical assessment of various known and perceived events crucial to advancing designs for sustainable products and processes. Specific events are perceived primarily to overcome gaps in known knowledge. This critical assessment helps one to consolidate existing knowledge into a model, impose a set of mutually inclusive or coherent constraints on the model to

“A novel modeling approach is successful for product developments and process improvements” Dr. K. Sampath is a Technology/Business Consultant in Johnstown, PA. He received a Ph.D. degree in Welding Engineering from The Ohio State University and a MBA degree from Cornell University. He has pioneered the Constraints Based Modeling Approach to provide innovative, low-cost, low-risk solutions to persistent materials processing issues, and has received three U.S. Patent awards

K. Sampath, Kreative Koncepts, 615 Demuth Street, Johnstown, PA 15904. Contact e-mail: rs127@yahoo.com.

substantially reduce the experimental space while developing an improved understanding of the effects of various constraints on sustainable product or process design, in relation to quality and performance, with no adverse effects on either the environment or the health and safety of workers.

The CBM approach uses two key principles:

- (1) consolidate prior and perceived knowledge into a coherent set of mutually inclusive constraints that explicitly address specific client requirements; and
- (2) based on the set of constraints, formulate controlled experiments to limit experimental space while reducing inherent risks, including environmental and regulatory risks, thereby allowing one to reach beyond the consolidated knowledge in developing novel, low-cost, low-risk, sustainable solutions to overcome persistent materials (processing and fabrication) issues.

The above key principles lend themselves for successful application to sustainable product and process designs. The purpose of this article is to describe two case studies that illustrate the use of CBM approach in fostering sustainable product and process designs. The first case on sustainable product design (Ref 1, 2) shows how the CBM approach proved successful in innovatively designing the chemical composition of chromium-free, high-strength steel welding electrodes while complying with chemical composition requirements for MIL-100S and MIL-120S electrodes specified in MIL-E-23765/2E (Ref 3) or its commercial equivalent A5.28 specification (Ref 4) issued by the American Welding Society. The second case on sustainable process design shows how the CBM approach (Ref 5) was successful in designing an innovative non-chromate conversion coating solution for use with corrosion protection of aluminum and its alloys. In both cases, successful application of the CBM approach also led to the award of U.S. Patents (Ref 6-8). The above two cases are described through the three steps:

- (1) Client needs,
- (2) Knowledge management, and
- (3) Model validation.

2. Case 1—Design of Advanced Welding Electrodes

2.1 Client Needs

High yield (HY) and high-strength low-alloy (HSLA) type steels with a minimum specified yield strength of 550 or 700 MPa are used extensively in U.S. Navy ship and submarine construction (Ref 9). Commercial applications for these high-performance steels include off-highway vehicles, bridges, pressure vessels, and storage tanks for petro-chemicals, nuclear wastes and other materials, etc.

The HY steels were developed in the 1960s and exhibit a predominantly tempered martensitic microstructure. The HY-80 and HY-100 steels are characterized by a high-carbon content (Ref 10) ranging from about 0.12 to 0.20 wt.% (percent by weight). Hydrogen-assisted cracking (HAC) in the weld heat-affected zone (HAZ) is a serious issue in fusion (arc) welding of these high-strength structural steels with a high-carbon content.

These steels, depending on actual carbon and alloy content, show a high potential to form twinned martensite and solid-state cracking in HAZ when the following conditions are *simultaneously* present: (1) a source of dissolved hydrogen; (2) high-residual tensile stress distribution; (3) a temperature range that did not allow significant solid-state diffusion of atomic hydrogen from the steel; and (4) a time delay following welding that allowed atomic hydrogen to accumulate at internal “flaws” in the steel, thereby leading to HAC. To eliminate or substantially reduce the occurrence of HAC in the weld HAZ, the HY steels require the application of preheat, interpass, and occasionally post-soak temperature controls during welding. These additional operations increase fabrication cost, produce considerable production delays, reduce overall productivity while increasing welder discomfort. The U.S. Navy has estimated that elimination or substantial reduction in temperature control during welding could save about \$10 M in the construction of an aircraft carrier, and \$15 M in the construction of a submarine in material (including energy expenses), labor and productivity, irrespective of the type of arc welding processes used.

Currently, various U.S. shipyards employ gas-metal arc welding (GMAW) process as the preferred fabrication process for constructing several ship structures, and primarily use Ar-5%CO₂ as weld shielding gas. MIL-E-23765/2E (Ref 3) specifies MIL-100S and MIL-120S as welding consumables useful for joining HY-80 and HY-100 steels. Table 1 specifies the chemical composition range and mechanical property requirements for MIL-100S and MIL-120S GMAW consumable electrodes. These electrodes often exhibit a carbon content in excess of 0.05 wt.%. Consequently, these welding electrodes also require significant preheat to reduce the occurrence of HAC in the weld metal (Ref 11).

High-strength low-alloy steels were developed in the 1980s primarily to reduce fabrication costs (Ref 12). In contrast to the HY steels, the HSLA-80 and HSLA-100 steels (Ref 13) have a lower carbon content (0.07 wt.% maximum) and exhibit a predominantly ferritic and bainitic microstructure, respectively. Unlike the martensitic microstructure, the ferritic and bainitic microstructures exhibit little or no susceptibility to HAC. Because of their low susceptibility to HAC, HSLA-80 and HSLA-100 steels require much less stringent preheating controls compared to the corresponding grade of HY steels.

Table 1 MIL-E-23765/2E chemical composition ranges and mechanical property requirements

Element	MIL-E-23765/2E	
	MIL 100S	MIL 120S
Carbon	0.08	0.09
Manganese	1.25-1.80	0.90-2.35
Silicon	0.20-0.55	0.60
Phosphorus	0.012	0.012
Sulfur	0.008	0.008
Nickel	1.40-2.10	1.0-3.0
Chromium	0.30	0.80
Molybdenum	0.25-0.55	0.30-1.00
Vanadium	0.05	0.03
Titanium	0.10	0.10
Zirconium	0.10	0.10
Aluminum	0.10	0.10
Copper	0.25	0.25
Other elements, Total	0.50	0.50
Iron	Balance	Balance
<i>Mechanical property in as-welded condition</i>		
Yield strength, MPa	565-758	703-841
Tensile strength, MPa
Elongation (%)	16	14
Minimum CVN, J at 18 °C	81	81
Minimum CVN, J at -50 °C	48	61

Therefore, HSLA-80 and HSLA-100 steels offer a huge potential for low-cost fabrication of very large structures.

However, HSLA-80 and HSLA-100 steels are currently fabricated with MIL-100S and MIL-120S solid-wire electrodes used for GMA welding of HY-80 and HY-100 steels. Since the currently available MIL-100S and MIL-120S solid-wire electrodes require preheat and interpass controls, and post-soak temperature control for MIL-120S, their use precludes the full economic advantages of HSLA steels (Ref 12). For the foregoing reasons, there is an immense economic need for developing advanced consumable, solid-wire electrodes for GMA welding of HSLA-80 and HSLA-100 steels. From logistical and quality assurance standpoints, the U.S. Navy manufacturers may prefer that the same set of electrodes be certified for use with the welding of HY-80 and HY-100 steels as well.

As the prime user, the U.S. Navy had identified that the candidate advanced GMA welding electrodes for high-strength steels used in naval ship construction should exhibit the additional characteristics (Ref 12): (1) eliminate or substantially reduce the need for preheat controls while joining higher strength steels such as HSLA-100, HY-100, HSLA-80, and HY-80; (2) show adequate resistance to HAC; (3) meet or exceed the mechanical property requirements of the existing MIL-100S or MIL-120S electrodes; (4) allow welding over a broad operational envelope in terms of plate thickness, welding position, and weld energy input; and (5) show minimal variation in weld mechanical properties (especially yield strength) when used over a broad operational envelope for welding HSLA-100, HY-100, HSLA-80, and HY-80 steels.

2.2 Knowledge Management

The primary emphasis of the CBM effort was to design advanced welding electrodes with excellent weldability that offer substantial savings in energy expenses. For the purpose of this work, weldability was defined as the ability to “recreate”

or “retain” high-performance microstructure that showed a minimal susceptibility to HAC. As the HSLA-80 and HSLA-100 steels have a low carbon content (0.07 wt.% maximum), exhibit a ferritic and bainitic microstructure, respectively, and show a minimal susceptibility to HAC, one could expect that weld metals with similar characteristics, including desired microstructures, would offer excellent weldability. Based on this premise, various client needs were converted into a set of mutually inclusive constraints that enabled one to identify and define appropriate chemical composition ranges for welding electrodes that provided high-performance weld metals with a predominantly ferritic or bainitic microstructure and a minimal susceptibility to HAC.

Initially, three constitutive equations that related chemical composition of candidate steel electrodes to certain metallurgical characteristics were used to set up a set of constraints. Each of these constitutive equations underscores one or more metallurgical characteristics such as strength, toughness, and weldability. The respective numerical ranges for the selected constitutive equations were obtained from an analysis of published literature. Specific numerical ranges were determined based on the possibility to achieve desirable range of mechanical properties (tensile strength, low-temperature toughness) for both MIL-100S and MIL-120S electrodes while improving their weldability in terms of resistance to HAC.

A composition having the features of the CBM is comprised of iron (Fe), and specific amounts (in percent by weight) of carbon (C), manganese (Mn), nickel (Ni), chromium (Cr), molybdenum (Mo), silicon (Si), copper (Cu), vanadium (V), niobium (Nb), and boron (B) that concurrently satisfy the three equations:

$$B_{50}(\text{°C}) = 770 - (270 \times C) - (90 \times \text{Mn}) - (37 \times \text{Ni}) - (70 \times \text{Cr}) - (83 \times \text{Mo}), \quad (\text{Eq 1})$$

where the calculated value of B_{50} is 400-500 °C

$$M_S(\text{°C}) = 561 - (474 \times C) - (33 \times \text{Mn}) - (17 \times \text{Ni}) - (17 \times \text{Cr}) - (21 \times \text{Mo}), \quad (\text{Eq 2})$$

where the calculated value of M_S is 400-450 °C;

$$\text{CEN} = C + A(C) \times \{ \text{Si}/24 + \text{Mn}/6 + \text{Cu}/15 + \text{Ni}/20 + (\text{Cr} + \text{Mo} + \text{V} + \text{Nb})/5 + 5\text{B} \}, \quad (\text{Eq 3})$$

where $A(C) = 0.75 + 0.25 \tanh[20 \times (C - 0.12)]$, and where the calculated value of CEN is 0.28-0.41.

The first equation relates the chemical composition to B_{50} temperature, i.e., the temperature at which 50% bainite transformation occurs (Ref 14). Bainite is a transformation product of austenite and this transformation occurs between bainite-start (B_S) and bainite-finish (B_F) temperatures. The difference between B_S and B_F temperatures is 120 °C. The B_{50} temperature is midway between the B_S and B_F temperatures.

The bainite transformation is known to show dual characteristics, i.e., under certain conditions, bainite forms athermally from austenite through a displacive reaction involving a limited diffusion of carbon, while in certain other situations bainite may nucleate and grow into austenite exclusively through diffusion-control (Ref 15). When the bainite transformation occurs athermally, the quantity of bainite formed at a given temperature between B_S and B_F temperatures can be estimated from the ratio of the difference between B_S temperature and the

transformation temperature over 120 °C, the latter being the difference between B_S and B_F temperatures. For the limited purpose of the CBM effort, the bainite transformation in low-carbon, low-alloy steel weld metal was perceived to be athermal, so one could use the constitutive relationship between chemical composition and B_{50} temperature to achieve microstructure selection and control. Further, the athermal nature of the bainite transformation is also perceived to allow the use of a wide welding operational envelope, i.e., large changes in weld heat input conditions may still provide adequate control over weld metal microstructure and allow acceptable variations in weld mechanical properties.

Furthermore, the higher strength bainitic steels exhibit a B_{50} temperature in the range of 420-550 °C and in this range, the strength of these steels increases linearly with a decrease in B_{50} temperature (Ref 16, 17). Bainitic steels exhibit high-tensile strength (in 900-1200 MPa range) and good impact toughness at low temperature. Lowering the transformation temperature allows one to refine the grain size of the transformation product, leading to simultaneous increases in both tensile strength and ductility. Therefore, selection of a range of 400-500 °C for B_{50} temperature allowed one to match the tensile strength range for MIL-100S and MIL-120S electrodes.

The second equation relates the chemical composition to M_S temperature, i.e., the temperature at which martensite transformation starts (Ref 14). Martensite is another transformation product of austenite, but has a higher susceptibility to HAC. In other words, both bainite and martensite form only from austenite. The M_S temperature of high-strength bainitic steels is often well below their corresponding B_{50} temperature. Understandably, this characteristic can be manipulated as an additional constraint to design the chemical composition of a high-performance steel that will allow one to achieve desirable microstructure selection and control. For example, a careful lowering of the M_S temperature below the B_{50} temperature of a candidate steel allowed one to achieve a large volume fraction of bainite than martensite in the resultant microstructure, and thereby substantially reduced the susceptibility to HAC.

Based on the ranges for tensile strength, low-temperature toughness, and resistance to HAC of MIL-100S and MIL-120S electrodes, the desired range for M_S temperature is approximately 400-450 °C.

The third equation relates the chemical composition to the carbon equivalent number (CEN), which is often used to distinguish high-strength structural steels that may require preheating during weld fabrication (Ref 18). One could also use the CEN equation to assess the relative effects of different alloy elements on the need for preheat. Evidently carbon content has the greatest effect on the CEN. When considering weld metal, a substantial reduction in the carbon content of the welding consumable is necessary to obtain significant reduction in preheat levels. To further reduce the CEN and the sensitivity of weld metals to preheat controls, it is desirable to limit the levels of elements with the highest coefficients in the CEN equation (e.g., boron, chromium, molybdenum, vanadium, and niobium) and increase the levels of elements with the lowest coefficients in the CEN equation (e.g., silicon, nickel, copper, and manganese). The desired value for CEN of structural steels that may eliminate or substantially reduce the need for preheat and interpass temperature controls ranges between 0.28 and 0.41.

Besides compositional control to achieve mechanical property goals, the CBM approach also limited the combined oxygen and nitrogen content of the electrodes to preferably

below 550 ppm (Ref 19) consistent with dissolved gas content commonly obtainable with gas-shielded welding processes.

In the CBM approach, the above metallurgical characteristics and their numerical ranges, in turn, were used to identify carbon, manganese, nickel, and molybdenum as critical elements for compositional control, and to specify the compositional ranges for these individual alloy elements (Ref 20). Subsequently, a 2³ factorial design of experiments was used to develop a batch of eight welding electrodes. These electrodes were essentially free from chromium, and contained low-carbon (at about 0.03 wt.%). The 2³ factorial design used one low and another high level for manganese (1.5 and 1.8 wt.% as aim composition), nickel (2.5 and 3.8 wt.% as aim composition) and molybdenum (0.5 and 1.0 wt.% as aim composition). The eight electrodes contained other elements such as silicon, phosphorus, and sulfur at some nominal values. The compositions also included approximately 0.03 wt.% titanium as a deoxidizer, grain refiner, and “nitrogen getter” (Ref 20, 21) and thus attempted to control the amount of oxygen and nitrogen in the weld metal. Titanium addition also served to refine weld metal grains.

2.3 Model Validation

Table 2 shows the melt chemical composition of the solid-wire electrodes. Table 3 shows the calculated metallurgical characteristics of the solid-wire electrodes based primarily on their respective melt composition. Initially, a set of demonstration weldments was produced to evaluate the performance of these eight welding electrodes (Ref 22) and to downselect one electrode for additional weld testing over a much wider welding operational envelope. Results showed that three of the eight electrodes (#3, #4, and #7) met or exceeded MIL-100S requirements while two of the eight electrodes (#4 and #8) met or exceeded MIL-120S requirements. Microstructural and

fractographic analyses of the weldments showed that these advanced electrodes provided a predominantly bainitic microstructure in the weld metal.

Based on the encouraging results, electrode #3 was selected for additional weld evaluations. Table 4 shows the details of GMA weld schedules for the additional test weldments. These weldments provided acceptable weld mechanical properties over the entire range of welding conditions. Table 5 shows the corresponding weld metal mechanical property test results. These results also indicated that electrode #3 could be used as either MIL-100S or MIL-120S by choosing an appropriate welding operational envelope. Based on weld CVN impact toughness values of the weldments obtained from both HSLA-100 and HY-100 steels at comparable welding conditions, one could surmise that the use of HSLA-100 steel was more discriminating than the use of HY-100 steel in identifying advanced consumable electrodes that could be potential alternatives to conventional MIL-100S electrodes.

Figure 1 (Ref 1, 2) shows the variation of the all-weld metal yield strength with calculated weld cooling rate at 538 °C (Ref 23), confirming acceptable increase in weld metal yield strength with increasing weld cooling rate. The trend line showed the following statistical relationship, at a *r*² value of 0.99:

$$\text{All-weld metal yield strength (in MPa)} = 524 + \{65 \times \text{Ln}(\text{Calculated weld cooling rate at } 538^\circ\text{C in } ^\circ\text{C/s})\}.$$

The chief advantage of this CBM approach is that it helps one to distinguish high-performance welding electrode chemical compositions from rich and lean welding electrode chemical compositions that otherwise meet MIL-23765/2E or AWS 5.28 electrode specification requirements. It is well known that the use of rich and lean welding electrode chemical compositions often limits operational envelope, reduces performance or both, while increasing overall cost of fabrication.

Table 2 Chemical composition of bare wire gas-metal arc welding electrodes (Ref 1, 2)

No.	C	Mn	P	S	Si	Cr	Ni	Mo	V	Cu	Ti	B	O	N	H
1	0.027	1.51	0.001	0.0019	0.34	0.02	2.52	0.52	0.001	0.001	0.033	0.001	69	6	2.11
2	0.028	1.49	0.001	0.0018	0.37	0.01	2.38	0.99	0.001	0.001	0.031	0.001	47	9	1.51
3	0.028	1.54	0.001	0.0018	0.34	0.01	3.78	0.52	0.001	0.001	0.028	0.001	52	10	2.13
4	0.029	1.5	0.001	0.0018	0.35	0.01	3.73	0.98	0.002	0.001	0.03	0.001	78	6	1.46
5	0.03	1.82	0.001	0.0020	0.34	0.01	2.37	0.52	0.003	0.001	0.029	0.001	76	6	1.63
6	0.029	1.82	0.001	0.0021	0.35	0.01	2.38	0.98	0.003	0.001	0.029	0.001	66	7	1.15
7	0.026	1.82	0.001	0.0022	0.35	0.01	3.77	0.51	0.002	0.001	0.027	0.001	64	6	1.79
8	0.03	1.8	0.001	0.0019	0.33	0.01	3.72	0.99	0.003	0.001	0.025	0.0003	82	4	1.23

Chemical composition (#1 through 8) is expressed in wt.%. Balance is essentially Fe. Chemical composition determined from vacuum induction melt (VIM) billets. N, O, and H contents determined from bare solid-wire electrodes. N and O contents are expressed in parts per million (ppm). H content is expressed in mL/100 g of Fe. Bare wire size is 1.6 mm diameter

Table 3 Calculated metallurgical characteristics of bare wire welding electrodes (Ref 1, 2)

No.	B ₅₀ Temperature (°C)	M _S Temperature (°C)	Carbon equivalent number (CEN)	Combined (O + N) content (ppm)
1	489	444	0.29	75
2	457	437	0.33	56
3	440	422	0.32	62
4	407	414	0.36	84
5	467	435	0.31	82
6	428	426	0.36	73
7	417	414	0.34	70
8	379	403	0.39	86

Second, the CBM approach is quite useful in readily identifying an acceptable heat, which has a melt composition that meets the metallurgical criteria set by the CBM. Alternatively, the CBM approach allows one to reject a rich or a lean heat even when the melt composition is otherwise well within MIL-E-23765/2E or AWS 5.28 specification. When the metallurgical criteria are not met, a rich or a lean heat becomes an “out-lier.” Such a

decision eliminates or substantially reduces further processing costs and associated risks. This level of reliability and risk reduction while specifying an electrode chemical composition is not commonly achieved.

Thus, use of the above CBM approach greatly reduced various risks inherent in specifying electrode chemical composition while complying with MIL-E-23765/2E or AWS 5.28,

Table 4 GMA welding schedules for evaluation of electrode #3 (Ref 1, 2)

Weld #	Base plate	Energy input, kJ/mm	Welding position	Metal transfer	Preheat temperature, °C	Interpass temperature, °C	Calculated weld cooling rate at 538 °C in °C/s
1	HSLA-100	1.18	Flat	Spray	52	52	53
2	HSLA-100	1.77	Flat	Spray	66	66	32
3	HY-100	1.77	Flat	Spray	66	66	32
4	HSLA-100	2.17	Flat	Spray	16	52	26
5	HSLA-100	4.33	Flat	Spray	16	52	6
6	HSLA-100	4.33	Vertical-up	Pulsed	149	149	4
7	HSLA-100	4.33	Flat	Spray	135	149	3
8	HY-100	4.33	Flat	Spray	149	149	3

Table 5 Mechanical property test results of additional GMA welds (after Ref 1, 2)

Weld no.	Base plate	Calculated weld cooling rate at 538 °C in °C/s	Room-temperature all-weld tensile test				CVN impact test, J	
			Yield strength, MPa	Ultimate tensile strength, MPa	Elongation, %	Reduction in area, %	At -50 °C	At -18 °C
MIL-100S	HY-100/HY-80	...	565-758	...	16 min	...	48 min	81 min
MIL-120S	HY-100/HY-80	...	703-841	...	14 min	...	61 min	81 min
1	HSLA-100	53	786	822	19.2	63	117	168
2	HSLA-100	32	746	792	21.3	68	100	122
3	HY-100	32	753	801	22.3	67	103	130
4	HSLA-100	26	729	790	22.0	69	102	138
5	HSLA-100	6	638	725	23.5	71	99	152
6	HSLA-100	4	600	752	24.3	72	170	198
7	HSLA-100	3	609	709	24.3	71	66	129
8	HY-100	3	600	709	25.8	72	134	175

Tensile test results represent an average of two tests; CVN impact test results represent an average of five tests.

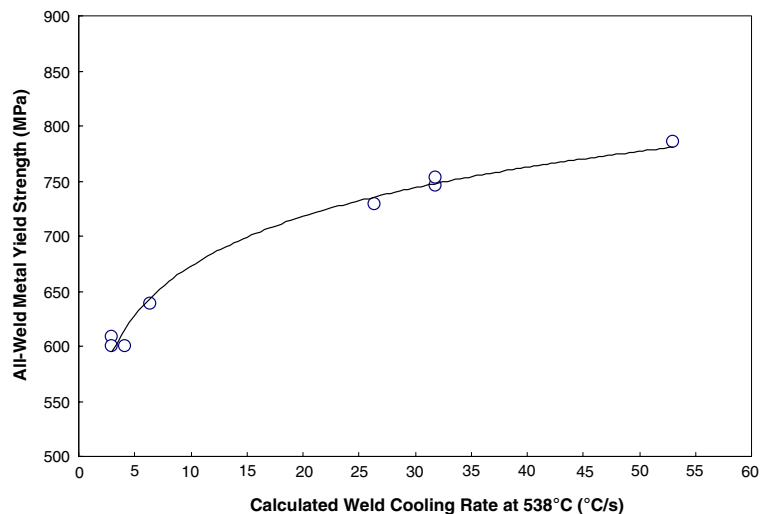


Fig. 1 Variation of weld metal yield strength with calculated weld colling rate (Ref 1, 2)

albeit a wider range for nickel content, and helped to identify advanced electrode chemical compositions that met weld mechanical properties over a wide welding operational envelope. Effective use of the CBM approach also allowed one to gain an improved understanding of the effects of weld metal chemical composition on processing (welding operational envelope), microstructure development, and mechanical properties including room-temperature and low-temperature fracture behavior.

3. Case 2—Non-Chromate Conversion Coating Process Design

3.1 Client Needs

Both chromate conversion coatings and paints based on chromates are widely used in preventing or mitigating corrosion-related problems in structures and components made of aluminum and its alloys (Ref 24). These surface coatings resist corrosion and wear, and also promote paint adhesion. Commonly, these protective coatings are produced by immersion, electrostatic spraying, swabbing, or brushing techniques that use solutions containing either chromates (as potassium or strontium chromate), dichromates (as potassium dichromate), phosphates (as orthophosphoric acid), or fluorides (as either sodium or potassium fluoride or hydrofluoric acid).

When a chromate conversion coating is applied to aluminum alloy components, the substrate surface reacts with the chemical solution. The metal surface is converted into a tight adherent coating, all or part of which consists of an oxidized form of the substrate metal. The chromium ions in the solution are partially reduced from a higher valency to a lower valency state (e.g., from hexavalent Cr(VI) to trivalent Cr(III) states), with a concurrent rise in the pH of the coating bath. When dried, the coating that is initially gelatinous (i.e., gel-like) undergoes hardening, becomes hydrophobic, less soluble in water, and more abrasion resistant. The resulting conversion coating on the surface of the aluminum component offers resistance to corrosion and an anchoring surface for organic finishes, such as a paint topcoat.

The chemical composition of the chromate conversion coating is indefinite as it contains varying amounts of reactants, reaction products, water of hydration, and other anions, such as fluorides and phosphates. In the presence of corrosive conditions, the hexavalent Cr(VI) ions “incorporated” into the coating leach out, and possibly tie-up the free electrons, and thereby provide exceptional corrosion resistance.

However, solutions containing hexavalent chromium ions, Cr(VI), have been determined to be carcinogens. The U.S. Environmental Protection Agency (EPA) has included hexavalent chromium on its list of toxic chemicals for voluntary replacement, and has promulgated strict air emission and waste disposal standards to curtail the use of hexavalent chromium. These developments have created a need for alternative chemical conversion coating compounds that do not contain Cr(VI) ion, but either meet or exceed the protective properties displayed by the hexavalent chromium-based compounds.

Furthermore, from legacy and cost standpoints, any alternative is required to serve as a “drop-in” substitute with only minor modifications to the present process stream so that it is readily acceptable to industry. However, while a cost-effective and an

environmentally benign alternative that provides protection comparable to that of chromium is needed, currently no known rational methods are available for identifying alternatives to Cr(VI). Although use of chromates as corrosion inhibitors has evolved over several decades, much of this use is based on empirical knowledge. For example, Cr(VI) in the coating is believed to provide both corrosion protection and a self-healing ability. Not only is it unclear exactly what functional role chromates play, it is not known what chromate replacement complexes must do to ensure long-life coating systems.

Furthermore, as with chromate conversion coatings, the corrosion inhibitor paint chemistry for aluminum substrates relies on the extensive use of Cr(VI) in the form of strontium chromate, which is incorporated into both the surface pretreatment and the primers as a highly effective corrosion inhibitor. Besides mandating the removal of chromates in conversion coatings and paint chemistries, the new environmental regulations are also forcing paint materials and processing technology to move away from the use of formulation chemistries involving volatile organic contaminants (VOCs) and hazardous air pollutants (HAPs). These ingredients must soon be substantially reduced or eliminated from the paint technology base. Although formulation technology has begun to move toward compliance, the available environmentally compliant paint systems have so far provided less than satisfactory performance. Current comparative evaluations show that adhesion, coating durability, weathering, and corrosion protection have suffered.

3.2 Knowledge Management

To develop effective non-chromate conversion coatings and paint formulations acceptable to industry, one needs to obtain a fundamental understanding of the chemical and/or physical processes and mechanisms of corrosion protection that occur when chromate-based coatings are applied on metal surfaces, especially aluminum and its alloys. Therefore, the primary emphasis of the CBM effort was to identify desirable features of a potential alternative to the chromate conversion coating process through a critical assessment of the chromate conversion coating process (Ref 5). This assessment revealed that the following features or characteristics are essential in defining the chromate conversion coating process:

- (1) The chromate bath is a clear acidic solution with a pH in the range of 1.2-2.2.
- (2) During chromating, precipitation of hydrated compounds occurs on the substrate and the pH of the bath increases at the substrate interface.
- (3) Several hydrated compounds containing chromate, nitrate, phosphate or a combination of these anions are formed.
- (4) The Cr(VI) to Cr(III) reduction reaction occurs with the liberation of hydrogen gas, formation of waters of hydration or both.
- (5) Fluoride, nitrate or phosphate anions present in the coating bath, perhaps as activators, also enter the surface coating.

Further, this critical assessment also revealed that the chief aspects of the chromate coating process are:

- (1) Cr(VI) to Cr(III) reduction reaction is essential to achieve corrosion protection,

- (2) increase in bath pH at the interface is necessary to promote precipitation of compounds in the coating,
- (3) resulting precipitation reaction involved hydrated compounds, and
- 4) ratio of Cr(III) to Cr(VI) in the coating must be controlled.

The precipitation reaction can be expected to occur when the products of the reaction (chromates, nitrates and phosphates of chromium or the substrate) show decreased solubility with increasing bath pH. In considering potential alternatives to the chromate conversion coating process, the CBM effort addressed the above chief features of the chromate conversion coating process. In particular, the CBM effort focused on identifying chemicals that show a decrease in solubility with increasing pH in the range of from 2.0 to 7.0, while also forming waters of hydration.

The CBM effort considered the electromotive force (EMF) series for imposing additional constraints to further reduce the experimental space. It is common knowledge that to obtain corrosion resistance, the cation of the chemicals that form the precipitate must be positive (i.e., less negative) in the EMF series relative to the substrate, and their EMF values should be close to each other. Table 6 shows the EMF series for various electrode reactions involving selected basis metals and their corresponding standard electrode potentials (Ref 25). CBM efforts considered methods or solutions that provided one or more chemicals satisfying the above sets of constraints that were also environmentally benign and cost effective.

Based on the above analysis, the following constraints, all of which are mutually inclusive, were used in constructing a CBM for identifying an alternative to the chromate conversion coating process:

- (1) The processing (coating bath) solution must be clear with no precipitates.
- (2) The processing solution must contain a wetting agent such as sodium alkyl aryl sulfonate to provide a uniform and continuous coating.
- (3) The processing solution must contain fluoride, perchlorate, nitrate, phosphate, sulfate or as many of these anions as necessary to activate the surface of the substrate and enter the coating as well.
- (4) The pH of the processing solution must be capable of being varied in the acidic range of pH 1.2-5.0.
- (5) The solution of these salts must react with the substrate, raise the pH of the coating bath locally at the bath/substrate interface and form hydrated precipitates that are insoluble in near neutral and alkaline solutions.
- (6) The precipitate that forms a hydrated compound must also contain cations in multiple (e.g., III and VI) valence states.
- (7) The cation forming the hydrated precipitate must be positive in the EMF series with respect to the substrate.
- (8) The precipitates that form on the substrate during processing should exhibit waters of hydration.
- (9) To preserve the waters of hydration in the coating, the processing temperature must be kept under 100 °C.

In addition to the above set of constraints, to further reduce the experimental space, two additional constraints were included based on an analysis of the ionic radii and coordination numbers for Al(III), Cr(III) and Cr(VI) ions. Table 7 shows the ionic radii and coordination numbers of candidate metallic cations in either the (III) or (VI) valence state (Ref 26). Among these candidate cations, it is interesting to note that Mn(III) and Mn(VI) have radii similar to those of Al(III), Cr(III), and Cr(VI) ions. Coincidentally, Sanchem, Inc., Chicago, Illinois has developed a proprietary Sanchem Safeguard non-chromate conversion coating process that uses potassium permanganate that contains manganese as Mn(VII).

Furthermore, Table 7 also includes data for the Ce(III) and Mo(VI) ions. Both these ions have been used in the “stainless aluminum” process developed at the University of Southern California (Ref 27). The “stainless aluminum” coating process uses cerium ions, Ce(III), to harden or strengthen the coating and Mo(VI) ions to provide corrosion resistance and the ability to self-heal. Understandably, when either of these two ions is used independently in a coating, the coating does not provide acceptable test results. As these two ions exhibit a size either larger than the Al(III), Cr(III), and Cr(VI) ions, or a non-matching coordination number with either the Cr(III) or Cr(VI) ions, one might expect that the reactions involving these chemicals would require long processing times and/or high temperatures.

Interestingly, both the proprietary Sanchem Safeguard conversion coating process and the stainless aluminum coating process appeared to support the additional set of constraints based on ionic radius. For example, as the proprietary conversion coating process uses potassium permanganate (KMnO₄) that contains manganese as Mn(VII), depending on the nature of the chemical reactions between the chemicals in the bath and the substrate, one may expect the potassium permanganate solution to provide both Mn(III) and Mn(VI) ions in the coating. However, at this time, it is not clear whether the chemical reactions involving potassium permanganate allowed Mn(III) and Mn(VI) ions to enter the coating and, if

Table 6 Electromotive force series (Ref 25)

No.	Electrode reaction	Standard electrode potential <i>E</i> (volts) at 25 °C
1	K = K ⁺ + e ⁻	-2.922
2	Ca = Ca ⁺⁺ + 2e ⁻	-2.87
3	Na = Na ⁺ + e ⁻	-2.712
4	Mg = Mg ⁺⁺ + 2e ⁻	-2.34
5	Be = Be ⁺⁺ + 2e ⁻	-1.70
6	Al = Al ⁺⁺⁺ + 3e ⁻	-1.67
7	Mn = Mn ⁺⁺ + 2e ⁻	-1.05
8	Zn = Zn ⁺⁺ + 2e ⁻	-0.762
9	Cr = Cr ⁺⁺⁺ + 3e ⁻	-0.71
10	Ga = Ga ⁺⁺⁺ + 3e ⁻	-0.52
11	Fe = Fe ⁺⁺ + 2e ⁻	-0.440
12	Cd = Cd ⁺⁺ + 2e ⁻	-0.402
13	In = In ⁺⁺⁺ + 3e ⁻	-0.340
14	Ti = Ti ⁺ + e ⁻	-0.336
15	Co = Co ⁺⁺ + 2e ⁻	-0.277
16	Ni = Ni ⁺⁺ + 2e ⁻	-0.250
17	Sn = Sn ⁺⁺ + 2e ⁻	-0.136
18	Pb = Pb ⁺⁺ + 2e ⁻	-0.126
19	H ₂ = 2H ⁺ + 2e ⁻	0.000
20	Cu = Cu ⁺⁺ + 2e ⁻	0.345
21	Cu = Cu ⁺ + e ⁻	0.522
22	2Hg = Hg ₂ ⁺⁺ + 2e ⁻	0.799
23	Ag = Ag ⁺ + e ⁻	0.800
24	Pd = Pd ⁺ + e ⁻	0.83
25	Hg = Hg ⁺⁺ + 2e ⁻	0.854
26	Pt = Pt ⁺⁺ + 2e ⁻	ca 1.2
27	Au = Au ⁺⁺⁺ + 3e ⁻	1.42
28	Au = Au ⁺ + e ⁻	1.68

Table 7 Coordination numbers and radii of selected metallic cations (Ref 26)

No.	Element	Metallic cation	Coordination number(s)	Ionic radius (Å)
1	Aluminum	Al(III)	4, 6	0.39, 0.54
2	Chromium	Cr(III)	6	0.62
3	Chromium	Cr(VI)	4	0.26
4	Cerium	Ce(III)	6, 8, 12	1.01, 1.14, 1.29
5	Gallium	Ga(III)	4, 6	0.47, 0.62
6	Manganese	Mn(III)	6	0.58
7	Manganese	Mn(VI)	4	0.26
8	Molybdenum	Mo(VI)	6, 7	0.59, 0.73
9	Scandium	Sc(III)	6, 8, 12	0.745, 0.87, 1.116
10	Selenium	Se(VI)	4, 6	0.50, 0.42
11	Titanium	Ti(III)	6	0.67
12	Tellurium	Te(III)	6	0.56
13	Vanadium	V(III)	6	0.64
14	Wolfram (Tungsten)	W(VI)	4, 6	0.42, 0.60

Note: When an ion exhibits two or more coordination numbers, the ionic radius increases with increasing coordination number, excepting for selenium

so, whether they exhibit the same set of coordination numbers as those of the Cr(III) and Cr(VI) ions, respectively, and the possible ratio of Mn(III) to Mn(VI) in the coating. Chemical analyses of the protective coatings produced with the proprietary Sanchem Safeguard conversion process are currently unavailable. The success of the process in producing protective coatings on a range of aluminum alloys is perhaps largely dependent on the effectiveness of the above substitutions.

As mentioned previously, Table 7 also identifies other candidate metallic cations in (III) and (VI) valence states that exhibit a coordination number similar to those of the Cr(III) and Cr(VI) ions. Chemicals that contain many of these metallic cations are inherently expensive. Despite this cost aspect, it is interesting to note that several previous investigations (Ref 5) have used many of these metallic cations to evaluate their ability to provide protective coatings, and such coatings have shown varying degrees of corrosion resistance.

The above CBM was constructed based on common industry observations and the underlying (known and perceived) scientific understanding. While the ratio of Cr(III) to Cr(VI) ions in a chromate conversion coating is perhaps quite important in achieving the desired protective properties, such a constraint for potential alternatives to chromate coating processes was not explicitly considered in the CBM. Rather it was intended to be achieved by controlling the pH of the coating bath. The relevance of the above constraints to the controlled experiment required subsequent validation by experiments and analysis of the data.

3.3 Model Validation

In order to validate the CBM effort, one had to first identify chemicals that can satisfy the variety of constraints imposed by the model. This identification required an examination of the specific characteristics of various chemicals, relative to specific substrate materials.

With regard to aluminum-based alloys, manganese-based chemicals appeared as potential alternatives to chromate-based solutions, based on the sizes of the Mn(III) and Mn(VI) ions versus those of Al(III), Cr(III), and Cr(VI) ions, and the electropositive nature of manganese (-1.05 V at 25 °C) relative to aluminum (-1.67 V at 25 °C) substrate. Mn(III) and Mn(VI) ions also offered the greatest promise in terms of availability, cost, and ease of handling.

Understandably, the success of any non-chromate conversion coating process that involved manganese ions in multiple valence states (e.g., III and VI) will depend largely on the effectiveness of their substitution, and achieving a desirable ratio of Mn(III) and Mn(VI) ions in the coating. One could expect that processing conditions that enhanced the thermodynamic and kinetic factors that allowed the substitution of Mn(III) and Mn(VI) ions into the gel should contribute to improving the corrosion resistance of the non-chromate conversion coating, while those processing conditions that limited the substitution of Mn(III) and Mn(VI) ions into the gel will contribute to the limited success or failure of the coating. The ratio of Mn(III) to Mn(VI) ions in the coating could also be a significant factor affecting the protective properties of the coating.

Based on the set of constraints proposed in the model, manganese-based chemicals were identified that (1) dissolved in acid to provide a clear solution with a pH ranging from about 2.0 to 5.0 and (2) reacted with the aluminum substrate to form a precipitate that is insoluble in near neutral solutions or showed decreasing solubility with increasing pH and also form waters of hydration. Table 8 shows a number of manganese-based chemicals that show solubility in acid (i.e., $\text{pH} < 7.0$), and the ability to add water of hydration, besides having limited solubility in water. Evidently, the coating bath must also contain reactants that will provide one of the chemicals listed in Table 8 as a reaction product.

The reactants could include chemical compounds with fluoride, perchlorate, nitrate, phosphate, or sulfate anions that would activate the substrate surface, a wetting agent, such as sodium alkyl aryl sulfonate, that would facilitate the formation of a uniform and continuous coating, and either a reducing or oxidizing agent to provide manganese ions in multiple valence states. Prior to reaction with aluminum, all of these chemicals must provide a clear solution, with a pH ranging from 2.0 to 5.0.

U.S. Patents 6,248,183 and 6,669,786 (Ref 7, 8) describe a non-chromate conversion coating process for aluminum alloys that uses a solution based on potassium manganate (K_2MnO_4). While this solution provided acceptable results, further refinements to both the coating bath and processing steps may produce non-chromate conversion coatings with exceptional performance.

Table 8 A select list of manganese-based chemical compounds

No.	Chemical name	Chemical formula	Solubility
1	Manganese acetate	Mn(OOCCH ₃) ₂ ·2H ₂ O	
2	Manganese orthophosphate	MnPO ₄ ·xH ₂ O	Slightly soluble in water
3	Manganous phosphate	Mn(PO ₄) ₂ ·7H ₂ O	Insoluble in water
4	Manganous phosphate	MnHPO ₄ ·3H ₂ O	Slightly soluble in water
5	Manganous pyrophosphate	MnP ₂ O ₇ ·3H ₂ O	Insoluble in water

The above case study shows that CBM approach is quite advantageous in identifying the desirable features of an alternative to the chromate conversion coating process, and appropriate chemical compounds that are more likely to provide effective alternatives to chromates and dichromates for producing non-chromate conversion coatings. This CBM effort identifies and recommends specific chemical compounds containing Mn(III) and Mn(VI) ions to replace Cr(III) and Cr(VI) ions, based on a variety of constraints that include ionic radii and coordination numbers comparable to those of Al(III), Cr(III) and Cr(VI) ions, the availability of the cation in multiple valence states, decreasing solubility of the reaction products with increasing pH and their ability to form water of hydration. Non-chromate conversion coating process for aluminum alloys that uses a bath containing potassium manganate validates the advantages offered by CBM.

In fact, the results of the CBM approach to conversion coating are also applicable in identifying appropriate chemicals suitable for paint chemistries. In a manner similar to Table 8, additional lists of selected chemicals could be generated based on the other cations (Ce, Ga, Mo, Sc, Se, Te, Ti, V, and W) listed in Table 7. The electronegativity of these elements relative to the substrate (Table 6) must first be established. If the element is electropositive with respect to the selected substrate, then a chemicals database can be used to identify chemical compounds based on these cations that exhibit solubility in an acid, reduced solubility with increasing pH (or insolubility in water), an ability to form waters of hydration and also provide cations in multiple valence states. After ascertaining those characteristics, a clear coating bath can be prepared which contains the appropriate reactants, activators, and wetting agents. Testing and evaluation could then follow.

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