

under an inert, or preferably, a reducing atmosphere such as a  $H_2$ -containing atmosphere (preferably at least 1000 ppm  $H_2$ , in some embodiments 1 to 10%  $H_2$ ). Preheat under a reducing atmosphere was observed to produce superior oxide coatings with little or no spalling. It is believed that this control of preheat conditions results in superior coatings because it minimizes the formation of nickel oxide. Great care must be taken selecting a truly "inert" atmosphere because atmospheres conventionally considered as inert atmospheres yield inferior results. That is because nickel oxide can theoretically form even at  $10^{-10}$  atm oxygen and chromia at  $10^{-21}$  atm oxygen; such extreme levels of purity are not available in commercially available gases. Therefore, reducing atmospheres are preferred.

[0095] Conventional wisdom suggests that the higher the temperature, the faster the oxidation rate. Surprisingly, we discovered that the oxide grew faster at  $1000^\circ C.$  than at  $1050^\circ C.$  One possible explanation is that the high temperature oxide could be denser, thus discouraging faster growth. The lower temperature oxide could be more porous thus allowing faster oxide growth. On the other hand, too high a temperature will promote interdiffusion between the aluminide layer and the substrate, and the aluminide will disappear into the bulk of the alloy. Therefore, the thermally-grown oxide is preferably conducted in the temperature range of  $1000$  to  $1100^\circ C.$ , more preferably  $1025$ - $1075^\circ C.$  In the presence of excess oxygen, for example flowing air, the oxidation treatment is preferably conducted for 30 to 6000 min, more preferably 60 to 1500 min.

[0096] It should be recognized that the term "alumina" can be used to refer to a material containing aluminum oxides in the presence of additional metals. In the descriptions herein, unless specified, the term "alumina" encompasses substantially pure material ("consists essentially of alumina") and/or aluminum oxides containing modifiers.

[0097] Thinner layers are less prone to cracking; therefore, the thermally-grown oxide layer is preferably  $5 \mu m$  thick or less, more preferably  $1 \mu m$  thick or less, and in some embodiments  $0.1 \mu m$  to  $0.5 \mu m$  thick. In some preferred embodiments, the articles have an oxide thickness of a thermally grown scale of less than 10 micrometers, and in some embodiments an oxide thickness of a thermally grown scale in the range of about 1 to about 5 micrometers. In some embodiments, thicker oxide layers may be useful, such as for a higher surface area catalyst support. In some preferred embodiments, the articles have an oxide thickness of a washcoat of less than 10 micrometers, and in some embodiments an oxide thickness of a washcoat in the range of about 1 to about 5 micrometers. Typically, these thicknesses are measured with an optical or electron microscope. Generally, the thermally-grown oxide layer can be visually identified; the underlying aluminide layer is metallic in nature and contains no more than 5 wt % oxygen atoms; surface washcoat layers may be distinguished from the thermally-grown oxide by differences in density, porosity or crystal phase.

[0098] The aluminidized surface can be modified by the addition of alkaline earth elements (Be, Mg, Ca, Sr, Ba), rare earth elements (Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Th, Dy, Ho, Er, Tm, Yb, Lu) or combinations of these. The addition of these elements is followed by a reaction in an oxidizing atmosphere to form a mixed oxide scale. When the modi-

fying element is La, for example, the scale contains  $LaAlO_x$ , lanthanum aluminate. In some embodiments, a stabilized alumina surface can be formed by adding a rare earth element such as La, coated with a layer of alumina sol, then doped with an alkaline earth element such as Ca followed by a heat treatment.

[0099] La was demonstrated to be effective in improving the adhesion between the sol-alumina coating and the alumina scale. Inconel™ 617 substrate after aluminidization and heat treatment was coated with an aqueous solution of La nitrate, followed by drying and air calcination at  $1,000^\circ C.$  for 4 hr. It was then coated with sol-alumina and exposed to the corrosion testing environment at  $960^\circ C.$  for 1,000 hr. The sol-alumina coating survived well, with no visible signs of damage such as flaking or cracking. In contrast, similar testing with an Inconel™ 617 substrate after aluminidization and heat treatment and coated with sol-alumina without pretreatment with an aqueous solution of La nitrate, showed that most of the sol-alumina coating was lost after only 100 hr of testing, suggesting insufficient adhesion between the sol-alumina and the alpha-alumina scale on the aluminide.

[0100] The benefit of La as an adhesion promoter is believed to be associated with its reaction with the alpha alumina scale to change the surface to a more chemically active La aluminate. Surface X-ray diffraction (XRD) showed the formation of  $LaAlO_3$ . Without La addition, only alpha alumina and some background nickel aluminide could be detected by surface XRD.

[0101] Flow Rates

[0102] The aluminide layer is preferably formed by reacting a surface with a gaseous reactant mixture under dynamic flow conditions. The aluminum needed for aluminide formation can be deposited in a microchannel by flowing  $AlCl_3$  and  $H_2$  into a microchannel. In a multichannel device, the Al can be deposited only on selected channels (such as by plugging certain channels to exclude the aluminum precursors during a CVD treatment). The aluminum layer can also be applied onto selected portions of a microchannel device by controlling relative pressures. For example, in a microchannel device that contains at least two channels separated by a wall and in which the two channels are connected to each other via orifices in the wall,  $AlCl_3$  flows through a first channel while  $H_2$ , at a higher pressure, flows through a second channel and through the orifices into the first channel.

[0103] Static gas treatments can be conducted by filling the desired areas with the reactive gases with interim gas pumping if needed.

[0104] It has been found that excessively high flow rates can lead to uneven coatings. An example of this problem can be seen in FIG. 2.

[0105] Two flow metrics have been established for characterizing the extent of shear and jet impaction. For mechanical shear, the total wall shear stress (two tangential components and one normal component) has been selected as the relevant metric. Likewise dynamic pressure, which is equal to the momentum flux of the jet plume, has been chosen as a means of monitoring the effects jet impaction on coating formation.

[0106] Computational fluid dynamic (CFD) simulations of several device aluminidization tests were conducted to con-