Fundamentals : Phase Relationships and Microstructures

Nitrogen in iron and steel

V. G. GAVRILJUK

A short review of beneficial effects of nitrogen in steel is given including mechanical and corrosion properties, and the data of interatomic interactions and distribution of solute atoms in solid solutions are discussed with the aim of explanation of the physical nature of nitrogen steels. The concept is presented according to which alloying by nitrogen enhances the metallic component of interatomic bonds and provides more homogeneous distribution of substitutional solutes through short range ordering of nitrogen atoms and strong chemical interaction between nitrogen and alloying elements, which results in the high thermodynamical stability of nitrogen austenitic steels. The opposite tendency to clustering and concentration inhomogeneity of austenitic steels due to carbon is shown. Inheritance of the atomic distribution by martensite is discussed in terms of short range atomic order and data on crystal structure of precipitations during tempering of nitrogen martensite are presented as compared to carbon and carbon + nitrogen martensites.

Nitrogen addition to bcc-Fe

J. C. RAWERS et al.

High pressure melting was used to increase the nitrogen concentration in iron-carbon alloys. Nitrogen concentration in the alloys followed Sieverts' law. Increasing the carbon concentration decreased the nitrogen concentration. Alloy concentrations above approximately 0.5 wt% nitrogen and carbon resulted in stabilizing the austenitic phase and eliminated the formation of nitrides and carbides.

Prediction of the solubility of nitrogen in molten duplex stainless steel

D. R. ANSON et al.

The influence of temperature and effects of alloying elements on the solubility of nitrogen in pure iron and iron alloys have been investigated in a pure nitrogen gas atmosphere. Both decrease in temperature and additions of Cr, Mn and Mo are found to increase the solubility of nitrogen in Fe-Cr alloys, whilst increase in temperature and additions of Ni and C are found to decrease the solubility of nitrogen.

The first and second order interaction parameters e^j_{NFe} and r^j_{NFe} have been calculated, with reference to the infinitely dilute solution of nitrogen in liquid pure iron, giving good agreement with the recent results of other workers.

A more relevant reference state to the duplex phase field has been selected to be an Fe-20Cr alloy and further interaction parameters, $e^j_{NFe20Cr}$, measured. Equations have been derived for the prediction of nitrogen solubility in molten duplex stainless steels containing 20-30 mass % Cr, which obey Sieverts law at pressures of nitrogen up to 1 atm.

$$\log\%N^{alloy}_{T,P_{N_2}} = \log\sqrt{P_{N_2}} + \log\%N^{Fe20Cr}_{T,P_{N_2}} - \log f^{alloy}_{T,P_{N_2}}$$

where

$$\log f^{alloy}_{T,P_{N_2}} = \left[e^{Cr}_{NFe20Cr} \times (\%Cr - 20) + \sum_{j=1, j \neq Cr}^{n} e^j_{NFe20Cr} \times \%j \right]_{T,P_{N_2}}$$

Where values of $e^j_{NFe20Cr}$ are given in the text and are applicable between 1 550 and 1 650°C.

Features of surface nitriding revealed by Mössbauer spectroscopy

C. CORDIER-ROBERT et al.

Two different nitriding surface treatments of austenitic stainless steel have been studied: gaseous nitriding in a NH_3-H_2 mixture performed at temperatures between 700 and 900°C and nitrogen ion implantation with different dose rates between 5×10^{16} to 1.5×10^{17} N_2^+ions cm^{-2} and different current densities between 1 to 5 $\mu A\ cm^{-2}$. The microstructure of the coating was studied by X ray diffraction and Mössbauer spectroscopy. The discussion emphasizes the role of thermodynamical equilibrium conditions at higt temperatures and of the process parameters at low temperatures on the hases which constitute the layer.

Atom-probe-and X-ray diffraction analysis of the composition and structure of precipitates formed on tempering of ternary iron-carbon-nitrogen martensites

A. J. BÖTTGER et al.

X-ray diffraction analysis showed that both α''-type precipitates (as in Fe-N) and ε/η-type precipitates (as in Fe-C) develop in ternary Fe-C-N martensite upon tempering below 450 K. Atom-probe analysis was used to study the distribution of the interstitial atoms on a local scale. Most of the enriched regions formed after tempering contain both nitrogen and carbon atoms, but in an enriched region one type of interstitial is dominant. The carbon-rich regions contain a significantly larger amount of total interstitial atoms than the nitrogen-rich regions. The total interstitial amounts are close to that in ε/η for the carbon-rich regions and close of that in α'' for the nitrogen-rich regions. This suggests that upon tempering Fe-C-N martensite nitrogen atoms reside preferentially in an α''-type structure and carbon atoms reside preferentially in an ε/η-type structure, but that coprecipitation of nitrogen and carbon atoms occurs to a limited extent as well.

Precipitation behaviour and stability of nitrides in high nitrogen martensitic 9% and 12% chromium steels

A. GOECMEN et al.

Precipitation behaviour and stability of nitrides has been investigated in two high nitrogen, high vanadium containing martensitic 9-12% chromium steels under different heat treatment conditions. Microstructural evolution during the heat treatments was studied by hardness measurements, optical microscopy, transmission electron microscopy and energy dispersive X-ray analysis.

Nitrides with f.c.c. structure were found to precipitate very uniformly and densely during aging in the austenite (ausaging) as well as during aging in the ferrite (tempering) at temperatures between 823 and 973K. Microstructural evolution during tempering was influenced by precipitation of the nitrides in the austenite prior to the martensitic transformation. It is shown that the hardness of martensite and tempered martensite depend strongly on the size and distribution of nitrides. Niobium is dissolved in primary vanadium nitrides. Dissolution and reprecipitation of these nitrides in the austenite was found to be influenced by the presence of niobium. Ausaging treatment of a niobium containing alloy at 898K has a more significant effect on the martensite hardness than a niobium free alloy.

The stability of dense precipitation states produced in the austenite prior to the martensitic transformation is discussed in terms of the development of non uniform precipitation states during tempering of the martensite. The uniformity of the precipitation states is stabilized by a pre-overaging treatment in the austenite. It is shown for a martensitic 12% chromium alloy, that a pre-ausaging treatment retards the formation of the rapid coarsening hexagonal chromium nitride which dissolves a high amount of vanadium during tempering at 973K. As a result the tempering resistance becomes improved by maintaining an increased density of face centered cubic nitrides precipitated in the austenite.

Corrosion, Oxidation and Corrosion Resisting Steels

The role of nitrogen in the corrosion of iron and steels (Review)

H. J. GRABKE

The beneficial effect of nitrogen in steels in resistance against localized corrosion, pitting and crevice corrosion is well proven, but not yet fully understood. The results on dissolution of nitrogen steels in acids are controversial, but the dissolution of Fe-N alloys is enhanced compared to pure iron. Many surface analytical studies have been conducted in the recent years to find out about the state of nitrogen, and mainly the presence of $N^{\delta-}$ in the metal surface and NH_3 or NH_4^+ in the passive layer are well established, and moreover, NH_4^+ is the species transferred into the electrolyte in a wide range of potentials. Formation of NH_4^+ will somewhat buffer the acidification in pits. The possible role of N in the steps of pitting, initiation, growth and possible repassivation are discussed, and most important appears the favourable effect on passivation, and repassivation, which is effective also for Fe-N alloys. Many authors assume formation of stable Cr-and Mo-nitrides in the steel surface upon dissolution, and retardation of pit growth by these nitrides, however, this mechanism would not apply for Fe-N alloys.

Desorption of the aggressive anions induced by the segregated $N^{\delta-}$ just after the local failure of the passive layer is proposed to be the mechanism by which nitrogen favours the rapid repassivation of pits.

In-situ observation of dynamic reacting species at pit precursors of nitrogen-bearing austenitic stainless steels

T. Misawa et al.

Anodic steady state polarization and potentiodynamic polarization studies were carried out for nitrogen-bearing austenitic stainless steels in 0.6 kmol. m^{-3} NaCl solution at room temperature. The pitting potential measurement indicated that the pitting resistance increased with increase in nitrogen addition. In-situ distribution and imaging of H^+ and Cl^- at the pit precursors were identified using scanning electrochemical microscopy (SECM) in the chronoamperometric mode, and the observation of dynamic reacting species at the pit initiation stage was made using laser Raman spectroscopy. SECM study gave useful information about the distribution and imaging of H^+ and Cl^- at the pit precursors. Using in-situ Raman spectroscopy, nitrate ions at the pit precursor region were observed for the first time. There was no evidence for the presence of ammonia/ammonium ion at the pit precursor stage. The formation of nitrate ion was attributed to the combination of nitrogen and oxygen ions in the passive film. It is concluded that nitrate ions were incorporated into the passive film along with hydrated chloride ions, and help in the self-repair of the passive film during pit initiation.

Effect of alloying nitrogen on crevice corrosion of austenitic stainless steels

S. Azuma et al.

The effect of alloying nitrogen was investigated on crevice corrosion of the 10 % Mn-25 % Ni-25 %Cr-(0∼0.36) % N austenitic steels. From the immersion test results for the multiple crevice specimens in natural seawater, the probability of the occurrence of the crevice corrosion was not dependent upon the nitrogen content, while the penetration depth was decreased with increased nitrogen content. The electrochemical measurements were carried out to clarify the effect of nitrogen on each stage: initiation, propagation and repassivation. The acidification of anolyte and the active dissolution were suppressed by the addition of nitrogen. Also, the transient current for passivation after polishing revealed that the nitrogen kinetically accelerated the passivation in acidic chloride environments. On the other hand, the nitrogen was found to have no effect on the depassivation pH (pH_D) and the repassivation potential (E_R). The concentration of ammonium ion in the anolyte was increased with increasing nitrogen content. The beneficial effect of nitrogen was considered to be in prolonging the incubation period and decreasing the penetration rate by the formation of ammonium ion from the alloyed nitrogen.

Relationship between pitting and intergranular corrosion of nitrogen-bearing austenitic stainless steels

U. Kamachi Mudali et al.

Nitrogen-bearing types 304 and 316 stainless steels thermally aged at 823, 873 and 923K for various durations were investigated to understand the relation between the sensitized microstructure (intergranular corrosion) and pitting corrosion resistance. The sensitized microstructure was assessed as per ASTM A262 practice A (electrolytic etch test) and electrochemical potentiokinetic reactivation (EPR) tests; and pitting corrosion resistance was evaluated in an acidic chloride medium by potentiodynamic anodic polarisation method. The results indicated that the pitting resistance decreased as the degree of sensitization increased, and this was attributed to the formation of a heterogeneous microstructure consisting of Cr-rich $M_{23}C_6$ carbides, Cr-depleted regions and the carbide/matrix interfaces resulting from the sensitizing treatment. Pitting attack was found at triple points, grain boundaries and precipitate/matrix interfaces. Time-temperature-sensitization-pitting diagrams were developed for both the alloys based on the results, interrelating the sensitized microstructure and the pitting attack.

Effect of elemental partitioning on pitting resistance of high nitrogen duplex stainless steels

H. Vannevik et al.

The present paper describes an investigation on highly alloyed duplex stainless steels with nitrogen concentrations varying in the range 0.31-0.44 %. The distribution of alloying elements obtained in the electron microprobe (EPMA) was compared with predictions obtained by the thermodynamic computer program Thermo-Calc. Based on calculated and measured chemical composition of the two phases, pitting resistance equivalent (PRE) values were calculated. The critical pitting temperature (CPT) was determined and related to the PRE of the weakest phase, which turned out to be ferrite in the present case. Thermo-Calc proved to be capable of predicting PRE-values as a function of temperature in ferrite and austenite, thereby offering a means of balancing the partitioning of alloying elements between ferrite and austenite. This reduces the number of laboratory melts when developing duplex stainless steels.

Corrosion resistance of nitrogen bearing martensitic stainless steels

A. A. Ono et al.

It has been mentioned that nitrogen enhances the corrosion resistance of the martensitic stainless steels. In this work, by means of electrochemical and mass loss tests, the corrosion resistance of three experimental martensitic stainless steels, with partial substitution of carbon by nitrogen were investigated. Martensitic stainless steels type AISI 410 and AISI 420 were also tested, for comparison, and all teels were tested in both hardened and tempered conditions.

The resistance to general corrosion in 0.5M H_2SO_4 was evaluated by mass loss tests and by potentiodynamic polarization tests, the last through the critical current density and the passive current density. The resistance to pitting corrosion was evaluated by potentiodynamic polarization tests in 0.01M NaCl + 0.01M Na_2SO_4, through the pitting potential.

The results of both general corrosion and pitting corrosion tests show that the nitrogen, when present in the solid solution condition, improves the corrosion resistance. It was observed that with the partial substitution of carbon by nitrogen, the passive current densities were lower, in 0.5M H_2SO_4, and the pitting potentials were higher, in the 0.01M NaCl + 0.01M Na_2SO_4 solution.

The results are discussed basically through the different chemical composition of the steels and the microstructure observed in each sample.

Sensitization behaviour and corrosion resistance of austenitic stainless steels alloyed with nitrogen and manganese

R. F. A. Jargelius-Pettersson

The influence of alloying levels in the range (in mass%) of 0.01-0.5 nitrogen and 0.2-10 manganese on pitting corrosion resistance has been investigated for austenitic stainless steels with a base composition (in mass%) of 20Cr 18Ni 4.5Mo. The beneficial effect of nitrogen alloying is confirmed, while the detrimental effect of manganese alloying can be offsetby the higher nitrogen contents attainable in such steels. The effect of sensitizing heat treatments at 800 and 900°C on resistance to pitting and inter granular corrosion is also evaluated and correlated to the precipitation of secondary phases.

High temperature oxidation behavior of high nitrogen ferritic steels

F. Masuyama et al.

High temperature oxidation behavior of a high nitrogen steel with about 0.15mass% nitrogen was studies, comparing with a base material of 9Cr-0.5Mo-1.8W-0.2V-0.05Nb-0.04N steel. Weight gains were measured and microstructural observation and analyses were carried out using SEM, X-ray diffraction, EPMA and ESCA for the specimens heated in air at temperatures of 500 to 900°C and for 10 000 h at maximum. The weight gain due to oxidation in the high nitrogen steel was far smaller than that in the base material, and about one fifth of that in the base material at 10 000 h. In the high nitrogen steel, the depletion of Cr concentration at the metal surface was smaller than in the base material, and this was considered to be a possible cause of the intensified oxidation resistance of high nitrogen steel.

Effect of nitrogen, carbon and tungsten on high-temperature oxidation of 12% Cr-15% Mn austenitic steel

Y.Hosoi et al.

Oxidation behavior of Fe-12% Cr-15% Mn alloy has been studied in air at 773 to 973K. The oxidation rate of the alloy was very low at 773K, and the effect of each alloying element on the oxidation did not identified. At above 873K, the oxidation behavior was affected by the ratio of N/C and tungsten content in the alloy; the increase of N/C and tungsten content increased oxidation resistance of the alloy. Results of EPMA showed that thin Fe-Cr nitride layer was formed adjacent to the alloy surface when the ratio of N/C was proper, which was useful to prevent the oxidation of alloy. It also showed that homogeneous mono layer oxide was formed on the W-containing alloy, whereas four layer oxide was formed on the W-free alloy. Beneficial effect of tungsten may be related to this homogenization action. Small addition of vanadium and titanium was also effective to improve the oxidation resistance of the alloy. It is confirmed that the oxide formed on the alloy with good oxidation resistance was mainly composed of $(Mn, Cr)_2O_3$.

Mechanical Properties and Alloy Development

Nitrogen bearing martensitic stainless steels: microstructure and properties

M.B.Horouitz et al.

Three experimental nitrogen bearing martensitic stainless steels (Nitrogen content ranging from 1 600 to 1 900ppm) were produced in an air induction furnace and the N was added into the melt as Fe-Cr-N master alloy or gas nitrogen. These alloys with (C + N) content equal to 0.32wt% were compared with a commercial AISI 420 steel. The alloys were homogenized, forged, quenched in air (alloys I and II) or in oil (alloys III and AISI 420) from temperatures between 1 073 to 1 423K. The austenitizing temperature of 1 273K was chosen and the specimens were tempered in the range of 373 to 973K for 1 h. SEM of the 773K tempered nitrogen steels did not show any visible precipitates. The AISI 420 alloy, however, exhibited a high density of chromium carbide precipitates when heat treated in the same manner. TEM observation of the alloy III did not show clearly fine and well distributed precipitates. The nitrogen bearing steels showed better corrosion resistance in the 773K tempered condition than the as quenched AISI 420 as a consequence of lower precipitate size, stoichiometry and distribution of precipitates.

Effect of nitride (Cr_2N) precipitation on the mechanical, corrosion, and wear properties of austenitic stainless steel

J. W.Simmons et al.

High-nitrogen austenitic stainless steels are thermally unstable and susceptible to nitride precipitation (primarily Cr_2N) during elevated temperature exposure. This paper describes the effect of Cr_2N precipitation on the mechanical, corrosion, and abrasive wear properties of a high-nitrogen austenitic stainless steel, nominally Fe-19Cr-5Mn-5Ni-3Mo-0.02C-0.7N. In the annealed state, Cr-rich nitrides (Cr_2N) precipitate sequentially as intergranular celluiar, and finally, intragranular precipitates. Cold working, prior to aging, increases grain boundary and intragranular precipitation kinetics, but retards cellular phase formation.

Nitride precipitation has only a minor influence on the yield and ultimate tensile strength of annealed materials, but causes embrittlement which is enhanced at high strain rate condlition such as impact testing by the accelerated precipitation kinetics associated with prior deformation. Nitride precipitation results in sensitization which is also accelerated by prior deformation. The degree of sensitization, as measured by electrochemical potentiokinetic reactivation (EPR) testing, correlates to intergranular, cellular, and intragranular Cr-depletion. Although the degree of sensitization is defined by both the Cr-minimum and width of Cr-depleted region, a Cr level below approximately 14wt% is required for sensitization. Precipitation also results in a greater corrosion susceptibility as determined by potentiodynamic polarization scans. The wear behavior of the 0.7wt% N alloy is little affected by the precipitation of Cr_2N since the volume fraction and size (compared to the abrasive) of the Cr_2N precipitates is insufficient to alter the wear resistance of the alloy.

Effect of thermo-mechanical treatment on mechanical properties of high-nitrogen containing Cr-Mn-Ni austenitic stainless steels

Y.IKegami et al.

To develop a high strength nonmagnetic stainless steel with excellent toughness, thermo-mechanical control process (TMCP) was applied to hot-forged products of Cr-Mn-Ni austenitic stainless steels with various levels of C and N. The yield strength in the as-hot-forged condition increases with increasing nitrogen contents. Carbon addition is detrimental to toughness because it promotes carbide precipitation at the grain boundary during hot forging, causing intergranular fracture at 293K. In a low carbon and high nitrogen steel, 0.2% yield strength increases and toughness slightly decreases with lowering finishforging temperature. It was found that a steel with a chemical composition of Fe-0.06C-20Cr-15Mn-4Ni-2Mo-0.64N can be strengthened by TMCP to a level of more than 1 000 MPa in 0.2 % yield strength with maintaining its ductility and toughness. This excellent strength-toughness balance can be explained by austenite grain refinement and substructures generated by TMCP as well as strong solution hardening and grain size hardening by nitrogen.

Sensitivity of a high nitrogen austenitic stainless steel to fatigue crack initiation

J.-B. Vogt et al.

The low cycle fatigue behaviour of a 0.9 % N Cr-Mn austenitic stainless has been investigated at room temperature and at 77 K at total strains ranging from $\Delta\varepsilon_t$ = 0.6 to 2.5 %. The macroscopic behaviour, cyclic stress amplitude and accommodation period, is strongly influenced by the test temperature. The fatigue resistance has been associated to surface plasticity and to crack initiation. Cycling at low temperature or at room temperature at high strain amplitude favours crack initiation at grain boundaries which is detrimental for fatigue resistance. However, it is found that the fatigue cracks tend to initiate transgranularly which is beneficial for fatigue resistance when the alloy is previously aged at 350°C.

Effect of enhancement in surface nitrogen concentration on the corrosion and fatigue properties of austenitic steel wire rod

G.Paul et al.

Austenitic steel rod for wire production with a nitrogen content of 0.23 % has been nitrided to produce an enhanced nitrogen surface layer. The level of nitrogen and depth of penetration is controlled by the temperature, gas potential and the residence time in the furnace. The cooling rate from the nitriding temperature is also shown to be important in control of the nitrogen distribution. The alloys were then subjected to thermal treatments and the effect of those on the microstructure of the rods was assessed. Measurements of the strength, fatigue resistance, corrosion resistance and corrosion fatigue resistance in salt-water were made and these are interpreted in terms of the nitrogen distribution in the alloys. The consequences of these effects for production and use of wire from such rod is discussed and suggestions are made for a production sequence for improved high-nitrogen alloy wire.

Mechanical properties of atustenitic high-nitrogen Cr-Ni and Cr-Mn steels at low temperature

R.J.ILOLA et al.

Mechanical properties of solution annealed austenitic 19Cr-8Ni-(0.26-0.5N), 22Cr-12 Mn-1.0N and 19Cr-15Mn-0.8N steels were investigated by means of tensile and Charpy-V impact toughness tests between room temperature and 77K. Solution annealing temperature was selected in order to prevent Cr_2N formation. Fracture surfaces were investigated using SEM (scanning electron microscope). Austenite stability against α'-martensite formation during cooling or deformation in tensile and Charpy-V tests was determined using magnetic measurements. Austenitic high-nitrogen Cr-Ni and Cr-Mn steels exhibited excellent strength, ductility and toughness at room temperature. At 77K, yield strength was increased, but ductility and toughness were decreased markedly, and ductile-to-brittle behaviour associated with brittle transgranular and intergranular fracture was observed. Results are compared with AISI 304N steel (0.16wt% N) which retained excellent ductility and impact toughness at 77 K.

Strength properties and microstructure of high Mn-Cr austenitic steels as potential high temperature materials

K.MIYAHARA et al.

The present authors have investigated the high temperature strength, toughness and microstructural phase instability of 12 % Cr-15 % Mn steels, for the development of high Mn-Cr austenitic steels as heat resisting materials. While high content of carbon and nitrogen (0.1 to 0.2mass% C and N) and combined addition of vanadium and titanium were effective to increase the creep-rupture strength considerably compared with that of the regular type 316 steel or Tenelon, such addition of the elements deteriorated the toughness of the materials because of the large amounts of coarse precipitates of type $M_{23}C_6$ carbide and also fine precipitates of TiN. It was clarified that the reducing of carbon content to 0.02 mass% C improved much the toughness of the 12 % Cr-15 % Mn steel and also produced the creep-rupture strength which is comparable with that of the 316 steel.

Microstructure and deformation behavior of high nitrogen duplex stainless steels

N.AKDUT et al.

The deformation of duplex structures in general and duplex stainless steels in particular is very complex. The existence of the massive second phase leads to numerous unexpected features, *i.e.* the microstructure is the most decisive influence parameter on the deformation behavior of duplex structures. In the case of DSS additionally the chemical composition has to be taken into account.

With increasing rolling deformation at room temperature several deformation mechanisms occur, *e.g.* shear relaxation, twinning of austenite, deformation induced martensitic transformation of the austenitic phase, crack formation (and crack healing accompanied by the refinement of the microstructure) and dynamic recovery. In α/γ-duplex stainless steels (DSS) additionally the phase boundaries (PB) are obstacles for deformation. Therefore, here large deformation zones were built up during deformation which contribute to the complex deformation behavior.

Since nitrogen reduces the SFE and, thereby, hardens the austenitic phase and promotes planar slip which is not homogeneously distributed in the austenitic grains but localized, ferrite becomes the more ductile phase in DSS. Furthermore, as a very strong austenite stabilizing element, N causes the change of the matrix phase from ferrite to austenite and leads to the ductile to brittle transition of austenite which also influences the deformation behavior.

It occurred that there are equal deformation modes like the hindrance of shear band formation, shear band cracking and "selective phase boundary sliding", which are obviously valid for all duplex structures, and other ones, due to the nitrogen content (*e.g.* brittleness) or the existence of the second phase (*e.g.* increased strain hardening rate).

High nitrogen containing Ni-free austenitic steels for medical applications

J.MENZEL et al.

New nickel-free Cr Mn Mo austenites with up to 1 % nitrogen developed by VSG exhibit properties which correspond particularly well to medical engineering requirements. The combination of strength, toughness, corrosion resistance, wear resistance and cost-efficiency which these alloys display is not attained by any other material.

Nickel free high nitrogen steels

P.J.UGGOWITZER et al.

The paper presents the philosophy of the development and the resulting properties of a new austenitic stainless steel. The steel contains 15-18% chromium, 3-6% molybdenum, 10-12% manganese, and about 0.9% nitrogen. The most important feature of this steel is the complete absence of nickel as alloying element. The austenitic microstructure is obtained exclusively by adding nitrogen. Besides being nickel free, the steel is further characterized by an excellent corrosion resistance, the absence of ferromagnetism, and outstanding mechanical properties. The unique combination of these properties makes this steel most interesting for its use in items which are in direct contact with the human body. By using these new steels, nickel allergy can be prevented.

Processing and Manufacturing : Nitriding, Powder Metallurgy and Welding

Manufacture and application of high nitrogen steels

H.BERNS et al.

The introduction of nitrogen by alloying, pressure metallurgy, powder metallurgy and solid state diffusion is briefly reviewed. Examples of martensitic, austenitic, duplex and dual phase HNS are given and applications already realized or tentative ones are presented.

High nitrogen steel powder for the production of near net shape parts

T.EI GAMMAL et al.

The Plasma-Rotating-Electrode-Process is a powder metallurgical process for the production of high nitrogen steel utilizing the activated, ionized or dissociated state of the nitrogen in plasma for the nitrogenization of steel. The powder produced is characterized by its high nitrogen level far in excess of the nitrogen content under normal condition and its nearly ideal spherical form.

The influences of rotational speed and nitrogen content in the plasma gas on powder sizes and nitrogen content of the powders respectively are pointed out. The microstructure of the powder has been investigated at different heat treatment conditions. The initial material (before nitrogenization) was an austenitic steel grade 304. After a solution heat treatment the powder is almost free of precipitates. After an annealing treatment at moderate temperatures (600 to 800°C) different forms of nitrides occur in dependence of temperature and time. The observed nitrides are described.

The microhardness of the powder increases with increasing nitrogen content. In the solution heat treated state the corrosion resistance of the powder increase if the nitrogen can be kept in interstitial solution. The powder is well adapted for extrusion process.

Structural control of stainless steel by nitrogen absorption in solid state

N.NAKAMURA et al.

Nitrogen addition to stainless steels is very effective for improving mechanical properties and corrosion resistance. Powder metallurgy process, which is the sintering of stainless powder in N_2 gas atmosphere, has some beneficial points to the production of high nitrogen stainless steels, because a large amount of nitrogen can be absorbed into powder particles in a very short time.

In this paper, the behavior of nitrogen absorption into an Fe-23mass % Cr ferritic alloy powder was investigated in association with the structural changes. The results obtained are as follows : (1) Since the amount of nitrogen absorbed is dependent on the surface equilibrium between N_2 gas and nitrogen content of steels, the saturation nitrogen content increases with lowed sintering temperature. (2) At 1 473 K in 1atm-N_2 gas, the saturation nitrogen content of an Fe-23mass % Cr alloy is about 1 mass% N and the nitrogen absorption causes a structural change of the matrix from ferrite to austenite. The nitrogen content is also enough to give a stable austenitic structure at room temperature for the alloy. (3) The Fe-23 mass% Cr-1 mass% N alloy developed by the above sintering treatment has a high yield stregth and a moderate elongation in spite of containing about 12 vol% of retained pores. Such good mechanical properties are attributed to the solid-solution of a great deal of nitrogen into the steel.

High nitrogen austenitic cases in stainless steels

H.BERNS et al.

Utilising the high nitrogen solubility of the austenitic phase nitrogen can be introduced into the surface of a near net shape part by a new diffusion process called "solution nitriding". The result is a fully austenitic case around a martensitic, austenitic-ferritic or austenitic core as depicted in the Schaeffler diagram. This high strength yet very tough high nitrogen case shows improved wear and corrosion properties. Especially the wear rate by cavitation is extremely reduced because of a different strengthening behaviour as compared to conventional steels. As long as nitrogen is totally dissolved in the case the corrosion properties are not impaired. The formation of nitrides during solution nitriding, which consume chromium and in consequence lower the corrosion resistance, can be beneficial for applications under mainly erosive loading.

Dissolution and reprecipitation of nitrides in an austenitic stainless steel produced by powder metallurgy

S.L.LEE et al.

Production of nitrogen-alloyed AISI 316 steel containing titanium has been studied using a powder metallurgy route. The material is prepared by nitriding titanium-free 316 powder in an ammonia/nitrogen gas mixture at temperatures below 900°C and then blending with the titanium alloyed steel to give the required total nitrogen content in the alloy. Alloys with sufficient nitrogen for precipitation of titanium nitride (TiN) and an excess of 0.2 % N in solid solution were prepared. The blend powders were cold isostatically pressed into cylindrical samples and sintered at temperatures between 1 100 and 1 350°C. Samples were also extruded at 1 200°C without prior sintering.

The results show that the titanium alloyed powder is not fully austenitic in the as-sprayed form but the austenite phase is stabilised by the presence of nitrogen. The as-nitrided powder contains a considerable amount of chromium nitride and the microstructure of the sintered or extruded steel is controlled by the behaviour of that phase.

The best conditions for densification are found to be at 1 350°C in a vacuum furnace with a partial pressure of nitrogen gas applied as the temperature approaches the sintering maximum, followed by a hold for one hour. This gives a material of relatively high density with a controlled nitrogen distribution, high hardness and a fully austenitic structure. During the heating cycle and while the pore structure remains open the vacuum results in the decomposition of some chromium nitride and redistribution of nitrogen into solid solution, but as this is above the atmospheric solubility limit some of it is lost to the atmosphere.

The process is limited by the onset of pore closure at maximum sintering temperature. The rate of decomposition of the nitride in the solid state is slow and if the sintering temperature is low then the process of decomposition of the nitrides is incomplete, residual (coarse) chromium nitride remains and the properties are poor. This is also the case in extruded samples which contain remains of the original nitrided particles even after heat treatment. However, when the sintering regime involves liquid phase sintering, the process of dissolution of the original chromium nitride goes to completion, fine titanium nitride remains and a high - density strengthened component is achieved.

Development of properties of P/M austenitic stainless steels by nitrogen infusion

J.J.ROMU et al.

Properties of nitrogen alloyed P/M austenitic stainless steels manufactured by Hot Isostatic Pressing (HIP) of gas atomized powders were studied. Nitrogen contents beyond the solubility limit of nitrogen in the melt were obtained by solid state nitriding in a fluidized bed furnace. As a disadvantage of the fluidized bed nitriding, the oxygen contents in the powder and the final product increased. Nitrogen alloying increases the strength level, as well as the corrosion and wear resistance of P/M austenitic stainless steels. Nitride precipitation is detrimental to corrosion resistance and ductility, but beneficial to yield strength and wear resistance.

Consolidation, mechanical properties, and phase stability of mechanically alloyed Fe-N powder compositions

J.RAWERS et al.

Mechanical processing of iron powder and mechanical alloying of iron-aluminium, carbon, and nitrogen powder compositions resulted in a highly refined bcc-Fe nanograin microstructure. The milled microstructures were thermally stable. The refined nanostructure was retained while producing a fulldense compact by explosive compaction. Evaluation of macrostructure properties were obtained after compaction. Tensile strength, derived from hardness data, suggest that tensile strengths could exceed 3GPa.

Preparation of amorphous high nitrogen iron alloys with ternary additions by mechanical alloying

H.MIURA et al.

In order to prepare amorphous high nitrogen iron alloys, mechanical alloying (MA) of elemental powder mixtures with Fe-9.85mass% N alloy powder of $Fe_{(100-y)-x}A_yN_x$ (at%) (A = Mn, Cr, Mo, W, V, Nb, Ta, Co or N ; x = 0-20 ; y=0-25) was performed in an argon atmosphere using a planetary ball mill. Effect of the ternary additives A on MA of the Fe-N materials is investigated in terms of the interaction parameter W_{AN} of the additives A. The interaction parameter W_{AN} represents the difference in bonding energy of A-N atomic pair (U_{AN}) and that of Fe-N pair (U_{FeN}) in the ternary Fe-A-N solution, *i.e.* $W_{AN} = U_{AN}-U_{FeN}$, and the values of W_{AN} were calculated using thermodynamic data at 1 273 K on austenite. The value of W_{AN} is clearly dependent on the position of the elements A in the periodic table and a similar tendency in the dependencies exists in any liquid or solid solutions of Fe-A-N. Thus, this is also expected to hold for Fe-A-N materials processed by MA.

In the MA processing, the ternary additives A with a moderately negative W_{AN} value of −330 to −980kJ/mol, such as Cr, Nb, and Ta, markedly promote solid-state reactions, leading to formation of amorphous high nitrogen iron alloys having x = 8.5-20 after 720ks of processing by adding about 13-15 at% of these additives to Fe-N materials, in contrast to the additives Co and Ni with the positive W_{AN} value. However, for the MA sample with the additive Ti, the formation of TiN was seen during MA, before progress of the intermixing of atomic species due to its extreamly negative W_{AN} value (−4 110kJ/mol). In addition, the additive Mn with the less negative value of W_{AN} (−104kJ/mol) did not effectively act on MA of Fe-N materials. Similar effects of such additive were also obtained in MA materials with austenitic stainless steel compositions.

Mechanical alloying of nitrogen into iron powders

J.RAWERS et al.

Mechanical alloying of nitrogen into bcc-Fe powder is a very effective and efficient means of obtaining very high concentration of nitrogen in micron-size iron particles. Mechanical alloying increases the concentration of nitrogen in the iron powder far in excess of the bcc-Fe lattice low nitrogen solubility, however most of the infused nitrogen resides on the nano-size grain boundaries and in nano-size bcc-Fe that forms during mechanical alloying.

Mechanical alloying of iron nitrides designed for structural and functional applications

J. Foct et al.

Mechanical alloying (MA) of iron nitrides and ferrous nitrogen solid solution is studied and discussed in order to determine which role does an interstitial such as N play in the MA process and what is the influence of the N_2 molecule in respect to the reaction between the gas and the solid phase. Emphasis has been put on the influence of ball milling conditions on the microstructure. The conditions for transferring laboratory result to an industrial process are discussed.

Influence of shielding gas composition and welding parameters on the N-content and corrosion properties of welds in Nalloyed stainless steel grades

S. Hertzman et al.

TIG welding using different heat inputs, arc lengths and shielding gas nitrogen contents was performed. The aim was to evaluate the possibilities to avoid nitrogen losses on welding or even increase the weld metal nitrogen content and thereby improve the corrosion properties and, in the case of duplex grades, also to improve the phase balance. Three different nitrogen-alloyed duplex grades and one superaustenitic grade were investigated. The corrosion resistance in terms of CPT, Critical Pitting Temperature, of the super duplex material was found to be strongly correlated to the nitrogen content of the weld metal. In the case of the superaustenitic weld metal, the increased nitrogen content was found to be associated with an increased pore formation, leading to a lower corrosion resistance and thereby masking the positive effect of the increased nitrogen content.

In order to illuminate the nitrogen exchange reactions between the arc, weld pool, and shielding gas, stationary weld experiments were also performed. The results from these stationary trials indicated that the net weld pool nitrogen content could be qualitatively understood if the various fluxes involved in the nitrogen transport between the plasma arc and weld pool, weld pool-shielding gas were considered. At short times the weld pool was limited in area and the nitrogen content of the weld pool increased due to high nitrogen activity in the arc. At longer times the nitrogen escaped from the weld pool to the shielding gas. This flux became then the dominating factor due to the increased weld pool area exposed to the shielding gas. The situation then approached the equilibrium conditions that were expected from the gas nitrogen activity and weld pool alloy composition according to thermodynamic calculations using the Thermo-Calc database.

Nitrogen content of 316L weld metal and its fine particle by means of high-pressure MIG arc welding

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The suitability of the high nitrogen pressure Metal Inert Gas (MIG) ARC welding process (constant arc length condition) for high nitrogen containing stainless steel was investigated. The formation of fine stainless steel fine particles by the high nitrogen pressure MIG arc welding process was examined. The welding atmosphere consisted of pressurized N_2 gas. Nitrogen absorption of 316L stainless steel weld metal and its fine particle in the high nitrogen pressure MIG process was studied. The effect of nitrogen contents in remelted weld metal and changes in the microstructure of the weld metal were observed.

The nitrogen content of weld metal and the number of fine particles increased with increasing pressure of N_2.

Approximately 0.6 and 2.4mass% nitrogen was absorbed in the weld metal and fine particles at pressure of N_2 6 Mpa and 3 Ma nitrogen respectively. Nitrogen content of the weld metal was lower than that representing equilibrium solubility of 316L stainless steel at close to the melting point.