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Some special features of formation of manyfunctional powders steels structure

Antsiferov V. N. , Oglezneva S. A. , Grevnov L. M.

(Research Centre of Powder Materials Science, Perm 614013)

Abstract: It has been studied connection between composition, structure and properties of powder steels using technology of their own. Nitrogen containing powders were obtained by mechanical allowing (MA) of Fe-Cr and Fe Cr Ni-C mixtures in a high-energy planetary mill in the gaseous nitrogen environment. The contents of nitrogen after MA was 0. 7% in Fe-Cr-N and 2. 1% in Fe-Cr-Ni-C-N mixes. Phase composition after the mechanical alloying was: in system Fe-Cr-N - solid solution of chrome in iron and α - Fe, in system Fe-Cr-Ni-C-N-40% γ-phase (vol. fraction) , α - Fe and solid solution Cr-Fe.

There are investigated physical-mechanical, tribo-technical and specify properties of the nitrous steels, are fixed the base dependences between parameters of process of MA and structure of steels. Introduction of nitrogen by rather new method of MA, as against saturation of melts, allows to run phase composition - to generate structure with more dispersible and uniform nitrides or with the nitrous austenite (depending on purpose of steel).

It is demonstrated by means of X-ray diffraction and method of Raman spectrum analysis, that in a sintering process of powder steels, obtained by introduction of carbon in the form of cast-iron powder, a formation of metallofullerite phase Fe_xC_{60} at determined conditions. The possibility of fullerenes conception in powder carbon steels, diffusion of iron atoms at fullerite lattice and formation of metallofullerites during contact interaction of fullerene with iron is confirmed experimentally.

Dependence of synthesis activity of fullerences from temperature of sintering, type and quantity of alloy elements is determined.

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Synthesis of fullerenes and introduction of nitrogen in powder steels by mechanical alloying are considering in the study for the widening of functional possibility of powder steels .

1 Synthesis of fullerenes in powdered steels

In 1985 there was experimentally discovered a new allotropic modification of carbon-fullerenes [1]. The compounds of fullerenes with metals are of high interest to the material scientists. There is known the existence of the metallofullerite phases type Fe_xC_{60} and of the fullerene-bearing materials on their basis[2]. It is shown [3] that during sharp quenching the fullerenes formed in the structure of steel synthesize into the diamond-like compounds.

It is established[4] that in the course of sintering the powdered composition of ferrum and eutectic iron

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there takes place the formation of the Fe_xC_{60} metallofullerite having the lattice of face-centred cube with the spacing of 12.3 . It is also known [5] that in the course of sintering the powdered nickel steel there takes place the low-temperature solid-phase synthesis of the Fe_xC_{60} metallofullerite with the face-centred lattice having the spacing of 14.4Å.

This study investigates the formation of fullerene-bearing phases in the ferrum-based alloys produced by the method of powder metallurgy. It was interesting to study the effect of porosity on the synthesis of fullerene-bearing phases.

The specimens of the mixture of ferrum powder and eutectic iron particles were compacted at pressures of 200-800 MPa. Besides, the mixture was used in the free bulk state. Composition of the mixture of ferrum powder and eutectic iron was chosen such that thespecimens contained 1.2% of carbon.

The specimens were sintered so that at heating the high-carbon component (iron) melted while the low-carbon component (ferrum powder) remained in its solid state.

It was established that the relative density of sintered specimens of the ferrum-iron-composition was 57% for free bulk, while that of the specimens compacted at the pressures of 200, 400, 600 and 800 MPa was 68%, 77%, 82% and 85% , respectively. It is shown by X-ray powder diffraction and Raman spectra method that in the course of sintering the powdered composition of ferrum and iron there takes place the formation of the metallofullerite phases type Fe_xC_{60}.

The investigations showed that synthesis of the fullerene-bearing phases proceeds more actively in the specimens of lower density. Thus, for example, the diffractograms taken from specimens with relative density of 57% give the lines of 7.12, 4.13, 3.55 and 3.34 ; for the specimen with relative density of 68% - 7.09 and 3.56 ; for the specimen with relative density of 82% -3.56 ; in the specimen with relative density of 85 % synthesis of the fullerenes did not take place at all. As follows from the results obtained, there are formed two types of metallofullerite with the face-centred cubic lattice, the lines of which are superposed on each other. Besides, there occur the lines of the C_{60} fullerite: 4.10 (222) and 3.57 (400) Å

It is established that the lattice spacing of both metallofullerite 1 and metallofullerite 2 grows with increasing duration from 15 up to 120 minutes. Lattice spacing of the first phase increases from 12.3435 Å to 12.4798 Å and with the second phase from 13.7828 Å to 14.5192Å. This can be probably explained by the fact that in the course of sintering there firstly forms the C_{60} fullerene and then the fullerenes interact with ferrum to form the Fe_xC_{60} compound. The atoms of ferrum arrange between the molecules of fullerite and increase the size of lattice. The lattice spacing depends upon the ratio of carbon and ferrum atoms in the Fe_xC_{60} structure.

The studies performed show that in the course of sintering there are formed two types of fullerene-bearing phases which have the face-centred cubic lattice but differ in the lattice spacing. Lattice spacing of the fullerene-bearing phases grows with increasing duration of sintering which is associated with transformation of the C_{60} fullerite lattice into the Fe_xC_{60} metallofullerite lattice. Synthesis of the fullerene-bearing phases proceeds more actively in the specimens of lower density. The results obtained are an important step toward development of the technology for producing new fullerene-bearing materials which can be used for manufacture of the articles with improved performance characteristics of the structural and tribotechnical purpose, of the metal-diamond tools and other articles.

2 Nitrogen containing powdered steels

As the alloying element nitrogen is capable to replace successfully a nickel and manganese due to shaping of nitrogenous austenite, steadier, than carbonaceous [6]. The increase in the contents of nitrogen in austenite results in a strength improvement and plasticity of alloys[7]. Martempering of properties of the steels alloyed by nitrogen, is attained at concentrating of nitrogen 1.1%-1.3%(mass fraction), that considerably exceeds breaking points of his(its) solubility in metals under equilibrum conditions[8,9], therefore for dissolution of nitrogen the role of dislocations where more favourable conditions for their disposing are created energetically is great. The quantity of the nitrogen concentrated at dislocations, increases with their density dependent on extent of a cold strain of metal, i. e. from evolution of his(its) metastablis defective structure[10]. (the chemical inhomogeneity, the raised(increased) unsoundness of a crystalline structure, the porosity, hereditary fineness [11]) intensify habits of a structure of powdered metals diffusion processes, raise a diffusion constant. Therefore a perspectiv way of reception of steels with the contents of nitrogen is higher equilibrum basic new method of a mechanical alloy building of powders of metal is introduction of nitrogen occurs during long fine crushing metals in nitrogen or ammonia.

Nitrogen containing powders were obtained by mechanical alloying (MA) of Fe-21% Cr and Fe-21% Cr-7% Ni-0.5%C mixtures in a high-energy planetary mill in the gaseous nitrogen environment with ratio of spheres and a powder weights 30:1. The contents of nitrogen after MA was up to 0.7% in mixes. The ending of process of mechanical alloying fixed on structural change at various scale levels: reduction of particle size and narrowing of distribution of sizes at a macro-level, formation of solid solutions and homogenization of a mix - on meso-level, change of lattice constants at a micro-level. Phase composition after the mechanical alloying was: in system Fe-Cr-N-solid solution of chrome in iron and α-Fe, in system Fe-Cr-Ni-C-N-about 40% (vol fraction) γ-phase, α-Fe and solid solution Cr-Fe.

It is established the increase of concentration of nitrogen and containing of γ-phase at MA and after sintering in nitrogenium. Optimal temperature-time parameters of sintering are fixed: the environment of sintering-dissociated ammonia, temperature-1170℃, isothermal endurance 3 hours for Cr-Ni-steel and 4-5 hours for Cr-steel when almost 100% of γ-phase was obtained. Duration of sintering time is caused by formation of fixed phase composition-at the first stages of sintering nitrides of chrome and iron are formed, and then at increase in time of isothermal homogenization nitrides dissolve with formation of the nitrous austenite. Presumably, the mechanism of formation of austenitic structure at sintering in view of obtained experimental data can be such: at mechanical alloying nitrogen has an opportunity "to slam" in defect areas of iron and chrome.

There are received steels with the nonequilibrium contents of nitrogen 0.7%-2.1%. Microstructure of steels after the sintering were dispersible and contained austenite and martensite. There are investigated physical-mechanical, tribo-technical and specify properties of the nitrous steels, are fixed the base dependences between parameters of process of MA and structure of steels. Introduction of nitrogen by rather new method of MA, as against saturation of melts, allows to run phase composition to generate structure with more dispersible and uniform nitrides or with the nitrous austenite (depending on purpose of steel). Rust resistance of the developed powder steels 2 points in conditions of an industrial environment and 5 points in solute NaCl, wear resistance in 10 times exceeds wear resistance molten X18H9T.

References

[1] Kroto H W, Heath J R, O'Brien S C, et al. Nature, 1985,(318):162.

[2] Robert C Job. Solid metal-carbon matrix of metallofullerites and method of forming same[P]. US Patent: 0528342.

[3] Robert C Job. Method of producing diamond crystals from metallfullerite matrix and resulting product[P]. US

Patent: 5449491.

[4] Antsyferov V N, Gilyev V G, Grevnov L M, et al. Formation of fullerene-based phases in Fe-C and Fe-C_{60} systems[J], Перспективные материалы, 1999, (6): 5.

[5] Antsyferov V N, Gilyev V G, Oglezneva S A, et al. Low-temperature solid-phase synthesis of metallofullerites [J], Перспективные материалы, 2000, (1) :11.

[6] Морозов А. Н. Водород и азот в стали М. : Металлургия, 1966. 283 с.

[7] Устиновщиков Ю. И. , Рац А. В. , Банных О. А. u gn. Свойства структур, формирующихся после закалки Fe-18% Cr-(0.9-1.3)% N-сплавов с добавками и без добавок никеля // Известия ВУЗов. Черная металлургия №7, 1997. С. 48-51.

[8] Устиновщиков Ю. И. , Рац А. В. , Банных О. А. , Блинов В. М. Структура высокоазотистых сплавов Fe -18 % Cr // Металлы №1, 1996. С. 67-73.

[9] Устиновщиков Ю. И. , Рац А. В. , Банных О. А. , Блинов В. М. Структура азотистого аустенита. // Известия ВУЗов. Черная металлургия №2, 1999. С. 57-60.

[10] Попович А. А. , Арестов О. В. , Кучма А. С. Механохимический способ получения и упрочнения сплавов на основе железа // Перспективные материалы, технологии, конструкции: Сб. науч. тр. Красноярск: САА, 1998. № 4. С. 530-534.

[11] Анциферов В. Н. , Буланов В. Я. , Богодухов С. И. , Гревнов Л. М. Термохимическая обработка порошковых сталей // Екатеринбург, 1997. 482 с.