mixture. In a related aspect, a catalyst or catalyst intermediate is formed on substrates having such a nickel aluminide surface. Of course, the invention also includes methods of making catalysts or microchannel apparatus comprising coating a substrate (preferably a Ni-based alloy) with chemically vapor deposited aluminum that is simultaneously and/or subsequently converted to an aluminide (such as NiAl).

[0067] A NiAl layer can be formed by exposing a Ni-based alloy to $AlCl_3$ and H_2 at high temperature, preferably at least 700° C., in some embodiments 900 to 1200° C. Aluminum is deposited at the surface as a result of the reaction between $AlCl_3$ and H_2. At temperature, Ni from the substrate would diffuse towards the surface and react with the aluminum to form a surface layer of nickel aluminide. The Ni source could be Ni in a Ni-based alloy substrate, an electrolytically plated Ni layer or a vapor deposited Ni layer that can be deposited over a substrate prior to aluminidization. It is believed that other metal aluminides (such as Co or Fe) could be formed under similar conditions.

[0068] Preferably, the aluminidization process is conducted with good control of flow to the device through a manifold. For example, good control can be obtained by passing flow into microchannels through a leak-free manifold. Preferably the aluminidization process is carried out at 100 Torr (2 pounds per square inch absolute, psia) to 1800 Torr (35 psia), more preferably between 400 Torr (8 psia) and 1300 Torr (25 psia).

[0069] In preferred embodiments, nickel aluminide contains 13 to 32% aluminum, more preferably to 32%; and still more preferably consists essentially of beta-NiAl. If Al falls significantly below the 13% weight % level of the gamma-prime phase, it may be expected to negatively affect the quality of the thermally-grown alumina scale.

[0070] In some embodiments, the metal aluminide layer has a thickness of 1 to 100 micrometers (μm); in some embodiments a thickness of 2 to 50 μm; and in some embodiments a thickness of 5 to 25 μm. In some embodiments, the aluminide layer is completely oxidized; however, this is generally not preferred.

[0071] The metal surface upon which the metal aluminide is formed is preferably substantially free of oxides. Optionally the surface can be cleaned, polished, or otherwise treated to remove such oxides if any are present.

[0072] A reactor can be formed by a catalyst that is disposed as a coating on an internal wall (where the walls can be simple walls or shaped walls). Alternatively, or in addition, inserts such as fins, plates, wires, meshes, or foams can be inserted within a channel. These inserts can provide additional surface area and effect flow characteristics. An aluminization process can be used to fix inserts onto a wall of a device (such as a reactor); the resulting aluminum layer (or aluminum oxide, or aluminum, or metal aluminide, or a mixture of these) fills some voids and greatly improves thermal conduction between the insert and device wall (such as reactor wall).

[0073] Effect of Oxide Presence During Aluminidization Process

[0074] An Inconel™ 617 coupon was heat treated in air at 400° C. for 1 hr to purposely grow some native oxide of chromia before being aluminized. A thin dotted line of inclusions in the aluminide is observed in the coupon with native oxide before aluminization. Such a line of inclusions could become a weak point in terms of adhesion.

[0075] In early attempts at the aluminidization of a multichannel device, it was discovered that the channels nearest the gas inlet (that is, the inlet for the aluminum compounds) showed the most inclusions while the channels furthest away showed the least. This is believed to have been caused by surface oxides in the tubing or manifolding in the pathway of the aluminum compounds prior to the microchannels. The presence of surface oxide in the tubing was confirmed by EDS. To avoid these defects, care should be taken to avoid the use of components that have surface oxides in the aluminidization process, especially surface oxides along the fluid pathway (that is, the pathway carrying aluminum compounds) leading to a microchannel device. In some preferred techniques, the tubing and/or other fluid pathways are subjected to a treatment to remove surface oxides (brightened), such as by a hydrogen treatment. Of course, before aluminidization, the microchannels may also be subjected to a treatment for the removal of surface oxide.

[0076] In preferred embodiments, the aluminide layer and the interfaces of the aluminide layer with the alloy substrate and an oxide layer (if present) is preferably substantially without voids or inclusions that are larger than 10 μm, more preferably substantially without voids or inclusions that are larger than 3 μm. "Substantially without voids or inclusions" excludes coatings having numerous (that is, more than about 5 large or a single very large) defects in 50 μm of length along a channel, but wouldn't exclude a structure that shows a small number of isolated defects.

[0077] Thermally Grown Oxide

[0078] A metal aluminide layer or more preferably a NiAl layer, can be heated in the presence of oxygen or other oxidizing gas to grow a layer of aluminum oxide. It was surprisingly discovered that when the surface was heated to the treatment temperature in the absence of O_2 or other oxidizing gas prior to the oxide growth at temperature, a significantly improved oxide coating resulted. The oxide layer grown by heating the surface to the treatment temperature in the presence of oxygen exhibited spalling while the layer grown by heating the surface from ambient temperature to the treatment temperature in the absence of oxygen did not. Oxygen can be substantially excluded from the heat up step of the heat treatment process.

[0079] A convenient and preferred method of excluding oxygen from the surface while heating the surface from ambient temperature to treatment temperature involves exposure to hydrogen. The hydrogen effectively reduces the oxidizing power of the atmosphere during heat up to prevent premature growth of the oxide scale. Other gases that reduce the oxidizing power of the gas, such as NH3, CO, CH4, hydrocarbons, or the like, or some combination of these could also be used. These gases could be used in combination with inert gases, such as N2, Ar, He, Ne, or combinations of these.

[0080] The oxide layer is formed by exposing the surface to an oxidizing atmosphere at the treatment temperature. The oxidizing gas could be air, diluted air, oxygen, CO_2, steam, NOx or any mixture of these gases or other gases that have substantial oxidizing power. The temperature of oxide