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## Formed Metal Products and Methods of Making the Same

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## FORMED METAL PRODUCTS AND METHODS OF MAKING THE SAME

### FIELD

5 The present disclosure relates to the field of aluminum alloys and more specifically to methods of processing aluminum alloy products.

### BACKGROUND

10 Aluminum alloys with high strength are desirable for improved product performance in many applications, including automotive and other transportation applications (including, for example and without limitation, trucks, trailers, trains, aerospace, and marine applications), and electronics applications, among others. In some cases, such alloys should exhibit, among other properties, high formability (e.g., an ability to be formed into a desired shape). Additionally, aluminum alloys require lubricants to facilitate the forming process. Lubricants must be removed for downstream processing, for example, painting, but are difficult and costly to remove.

15

### SUMMARY

Described herein are methods of producing a formed metal product, including providing a metal blank; applying a formability film to at least a portion of the metal blank to provide at least a partially coated metal blank, wherein the formability film is water soluble and wherein the formability film is up to about 1000 microns thick; forming the at least partially coated metal blank to provide the formed metal product; and removing the formability film from the formed metal product. In some non-limiting examples, the metal blank can be an aluminum or aluminum alloy blank, a steel blank, a magnesium or magnesium alloy blank, a titanium or titanium alloy blank, a copper or copper alloy blank, any suitable metal or metal alloy blank, or any combination thereof.

20 In certain examples, the metal product comprises a 5xxx series aluminum alloy, a 6xxx series aluminum alloy, or a 7xxx series aluminum alloy.

25

In certain aspects, the formability film can be any suitable water soluble film (e.g., a water soluble natural polymer film, a water soluble synthetic polymer film, or a combination thereof). In certain examples, the formability film provides improved formability of at least a portion of the metal blank as compared to a metal blank devoid of a formability film (e.g., improved formability includes increasing elongation before fracture at least about 50 % (e.g., at least about 75 %, at least

30

about 100 %, at least about 110 %, or at least about 125 %) as compared to a metal blank devoid of a formability film). In some cases, applying the formability film can be performed by physical vapor deposition, chemical vapor deposition, solution deposition, or any combination thereof.

5 In some non-limiting examples, forming includes stamping, drawing, bending, extruding, curving, forging, stretching, recessing, die forming, indenting, shearing, or any combination thereof. Further, removing the formability film from the formed metal product comprises rinsing (e.g., rinsing with water), combusting, or a combination thereof. In some non-limiting examples, removing the formability film includes depositing a chemical additive such as an adhesion promoter, a corrosion inhibitor, a coupling agent, an antimicrobial agent, a welding primer, a riveting primer, or any combination thereof.

10 Also described herein is a metal product produced according to the methods described herein having a removable formability layer that can provide an increase in elongation before fracture of at least about 50 % (e.g., at least about 75 %, at least about 100 %, at least about 110 %, or at least about 125 %) as compared to a metal product devoid of a formability layer. In certain aspects, the removable formability layer is water soluble. In certain aspects, the method described herein further comprises pretreating the metal blank with a pretreatment before applying the formability film. The pretreating step comprises applying an adhesion promoter, a corrosion inhibitor, a coupling agent, an antimicrobial agent, a welding primer, a riveting primer, or any combination thereof. Thus, in some examples, removing the formability film from the formed metal product comprises exposing the pretreatment to a surrounding environment. Additionally, the formability layer can have a thickness of up to about 1000 microns.

15 In certain examples, the preprime described herein comprises a chemical additive that can be an adhesion promoter, a corrosion inhibitor, a coupling agent, an antimicrobial agent, a welding primer, a riveting primer, or any combination thereof. Thus, in certain aspects, the chemical additive can be an adhesion promoter and the metal product can have an improved bond durability when compared to metal products devoid of a preprime having an adhesion promoter (e.g., the metal product having improved bond durability survives a bond durability test through up to about 25 125 % more cycles when compared to metal products devoid of a preprime having an adhesion promoter). Additionally, in certain examples, the chemical additive can be a corrosion inhibitor, and the metal product can have improved corrosion resistance when compared to metal products devoid of a preprime having a corrosion inhibitor (e.g., the metal product having improved 30

corrosion resistance exhibits up to about a 125 % decrease in corrosion attack pit depth when compared to metal products devoid of a preprime having a corrosion inhibitor). In some cases, the preprime can be a hybrid organic-inorganic preprime or a heat-resistant hybrid organic-inorganic preprime. In some non-limiting examples, the metal product has a reduced coefficient of friction, wherein the reduced coefficient of friction comprises a stable coefficient of friction less than 0.15.

In some non-limiting examples, the metal product is an automotive structural part, an aerospace structural part, a transportation structural part, an automotive body part, an aerospace skin panel, a transportation body part, an architectural part, an aesthetic part, or an electronics device housing. In certain examples, the metal product comprises a 5xxx series aluminum alloy, a 6xxx series aluminum alloy, or a 7xxx series aluminum alloy.

Also described herein is a method of producing a formed metal product, comprising: providing a metal blank; applying a preprime to at least a portion of the metal blank to provide at least a partially coated metal blank, wherein the preprime is a polyurethane-polyamide network polymer, and wherein the preprime is up to about 1000 microns thick; and forming the coated metal blank to provide a formed metal product. In some cases, the metal blank comprises an aluminum or aluminum alloy blank, a steel blank, a magnesium or magnesium alloy blank, a titanium or titanium alloy blank, a copper or copper alloy blank, any suitable metal or metal alloy blank, or any combination thereof. In certain examples, the metal product comprises a 5xxx series aluminum alloy, a 6xxx series aluminum alloy, or a 7xxx series aluminum alloy. In certain aspects, the preprime provides an improved formability of at least a portion of the metal blank as compared to a metal blank devoid of a preprime. In some non-limiting examples, the improved formability comprises increasing elongation before fracture by at least about 50 % (e.g., at least about 75 %, at least about 100 %, at least about 110 %, or at least about 125 %) as compared to a metal blank devoid of a formability film. In some cases, the preprime can be applied by physical vapor deposition, chemical vapor deposition, solution deposition, or any combination thereof. Additionally, forming the metal blank comprises stamping, drawing, bending, extruding, curving, forging, stretching, recessing, die forming, indenting, shearing, or any combination thereof.

Other objects and advantages will be apparent from the following detailed description of non-limiting examples and figures.

## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic of a network polymer according to methods described herein.

Figure 2 is a digital image showing the formability of aluminum alloys subjected to a cupping test according to methods described herein.

5 Figure 3 is a graph showing the coefficient of friction of coatings described herein.

Figure 4 is a digital image showing the formability of aluminum alloys subjected to a cupping test according to methods described herein.

Figure 5 is a graph showing the results of a cupping test according to methods described herein.

10 Figure 6 is a digital image showing the formability of aluminum alloys subjected to a cupping test according to methods described herein.

Figure 7 is a graph showing the results of a cupping test according to methods described herein.

Figure 8 is a graph showing the coefficient of friction of coatings described herein.

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## DETAILED DESCRIPTION

Described herein are methods of producing a formed metal product, including providing a metal blank, applying a water soluble formability film to the at least a portion of the metal blank to provide an at least partially coated metal blank, forming the coated metal blank to provide the formed metal product, and removing the formability film from the formed metal product, for  
20 example, an aluminum alloy product. In some non-limiting examples, the water soluble formability film is a water soluble polymer film up to about 1000 microns ( $\mu\text{m}$ ) thick. In certain aspects, applying a formability film to a metal blank as described herein significantly increases the formability of the metal blank. In some cases, the formability (described in terms of elongation  
25 before fracture) of the metal blank can be increased by at least 50 %, and in some examples at least 125 % where the formability film is applied to the metal blank. Accordingly, the formability film can be selectively applied to desired portions of the metal blank, providing areas of higher formability than uncoated portions.

A removable formability film, as described herein, can improve the formability of an  
30 aluminum alloy and replace lubricants that are necessary for the forming process. The formability can be improved such that the elongation before fracture of the metal is increased by at least 50 %.

Additionally, applying a formability film to the metal can act as a lubricant for certain forming processes, including stamping, curving, die forming, indenting, and the like. Further, employing a water soluble formability film eliminates lubricant removal for downstream processing.

Also described herein are methods of producing a formed metal product, including providing a metal blank, applying a preprime network polymer to at least a portion of the metal blank to provide an at least partially preprime-coated metal blank, and forming the at least partially preprime-coated metal blank to provide the formed metal product, for example, an aluminum alloy product. In some non-limiting examples, the preprime is up to about 1000 microns ( $\mu\text{m}$ ) thick. A preprime, as described herein, can improve the formability of an aluminum alloy and replace lubricants that are necessary for the forming process. Similar to the formability film described above, the formability can be improved such that the elongation before fracture of the metal is increased by at least 50 %, and in some examples at least about 125 %. Additionally, applying a preprime to the metal can act as a lubricant for certain forming processes, including stamping, curving, die forming, indenting, and the like. Further, employing a preprime eliminates lubricant removal for downstream processing. In certain aspects, the preprime can include chemical additives that provide additional surface treatment properties. The methods of processing the aluminum alloy products described herein provide a more efficient method for producing aluminum alloy products, as required by end users (e.g., original equipment manufacturers (OEMs)).

20

### *Preparing and Processing Methods*

Described herein are methods of producing a formed metal product. In some examples, the formed metal product is aluminum, an aluminum alloy, magnesium, a magnesium-based material, titanium, a titanium-based material, copper, a copper-based material, steel, a steel-based material, bronze, a bronze-based material, brass, a brass-based material, a composite, a sheet used in composites, or any other suitable metal or combination of materials. The product may include monolithic materials, as well as non-monolithic materials such as roll-bonded materials, clad materials, composite materials (such as, but not limited to, carbon fiber-containing materials), or various other materials. In some examples, the metal product is a metal coil, a metal strip, a metal plate, a metal sheet, a metal billet, a metal ingot, or the like. In some cases, the systems and methods described herein can be used with a non-metal product.

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In some non-limiting examples, the formed metal product includes an aluminum alloy. The aluminum alloy can include a 1xxx series aluminum alloy, a 2xxx series aluminum alloy, a 3xxx series aluminum alloy, a 4xxx series aluminum alloy, a 5xxx series aluminum alloy, a 6xxx series aluminum alloy, a 7xxx series aluminum alloy, or an 8xxx series aluminum alloy.

5           Optionally, the aluminum alloy as described herein can be a 1xxx series aluminum alloy according to one of the following aluminum alloy designations: AA1100, AA1100A, AA1200, AA1200A, AA1300, AA1110, AA1120, AA1230, AA1230A, AA1235, AA1435, AA1145, AA1345, AA1445, AA1150, AA1350, AA1350A, AA1450, AA1370, AA1275, AA1185, AA1285, AA1385, AA1188, AA1190, AA1290, AA1193, AA1198, or AA1199.

10           Optionally, the aluminum alloy as described herein can be a 2xxx series aluminum alloy according to one of the following aluminum alloy designations: AA2001, A2002, AA2004, AA2005, AA2006, AA2007, AA2007A, AA2007B, AA2008, AA2009, AA2010, AA2011, AA2011A, AA2111, AA2111A, AA2111B, AA2012, AA2013, AA2014, AA2014A, AA2214, AA2015, AA2016, AA2017, AA2017A, AA2117, AA2018, AA2218, AA2618, AA2618A,  
15 AA2219, AA2319, AA2419, AA2519, AA2021, AA2022, AA2023, AA2024, AA2024A, AA2124, AA2224, AA2224A, AA2324, AA2424, AA2524, AA2624, AA2724, AA2824, AA2025, AA2026, AA2027, AA2028, AA2028A, AA2028B, AA2028C, AA2029, AA2030, AA2031, AA2032, AA2034, AA2036, AA2037, AA2038, AA2039, AA2139, AA2040, AA2041, AA2044, AA2045, AA2050, AA2055, AA2056, AA2060, AA2065, AA2070, AA2076, AA2090,  
20 AA2091, AA2094, AA2095, AA2195, AA2295, AA2196, AA2296, AA2097, AA2197, AA2297, AA2397, AA2098, AA2198, AA2099, or AA2199.

          Optionally, the aluminum alloy as described herein can be a 3xxx series aluminum alloy according to one of the following aluminum alloy designations: AA3002, AA3102, AA3003, AA3103, AA3103A, AA3103B, AA3203, AA3403, AA3004, AA3004A, AA3104, AA3204,  
25 AA3304, AA3005, AA3005A, AA3105, AA3105A, AA3105B, AA3007, AA3107, AA3207, AA3207A, AA3307, AA3009, AA3010, AA3110, AA3011, AA3012, AA3012A, AA3013, AA3014, AA3015, AA3016, AA3017, AA3019, AA3020, AA3021, AA3025, AA3026, AA3030, AA3130, or AA3065.

          Optionally, the aluminum alloy as described herein can be a 4xxx series aluminum alloy  
30 according to one of the following aluminum alloy designations: AA4004, AA4104, AA4006, AA4007, AA4008, AA4009, AA4010, AA4013, AA4014, AA4015, AA4015A, AA4115,



AA4016, AA4017, AA4018, AA4019, AA4020, AA4021, AA4026, AA4032, AA4043, AA4043A, AA4143, AA4343, AA4643, AA4943, AA4044, AA4045, AA4145, AA4145A, AA4046, AA4047, AA4047A, or AA4147.

Optionally, the aluminum alloy as described herein can be a 5xxx series aluminum alloy according to one of the following aluminum alloy designations: AA5005, AA5005A, AA5205, AA5305, AA5505, AA5605, AA5006, AA5106, AA5010, AA5110, AA5110A, AA5210, AA5310, AA5016, AA5017, AA5018, AA5018A, AA5019, AA5019A, AA5119, AA5119A, AA5021, AA5022, AA5023, AA5024, AA5026, AA5027, AA5028, AA5040, AA5140, AA5041, AA5042, AA5043, AA5049, AA5149, AA5249, AA5349, AA5449, AA5449A, AA5050, AA5050A, AA5050C, AA5150, AA5051, AA5051A, AA5151, AA5251, AA5251A, AA5351, AA5451, AA5052, AA5252, AA5352, AA5154, AA5154A, AA5154B, AA5154C, AA5254, AA5354, AA5454, AA5554, AA5654, AA5654A, AA5754, AA5854, AA5954, AA5056, AA5356, AA5356A, AA5456, AA5456A, AA5456B, AA5556, AA5556A, AA5556B, AA5556C, AA5257, AA5457, AA5557, AA5657, AA5058, AA5059, AA5070, AA5180, AA5180A, AA5082, AA5182, AA5083, AA5183, AA5183A, AA5283, AA5283A, AA5283B, AA5383, AA5483, AA5086, AA5186, AA5087, AA5187, or AA5088.

Optionally, the aluminum alloy as described herein can be a 6xxx series aluminum alloy according to one of the following aluminum alloy designations: AA6101, AA6101A, AA6101B, AA6201, AA6201A, AA6401, AA6501, AA6002, AA6003, AA6103, AA6005, AA6005A, AA6005B, AA6005C, AA6105, AA6205, AA6305, AA6006, AA6106, AA6206, AA6306, AA6008, AA6009, AA6010, AA6110, AA6110A, AA6011, AA6111, AA6012, AA6012A, AA6013, AA6113, AA6014, AA6015, AA6016, AA6016A, AA6116, AA6018, AA6019, AA6020, AA6021, AA6022, AA6023, AA6024, AA6025, AA6026, AA6027, AA6028, AA6031, AA6032, AA6033, AA6040, AA6041, AA6042, AA6043, AA6151, AA6351, AA6351A, AA6451, AA6951, AA6053, AA6055, AA6056, AA6156, AA6060, AA6160, AA6260, AA6360, AA6460, AA6460B, AA6560, AA6660, AA6061, AA6061A, AA6261, AA6361, AA6162, AA6262, AA6262A, AA6063, AA6063A, AA6463, AA6463A, AA6763, AA6963, AA6064, AA6064A, AA6065, AA6066, AA6068, AA6069, AA6070, AA6081, AA6181, AA6181A, AA6082, AA6082A, AA6182, AA6091, or AA6092.

Optionally, the aluminum alloy as described herein can be a 7xxx series aluminum alloy according to one of the following aluminum alloy designations: AA7011, AA7019, AA7020,

AA7021, AA7039, AA7072, AA7075, AA7085, AA7108, AA7108A, AA7015, AA7017, AA7018, AA7019A, AA7024, AA7025, AA7028, AA7030, AA7031, AA7033, AA7035, AA7035A, AA7046, AA7046A, AA7003, AA7004, AA7005, AA7009, AA7010, AA7011, AA7012, AA7014, AA7016, AA7116, AA7122, AA7023, AA7026, AA7029, AA7129, AA7229, 5 AA7032, AA7033, AA7034, AA7036, AA7136, AA7037, AA7040, AA7140, AA7041, AA7049, AA7049A, AA7149, AA7249, AA7349, AA7449, AA7050, AA7050A, AA7150, AA7250, AA7055, AA7155, AA7255, AA7056, AA7060, AA7064, AA7065, AA7068, AA7168, AA7175, AA7475, AA7076, AA7178, AA7278, AA7278A, AA7081, AA7181, AA7185, AA7090, AA7093, AA7095, or AA7099.

10           Optionally, the aluminum alloy as described herein can be an 8xxx series aluminum alloy according to one of the following aluminum alloy designations: AA8005, AA8006, AA8007, AA8008, AA8010, AA8011, AA8011A, AA8111, AA8211, AA8112, AA8014, AA8015, AA8016, AA8017, AA8018, AA8019, AA8021, AA8021A, AA8021B, AA8022, AA8023, AA8024, AA8025, AA8026, AA8030, AA8130, AA8040, AA8050, AA8150, AA8076, 15 AA8076A, AA8176, AA8077, AA8177, AA8079, AA8090, AA8091, or AA8093.

In some examples, the aluminum alloy is a monolithic alloy. In some examples, the aluminum alloy is a clad aluminum alloy, having a core layer and one or two cladding layers. In some cases, the core layer may be different from one or both of the cladding layers. As described herein, the metal product (e.g., a metal blank) is a 5xxx series aluminum alloy, a 6xxx series 20 aluminum alloy, or a 7xxx series aluminum alloy.

In some non-limiting examples, providing a metal blank can include providing a metal plate, a metal shate, a metal sheet, a metal foil, any suitable metal blank, or any combination thereof. For example, a metal plate blank can have a gauge (i.e., a thickness) of from greater than about 15 millimeters (mm) to about 200 mm. For example, a metal plate blank can have a thickness 25 of greater than about 15 mm, 16 mm, 17 mm, 18 mm, 19 mm, 20 mm, 21 mm, 22 mm, 23 mm, 24 mm, 25 mm, 26 mm, 27 mm, 28 mm, 29 mm, 30 mm, 31 mm, 32 mm, 33 mm, 34 mm, 35 mm, 36 mm, 37 mm, 38 mm, 39 mm, 40 mm, 41 mm, 42 mm, 43 mm, 44 mm, 45 mm, 46 mm, 47 mm, 48 mm, 49 mm, 50 mm, 51 mm, 52 mm, 53 mm, 54 mm, 55 mm, 56 mm, 57 mm, 58 mm, 59 mm, 60 mm, 61 mm, 62 mm, 63 mm, 64 mm, 65 mm, 66 mm, 67 mm, 68 mm, 69 mm, 70 mm, 71 mm, 72 30 mm, 73 mm, 74 mm, 75 mm, 76 mm, 77 mm, 78 mm, 79 mm, 80 mm, 81 mm, 82 mm, 83 mm, 84 mm, 85 mm, 86 mm, 87 mm, 88 mm, 89 mm, 90 mm, 91 mm, 92 mm, 93 mm, 94 mm, 95 mm, 96

mm, 97 mm, 98 mm, 99 mm, 100 mm, 101 mm, 102 mm, 103 mm, 104 mm, 105 mm, 106 mm, 107 mm, 108 mm, 109 mm, 110 mm, 111 mm, 112 mm, 113 mm, 114 mm, 115 mm, 116 mm, 117 mm, 118 mm, 119 mm, 120 mm, 121 mm, 122 mm, 123 mm, 124 mm, 125 mm, 126 mm, 127 mm, 128 mm, 129 mm, 130 mm, 131 mm, 132 mm, 133 mm, 134 mm, 135 mm, 136 mm, 137 mm, 138 mm, 139 mm, 140 mm, 141 mm, 142 mm, 143 mm, 144 mm, 145 mm, 146 mm, 147 mm, 148 mm, 149 mm, 150 mm, 151 mm, 152 mm, 153 mm, 154 mm, 155 mm, 156 mm, 157 mm, 158 mm, 159 mm, 160 mm, 161 mm, 162 mm, 163 mm, 164 mm, 165 mm, 166 mm, 167 mm, 168 mm, 169 mm, 170 mm, 171 mm, 172 mm, 173 mm, 174 mm, 175 mm, 176 mm, 177 mm, 178 mm, 179 mm, 180 mm, 181 mm, 182 mm, 183 mm, 184 mm, 185 mm, 186 mm, 187 mm, 188 mm, 189 mm, 190 mm, 191 mm, 192 mm, 193 mm, 194 mm, 195 mm, 196 mm, 197 mm, 198 mm, 199 mm, or 200 mm.

In some cases, the metal blank is a metal shate blank. The metal shate blank can have a thickness of from about 4 mm to about 15 mm. For example, the metal shate blank can have a thickness of about 4 mm, 5 mm, 6 mm, 7 mm, 8 mm, 9 mm, 10 mm, 11 mm, 12 mm, 13 mm, 14 mm, or 15 mm.

In some cases, the metal blank is a metal sheet blank. The metal sheet blank can have a thickness of from about 0.2 mm to less than about 4 mm. For example, the metal sheet blank can have a thickness of about 0.2 mm, 0.3 mm, 0.4 mm, 0.5 mm, 0.6 mm, 0.7 mm, 0.8 mm, 0.9 mm, 1 mm, 1.1 mm, 1.2 mm, 1.3 mm, 1.4 mm, 1.5 mm, 1.6 mm, 1.7 mm, 1.8 mm, 1.9 mm, 2 mm, 2.1 mm, 2.2 mm, 2.3 mm, 2.4 mm, 2.5 mm, 2.6 mm, 2.7 mm, 2.8 mm, 2.9 mm, 3 mm, 3.1 mm, 3.2 mm, 3.3 mm, 3.4 mm, 3.5 mm, 3.6 mm, 3.7 mm, 3.8 mm, 3.9 mm, or less than 4 mm.

In certain aspects, the metal blank can be a metal foil blank. The metal foil blank can have a thickness of from about 0.05 mm to less than about 0.2 mm. For example, the metal foil blank can have a thickness of about 0.05 mm, 0.06 mm, 0.07 mm, 0.08 mm, 0.09 mm, 0.1 mm, 0.11 mm, 0.12 mm, 0.13 mm, 0.14 mm, 0.15 mm, 0.16 mm, 0.17 mm, 0.18 mm, 0.19 mm, or less than 0.2 mm.

In certain examples, a process for coating a metal blank with a formability film and/or a preprime can include cleaning the metal blank, rinsing the metal blank after cleaning, coating the metal blank with the formability film and/or preprime, optionally rinsing the metal blank after coating, curing the formability film and/or preprime, and storing the metal blank (e.g., stacking

metal blanks or rolling the metal blank into a coil). In some cases, the metal blank can be artificially aged before coating (e.g., the metal blank can be artificially aged to a T6 temper, a T7 temper, a T8x temper, or any desired temper). For example, a process for coating an aged metal blank can include solution heat treating the metal blank and/or artificially aging the metal blank before  
 5 cleaning the metal blank, rinsing the metal blank after cleaning, coating the metal blank with the formability film and/or preprime, optionally rinsing the metal blank after coating, curing the formability film and/or preprime, and storing the metal blank.

#### A. Forming with a Removable Formability Film

10 As described herein, the methods include applying a formability film to the metal blank to provide a coated metal blank. In certain examples, the methods include applying the formability film to at least a portion of the metal blank to provide a partially coated metal blank. As used herein, “at least a portion” of the metal blank refers to at least 1 % of a surface area of the metal blank. For example, at least a portion of the metal blank can include about 1 %, about 2 %, about  
 15 3 %, about 4 %, about 5 %, about 6 %, about 7 %, about 8 %, about 9 %, about 10 %, about 11 %, about 12 %, about 13 %, about 14 %, about 15 %, about 16 %, about 17 %, about 18 %, about 19 %, about 20 %, about 21 %, about 22 %, about 23 %, about 24 %, about 25 %, about 26 %, about 27 %, about 28 %, about 29 %, about 30 %, about 31 %, about 32 %, about 33 %, about 34 %, about 35 %, about 36 %, about 37 %, about 38 %, about 39 %, about 40 %, about 41 %, about 42  
 20 %, about 43 %, about 44 %, about 45 %, about 46 %, about 47 %, about 48 %, about 49 %, about 50 %, about 51 %, about 52 %, about 53 %, about 54 %, about 55 %, about 56 %, about 57 %, about 58 %, about 59 %, about 60 %, about 61 %, about 62 %, about 63 %, about 64 %, about 65 %, about 66 %, about 67 %, about 68 %, about 69 %, about 70 %, about 71 %, about 72 %, about 73 %, about 74 %, about 75 %, about 76 %, about 77 %, about 78 %, about 79 %, about 80 %, about 81 %, about 82 %, about 83 %, about 84 %, about 85 %, about 86 %, about 87 %, about 88  
 25 %, about 89 %, about 90 %, about 91 %, about 92 %, about 93 %, about 94 %, about 95 %, about 96 %, about 97 %, about 98 %, or about 99 % of the surface area of the metal blank. In some aspects, the portion includes 100 % of the surface area of the metal blank. Further, the surface area of the metal blank can include a surface area of at least a first side of the metal blank, a surface area of at least a second side of the metal blank that is opposite the first side of the metal blank, a  
 30 surface area of at least a third side of the metal blank that is disposed between the first side and the

second side and spanning a thickness of the metal blank, and/or a surface area of at least a fourth side of the metal blank that is opposite the third side, also spanning the thickness of the metal blank.

5 Applying the formability film can be performed by any one of physical vapor deposition (PVD) (e.g., a liquid polymer is evaporated or a solid polymer is sublimed), chemical vapor deposition (CVD) (e.g., a solid film is deposited on the metal blank through a chemical reaction of a gas mixture), or solution deposition (e.g., roll coating, spray coating, immersion coating, drop coating, enrobing, squeegee coating, or any combination thereof). In the example of PVD, a suitable polymer solid can be heated to a sublimation point and the vaporized polymer molecules  
10 can travel to the metal blank and adhere to the metal blank. Likewise, a liquid polymer solution can be heated to an evaporation point and the vaporized polymer molecules can travel to the metal blank and adhere to the metal blank. The vaporized polymer molecules adhering to the metal blank can nucleate with other vaporized polymer molecules. Nucleated polymer molecules can coalesce and form a continuous film.

15 In the example of CVD, the formability film can be deposited by a chemical reaction including pyrolysis, photolysis, reduction, oxidation, or a reduction-oxidation (redox) reaction. In certain aspects, vaporized monomeric reactant molecules can travel to the metal blank and adhere to the metal blank. The monomeric reactant molecules can be reacted with each other, or optionally with other reactant molecules, to polymerize. Polymerizing the monomeric reactant molecules can  
20 provide the formability film on the metal blank.

In the example of solution deposition, the formability film can be deposited from a liquid polymer solution. For example, the formability film can be deposited by coating a liquid polymer solution onto the metal blank and curing the applied polymer solution to provide the formability film (e.g., by air drying or by heating). In certain aspects, any suitable solution coating process can  
25 be used.

In the example of applying the formability film to at least a portion of the metal blank, the partially coated metal blank is a metal blank having at least one portion exhibiting a higher formability than the remainder of the metal blank. For example, the partially coated metal blank can have a first portion that is coated with the formability film and a second portion that is not  
30 coated. Thus, when subjected to forming, the first portion can exhibit a higher formability than the second portion. Accordingly, the formability of the metal blank can be locally tuned. Locally

tuning the formability of the metal blank can provide variably formed and complex metal products as desired.

In some non-limiting examples, the formability film can be laminated onto the metal blank. Any suitable polymer film, such as those described below, can be brought into contact with the metal blank. For example, the polymer film can be coupled to the metal blank using mechanical bonding, dipolar interactions, or any suitable mechanism initiated by intimate contact between the metal blank and the polymer film. Laminating the polymer film onto the metal blank can provide the formability film.

As described above, the formability film is water soluble. As described herein, a water soluble film is a film that is removed from a surface by applying water to the film and/or surface. As described herein, a film that is removed from a surface encompasses at most 20 % of the formability film remaining on the surface of the metal blank and/or the formed metal product (e.g., from about 1 % to about 19 %, from about 2 % to about 18 %, from about 3 % to about 17 %, from about 4 % to about 16 %, from about 5 % to about 15 %, from about 6 % to about 14 %, from about 7 % to about 13 %, from about 8 % to about 12 %, or from about 9 % to about 11 %). For example, after a removing step (e.g., rinsing), up to about 20 % of the formability film remains on the surface, up to about 19 % of the formability film remains on the surface, up to about 18 % of the formability film remains on the surface, up to about 17 % of the formability film remains on the surface, up to about 16 % of the formability film remains on the surface, up to about 15 % of the formability film remains on the surface, up to about 14 % of the formability film remains on the surface, up to about 13 % of the formability film remains on the surface, up to about 12 % of the formability film remains on the surface, up to about 11 % of the formability film remains on the surface, up to about 10 % of the formability film remains on the surface, up to about 9 % of the formability film remains on the surface, up to about 8 % of the formability film remains on the surface, up to about 7 % of the formability film remains on the surface, up to about 6 % of the formability film remains on the surface, up to about 5 % of the formability film remains on the surface, up to about 4 % of the formability film remains on the surface, up to about 3 % of the formability film remains on the surface, up to about 2 % of the formability film remains on the surface, or up to about 1 % of the formability film remains on the surface. In certain aspects, for example, rinsing under ultrasonic agitation, employing an acid etch step, an anodizing step, a polishing step, an ablation step, or any combination thereof, the formability film is completely

removed from the surface (e.g., 0 % of the formability film remains on the surface). In certain aspects, the formability film can be a water soluble natural polymer film, a water soluble synthetic polymer film, any other suitable water soluble film, or any combination thereof. In certain aspects the formability film can include acrylics, polyesters, fluoropolymers, polyurethane, or a mixture thereof. For example, the formability film can be a polyethylene glycol (PEG) film, a hydroxypropyl cellulose film, a polyacrylic acid (PAA) film, a poly(methacrylic acid) film, a polyvinyl alcohol (PVA) film, a poly(styrenesulfonic acid) film, a carboxymethyl cellulose film, a polyanionic cellulose film, a hydroxypropyl methylcellulose film, a polyethylene oxide (PEO) film, a dextran film, a pullulan film, a polyvinylfluoride film, a polyvinylidene fluoride film, a polytetrafluoroethylene film, a polychlorotrifluoroethylene film, a polyethylenetetrafluoroethylene film, a polyethylenechlorotrifluoroethylene film, a perfluorinated elastomer film, a perfluoropolyether film, a perfluorosulfonic acid film, any suitable low coefficient of friction film, any suitable water soluble polymer film, or any combination thereof.

In some cases, the formability film is from about 10 nm (0.01  $\mu\text{m}$ ) thick up to about 500  $\mu\text{m}$  thick (e.g., from about 1  $\mu\text{m}$  to about 490  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 480  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 470  $\mu\text{m}$ , from about 15  $\mu\text{m}$  to about 460  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 450  $\mu\text{m}$ , from about 25  $\mu\text{m}$  to about 440  $\mu\text{m}$ , from about 30  $\mu\text{m}$  to about 435  $\mu\text{m}$ , from about 35  $\mu\text{m}$  to about 430  $\mu\text{m}$ , from about 40  $\mu\text{m}$  to about 425  $\mu\text{m}$ , from about 45  $\mu\text{m}$  to about 420  $\mu\text{m}$ , from about 50  $\mu\text{m}$  to about 415  $\mu\text{m}$ , from about 55  $\mu\text{m}$  to about 410  $\mu\text{m}$ , from about 60  $\mu\text{m}$  to about 405  $\mu\text{m}$ , from about 65  $\mu\text{m}$  to about 400  $\mu\text{m}$ , from about 75  $\mu\text{m}$  to about 375  $\mu\text{m}$ , from about 100  $\mu\text{m}$  to about 350  $\mu\text{m}$ , from about 125  $\mu\text{m}$  to about 300  $\mu\text{m}$ , from about 150  $\mu\text{m}$  to about 250  $\mu\text{m}$ , or from about 175  $\mu\text{m}$  to about 225  $\mu\text{m}$ ). For example, the formability film can be up to about 0.01  $\mu\text{m}$ , 0.05  $\mu\text{m}$ , 0.1  $\mu\text{m}$ , 0.2  $\mu\text{m}$ , 0.3  $\mu\text{m}$ , 0.4  $\mu\text{m}$ , 0.5  $\mu\text{m}$ , 0.6  $\mu\text{m}$ , 0.7  $\mu\text{m}$ , 0.8  $\mu\text{m}$ , 0.9  $\mu\text{m}$ , 1  $\mu\text{m}$ , 2  $\mu\text{m}$ , 3  $\mu\text{m}$ , 4  $\mu\text{m}$ , 5  $\mu\text{m}$ , 6  $\mu\text{m}$ , 7  $\mu\text{m}$ , 8  $\mu\text{m}$ , 9  $\mu\text{m}$ , 10  $\mu\text{m}$ , 11  $\mu\text{m}$ , 12  $\mu\text{m}$ , 13  $\mu\text{m}$ , 14  $\mu\text{m}$ , 15  $\mu\text{m}$ , 16  $\mu\text{m}$ , 17  $\mu\text{m}$ , 18  $\mu\text{m}$ , 19  $\mu\text{m}$ , 20  $\mu\text{m}$ , 21  $\mu\text{m}$ , 22  $\mu\text{m}$ , 23  $\mu\text{m}$ , 24  $\mu\text{m}$ , 25  $\mu\text{m}$ , 26  $\mu\text{m}$ , 27  $\mu\text{m}$ , 28  $\mu\text{m}$ , 29  $\mu\text{m}$ , 30  $\mu\text{m}$ , 31  $\mu\text{m}$ , 32  $\mu\text{m}$ , 33  $\mu\text{m}$ , 34  $\mu\text{m}$ , 35  $\mu\text{m}$ , 36  $\mu\text{m}$ , 37  $\mu\text{m}$ , 38  $\mu\text{m}$ , 39  $\mu\text{m}$ , 40  $\mu\text{m}$ , 41  $\mu\text{m}$ , 42  $\mu\text{m}$ , 43  $\mu\text{m}$ , 44  $\mu\text{m}$ , 45  $\mu\text{m}$ , 46  $\mu\text{m}$ , 47  $\mu\text{m}$ , 48  $\mu\text{m}$ , 49  $\mu\text{m}$ , 50  $\mu\text{m}$ , 51  $\mu\text{m}$ , 52  $\mu\text{m}$ , 53  $\mu\text{m}$ , 54  $\mu\text{m}$ , 55  $\mu\text{m}$ , 56  $\mu\text{m}$ , 57  $\mu\text{m}$ , 58  $\mu\text{m}$ , 59  $\mu\text{m}$ , 60  $\mu\text{m}$ , 61  $\mu\text{m}$ , 62  $\mu\text{m}$ , 63  $\mu\text{m}$ , 64  $\mu\text{m}$ , 65  $\mu\text{m}$ , 66  $\mu\text{m}$ , 67  $\mu\text{m}$ , 68  $\mu\text{m}$ , 69  $\mu\text{m}$ , 70  $\mu\text{m}$ , 71  $\mu\text{m}$ , 72  $\mu\text{m}$ , 73  $\mu\text{m}$ , 74  $\mu\text{m}$ , 75  $\mu\text{m}$ , 76  $\mu\text{m}$ , 77  $\mu\text{m}$ , 78  $\mu\text{m}$ , 79  $\mu\text{m}$ , 80  $\mu\text{m}$ , 81  $\mu\text{m}$ , 82  $\mu\text{m}$ , 83  $\mu\text{m}$ , 84  $\mu\text{m}$ , 85  $\mu\text{m}$ , 86  $\mu\text{m}$ , 87  $\mu\text{m}$ , 88  $\mu\text{m}$ , 89  $\mu\text{m}$ , 90  $\mu\text{m}$ , 91  $\mu\text{m}$ , 92  $\mu\text{m}$ , 93  $\mu\text{m}$ , 94  $\mu\text{m}$ , 95  $\mu\text{m}$ , 96  $\mu\text{m}$ , 97  $\mu\text{m}$ , 98  $\mu\text{m}$ , 99  $\mu\text{m}$ , 100  $\mu\text{m}$ , 110  $\mu\text{m}$ , 120  $\mu\text{m}$ , 130

5  $\mu\text{m}$ , 140  $\mu\text{m}$ , 150  $\mu\text{m}$ , 160  $\mu\text{m}$ , 170  $\mu\text{m}$ , 180  $\mu\text{m}$ , 190  $\mu\text{m}$ , 200  $\mu\text{m}$ , 210  $\mu\text{m}$ , 220  $\mu\text{m}$ , 230  $\mu\text{m}$ , 240  $\mu\text{m}$ , 250  $\mu\text{m}$ , 260  $\mu\text{m}$ , 270  $\mu\text{m}$ , 280  $\mu\text{m}$ , 290  $\mu\text{m}$ , 300  $\mu\text{m}$ , 310  $\mu\text{m}$ , 320  $\mu\text{m}$ , 330  $\mu\text{m}$ , 340  $\mu\text{m}$ , 350  $\mu\text{m}$ , 360  $\mu\text{m}$ , 370  $\mu\text{m}$ , 380  $\mu\text{m}$ , 390  $\mu\text{m}$ , 400  $\mu\text{m}$ , 410  $\mu\text{m}$ , 420  $\mu\text{m}$ , 430  $\mu\text{m}$ , 440  $\mu\text{m}$ , 450  $\mu\text{m}$ , 460  $\mu\text{m}$ , 470  $\mu\text{m}$ , 480  $\mu\text{m}$ , 490  $\mu\text{m}$ , 500  $\mu\text{m}$ , 510  $\mu\text{m}$ , 520  $\mu\text{m}$ , 530  $\mu\text{m}$ , 540  $\mu\text{m}$ , 550  $\mu\text{m}$ , 560  $\mu\text{m}$ , 570  $\mu\text{m}$ , 580  $\mu\text{m}$ , 590  $\mu\text{m}$ , 600  $\mu\text{m}$ , 610  $\mu\text{m}$ , 620  $\mu\text{m}$ , 630  $\mu\text{m}$ , 640  $\mu\text{m}$ , 650  $\mu\text{m}$ , 660  $\mu\text{m}$ , 670  $\mu\text{m}$ , 680  $\mu\text{m}$ , 690  $\mu\text{m}$ , 700  $\mu\text{m}$ , 710  $\mu\text{m}$ , 720  $\mu\text{m}$ , 730  $\mu\text{m}$ , 740  $\mu\text{m}$ , 750  $\mu\text{m}$ , 760  $\mu\text{m}$ , 770  $\mu\text{m}$ , 780  $\mu\text{m}$ , 790  $\mu\text{m}$ , 800  $\mu\text{m}$ , 810  $\mu\text{m}$ , 820  $\mu\text{m}$ , 830  $\mu\text{m}$ , 840  $\mu\text{m}$ , 850  $\mu\text{m}$ , 860  $\mu\text{m}$ , 870  $\mu\text{m}$ , 880  $\mu\text{m}$ , 890  $\mu\text{m}$ , 900  $\mu\text{m}$ , 910  $\mu\text{m}$ , 920  $\mu\text{m}$ , 930  $\mu\text{m}$ , 940  $\mu\text{m}$ , 950  $\mu\text{m}$ , 960  $\mu\text{m}$ , 970  $\mu\text{m}$ , 980  $\mu\text{m}$ , 990  $\mu\text{m}$ , or 1000  $\mu\text{m}$ .

10 In some aspects, the formability film described herein improves a formability of the metal blank to provide a formed metal product. Forming the coated metal blank to provide a formed metal product can include stamping, drawing, bending, extruding, curving, forging, stretching, recessing, die forming, indenting, shearing, or any combination thereof. In some examples, forming can be performed at room temperature. In some cases, forming can be performed at an elevated temperature (e.g., warm forming and/or hot forming). Elevated temperature forming
 15 depends on the material characteristics of the formability film. For example, warm forming can be performed at temperatures less than a melting temperature ( $T_m$ ) of the formability film to preserve the formability film for downstream processing (e.g., when the formability film can be a lubricant). For example, warm forming can be performed up to about 75 % of the  $T_m$ . For example, warm forming can be performed at a temperature of about 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 7 %, 8 %, 9
 20 %, 10 %, 11 %, 12 %, 13 %, 14 %, 15 %, 16 %, 17 %, 18 %, 19 %, 20 %, 21 %, 22 %, 23 %, 24 %, 25 %, 26 %, 27 %, 28 %, 29 %, 30 %, 31 %, 32 %, 33 %, 34 %, 35 %, 36 %, 37 %, 38 %, 39 %, 40 %, 41 %, 42 %, 43 %, 44 %, 45 %, 46 %, 47 %, 48 %, 49 %, 50 %, 51 %, 52 %, 53 %, 54 %, 55 %, 56 %, 57 %, 58 %, 59 %, 60 %, 61 %, 62 %, 63 %, 64 %, 65 %, 66 %, 67 %, 68 %, 69 %, 70 %, 71 %, 72 %, 73 %, 74 %, or 75 % of the  $T_m$ . In some cases, warm forming can be
 25 performed at temperatures less than a glass transition temperature ( $T_g$ ) of the formability film.

In some cases, hot forming can be performed at temperatures greater than the  $T_m$  of the formability film, or greater than a degradation temperature of the formability film. In some cases, hot forming can be employed to remove the formability film by melting, sintering, charring, combusting, and/or degrading the formability film. For example, hot forming can be performed at
 30 a temperature of at least about 400 °C (e.g., at least about at least about 400 °C, at least about 410 °C, at least about 420 °C, at least about 430 °C, at least about 440 °C, at least about 450 °C, at



least about 460 °C, at least about 470 °C, at least about 480 °C, at least about 490 °C, at least about 500 °C, at least about 510 °C, at least about 520 °C, at least about 530 °C, at least about 540 °C, or at least about 550 °C).

##### 5 *Removing the Removable Formability Film From the Formed Metal Product*

As described herein, the formability film can be a removable film (e.g., a sacrificial film that benefits the forming process only). In certain aspects, the elevated temperature forming can be performed at a temperature sufficient to melt and/or sinter the formability film (e.g., to remove the formability film during the forming process). For example, hot forming can be performed at  
10 temperatures greater than the  $T_m$  temperature and/or greater than a decomposition temperature of the formability film.

The formability film, as described herein, can be a water soluble formability film. After forming, removing the formability film from the formed metal product is performed by rinsing, combusting, or any combination thereof (e.g., rinsing with water). In some examples, the water-  
15 soluble formability film can be removed with tap water, reverse osmosis water, distilled water, demineralized water, and/or deionized water. In some cases, rinsing the formability film is performed as an independent processing step. For example, the formed metal product can be subjected to a rinse after forming. The rinse can be performed by spraying, immersing, any suitable  
20 water application technique, or any combination thereof. In some examples, the rinse can be performed for up to about 60 seconds (s) (e.g., up to about 1 s, about 2 s, about 3 s, about 4 s, about 5 s, about 6 s, about 7 s, about 8 s, about 9 s, about 10 s, about 11 s, about 12 s, about 13 s, about 14 s, about 15 s, about 16 s, about 17 s, about 18 s, about 19 s, about 20 s, about 21 s, about 22 s, about 23 s, about 24 s, about 25 s, about 26 s, about 27 s, about 28 s, about 29 s, about 30 s, about 31 s, about 32 s, about 33 s, about 34 s, about 35 s, about 36 s, about 37 s, about 38 s, about 39 s,  
25 about 40 s, about 41 s, about 42 s, about 43 s, about 44 s, about 45 s, about 46 s, about 47 s, about 48 s, about 49 s, about 50 s, about 51 s, about 52 s, about 53 s, about 54 s, about 55 s, about 56 s, about 57 s, about 58 s, about 59 s, or about 60 s). In some cases, rinsing the formability film is performed as part of an optional downstream process, for example, as a part of a painting, electrocoating (E-coating), zinc phosphating, laminating, lacquering, any other suitable post-  
30 forming product processing, or any combination thereof, wherein the formed metal product is

cleaned and/or rinsed before processing. For example, a formed metal product can be cleaned before a coating step in a water-based cleaning process.

Such a cleaning process can remove the formability film without any further processing, for example, without the need for removing a lubricant used in the forming step. In some cases, wet (e.g., oil-based lubricants) and/or dry (e.g., graphite or silicate based lubricants) are not removable by a water-based cleaning step, and require additional processing to prepare the formed metal product for coating. Thus, a water-soluble formability film lowers production costs, energy consumption, volatile organic compound use, and environmental impact. In some cases, the formability film is removed by combusting. For example, heat treating the formed metal product in a post-forming heat treatment can melt the formability film, can pyrolyze the formability film, can sublime the formability film, or any combination thereof.

In some cases, the formability film, as described herein, provides lubrication for the forming process. As such, the formability film is a suitable replacement for the wet and/or dry lubricants described above. In certain aspects, the formability films can be a sacrificial substrate for the lubricants described above. For example, the lubricants used in the forming process can be applied onto the formability film. The metal blank can then be formed into a formed metal product. After forming, the lubricant (e.g., the wet lubricant or the dry lubricant described above) and the formability film can be removed simultaneously by rinsing or combusting. Thus, using the formability film as a lubricant, or as a sacrificial substrate for a difficult to remove lubricant, provides a more efficient lubricant removal mechanism.

In some non-limiting examples, the methods described herein include pretreating the metal blank before applying the formability film. Pretreating can include, for example, applying an adhesion promoter, a corrosion inhibitor, a coupling agent, an antimicrobial agent, a welding primer, a riveting primer, or any combination thereof. Thus, removing the formability film from the formed metal product can expose the pretreatment to the surrounding environment for downstream processing. For example, removing the formability film from the formed metal product can expose an adhesion promoter that can aid in bonding the formed metal product to other metal products.

### B. Forming with a Preprime Network Polymer Film

As described herein, the methods include applying a preprime to the metal blank to provide a coated metal blank. In certain aspects, the preprime is a polyurethane-polyamide network polymer. In certain aspects, the polyurethane-polyamide network polymer is a crosslinked polyurethane network containing polyamide particles. In some cases, the crosslinker is an isocyanate functional group ( $-N=C=O$ ). In some non-limiting examples, the isocyanate functional group is attached to a hydroxyl ( $-OH$ ) of the polyamide. In some cases, the isocyanate functional group is attached to a hydroxyl ( $-OH$ ) of a polyester resin. In certain aspects, the isocyanate functional groups can form a crosslinked network including polyamide, polyester resin, and isocyanate. In certain aspects, the isocyanate functional group is employed as a functionalized aliphatic molecule introduced into the matrix. For example, the functionalized aliphatic molecule can be isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), 4,4'-methylenebis(cyclohexyl isocyanate) (MDI), any isocyanate functionalized aliphatic molecule, or any combination thereof. In some cases, the preprime includes carbon black particles.

In certain examples, the preprime can include up to about 30 wt. % polyamide (e.g., from about 5 % polyamide to about 30 % polyamide, from about 6 % polyamide to about 28 % polyamide, from about 7 % polyamide to about 26 % polyamide, from about 8 % polyamide to about 24 % polyamide, from about 9 % polyamide to about 22 % polyamide, or from about 10 % polyamide to about 20 % polyamide). For example, the polyamide content can be up to about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23%, about 24%, about 25%, about 26%, about 27%, about 28%, about 29%, or about 30% based on the weight of the preprime. In some aspects, the polyurethane provides a low friction interface between, for example, a forming die and the metal blank. In certain other cases, the polyurethane provides a backbone for polyamide particles. The polyamide particles provide a flexible and elastic coating. In some aspects, the preprime can include up to about 3 wt. % carbon black particles (e.g., from about 1 % to about 3 %, from about 2 % to about 3 %, or from about 0.5 % to about 2.75 %). For example, the preprime can include about 0.1 %, about 0.2 %, about 0.3 %, about 0.4 %, about 0.5 %, about 0.6 %, about 0.7 %, about 0.8 %, about 0.9 %, about 1 %, about 1.1 %, about 1.2 %, about 1.3 %, about 1.4 %, about 1.5 %, about 1.6 %, about 1.7 %, about 1.8 %, about 1.9 %, about 2 %, about 2.1 %, about

2.2 %, about 2.3 %, about 2.4 %, about 2.5 %, about 2.6 %, about 2.7 %, about 2.8 %, about 2.9 %, or about 3 %. In some examples, carbon black particles are not present. The carbon black particles can have a particle size less than about 5  $\mu\text{m}$  (e.g., from about 50 nm to about 5  $\mu\text{m}$ , from about 100 nm to about 4.5  $\mu\text{m}$ , from about 200 nm to about 4  $\mu\text{m}$ , from about 500 nm to about 3.5  $\mu\text{m}$ , or from about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ ). For example, the carbon black particles can have a particle size of about 0.05  $\mu\text{m}$ , about 0.1  $\mu\text{m}$ , about 0.2  $\mu\text{m}$ , about 0.3  $\mu\text{m}$ , about 0.4  $\mu\text{m}$ , about 0.5  $\mu\text{m}$ , about 0.6  $\mu\text{m}$ , about 0.7  $\mu\text{m}$ , about 0.8  $\mu\text{m}$ , about 0.9  $\mu\text{m}$ , about 1  $\mu\text{m}$ , about 1.1  $\mu\text{m}$ , about 1.2  $\mu\text{m}$ , about 1.3  $\mu\text{m}$ , about 1.4  $\mu\text{m}$ , about 1.5  $\mu\text{m}$ , about 1.6  $\mu\text{m}$ , about 1.7  $\mu\text{m}$ , about 1.8  $\mu\text{m}$ , about 1.9  $\mu\text{m}$ , about 2  $\mu\text{m}$ , about 2.1  $\mu\text{m}$ , about 2.2  $\mu\text{m}$ , about 2.3  $\mu\text{m}$ , about 2.4  $\mu\text{m}$ , about 2.5  $\mu\text{m}$ , about 2.6  $\mu\text{m}$ , about 2.7  $\mu\text{m}$ , about 2.8  $\mu\text{m}$ , about 2.9  $\mu\text{m}$ , about 3  $\mu\text{m}$ , about 3.1  $\mu\text{m}$ , about 3.2  $\mu\text{m}$ , about 3.3  $\mu\text{m}$ , about 3.4  $\mu\text{m}$ , about 3.5  $\mu\text{m}$ , about 3.6  $\mu\text{m}$ , about 3.7  $\mu\text{m}$ , about 3.8  $\mu\text{m}$ , about 3.9  $\mu\text{m}$ , about 4  $\mu\text{m}$ , about 4.1  $\mu\text{m}$ , about 4.2  $\mu\text{m}$ , about 4.3  $\mu\text{m}$ , about 4.4  $\mu\text{m}$ , about 4.5  $\mu\text{m}$ , about 4.6  $\mu\text{m}$ , about 4.7  $\mu\text{m}$ , about 4.8  $\mu\text{m}$ , about 4.9  $\mu\text{m}$ , or about 5  $\mu\text{m}$ . Thus, the polyurethane-polyamide network polymer (i.e., the preprime) provides a flexible, elastic, friction-reducing coating for the metal blank.

The preprime can be applied to the metal blank using any suitable method, such as by a solution deposition method (e.g., roll coating, spray coating, immersion coating, drop coating, enrobing, squeegee coating, or any combination thereof). In the example of solution deposition, the preprime can be deposited onto the metal blank from a liquid polymer solution (e.g., a liquid preprime solution). For example, the preprime can be deposited by coating the liquid preprime solution onto the metal blank and curing the applied preprime solution to provide a preprime coating on the metal blank. In some examples, curing the applied preprime solution can include heating the metal blank to a temperature of up to about 250  $^{\circ}\text{C}$ . For example, curing can be performed at a temperature of up to about 190  $^{\circ}\text{C}$ , about 195  $^{\circ}\text{C}$ , about 200  $^{\circ}\text{C}$ , about 205  $^{\circ}\text{C}$ , about 210  $^{\circ}\text{C}$ , about 215  $^{\circ}\text{C}$ , about 220  $^{\circ}\text{C}$ , about 225  $^{\circ}\text{C}$ , about 230  $^{\circ}\text{C}$ , about 235  $^{\circ}\text{C}$ , about 240  $^{\circ}\text{C}$ , about 245  $^{\circ}\text{C}$ , or about 250  $^{\circ}\text{C}$ . In a further example, the curing can be performed for up to about 60 minutes (e.g., about 10 minutes, about 15 minutes, about 20 minutes, about 25 minutes, about 30 minutes, about 35 minutes, about 40 minutes, about 45 minutes, about 50 minutes, about 55 minutes, or about 60 minutes). For example, the curing can be performed for from 1 second to 55 minutes, from 1 second to 50 minutes, from 1 second to 45 minutes, from 1 second to from 1 second to 40 minutes, from 1 second to 35 minutes, from 1 second to 30 minutes, from 1 second

to 25 minutes, from 1 second to 20 minutes, from 1 second to 15 minutes, from 1 second to 600 seconds, from 1 second to 500 seconds, from 1 second to 400 seconds, from 1 second to 300 seconds, from 1 second to 200 seconds, from 1 second to 100 seconds, from 1 second to 60 seconds, from 1 second to 45 seconds, from 1 second to 30 seconds, or anywhere in between.

5            In some non-limiting examples, the preprime can be laminated onto the metal blank. Accordingly, a polyurethane-polyamide network polymer film can be brought into contact with the metal blank. For example, the polyurethane-polyamide network polymer film can be coupled to the metal blank using mechanical bonding, dipolar interactions, or any suitable mechanism initiated by intimate contact between the metal blank and the polymer film. Laminating the  
10 polymer film onto the metal blank can provide the preprime coating.

          In certain cases, curing the preprime coating provides a crosslinked network polymer film that is insoluble in various liquid solvents. For example, the preprime coating can be a crosslinked polymer film that is not soluble in water (e.g., tap water, reverse osmosis water, distilled water, demineralized water, and/or deionized water), certain organic solvents (e.g., acetone, benzene, *n*-  
15 butyl acetate, carbon tetrachloride, cyclohexane, *n*-decane, dibutyl amine, difluorodichloromethane, 1,4-dioxane, methanol, ethanol, toluene, xylene, hexanes, dichloromethane, tetrahydrofuran, and the like), and/or certain inorganic solvents (e.g., ammonia, sulfur dioxide, sulfuryl chloride, sulfuryl chloride fluoride, phosphoryl chloride, dinitrogen tetroxide, antimony trichloride, bromine pentafluoride, hydrogen fluoride, sulfuric acid, or the  
20 like).

          In certain aspects, the cured preprime coating can have a structure depicted in Figure 1. Polyurethane molecules (indicated by cross-hatched boxes) can provide a homogenous network containing polyamide moieties (indicated by open circles) covalently attached throughout. The homogenous network can be crosslinked by curing the polyester resin and polyamide having the  
25 isocyanate functional groups as described above (indicated by straight lines), providing the preprime coating.

          In some cases, the preprime coating is from about 10 nm (0.01  $\mu\text{m}$ ) thick up to about 500  $\mu\text{m}$  thick (e.g., from about 1  $\mu\text{m}$  to about 490  $\mu\text{m}$ , from about 5  $\mu\text{m}$  to about 480  $\mu\text{m}$ , from about 10  $\mu\text{m}$  to about 470  $\mu\text{m}$ , from about 15  $\mu\text{m}$  to about 460  $\mu\text{m}$ , from about 20  $\mu\text{m}$  to about 450  $\mu\text{m}$ ,  
30 from about 25  $\mu\text{m}$  to about 440  $\mu\text{m}$ , from about 30  $\mu\text{m}$  to about 435  $\mu\text{m}$ , from about 35  $\mu\text{m}$  to about 430  $\mu\text{m}$ , from about 40  $\mu\text{m}$  to about 425  $\mu\text{m}$ , from about 45  $\mu\text{m}$  to about 420  $\mu\text{m}$ , from about

50  $\mu\text{m}$  to about 415  $\mu\text{m}$ , from about 55  $\mu\text{m}$  to about 410  $\mu\text{m}$ , from about 60  $\mu\text{m}$  to about 405  $\mu\text{m}$ , from about 65  $\mu\text{m}$  to about 400  $\mu\text{m}$ , from about 75  $\mu\text{m}$  to about 375  $\mu\text{m}$ , from about 100  $\mu\text{m}$  to about 350  $\mu\text{m}$ , from about 125  $\mu\text{m}$  to about 300  $\mu\text{m}$ , from about 150  $\mu\text{m}$  to about 250  $\mu\text{m}$ , or from about 175  $\mu\text{m}$  to about 225  $\mu\text{m}$ ). For example, the preprime coating can be up to about 0.5  $\mu\text{m}$ , 1  $\mu\text{m}$ , 2  $\mu\text{m}$ , 3  $\mu\text{m}$ , 4  $\mu\text{m}$ , 5  $\mu\text{m}$ , 6  $\mu\text{m}$ , 7  $\mu\text{m}$ , 8  $\mu\text{m}$ , 9  $\mu\text{m}$ , 10  $\mu\text{m}$ , 11  $\mu\text{m}$ , 12  $\mu\text{m}$ , 13  $\mu\text{m}$ , 14  $\mu\text{m}$ , 15  $\mu\text{m}$ , 16  $\mu\text{m}$ , 17  $\mu\text{m}$ , 18  $\mu\text{m}$ , 19  $\mu\text{m}$ , 20  $\mu\text{m}$ , 21  $\mu\text{m}$ , 22  $\mu\text{m}$ , 23  $\mu\text{m}$ , 24  $\mu\text{m}$ , 25  $\mu\text{m}$ , 26  $\mu\text{m}$ , 27  $\mu\text{m}$ , 28  $\mu\text{m}$ , 29  $\mu\text{m}$ , 30  $\mu\text{m}$ , 31  $\mu\text{m}$ , 32  $\mu\text{m}$ , 33  $\mu\text{m}$ , 34  $\mu\text{m}$ , 35  $\mu\text{m}$ , 36  $\mu\text{m}$ , 37  $\mu\text{m}$ , 38  $\mu\text{m}$ , 39  $\mu\text{m}$ , 40  $\mu\text{m}$ , 41  $\mu\text{m}$ , 42  $\mu\text{m}$ , 43  $\mu\text{m}$ , 44  $\mu\text{m}$ , 45  $\mu\text{m}$ , 46  $\mu\text{m}$ , 47  $\mu\text{m}$ , 48  $\mu\text{m}$ , 49  $\mu\text{m}$ , 50  $\mu\text{m}$ , 51  $\mu\text{m}$ , 52  $\mu\text{m}$ , 53  $\mu\text{m}$ , 54  $\mu\text{m}$ , 55  $\mu\text{m}$ , 56  $\mu\text{m}$ , 57  $\mu\text{m}$ , 58  $\mu\text{m}$ , 59  $\mu\text{m}$ , 60  $\mu\text{m}$ , 61  $\mu\text{m}$ , 62  $\mu\text{m}$ , 63  $\mu\text{m}$ , 64  $\mu\text{m}$ , 65  $\mu\text{m}$ , 66  $\mu\text{m}$ , 67  $\mu\text{m}$ , 68  $\mu\text{m}$ , 69  $\mu\text{m}$ , 70  $\mu\text{m}$ , 71  $\mu\text{m}$ , 72  $\mu\text{m}$ , 73  $\mu\text{m}$ , 74  $\mu\text{m}$ , 75  $\mu\text{m}$ , 76  $\mu\text{m}$ , 77  $\mu\text{m}$ , 78  $\mu\text{m}$ , 79  $\mu\text{m}$ , 80  $\mu\text{m}$ , 81  $\mu\text{m}$ , 82  $\mu\text{m}$ , 83  $\mu\text{m}$ , 84  $\mu\text{m}$ , 85  $\mu\text{m}$ , 86  $\mu\text{m}$ , 87  $\mu\text{m}$ , 88  $\mu\text{m}$ , 89  $\mu\text{m}$ , 90  $\mu\text{m}$ , 91  $\mu\text{m}$ , 92  $\mu\text{m}$ , 93  $\mu\text{m}$ , 94  $\mu\text{m}$ , 95  $\mu\text{m}$ , 96  $\mu\text{m}$ , 97  $\mu\text{m}$ , 98  $\mu\text{m}$ , 99  $\mu\text{m}$ , 100  $\mu\text{m}$ , 110  $\mu\text{m}$ , 120  $\mu\text{m}$ , 130  $\mu\text{m}$ , 140  $\mu\text{m}$ , 150  $\mu\text{m}$ , 160  $\mu\text{m}$ , 170  $\mu\text{m}$ , 180  $\mu\text{m}$ , 190  $\mu\text{m}$ , 200  $\mu\text{m}$ , 210  $\mu\text{m}$ , 220  $\mu\text{m}$ , 230  $\mu\text{m}$ , 240  $\mu\text{m}$ , 250  $\mu\text{m}$ , 260  $\mu\text{m}$ , 270  $\mu\text{m}$ , 280  $\mu\text{m}$ , 290  $\mu\text{m}$ , 300  $\mu\text{m}$ , 310  $\mu\text{m}$ , 320  $\mu\text{m}$ , 330  $\mu\text{m}$ , 340  $\mu\text{m}$ , 350  $\mu\text{m}$ , 360  $\mu\text{m}$ , 370  $\mu\text{m}$ , 380  $\mu\text{m}$ , 390  $\mu\text{m}$ , 400  $\mu\text{m}$ , 410  $\mu\text{m}$ , 420  $\mu\text{m}$ , 430  $\mu\text{m}$ , 440  $\mu\text{m}$ , 450  $\mu\text{m}$ , 460  $\mu\text{m}$ , 470  $\mu\text{m}$ , 480  $\mu\text{m}$ , 490  $\mu\text{m}$ , 500  $\mu\text{m}$ , 510  $\mu\text{m}$ , 520  $\mu\text{m}$ , 530  $\mu\text{m}$ , 540  $\mu\text{m}$ , 550  $\mu\text{m}$ , 560  $\mu\text{m}$ , 570  $\mu\text{m}$ , 580  $\mu\text{m}$ , 590  $\mu\text{m}$ , 600  $\mu\text{m}$ , 610  $\mu\text{m}$ , 620  $\mu\text{m}$ , 630  $\mu\text{m}$ , 640  $\mu\text{m}$ , 650  $\mu\text{m}$ , 660  $\mu\text{m}$ , 670  $\mu\text{m}$ , 680  $\mu\text{m}$ , 690  $\mu\text{m}$ , 700  $\mu\text{m}$ , 710  $\mu\text{m}$ , 720  $\mu\text{m}$ , 730  $\mu\text{m}$ , 740  $\mu\text{m}$ , 750  $\mu\text{m}$ , 760  $\mu\text{m}$ , 770  $\mu\text{m}$ , 780  $\mu\text{m}$ , 790  $\mu\text{m}$ , 800  $\mu\text{m}$ , 810  $\mu\text{m}$ , 820  $\mu\text{m}$ , 830  $\mu\text{m}$ , 840  $\mu\text{m}$ , 850  $\mu\text{m}$ , 860  $\mu\text{m}$ , 870  $\mu\text{m}$ , 880  $\mu\text{m}$ , 890  $\mu\text{m}$ , 900  $\mu\text{m}$ , 910  $\mu\text{m}$ , 920  $\mu\text{m}$ , 930  $\mu\text{m}$ , 940  $\mu\text{m}$ , 950  $\mu\text{m}$ , 960  $\mu\text{m}$ , 970  $\mu\text{m}$ , 980  $\mu\text{m}$ , 990  $\mu\text{m}$ , or 1000  $\mu\text{m}$ .

In some aspects, the preprime coating described herein improves a formability of the metal blank to provide a formed metal product. Forming the preprime coated metal blank to provide a formed metal product can include stamping, drawing, bending, extruding, curving, forging, stretching, recessing, die forming, indenting, shearing, or any combination thereof. In some examples, forming can be performed at room temperature. In some cases, forming can be performed at an elevated temperature (e.g., warm forming and/or hot forming). Parameters of elevated temperature forming depend on the material characteristics of the preprime coating, and whether it is desired that the preprime coating remains on the metal blank. For example, warm forming can be performed at temperatures less than a melting temperature ( $T_m$ ) of the preprime coating (e.g., about 150 °C) to preserve the preprime coating for downstream processing (e.g.,

when the preprime coating can be a lubricant). In some examples, warm forming can be performed up to about 75 % of the  $T_m$ . For example, warm forming can be performed at a temperature of about 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 7 %, 8 %, 9 %, 10 %, 11 %, 12 %, 13 %, 14 %, 15 %, 16 %, 17 %, 18 %, 19 %, 20 %, 21 %, 22 %, 23 %, 24 %, 25 %, 26 %, 27 %, 28 %, 29 %, 30 %, 31 %, 32 %, 33 %, 34 %, 35 %, 36 %, 37 %, 38 %, 39 %, 40 %, 41 %, 42 %, 43 %, 44 %, 45 %, 46 %, 47 %, 48 %, 49 %, 50 %, 51 %, 52 %, 53 %, 54 %, 55 %, 56 %, 57 %, 58 %, 59 %, 60 %, 61 %, 62 %, 63 %, 64 %, 65 %, 66 %, 67 %, 68 %, 69 %, 70 %, 71 %, 72 %, 73 %, 74 %, or 75 % of the  $T_m$ .

In some non-limiting examples, the preprime coating can be a sacrificial coating. In some cases, warm forming and/or hot forming can be performed at temperatures greater than the  $T_m$  of the preprime coating, or greater than a degradation temperature of the preprime coating. In some cases, hot forming can be employed to remove the preprime coating by melting, sintering, charring, combusting, and/or degrading the preprime coating. For example, hot forming can be performed at a temperature of at least about 150 °C (e.g., at least about 150 °C, at least about 160 °C, at least about 170 °C, at least about 180 °C, at least about 190 °C, at least about 200 °C, at least about 210 °C, at least about 220 °C, at least about 230 °C, at least about 240 °C, at least about 250 °C, at least about 260 °C, at least about 270 °C, at least about 280 °C, at least about 290 °C, at least about 300 °C, at least about 310 °C, at least about 320 °C, at least about 330 °C, at least about 340 °C, at least about 350 °C, at least about 360 °C, at least about 370 °C, at least about 380 °C, at least about 390 °C, at least about 400 °C, at least about 410 °C, at least about 420 °C, at least about 430 °C, at least about 440 °C, at least about 450 °C, at least about 460 °C, at least about 470 °C, at least about 480 °C, at least about 490 °C, at least about 500 °C, at least about 510 °C, at least about 520 °C, at least about 530 °C, at least about 540 °C, or at least about 550 °C).

In certain aspects, the preprime can be applied to at least a portion of the metal blank, providing a partially preprime-coated metal blank having at least one portion exhibiting a higher formability than the remainder of the metal blank. For example, the partially preprime-coated metal blank can have a first portion that is coated with the preprime and a second portion that is not coated. Thus, when subjected to forming, the first portion can exhibit a higher formability than the second portion. As described above, the formability of the metal blank can be locally tuned by applying the preprime to at least a portion of the metal blank where a higher formability is desired.

Thus, locally tuning the formability of the metal blank can provide variably formed and complex metal products.

The preprime, as described herein, is a non-soluble coating. In some cases, the preprime coating can replace certain downstream processes, for example, painting, electrocoating (E-coating), and/or zinc phosphating. In some cases, the preprime coating, as described herein, provides lubrication for the forming process. As such, the preprime coating is a suitable replacement for the wet and/or dry lubricants described above.

In some non-limiting examples, the preprime coating includes a chemical additive such as an adhesion promoter, a corrosion inhibitor, a coupling agent, an antimicrobial agent, a welding primer, a riveting primer, or any combination thereof. For example, a chemical additive (e.g., an adhesion promoter, a corrosion inhibitor, or a combination thereof) can be incorporated into the preprime coating (e.g., during preparing a liquid solution). Thus, the preprime coating further imparts a surface treatment suitable for preparing the formed metal product for downstream processing, including joining, bonding, coating, any other suitable downstream processing, or any combination thereof.

### C. Forming with a Hybrid Organic-Inorganic Preprime

As described above, the methods include applying the preprime to the metal blank to provide a coated metal blank. In certain aspects, the preprime is a polyurethane-polyamide network polymer that optionally includes inorganic low coefficient of friction (COF) and/or heat-resistant materials, providing a hybrid organic-inorganic preprime. In certain aspects, the preprime can include dry lubricants (e.g., graphite, molybdenum disulfide, or the like), boron nitride (BN), nanodiamond materials, or a heat-resistant poly(tetrafluoroethylene) (PTFE). In certain examples, coating a metal blank with a hybrid organic-inorganic preprime allows the metal blank to be further subjected to thermal treatment processes, including artificial aging, paint baking, post-forming heat treatment, annealing, or any suitable heat treatment process.

In some cases, a heat-resistant hybrid organic-inorganic preprime can be applied to a metal blank prior to an artificial aging process. For example, the metal blank can be coated with the heat-resistant hybrid organic-inorganic preprime and heat to a temperature of up to about 150 °C (e.g., from about 25 °C to about 140 °C, from about 30 °C to about 125 °C, from about 50 °C to about 120 °C, or from 75 °C to about 125 °C). For example, the metal blank coated with the heat-resistant



hybrid organic-inorganic preprime can be heated to about 25 °C, about 30 °C, about 35 °C, about 40 °C, about 45 °C, about 50 °C, about 55 °C, about 60 °C, about 65 °C, about 70 °C, about 75 °C, about 80 °C, about 85 °C, about 90 °C, about 95 °C, about 100 °C, about 105 °C, about 110 °C, about 115 °C, about 120 °C, about 125 °C, about 130 °C, about 135 °C, about 140 °C, about 145 °C, or about 150 °C.

In certain cases, a heat-resistant hybrid organic-inorganic preprime can be applied to a metal blank prior to a solution heat treatment process. For example, the metal blank can be coated with the heat-resistant hybrid organic-inorganic preprime and heated to a temperature of up to about 500 °C (e.g., from about 250 °C to about 500 °C, from about 300 °C to about 480 °C, from about 350 °C to about 450 °C, or from about 375 °C to about 500 °C). For example, the metal blank coated with the heat-resistant hybrid organic-inorganic preprime can be heated to about 250 °C, about 255 °C, about 260 °C, about 265 °C, about 270 °C, about 275 °C, about 280 °C, about 285 °C, about 290 °C, about 295 °C, about 300 °C, about 305 °C, about 310 °C, about 315 °C, about 320 °C, about 325 °C, about 330 °C, about 335 °C, about 340 °C, about 345 °C, about 350 °C, about 355 °C, about 360 °C, about 365 °C, about 370 °C, about 375 °C, about 380 °C, about 385 °C, about 390 °C, about 395 °C, about 400 °C, about 405 °C, about 410 °C, about 415 °C, about 420 °C, about 425 °C, about 430 °C, about 435 °C, about 440 °C, about 445 °C, about 450 °C, about 455 °C, about 460 °C, about 465 °C, about 470 °C, about 475 °C, about 480 °C, about 485 °C, about 490 °C, about 495 °C, or about 500 °C.

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### *Metal Product Properties*

In certain examples, the formability film and/or the preprime coating provide improved formability of the metal blank as compared to a metal blank devoid of a formability film and/or a preprime coating (e.g., improved formability includes increasing elongation before fracture at least about 50 % as compared to a metal blank devoid of a formability film). Not to be bound by theory, providing a formability film and/or a preprime coating on a metal blank before forming allows the metal blank to be formed (i.e., deformed) to a greater extent than when forming a metal blank devoid of the formability film and/or the preprime coating. The formability film and/or the preprime coating, as described herein, reduce friction between the metal blank and a forming apparatus (e.g., a stamp, a die, a mandrel, a punch, a press, or the like). Reducing friction between the metal blank and the forming apparatus provides an increased elongation before fracture of the

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metal blank. For example, providing a metal blank with the formability film and/or the preprime coating increases the elongation before fracture of the metal blank up to about 125 % (e.g., from about 1 % to about 120 %, from about 5 % to about 110 %, from about 10 % to about 100 %, from about 20 % to about 90 %, from about 30 % to about 80 %, from about 40 % to about 70 %, or from about 50 % to about 60 %) compared to the elongation before fracture of a metal blank devoid of the formability film and/or the preprime coating. In some examples, the elongation before fracture is increased by up to about 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 7 %, 8 %, 9 %, 10 %, 11 %, 12 %, 13 %, 14 %, 15 %, 16 %, 17 %, 18 %, 19 %, 20 %, 21 %, 22 %, 23 %, 24 %, 25 %, 26 %, 27 %, 28 %, 29 %, 30 %, 31 %, 32 %, 33 %, 34 %, 35 %, 36 %, 37 %, 38 %, 39 %, 40 %, 41 %, 42 %, 43 %, 44 %, 45 %, 46 %, 47 %, 48 %, 49 %, 50 %, 51 %, 52 %, 53 %, 54 %, 55 %, 56 %, 57 %, 58 %, 59 %, 60 %, 61 %, 62 %, 63 %, 64 %, 65 %, 66 %, 67 %, 68 %, 69 %, 70 %, 71 %, 72 %, 73 %, 74 %, 75 %, 76 %, 77 %, 78 %, 79 %, 80 %, 81 %, 82 %, 83 %, 84 %, 85 %, 86 %, 87 %, 88 %, 89 %, 90 %, 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 %, 100 %, 101 %, 102 %, 103 %, 104 %, 105 %, 106 %, 107 %, 108 %, 109 %, 110 %, 111 %, 112 %, 113 %, 114 %, 115 %, 116 %, 117 %, 118 %, 119 %, 120 %, 121 %, 122 %, 123 %, 124 %, or 125 %.

Additionally, the bond durability and/or corrosion resistance can be improved up to about 125 % (e.g., from about 1 % to about 120 %, from about 5 % to about 110 %, from about 10 % to about 100 %, from about 20 % to about 90 %, from about 30 % to about 80 %, from about 40 % to about 70 %, or from about 50 % to about 60 %) when compared to a metal blank and/or formed metal product devoid of the pretreatment (e.g., the pretreatment applied before applying the formability film) or the preprime coating containing a chemical additive (e.g., an adhesion promoter chemical additive and/or a corrosion inhibitor chemical additive). Thus, the metal product can have an improved bond durability when compared to metal products devoid of a formability film and an adhesion promoter pretreatment, or devoid of a preprime having an adhesion promoter (e.g., the metal product having improved bond durability survives a bond durability test through up to about 125 % more cycles when compared to metal products devoid of a formability film and an adhesion promoter pretreatment, or devoid of a preprime having an adhesion promoter).

During bond durability testing, bonds are created between two metal products, such as by an epoxy adhesive. Then, the bonded metal products are subjected to strain and/or other conditions. For example, the bonded metal products may be immersed in a salt solution and then subjected to

humid conditions or drying conditions. After a series of cycles in one or more conditions, the bonds between the aluminum alloys are evaluated for chemical and mechanical failure. As described herein, the metal products can survive up to about 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 7 %, 8 %, 9 %, 10 %, 11 %, 12 %, 13 %, 14 %, 15 %, 16 %, 17 %, 18 %, 19 %, 20 %, 21 %, 22 %, 23 %, 24 %, 25 %, 26 %, 27 %, 28 %, 29 %, 30 %, 31 %, 32 %, 33 %, 34 %, 35 %, 36 %, 37 %, 38 %, 39 %, 40 %, 41 %, 42 %, 43 %, 44 %, 45 %, 46 %, 47 %, 48 %, 49 %, 50 %, 51 %, 52 %, 53 %, 54 %, 55 %, 56 %, 57 %, 58 %, 59 %, 60 %, 61 %, 62 %, 63 %, 64 %, 65 %, 66 %, 67 %, 68 %, 69 %, 70 %, 71 %, 72 %, 73 %, 74 %, 75 %, 76 %, 77 %, 78 %, 79 %, 80 %, 81 %, 82 %, 83 %, 84 %, 85 %, 86 %, 87 %, 88 %, 89 %, 90 %, 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 %, 100 %, 101 %, 102 %, 103 %, 104 %, 105 %, 106 %, 107 %, 108 %, 109 %, 110 %, 111 %, 112 %, 113 %, 114 %, 115 %, 116 %, 117 %, 118 %, 119 %, 120 %, 121 %, 122 %, 123 %, 124 %, or 125 % more bond durability test cycles when compared to metal products devoid of a formability film and an adhesion promoter pretreatment, or devoid of a preprime having an adhesion promoter.

Additionally, in certain examples, the metal product can have improved corrosion resistance when compared to metal products devoid of a formability film and a corrosion inhibitor pretreatment, or devoid of a preprime having a corrosion inhibitor (e.g., the metal product having improved corrosion resistance exhibits up to about a 125 % decrease in corrosion attack pit depth when compared to metal products devoid of a formability film and having a corrosion inhibitor pretreatment, or devoid of a preprime having a corrosion inhibitor).

During corrosion testing, the metal products are immersed in a salt solution for a period of time. Alternately, the metal products are subjected to a salt solution spray for a period of time. Following the immersion period or the spray period, the metal products are analyzed to determine the degree of corrosion that occurred, indicated by a pitting morphology, or corrosion attack pit depth. As described herein, the metal product can exhibit a corrosion attack pit depth reduction of up to about 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 7 %, 8 %, 9 %, 10 %, 11 %, 12 %, 13 %, 14 %, 15 %, 16 %, 17 %, 18 %, 19 %, 20 %, 21 %, 22 %, 23 %, 24 %, 25 %, 26 %, 27 %, 28 %, 29 %, 30 %, 31 %, 32 %, 33 %, 34 %, 35 %, 36 %, 37 %, 38 %, 39 %, 40 %, 41 %, 42 %, 43 %, 44 %, 45 %, 46 %, 47 %, 48 %, 49 %, 50 %, 51 %, 52 %, 53 %, 54 %, 55 %, 56 %, 57 %, 58 %, 59 %, 60 %, 61 %, 62 %, 63 %, 64 %, 65 %, 66 %, 67 %, 68 %, 69 %, 70 %, 71 %, 72 %, 73 %, 74 %, 75 %, 76 %, 77 %, 78 %, 79 %, 80 %, 81 %, 82 %, 83 %, 84 %, 85 %, 86 %, 87 %, 88 %, 89 %, 90 %, 91 %, 92 %, 93 %, 94 %, 95 %, 96 %, 97 %, 98 %, 99 %, 100 %, 101 %, 102 %, 103 %, 104 %, 105 %, 106 %, 107 %, 108 %, 109 %, 110 %, 111 %, 112 %, 113 %, 114 %, 115 %, 116 %, 117 %, 118 %, 119 %, 120 %, 121 %, 122 %, 123 %, 124 %, or 125 % more corrosion attack pit depth reduction when compared to metal products devoid of a formability film and a corrosion inhibitor pretreatment, or devoid of a preprime having a corrosion inhibitor).

105 %, 106 %, 107 %, 108 %, 109 %, 110 %, 111 %, 112 %, 113 %, 114 %, 115 %, 116 %, 117 %, 118 %, 119 %, 120 %, 121 %, 122 %, 123 %, 124 %, or 125 %.

As described above, the formability film and/or the preprime coating can be selectively applied to desired portions of the metal blank, providing areas of higher formability than uncoated portions. Thus, the formability of the metal blank can be varied across the area of the metal blank, such that a first area can have a higher formability than a second area. Accordingly, a complex shape can be imparted to a metal product in a single forming step wherein the first area having the higher formability can be driven further than the second area during forming. As such, the formability of a metal blank can be tuned across the area of the metal blank, wherein applying the formability film, the preprime coating, or any combination thereof to at least a portion of the metal blank, and optionally leaving at least a portion of the metal blank uncoated, can vary the formability across the area of the metal blank. Thus, complex custom stamps, dies, mandrels, or the like, can be employed to provide complex metal products in a single forming step.

In certain example, the metal product has a reduced coefficient of friction, wherein the reduced coefficient of friction when compared to metal products devoid of the formability film and/or the preprime. Additionally, in certain aspects the formability film and/or the preprime provides a metal product having a stable coefficient of friction that does not increase as the metal product is deformed in a forming process. For example, as shown in Figure 3, the samples coating with the comparative forming lubricant 210 exhibited a coefficient of friction that increase dramatically during testing, indicating a breakdown of the comparative forming lubricant and increased friction between the surface of the metal product and the test apparatus. Further, the metal products coated with the formability film and/or the preprime exhibited very low coefficients of friction, less than 0.15 as shown if Figures 3 and 8. For example, the metal products coated with the formability film and/or the preprime can have a coefficient of friction of less than about 0.15, less than about 0.14, less than about 0.13, less than about 0.12, less than about 0.11, less than about 0.1, less than about 0.09, less than about 0.08, less than about 0.07, less than about 0.06, less than about 0.05, less than about 0.04, less than about 0.03, less than about 0.02, or less than about 0.01.

Methods of Using

The alloy products and methods described herein can be used in automotive and/or transportation applications, including motor vehicle, aircraft, and railway applications, or any other desired application. In some examples, the products and methods can be used to prepare motor vehicle body part products, such as bumpers, side beams, roof beams, cross beams, pillar reinforcements (e.g., A-pillars, B-pillars, and C-pillars), crash ring components, inner panels, outer panels, side panels, inner hoods, outer hoods, or trunk lid panels. The aluminum alloy products and methods described herein can also be used in aircraft or railway vehicle applications, to prepare, for example, external and internal panels.

The products and methods described herein can also be used in electronics applications, to prepare, for example, external and internal encasements. For example, the products and methods described herein can also be used to prepare housings for electronic devices, including mobile phones and tablet computers. In some examples, the products can be used to prepare housings for the outer casing of mobile phones (e.g., smart phones) and tablet bottom chassis.

In certain aspects, the products and methods can be used to prepare aerospace vehicle body part products. For example, the disclosed products and methods can be used to prepare airplane body parts, such as skin alloys.

In some cases, the products and methods can be used to prepare architectural parts. For example, the disclosed products and methods can be used to prepare building panels, aesthetic parts, roofing panels, awnings, doors, window frames, and the like.

The products and methods can be used in any other desired application.

## EXAMPLES

Example 1: Formability and Coefficient of Friction of 6xxx Series Aluminum Alloys

As described above, applying a formability film and/or a preprime coating can reduce the amount of friction between the metal blank and, for example, a forming die. In the example of Figure 2, samples from a 6xxx series aluminum alloy were prepared and tested as follows. Test coupons were taken from a 0.9 mm gauge 6xxx series aluminum alloy blank. A first set of samples was tested as-removed from the blank. A second set of samples was treated with a comparative forming lubricant. A third set of samples was treated with the preprime coating described above

by coating the preprime solution onto the aluminum alloy blank and curing for 30 minutes at 225 °C. All samples were subjected to an Erichsen cupping test according to ISO standard 20482. Figure 2 is a digital image 100 showing the results of the cupping test. As shown in Figure 2, the as-removed sample 110 exhibited a 14 mm elongation before fracture, the sample treated with the comparative forming lubricant 120 exhibited a 22.6 mm elongation before fracture, and the sample treated with the preprime coating 130 exhibited a 35 mm elongation and did not fracture. As shown in Figure 2, the sample treated with the preprime coating 130 exhibited a 150 % increase in elongation before fracture over the as-removed sample 110, and a 50 % increase in elongation before fracture over the sample treated with the comparative forming lubricant 120. Thus, applying the preprime coating significantly increased the formability of the 6xxx series aluminum alloy by reducing friction between the aluminum alloy blank and the forming die, as further shown in Figure 3.

Figure 3 is a graph 200 showing the coefficient of friction of the comparative forming lubricant 210 versus the preprime coating 220 described above subjected to a four-ball wear test. A four-ball wear test was performed at a rotation speed of 100 RPM, under an applied load of 10 pounds, and at room temperature (e.g., about 22 °C). In a typical four-ball wear test, three steel balls are coated with a test material (e.g., the comparative forming lubricant as described herein, or the preprime as described herein) and clamped together. A fourth ball is placed into a space created by clamping the three balls together. The fourth ball is rotated while the three clamped balls are held in place. As shown in Figure 3, the preprime coating 220 maintained a low coefficient of friction throughout 1000 cycles of the four-ball wear test without exhibiting coefficient of friction break-down. However, the comparative forming lubricant 210 exhibited a coefficient of friction break-down after about 100 cycles. The preprime coating described herein provided improved formability, and demonstrated superior resistance to wear compared to the comparative forming lubricant. Thus, the preprime can be available for further downstream processing, utilized by an OEM (e.g., when it includes a chemical additive such as an adhesion promoter or corrosion inhibitor), or preserved to reduce wear effects when a formed metal product is placed into service. Accordingly, the preprime can be applied to the aluminum alloys before providing the aluminum alloys to an OEM. Heat treatable aluminum alloys (e.g., 6xxx series aluminum alloys and 7xxx series aluminum alloys) can be treated with the preprime and either naturally aged to provide

highly formable alloys in a T4 temper, or artificially aged to provide highly formable alloys in, for example, a T6 temper.

Example 2: Formability of 7xxx series Aluminum Alloys

5            In the example of Figure 4, samples from a 7xxx series aluminum alloy were prepared and tested as follows. Test coupons were taken from a rolled 7xxx series aluminum alloy blank. A first set of samples was treated with a comparative forming lubricant. A second set of samples was treated with a comparative forming lubricant and heat treated to provide the second set of samples in a T6 temper. A third set of samples was treated with the preprime coating described above by  
10            coating the preprime solution onto the aluminum alloy blank and curing for 30 minutes at 225 °C. All samples were subjected to an Erichsen cupping test according to ISO standard 20482 performed at room temperature. All samples were drawn to a draw depth of 25 mm. Figure 4 is a digital image 400 showing the results of the cupping test. As shown in Figure 4, the sample treated with the comparative forming lubricant 410 and the sample treated with the comparative forming  
15            lubricant and heat treated 420 both fractured in a 25 mm cup test. Surprisingly, the sample treated with the preprime coating 430 exhibited a 25 mm draw depth and did not fracture. Thus, applying the preprime coating significantly increased the room temperature formability of the 7xxx series aluminum alloy by reducing friction between the aluminum alloy blank and the forming die.

              Figure 5 is a graph 500 showing the draw depth of the cupping test samples in mm as a  
20            function of clamp load in kiloNewtons (kN). Each sample was drawn to a draw depth of 25 mm. Points plotted in the graph represent the fracture point, where applicable, of each sample. The sample treated with the preprime coating 430 (referred to as “Pre Prime” in Figure 5) did not fracture when drawn to 25 mm. The sample treated with the comparative forming lubricant 410 (referred to as “Sample 1” in Figure 5) and the sample treated with the comparative forming  
25            lubricant and heat treated 420 (referred to as “Sample 2” in Figure 5) both fractured before reaching the 25 mm draw depth. Additionally, the sample treated with the comparative forming lubricant 410 and the sample treated with the comparative forming lubricant and heat treated 420 (i.e., Samples 1 and 2) both fractured before reaching a draw depth of 25 mm under a clamp loads of  
30            20 kN. The sample treated with the preprime coating 430 (Pre Prime) reached a 25 mm draw depth under a clamp load of up to 370 kN, thus showing the effectiveness of the preprime coating in forming applications.

In the example of Figure 6, samples described above in the examples of Figures 4 and 5 were subjected to an Erichsen cupping test according to ISO standard 20482 performed at room temperature to a maximum draw depth of 85 mm. Figure 6 is a digital image 600 showing the results of the 85 mm cupping test. As shown in Figure 6, the sample treated with the comparative forming lubricant 610 and the sample treated with the comparative forming lubricant and heat treated 620 both fractured significantly before reaching the 85 mm draw depth and only withstood clamp loads of 20 kN and 30 kN, respectively. Surprisingly, the sample treated with the preprime coating 630 exhibited an 85 mm draw depth and did not fracture as shown in Figure 6. Thus, applying the preprime coating increased the room temperature formability of the 7xxx series aluminum alloy by at least 100 % by reducing friction between the aluminum alloy blank and the forming die.

Figure 7 is a graph 700 showing the draw depth of the cupping test samples in mm as a function of clamp load in kiloNewtons (kN). Each sample was drawn to a draw depth of 85 mm. Points plotted in the graph represent the fracture point, where applicable, of each sample. The sample treated with the preprime coating 630 (referred to as “Pre Prime” in Figure 7) did not fracture when drawn to 85 mm, surviving the maximum draw depth. The sample treated with the comparative forming lubricant 610 (referred to as “Sample 1” in Figure 7) only reached a draw depth of about 40 mm under a 20 kN clamp load, and the sample treated with the comparative forming lubricant and heat treated 620 (referred to as “Sample 2” in Figure 7) only reached a draw depth of about 25 mm under a 30 kN clamp load. Notably, the sample treated with the preprime coating 630 reached an 85 mm draw depth under a clamp load of up to 70 kN, showing the effectiveness of the preprime coating in forming applications. Thus, the preprime coating described herein allows a 7xxx series aluminum alloy to be formed at room temperature, eliminating any need to heat the 7xxx series aluminum alloy before forming.

25

### Example 3: Coefficient of Friction of 7xxx, 6xxx, and 5xxx Series Aluminum Alloys

Figure 8 is a graph showing the coefficient of friction (referred to as “COF” in Figure 8) of the comparative forming lubricant versus the preprime coating described above, subjected to a four-ball wear test, as described above. As shown in Figure 8, the samples treated with the preprime coating (referred to as “PrePrimed” in Figure 8) exhibited a significantly lower coefficient of friction when compared to the samples treated with the comparative forming

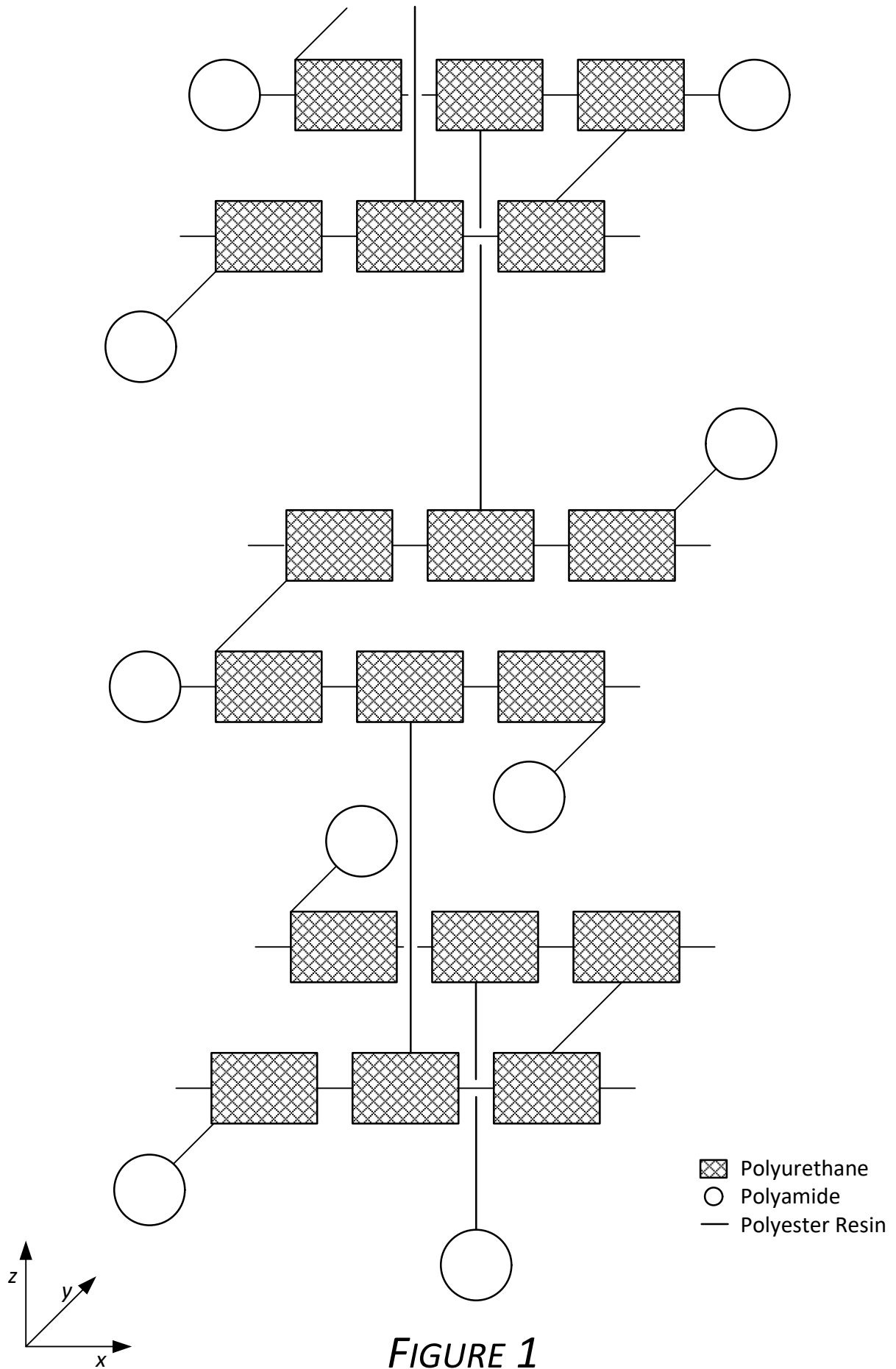
30



lubricant (referred to as “Lubed” in Figure 8). The samples included a 7xxx series aluminum alloy (left pair of histograms), a 5xxx series aluminum alloy (second from the left pair of histograms), and two 6xxx series aluminum alloys (third from the left pair of histograms and right histogram). The preprime coating described herein provided improved formability for a 7xxx series aluminum alloy, a 6xxx series aluminum alloy, and a 5xxx series aluminum alloy, and demonstrated superior resistance to wear compared to the comparative forming lubricant for each alloy designation. A lower COF can require a reduced punch force and reduced stress during forming, thus providing increased drawing and formability. The samples treated with the preprime coating exhibited up to a 100 % reduction in COF for the 7xxx series aluminum alloy. Further, the ability to form the alloys at room temperature reduces the cost of forming processes, and increases the tool life of drawing and forming equipment.

#### ABSTRACT

Provided herein are methods of forming a metal product, including applying a water soluble formability film to the metal blank and/or applying a network polymer preprime (e.g., a hybrid organic-inorganic preprime, or a heat-resistant hybrid preprime) to the metal blank, forming the metal blank into a formed metal product, and optionally removing the formability film. A removable formability film and/or a preprime can improve the formability of an aluminum alloy and replace lubricants that used for forming processes by reducing the coefficient of friction of the metal product surface. Further, employing a water soluble polymer film eliminates lubricant removal for downstream processing. The formability film and/or preprime can include chemical additives that provide additional surface properties. The methods of processing the aluminum alloy products described herein provide a more efficient method for producing aluminum alloy products, as required by end users (e.g., original equipment manufacturers (OEMs)).



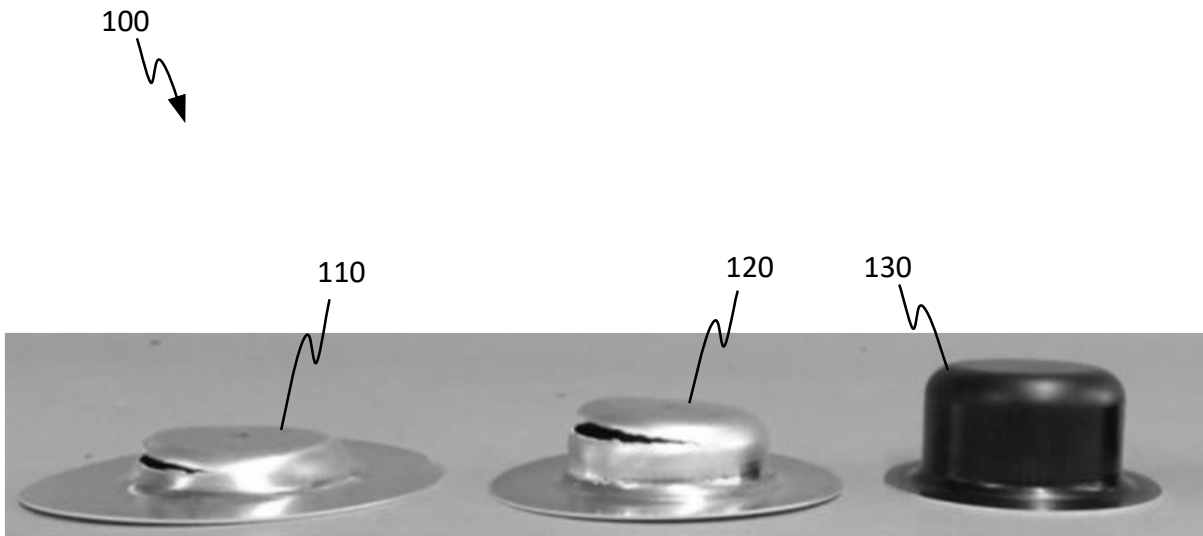


FIGURE 2

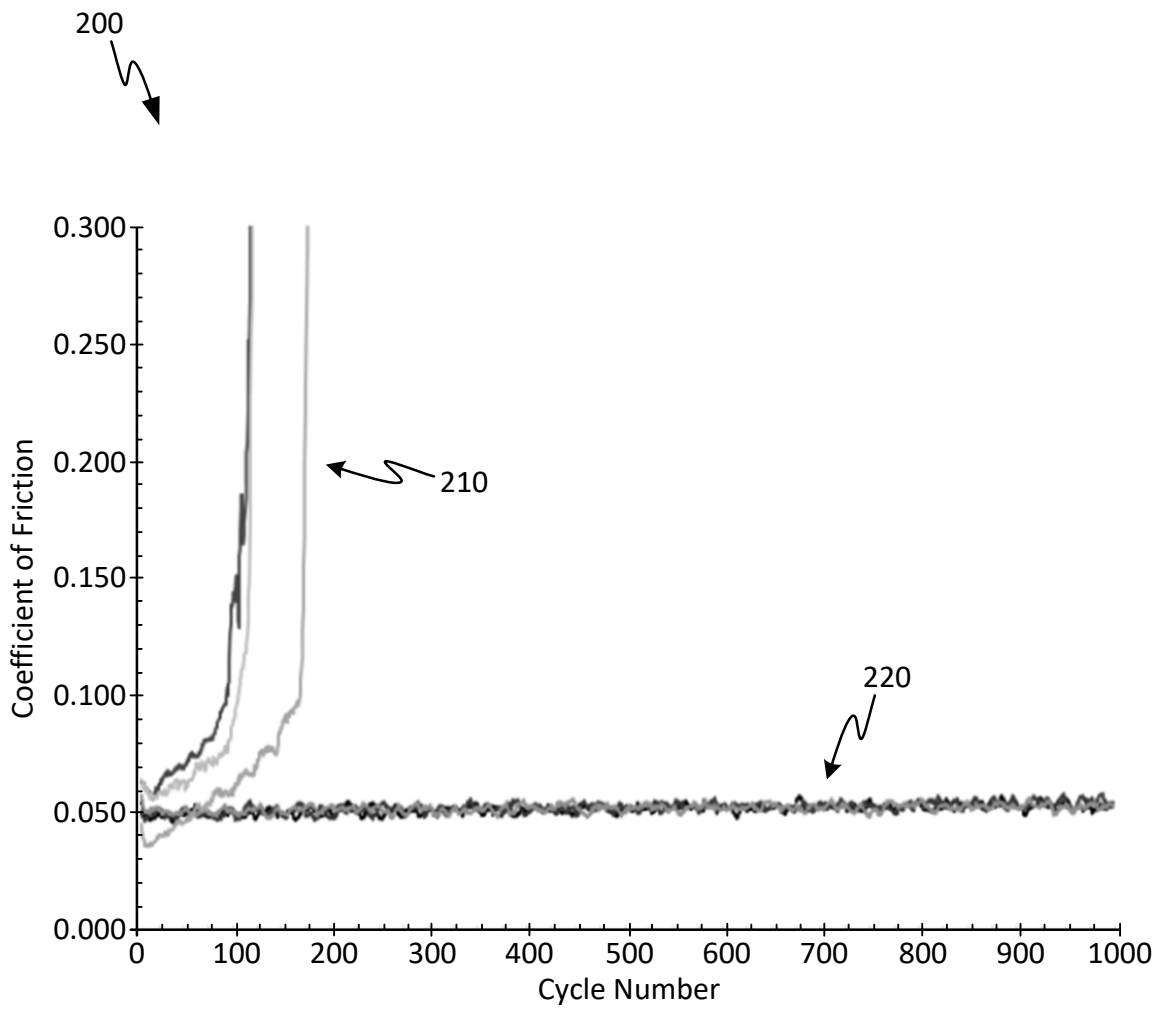


FIGURE 3

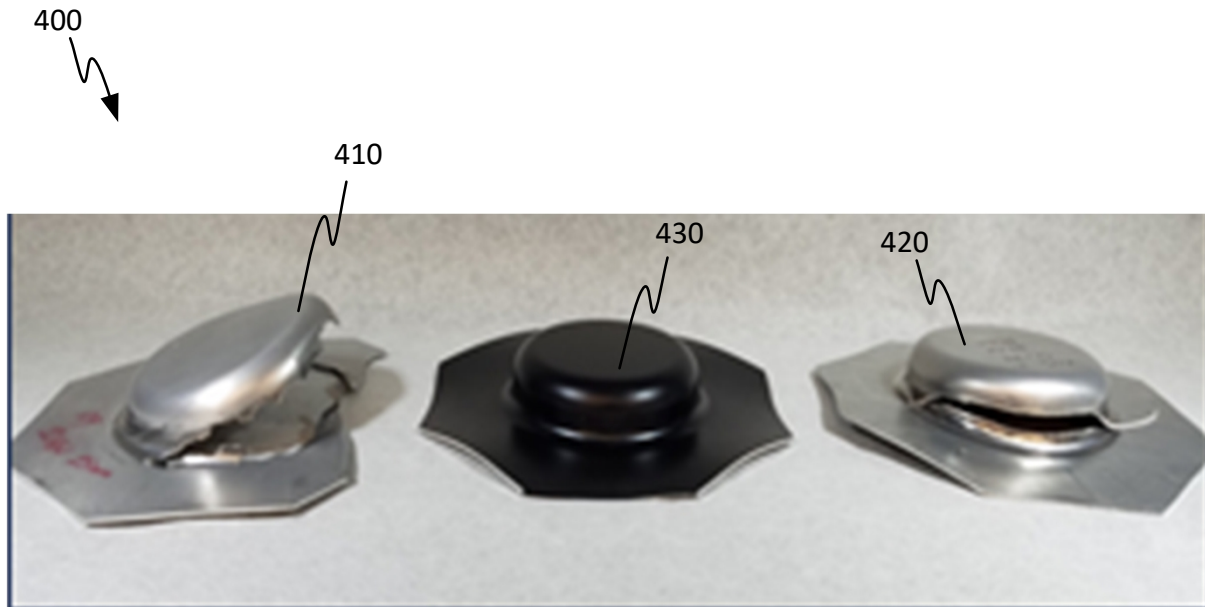


FIGURE 4

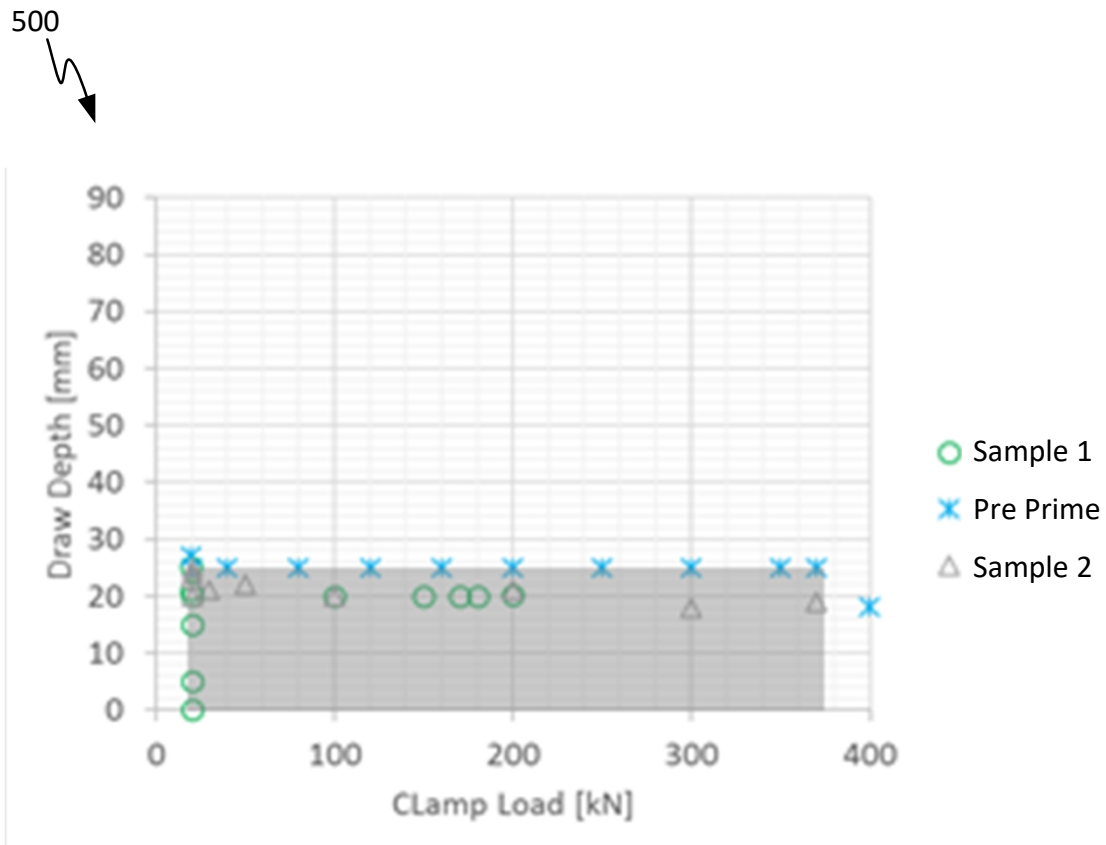


FIGURE 5

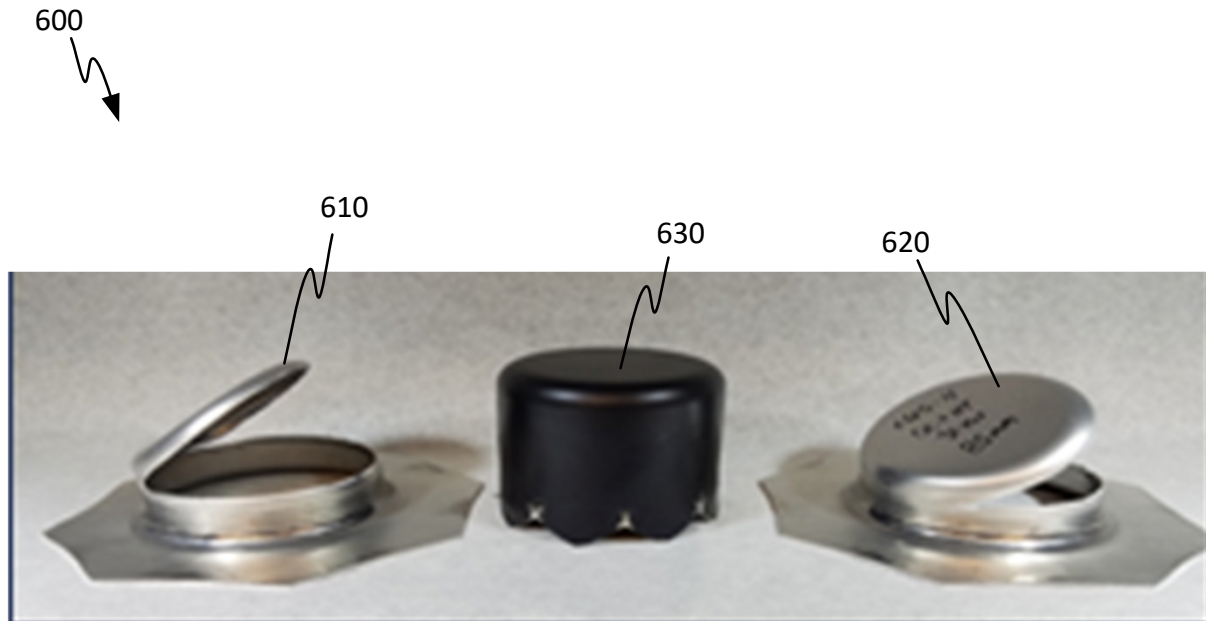


FIGURE 6

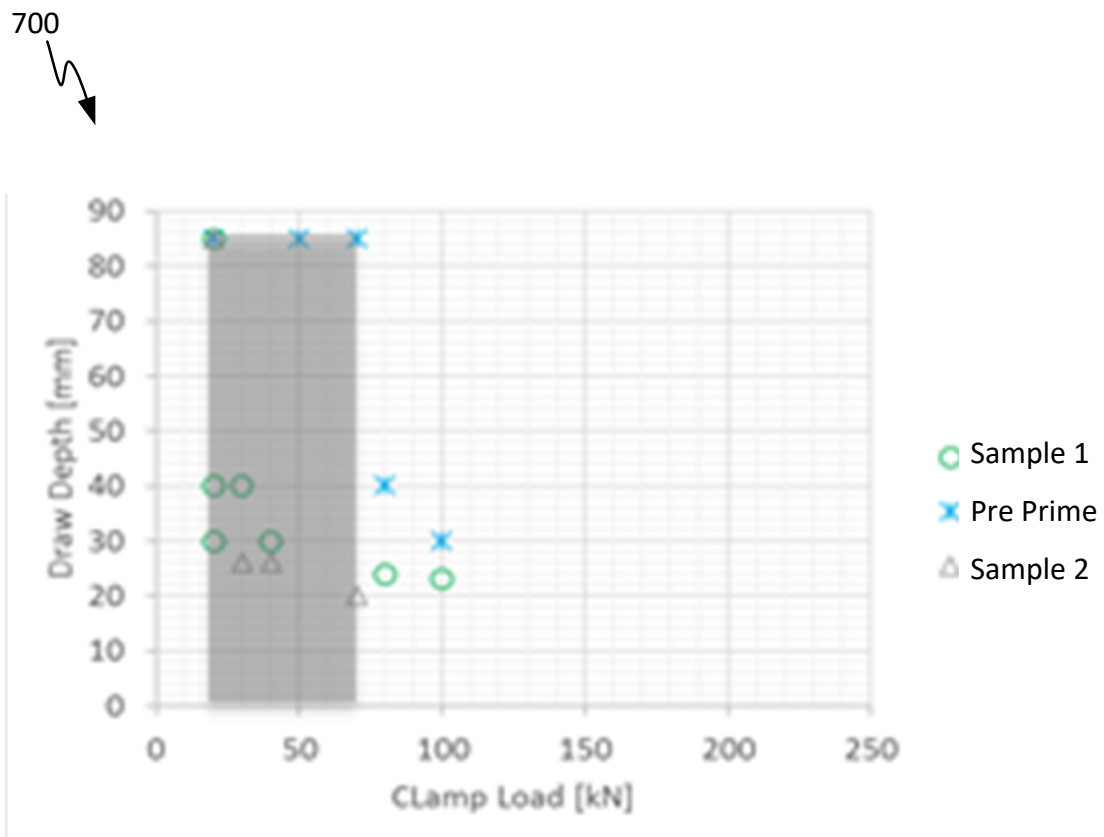
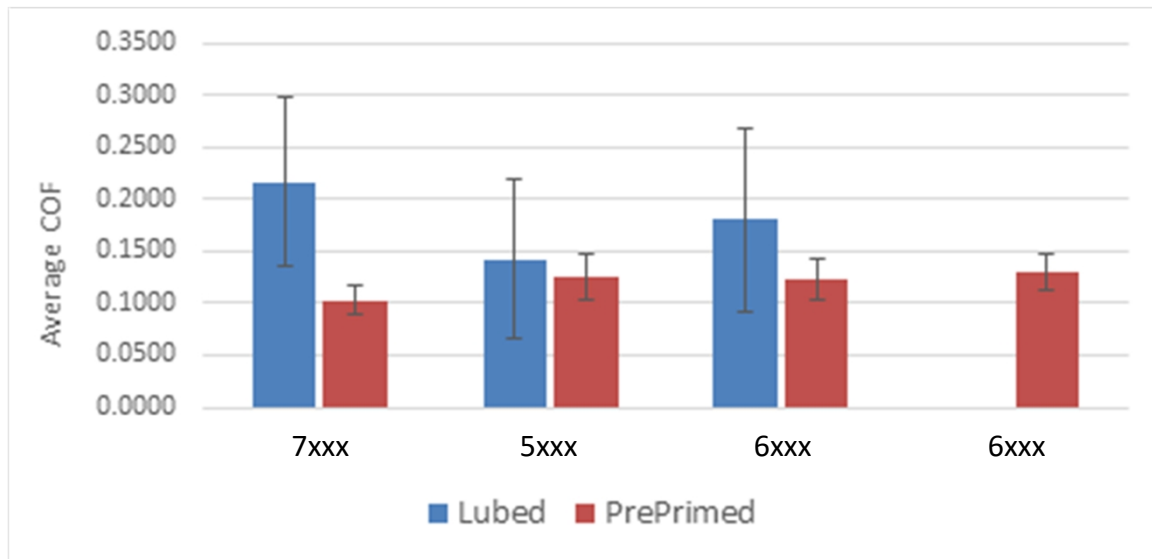


FIGURE 7



**FIGURE 8**