

Chapter 1 : Diffusion and surface alloying of gradient nanostructured metals

Diffusion Alloys was the first company world-wide to launch (in the s) chromising as a commercial industrial diffusion coating process. Properties and Uses of Chromising (Chromizing) Chromising, or chromising, can protect components from corrosion, wear, abrasion and oxidation.

The diffusion behavior in GNS metals is crucial for understanding the diffusion mechanism and relative characteristics of different interfaces that provide fundamental understanding for advancing the traditional surface alloying processes. In this paper, atomic diffusion, reactive diffusion, and surface alloying processes are reviewed for various metals with a preformed GNS surface layer. We emphasize the promoted atomic diffusion and reactive diffusion in the GNS surface layer that are related to a higher interfacial energy state with respect to those in relaxed coarse-grained samples. Accordingly, different surface alloying processes, such as nitriding and chromizing, have been modified significantly, and some diffusion-related properties have been enhanced. Finally, the perspectives on current research in this field are discussed. This architecture with a graded spatial variation of grain sizes offers a number of unique opportunities to enhance the properties of materials. It enables the delocalization of strains in the nano-grained structures, resulting in plastic deformation behavior fundamentally different from that of the free-standing homogeneous nano-grained and CG samples. For example, a considerable tensile ductility was achieved with the significantly enhanced strength in different metals with a gradient nanostructured GNS layer [], distinct from the traditional trade-offs between strength and ductility in conventional metals and alloys. In addition, GNS materials exhibit significantly enhanced wear resistance and fatigue resistance compared with their nano-grained and CG counterparts []. Investigating the diffusion behavior of GNS materials is an important topic mostly due to the following reasons: Numerous interfaces in the nanostructured layer make it possible to study interfacial diffusion and relative characteristics, such as interfacial structure, precipitation, phase transformation, plastic deformation, and chemical reaction, at lower temperatures. In comparison, it is difficult to obtain enough information on these aspects " particularly on the C-type diffusion regime as laid out in [8] " because of an insufficient number of interfaces in CG materials. A graded variation of interface types may accompany the graded distribution of grain sizes in a GNS layer. Such a microstructure provides a unique sample to study the effects of grain size and interface type on diffusion properties. Atomic diffusion is the essential factor in surface alloying processes such as nitriding and chromizing , and diffusion studies in GNS materials provide insights for modifying traditional surface alloying processes of engineering metallic materials. GNSs have been generated on various metals by methods with controlled surface plastic deformation []. In this paper, recent progress in the diffusion studies in GNS metals will be clarified to understand diffusion fundamentals and relationships between microstructure and diffusion in nanostructured materials, followed by some typical applications of GNS on advancing traditional surface alloying processes. Since then, studies have been performed to reveal the diffusion behavior of nanostructured metals worldwide. However, the measured results were rather scattered and even controversial. For instance, markedly promoted diffusion coefficients with a lower activation enthalpy were measured in the nanostructured Cu synthesized by IGC []. Moreover, interfacial diffusion coefficients in an Fe₃Si nanocomposite produced by crystallization CRY from a melt-spun amorphous sample were revealed to be even lower in comparison with those in the CG sample [18]. Particular attention has been paid to the diffusion behavior in nanostructured or ultrafine grained UFG materials produced by using severe plastic deformation SPD , mostly because of the bulk forms of nanostructures. Inconsistencies also exist in the experimental results. However, Kolobov et al. In this case, GBs might gather a large number of irregular extrinsic dislocation structures, so that extra free energy might be introduced in the interfaces, while misorientations across them remain stable [22,23]. In addition, the higher energy of nonequilibrium GBs as compared to conventional GBs has been demonstrated by the transformation of partial to complete GB wetting in Sn" Pb alloys during continuous strain by Straumal et al. However, this notion was confused by two works in the SPD Cu and Cu" Pb alloy [26,27] , in which various defects such as vacancy agglomerations, nanometer- and micrometer-sized voids were observed. These defects might be

linked and significantly accelerate atomic penetration in the materials. These microstructures characteristics provided unique opportunities to study the relationship between the diffusion property and microstructure into the nanometer scale. The diffusion studies in these materials will be reviewed and compared with results from other nanostructured metals in this section. In terms of the diffusion kinetics with Arrhenius dependence in the concerned temperature range, the pre-exponential factor and the activation enthalpy of Cr diffusion in the nanostructured Fe were calculated. Figure reproduced with permission from [31] , copyright Elsevier. The ratio of the value into the as-SMAT sample relative to the value into the CG sample decreased with elevating temperatures. Meanwhile, it was noticed that an isothermal preannealing might decrease the Cr-diffusion depth. Variations of Cr-diffusion depth with temperature in different low carbon steel samples: Figure reproduced with permission from [32] , copyright Elsevier. The results show that DGNS is about 8. The diffusivity increment is typically within $\hat{\epsilon}$ in nanostructured metals produced via the IGC or BMS techniques. Meanwhile, the interfacial diffusivities in nanostructured metals in the as-prepared states decrease significantly after preannealing treatments during which GBs may be relaxed, especially when evident grain growth has occurred. Additionally, no dependence on the preparation method or grain size is indicated. Therefore, the contribution from triple junctions, of which the amount increases with decreased grain size and the diffusivity should be further enhanced due to the larger excess volume [31,37] , might be insignificant within the present grain size scale. Diffusion studies in nanostructured metals prepared by different techniques.

Chapter 2 : Diffusion coating and products therefrom - Alloy Surfaces Company, Inc.

The results of an extensive study of the mechanism of formation of chromium diffusion coatings on ferrous alloys are described. The effects of the significant coating variables on the composition, thickness and microstructure of the coatings are discussed.

The paper presents the application of multitracer method of diffusion measurement in Cr-Mn steels. Two austenitic steels were investigated: The serial sectioning technique was used for simultaneous evaluation of diffusion coefficients of radioisotopes of chromium ^{51}Cr , manganese ^{54}Mn and iron ^{59}Fe at K and K. Diffusion coefficients of radiotracers at K were calculated on the basis of both: Moreover it was found that at K the diffusion rate of manganese is higher than that for iron and chromium while at K diffusion rates of chromium and manganese are comparable and higher than that for iron. Diffusion couples were annealed in an evacuated quartz ampoule at K for 90 and ks. A NH radical, which has played a key role to produce a nitrogen diffusion layer without the formation of the brittle compound layer, has been generated in a gas mixture of NH_3 and H_2 . One of the main advantages of the plasma radical nitriding is to improve the surface hardness by maintaining the roughness of the initial polished surface. The microstructures and material properties of the radical nitrided layer have been characterized in order to investigate the effects of various radical nitriding processing parameters. The hardness and surface roughness of the hardened layer were compared between two processes. In addition, PVD CrN coating has been deposited on both the radical nitrided substrates and conventional nitrided substrates by an arc ion plating AIP technique. The effect of two different of plasma nitriding treatments on the adhesive strength of the coating layer on the substrates was also investigated. Using plasma alloying technique, Q steel was firstly treated by W-Mo-Y Multi-elements co-diffusion followed by plasma nitriding process. And then the wear tests were conducted. The effects of technological parameters on alloying layer were studied. The structure, composition, phase and micro-hardness of alloying layer were analyzed by metalloscope, XRD, SEM and microhardness tester. Results show that the microstructure of W-Mo-Y Co-diffusion layer is columnar crystal; W, Mo contents decrease from the outside to the inside. The element Y is distributed mainly at the grain boundaries. After plasma nitriding process, the co-diffusion layer is strengthened and large amount of nitrides form and dispersedly distribute in the alloying layer. Compared with untreated samples, the wear resistance of alloying layer is improved by 2 times under abrasive wear conditions. Diffusion treatments of TiAl-based alloys The influence of the diffusion condition for the formation of intermetallic phases in the coating has been investigated. In the initial stage of diffusion treatment, TiAl_3 was formed on the outermost surface by the diffusion between liquid aluminum and the substrate. The maximum thickness of TiAl_3 during the initial stage increases as the diffusion temperature decreases.

Chapter 3 : What is Chromizing? - Definition from Corrosionpedia

The diffusion of aluminium into the surface of materials to increase the corrosion resistance of steels and other alloys has been carried out since the first patent by Tyco Van Aller in

This application is a continuation-in-part of application Ser. The process of diffusion coating a workpiece with chromium and then with aluminum, which process is characterized by loading the workpiece in a diffusion coating retort, then subjecting the retort to a diffusion-coating heat while introducing into it a chromizing vapor to cause the vapor to contact and chromize the workpiece, then without removing the workpiece, introducing into the retort an aluminizing powder pack to cause it to contact the workpiece, and then bringing the retort to diffusion aluminizing temperature to cause the chromized workpiece to be aluminized by said pack before the workpiece is removed from the retort. The combination of claim 1 in which the workpiece is a carbon steel that has its surface decarburized before the chromizing. The combination of claim 2 in which the decarburizing is effected in the retort and the workpiece is not removed from the retort between the decarburizing and the chromizing. The present invention relates to the coating of metals to increase their resistance to corrosion and other chemical attacks. Among the objects of the present invention is the provision of novel coating techniques and compositions for use therewith, as well as novel coated products, all suitable for commercial operations. Additional objects of the present invention include compositions and techniques for confining protective diffusion coatings to desired locations on workpieces such as jet engine components to be protected by the coatings. The foregoing as well as further objects of the present invention will be more fully understood from the following description of several of its exemplifications. According to one aspect of the present invention a ferrous metal such as in the compressor section of a turbine engine is very effectively protected against attack by a coating combination having as a first layer a baked mixture weighing between about 0. The flakes of aluminum very quickly spread over the surface to which they are applied as a dispersion in a liquid, and thus cover the entire surface in a very effective and thorough way. This is an important factor in providing the protection of the present invention. Interchanging the two layers so that the flake aluminum layer is against the surface of the substrate metal and the magnesium-phosphoric-chromic mixture overlies the flake aluminum layers also produces very good results. Such combinations with the layers in either order, or similar combinations in which all the coating ingredients are in one layer, are substantially more effective than the similar multi-layer combinations described in Ser. In some cases such diffusion aluminizing is best masked off from undesired portions of the surface of the workpiece being coated. Such masking problems arise more frequently with the superalloy components in the hot section of a turbine engine, where aluminizing and chromizing is widely practiced. Chromizing also increases dimensions. Turning now to a more detailed description of the present invention, the following is an example of a very effective flake-aluminum type coating combination typical of the present invention. Mg H₂ PO₄ 2 g. There was then sprayed over the thus-coated rotor, a dispersion of flake aluminum to form a layer about 0. The resulting product shows excellent resistance to corrosion when operated in a jet engine in salty marine atmosphere. The flake aluminum is easier to disperse in the water in a high concentration when the dispersion contains a little polyglycol as well as some dispersing agent, as described in U. These additives are driven off by the firing treatment. The adhesion of the flake aluminum coating and the corrosion resistance of the workpiece are increased when the dispersion of the flake aluminum contains some hexavalent chromium compound such as magnesium chromate, magnesium dichromate, chromic acid, ammonium chromate or ammonium dichromate. The final firing operation converts the magnesium chromate to water-insoluble material in addition to driving off any polyglycol and dispersing agent present in the aluminum dispersion. Repeating Example 1 but with the aluminum flake layer applied as a first coating and the magnesium-chromic-phosphoric layer as a top coating also gives very good results but care is needed to apply the top coating without disturbing the aluminum flakes in the first coating layer. It is preferred to include the magnesium chromate in the aluminum flake layer to better anchor those flakes when that layer is baked. Alternatively the aluminum flake layer can only be lightly baked so that the glycol dispersing aid is not completely driven off and helps hold the flake in place. It is also

helpful after the aluminum flake layer is baked, to apply over it a very thin stratum of porous filler such as fine alumina or silica particles, before the top layer is applied, as in the following example. Flake aluminum 12 g. Polyethylene glycol mixture ranging from penta- through hepta-ethylene glycol and having average molecular weight of 13 g. Para iso-nonyl phenyl ether of dodecaethylene glycol 1 g. Water to make cc. Over the resulting coating there was then sprayed an aqueous dispersion of colloidal alumina particles about 5 millimicrons in size to deposit a film weighing about 0. These blades have better corrosion resistance than those coated in Example 1. Colloidal silica can be substituted for the colloidal alumina without materially affecting the results. The colloidal film should weigh between about 0. When the pH of the colloidal layer is above 7 it is helpful to bring it down to below 7. The coating recipe of Example 2 also gives excellent results when applied to compressor blades made of titanium or titanium-base alloys. Indeed for coating such alloys the layer of flake aluminum can be omitted, along with the $MgCrO_4$ used to help anchor that aluminum. The resulting combination of colloidal silica or alumina layer, plus the top CrO_3 -- $MgCr_2 O_7$ -- $Mg H_2 PO_4 2$ layer provides very effective protection and is better than a single layer having the colloid particles included in the coating mixture from which the top layer is applied. It is helpful however to incorporate a little polytetrafluoroethylene in the top coating as described in U. On the other hand the aluminum flake layer by itself, with or without the $MgCrO_4$, is more adherent to the metal substrate particularly when the substrate is to be flexed. This protection includes galvanic action, as shown by the failure of rust to appear in scribed lines cut through the coating of the coated sheet, after the scribed sheet is exposed to salt spray for an extended period. Two or more layers of the leafing aluminum-hexavalent chromium compound can be applied with or without intervening bakes. In general the total build-up whether a single layer or multiple layers, should be from about 0. Prepared mixtures of this type are suitable for protecting jet engine compressor parts made of ferrous metal such as martensitic stainless steels, as well as protecting plain carbon and low alloy steels. Such coatings sometimes become scratched or marred in a localized area, and an aqueous dispersion of flake aluminum such as those described above, whether or not they contain dissolved magnesium chromate, or a mixture of magnesium chromate and phosphoric acid, can be readily brushed over the scratched or marred section, and permitted to dry. The touched-up portion then has the same aluminum flake appearance as the undamaged coating, and if the touch-up is confined to small areas the resulting corrosion resistance is not significantly different from that of an undamaged coating. This touch-up technique can be used on aluminum flake coatings deposited from mixtures with a hexavalent chromium compound like $MgCrO_4$, or from mixtures that contain magnesium chromate and phosphate as in Example 1. A layer of flake aluminum with $MgCrO_4$ is also very effective for providing a mirror surface on sheets of glass or silica or the like. Such a mirror surface is particularly brilliant when observed through the sheet which carries the layer. Mirrors of this type can be for example on Vycor-type glass tubes or the like used as sheaths for electric resistance heaters. The Vycor-type glass, being essentially silica remaining after the leaching of all other ingredients from glass, is itself resistant to high temperatures, and in use bakes the $MgCrO_4$ into water-insoluble condition. An aluminum substrate is also very effectively protected by the magnesium chromate formulations. In addition protective resins can be incorporated in such formulations to further increase the protection, as in U. The following is a good exemplification. **EXAMPLE 3** A hard aluminum compressor impeller for a jet helicopter engine, was cleaned and then sprayed with an emulsion of a hard polymeric methyl methacrylate resin in a dispersion of flake aluminum in aqueous magnesium dichromate. The recipe for the spray was: The thus coated impeller showed almost no attack after two weeks exposure to a salt spray, so that it was many times more resistant than the untreated impeller. Moreover whatever corrosion products form in use on the coated impeller of the present invention, are only loosely held, and they are easily brushed off, without disassembling the engine. The impeller is generally the sole compressor impeller in such a small engine, whether the engine is used in a helicopter or as a stationary power source, and it can be reached with a cleaning brush inserted through the air intake. It can have the structure shown in U. The $MgCr_2 O_7$ -resin coating layer can vary in thickness from about 0. The proportion of resin to $MgCr_2 O_7$ by weight, can vary from about 1: The following example demonstrates a very effective chromizing combined with a masked aluminizing. **EXAMPLE 4** A batch of first stage PWA blades for the hot section of a jet engine are cleaned by degreasing in

trichloroethylene and then lightly blasting with grit alumina propelled by an air jet at 30 psig. The packed retort was then covered by an outer retort as described and illustrated in U. The atmosphere in the outer retort is displaced by a stream of argon introduced through an inlet conduit opening near the bottom of the interior of the outer retort and exited through an outlet conduit opening near the top of the interior of the outer retort. Heating of the retort is initiated and the flow of argon maintained through the entire heat at a rate that assure essentially no entrance of air or moisture into the interior of the retorts. Where the outer retort has no leaks, an argon flow of about 5 standard cubic feet per hour is adequate. The blades have a very good chromized case 0. The foregoing chromizing pack is used without a break-in heat, and has so little metal content that it can be discarded after a single use. If desired, its metal content can be salvaged as by pouring a stream of the used pack through a horizontally moving air stream which deflects away the lighter particles permitting the metal particles to be collected. The pack of Example 4 can be modified by incorporating in it about 0. Chromized cases produced by a pack so modified have even less undesirable oxide visible on metallographic examination, and are of particularly high quality. In general the pack of Example 4 can have a chromium content of from about 0. The argon atmosphere of that example can be replaced in whole or in part by helium, neon or other inert gas or mixtures thereof. Other inert diluents like kaolin can be substituted for the alumina in its pack. The masked blades are then embedded in the following powder pack, the percentages being by weight: The most elaborate masking arrangement of the present invention uses a three-layer masking combination in which the workpiece-contacting layer is of the essentially inert type, the next layer of the depletion-preventing type, and the outermost layer of the sheath-forming type. Nickel aluminides present in any masking layer other than a sheath-forming layer, should have no more than about 3 atoms of aluminum for every four atoms of nickel. To make the masking layers easier to apply, it is helpful to add to the resin solution a little long-chain-hydrocarbon acid such as stearic acid that helps keep the particles of the masking composition dispersed in the volatilizable organic solvent in which they are suspended. As little as about 0. However dispersing aid concentrations of at least about 0. Hydrocarbon chain lengths as short as 12 carbons and as long as 50 carbons or more are suitable for the dispersing aid. Thus lauric acid, myristic acid, oleic acid, and even copolymers of ethylene and acrylic acid, are effective. The dispersing aid should also be soluble in the solvent in which the masking composition is suspended, and hydrocarbon type solvents including halogenated hydrocarbons give best results. The effectiveness of the dispersing aid is increased by also dissolving in the suspension a small amount of a surface-active agent, preferably a low-forming non-ionic surface-active agent such as polyethoxy ether of a linear primary alcohol like cetyl alcohol, or of an alkyl phenol. It should be noted in this connection that the surface-active agent when added without the long-chain-hydrocarbon acid, has substantially no effect on the masking suspension. The masking compositions of the present invention can be used to prevent chromizing or to prevent aluminizing. That layer can also weigh as much as about 2 grams per square centimeter, and can be composed of inert materials such as alumina, kaolin or MgO. Sheath formation seems to be caused by the sintering together of the nickel particles in the outer masking layer, under the influence of the diffusion atmosphere which causes diffusing metal to diffuse into the nickel of these particles. These particles thus grow in size. The Cr₂O₃ particles appear to form some chromium metal that becomes aluminized and sinters to a sheath. Sheath formation can also be effected by adding to the sheath-forming layer a metal powder like aluminum the particles of which sinter to the nickel particles. Excessive addition is to be avoided to keep the added metal from contaminating the workpiece. Thus an aluminum addition of this type should contribute no more than about one atom of aluminum for every atom of nickel. As little as one one-hundredth of that proportion of aluminum helps the sheath formation, particularly where only a light diffusion is being performed. The sheath-forming layer can be used to lock masking mixtures about a workpiece surface by partially or completely enveloping that surface.

Chapter 4 : Services | ATC-CES

Sudhangshu Bose, in High Temperature Coatings, Chromium-Modified Aluminide Coating for Ni Base Alloys. Chromizing or chromizing followed by aluminiding of high-temperature alloys is used to improve resistance to hot

corrosion and high-temperature oxidation (Sivakumar, ; Streiff and Boone,).

Chapter 5 : USA - Methods of chromizing molybdenum tungsten and their alloys - Google Patents

Diffusion Alloys Limited provides diffusion coating services for industrial gas turbine components, oil and gas, and process industries. The company offers aluminide diffusion coatings for.

Chapter 6 : What is Chromadizing? - Definition from Corrosionpedia

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Chapter 7 : Diffusion Carbide Layers Produced on Tool Steel in Chromium Chloride Atmosphere at Low Pr

Chromizing is a type of metallurgical process that involves diffusion of a single or several elements within a base material. The process is mainly composed of saturating through diffusion of predominantly steel or ferrous alloys with chromium.