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Research of the Possibility of Nanostructuring Functional Materials by Pre-Recrystallization Heat Treatment

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The paper is devoted to the research of the possibility of nanostructuring of functional materials, steels and ceramic sprayed coatings by pre-recrystallization heat treatment. The effect of the size of coherent X-ray scattering regions, the number of nanostructured elements and the subgrains misorientation angle on the physical and mechanical properties of technically pure iron and steel were experimentally studied. The possibility of thermal stabilization of a 62% polygonization nanoscale substructure during pre-recrystallization heat treatment at 500°C after combined plastic deformation is shown. A combination of 30% dynamic and 30% static deformations makes it possible to use such treatment in industry. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Physical and mechanical properties, thermal sprayed coatings, deformation of steels, pre-recrystallization heat treatment

The development level of modern engineering, in particular shipbuilding, is characterized by the use of increased intensity of operation modes of machine parts and mechanisms and requires constant updating and improvement of technologies and materials to meet the growing need for reliability and durability of products. Increased needs are met mainly by the physical and mechanical properties of the materials from which they are made. Therefore, an increase in these parameters is of great practical importance [1-3].

High rates of physical and mechanical properties of metals and alloys can be achieved by nanostructuring. Grinding of the grain (subgrain) structure to the nanoscale state is carried out mainly by the methods of intensive plastic deformation (IPD) [4-7]. Today, industrial methods for producing a nanostructure throughout the entire volume of a real product are quite complex and, as a result, expensive [8]. In this connection, the development of new methods of nanostructuring is an urgent task of modern materials science.

Since IPD methods are characterized by high cost, difficult equipment and are suitable only for small cross-section parts (up to 10 mm). One of the ways to solve the problem may be the use of pre-recrystallization heat treatment (PHT) of steels available for industrial conditions, the essence of which is fixing the polygonization substructure by cooling the material at the stage of formation of nanoscale subgrains [9-14].

The essence of processing is the deformation of metals or alloys with a reduction ratio of more than 20% at room temperature, heating to the temperature of the beginning of recrystallization, holding for 0.5 ... 10 minutes and subsequent cooling to room temperature at a speed that does not cause growth of the subgrain (not less than 5°C/ sec) [9-14].

Therefore, the aim of this work is to research the possibility of nanostructuring of functional materials by PHT.

For the study, the following samples were selected: technically pure iron of grades E10 and E12 (GOST 3836-83), carbon steels: St3 (quality certificate №05586 in accordance with EN 10204/3.1:2005), steels 20; 45 (GOST 1050-88) and U8 (GOST 1435-88), alloyed steels: 40H (GOST 2591-2006), 12H13; 20H13; 40H13; 12H18N10T (GOST 2590-2006), ZrO_2-7% Y_2O_3 plasma sprayed thermal barrier coating.

Dynamic deformation of the samples was carried out by shock cyclic action. Static deformation was carried out on a Losen Housen WLRK (Dusseldorf) hydraulic press with a load of up to 35000 kg. Heat treatment was carried out by a laboratory electric furnace SNOL-1.6.2.0.08/9-M1 and by a furnace with a KEN A-VT type silicon carbide heater (up to 1450°C). The temperature was controlled by chromel alumel THA thermocouples (GOST 6616-74) and PPR type S (platinum + 10% rhodium/platinum). The microstructure was analyzed using an MMR-2R metallographic microscope, ZEISS Gemini SEM 500 scanning electron microscope and a SUPRA55VP analytical field emission scanning electron microscope. The Vickers hardness (HV_5) was measured in accordance with the DSTU ISO 6507-4:2008 with a load of 5 kg on the indenter. The thermal conductivity of the coatings was also analyzed by dynamic calorimeter method using an IT-λ-400 meter. The X-ray diffraction patterns were obtained by DRON-3.0 diffractometer using molybdenum radiation ($\lambda = 0.071069$ nm). The sizes of X-ray coherent scattering regions (CSR) were calculated by Scherer formula, the method of harmonic analysis of diffraction profile shape and the point method. The relative number of nanosized elements was determined using the method of approximating the diffraction profile by Gauss function.

Since iron is the basis of steels and cast irons, which today make up about 90% of all construction materials used in engineering and everyday life, in subsequent studies, annealed samples of technically pure iron of grade E10 6×6×8 mm in size were used to determine the optimal temperature and holding time of PHT. These samples were deformed by 20, 40, 60 and 80% and heat treated at temperatures of 400, 500 and 600°C with holding time from 0.5 to 5 minutes [1].

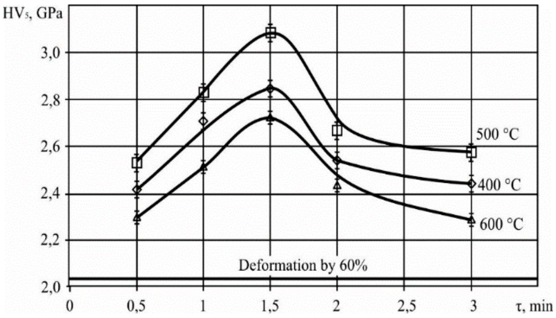

Fig. 1. shows the dependence of hardness on holding time and temperature of the PHT of technically pure iron deformed by 60%.

It is clear from Fig. 1 that after PHT the hardness of plastically deformed technically pure iron increases with extreme nature. Moreover, the maximum hardness after PHT is higher than after plastic deformation.

To analyze the effect of carbon amount on increase in hardness after PHT, samples of carbon steels 20, 40, 45, and U8 with the same deformation degree were studied [1]. Investigation of the carbon effect on maximum hardness during short holding time at a recrystallization temperature showed that the increase in hardness decreased with the increase in carbon content (Fig. 2).

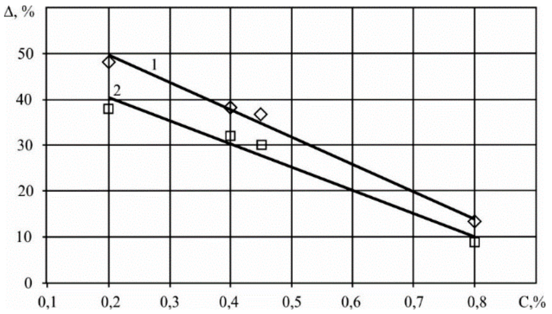

Fig. 2. The dependence of increase in hardness of steels after PHT on carbon amount: 1– HV_5; 2 – HRC.

Such dependence can be explained by the fact that with an increase in the amount of carbon in steel, the amount of cementite increases, which has high hardness and inhibits the formation of dislocation plexuses during plastic deformation [10]. Similar effect of reducing the increase in hardness after PHT is also observed in alloyed chromium steel. An increase in the chromium concentration in alloyed steel promotes the formation of carbides, which block dislocations during plastic deformation at the initial stage of polygonization.

Moreover, the physical and mechanical properties of plastically deformed steels are improved by using PHT (Table 1).

The mechanism of the improvement is associated with the grinding of the substructure, which is confirmed by a decrease in the size of CSR, which are identified with the size of subgrains (Table 2).

It is known [5] that nanostructuring improves the physical and mechanical properties of not only compact plastically deformed materials (steels), but also sprayed coatings. Therefore, the effect of PHT on the properties of ZrO_2-7% Y_2O_3 plasma sprayed thermal barrier coating was studied. Thermal spraying was carried out using the UPU-3D plasma spraying unit with PN-14M torch to a substrate from nickel heat-resistant alloy. Samples were prepared by abrasive treatment before spraying. The optimal regime of ZrO_2-7% Y_2O_3 plasma sprayed thermal barrier coating PHT was determined, which consists in heating to a temperature 1300°C, holding for 15 min and cooling in air, providing an increase in hardness of

Table 1. Physical and mechanical properties of steels depending on the type of treatment

Steel grades	Type of treatment	Tensile strength $\sigma_в$, MPa	Relative extension δ,%	Relative narrowing Ψ,%	Logarithmic decrement of damping oscillations δ, %	Thermal conductivity λ, W/(m·K)	Electrical resistance $\rho\times10^{-7}$, Ohm·m
Steel 20	Annealing 850°C, 60 min	360	16	57	2.5	51	1.91
	Deformation by 60%	624	3	9	4.1	31	2.9
	Deformation by 60% + PHT (500°C 1,5 min)	784	4	15	5.7	16	3.68
Steel 12H13	Annealing 720°C, 60 min	833	6	43	2.2	26	5.14
	Deformation by 60%	1162	1	18	3.2	23	7.47
	Deformation by 60% + PHT (600°C, 2 min)	1300	2	26	4.9	19	8.14

13%. Also, we note a decrease in thermal conductivity of the ceramic layer 15% (from 0.72 to 0.6 W/(m·K)) compared with the state after spraying. It can be explained by substructural changes.

A comparative analysis of micrographs showed that there are no changes in the structure of the coating before and after heat treatment. This indicates that the reinforcing effect is provided by structural elements whose size is less than 0.5 μm, which is explained by the resolution of the human eye and optical metallographic microscope.

Nanostructuring of steels and sprayed coatings by PHT provides a significant increase in physical and mechanical properties. But the proposed heat treatment [12] has a disadvantage like a short holding time at a recrystallization temperature of up to 5 minutes (for ceramics – 15 minutes), which limits its use – only for small parts.

In [15] the possibility of thermal stabilization of the polygonization substructure was investigated during PHT for technically pure iron (E12 grade) and nickel during 20...70 minutes and 10 ... 60 min, respectively. It consists in cold dynamic deformation by 30% and subsequent static deformation by 30% and PHT. Annealed samples of technically pure iron of grade E12 were deformed by various types of combined deformation and heat treated at 500°C

Table 2. Structure parameters of the studied materials before and after PHT

Material	Type of treatment	CSR size, nm
Technically pure iron	Annealing 800°C, 60 min	>200
	Deformation by 60%	131
	Deformation by 60% + PHT (500°C 1.5 min)	78
Steel 20	Annealing 850°C, 60 min	>200
	Deformation by 60%	149
	Deformation by 60% + PHT (500°C 1.5 min)	87
Steel 40	Annealing 820°C, 60 min	>>200
	Deformation by 60%	198
	Deformation by 60% + PHT (500°C 1.5 min)	137
Steel U8	Annealing 750°C, 60 min	>>200
	Deformation by 60%	159
	Deformation by 60% + PHT (500°C 2 min)	79
Steel 20H13	Annealing 720°C, 60 min	197
	Deformation by 60%	63
	Deformation by 60% + PHT (500°C 2 min)	44
Steel 12H18N10T	Annealing 860°C, 60 min	>200
	Deformation by 60%	144
	Deformation by 60% + PHT (500°C 2 min)	76

Table 3. Subgrains size and number of nanoscale subgrains of steel St3 before and after PHT

Type of treatment	Subgrains size, nm	Number of nanoscale subgrains, %
Combined deformation	94	55
Combined deformation and heat treatment 500°C, 2 min	89	66
Combined deformation and heat treatment 500°C, 60 min	92	62

with a holding time of up to 60 ... 70 minutes [15, 16]: cold rolling by 40% + 40% static deformation; cold rolling by 30% + 30% static deformation; 40% cold static deformation + 40% repeated static deformation at an angle of 90° to the first; cold dynamic deformation by 40% + 40% static deformation; cold dynamic deformation by 30% + 50% static deformation; cold dynamic deformation by 50% + 30% static deformation; 30% hot dynamic deformation at 880°C + 30% static deformation; hot dynamic deformation by 30% at 300°C + 30% static deformation.

Thus, the results showed that the highest stability of the polygonization substructure of technically pure iron (up to 60 min.) was obtained after dynamic deformation by 40% and 40% of static deformation at an angle of 90° to the first. The hardness of the substructure was 2.0 GPa, which is close to the hardness after static deformation by 60% (Fig. 1). Therefore, the combination of cold dynamic 30% and static 30% deformation (60% total) was chosen as the optimal type of deformation, because it provides a stable hardness of 2.1 GPa after PHT at 500°C for up to 70 min. In addition, this method is more technological. In further studies, this particular deformation method was used – a combination of cold dynamic deformation by 30% and static deformation by 30%.

Carbon steel grade St3 is one of the common structural materials that are used for the manufacture of welded structures, as well as the parts that are designed for operation under variable loads. Therefore, the study of changes in the substructure and hardness of combined deformed samples of steel St3 of size 3×5×5 mm after PHT is of scientific and practical interest. Annealed samples were deformed by combined deformation (30% dynamic and 30% static) and heat treated at a temperature of 500°C. Hardness after deformation was 1.92 GPa. Moreover, the maximum increase in hardness after PHT compared with the state after deformation is 22% and with a holding time of 60 min it is 17%.

Average size of CSR and relative number of nanoscale subgrains were measured by means of SEM analysis by computer metallography using Image Pro Plus software (Table 3).

From the data in Table 3 it follows that there is a decrease in the size of subgrains after PHT compared to the deformed state. The largest number of subgrains (66%) with a size of ≤ 100 nm in St3 steel is observed after a combination of dynamic by 30% and static deformation by 30% and followed by PHT at a temperature of 500°C, holding time 2 min, holding for 60 min provides 62% of nanosized subgrains .

Conclusions. It was observed that the average size of CSR (subgrain) in carbon and alloyed steels after plastic deformation by 60% and PHT with a holding time 1.5 ... 2 min is a nanoscale size. The tensile strength of steel 20 and 20H13 after plastic deformation by 60% and PHT with a holding time 1.5 ... 2 min compared with the deformed state increased by 26 and 12%, respectively. At the same time, ductility, electrical resistance increased and thermal conductivity decreased. The optimal regime of ZrO_2-7% Y_2O_3 plasma sprayed thermal barrier coating PHT was determined, which consists in heating to a temperature 1300°C, holding for 15 min and cooling in air, providing an increase in hardness of 13% and decrease in thermal conductivity of the ceramic layer 15% compared with the state after spraying. Combined plastic deformation (30% dynamically + 30% statically) of technically pure iron stabilizes the nanoscale substructure at a temperature of 500°C during 70 minutes. It was shown that the combined plastic deformation of steel St3 stabilizes the nanoscale substructure at 500°C in the amount of 62% during 60 minutes, which allows the use of such heat treatment in industrial conditions.

მასალათმცოდნეობა

ნანოსტრუქტურირებული ფუნქციონალური მასალების შესაძლებლობის კვლევა წინასწარი რეკრისტალიზაციის სითბური დამუშავებით

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(წარმოდგენილია აკადემიის წევრის გ. თავაძის მიერ)

წინამდებარე სტატია ეხება ნანოსტრუქტურირებული ფუნქციონალური მასალების, ფოლადისა და კერამიკული საფარის შესაძლებლობის კვლევას წინასწარი რეკრისტალიზაციის სითბური დამუშავებით. ექსპერიმენტულად შესასწავლილ იქნა კოჰერენტული რენტგენის სხივების გაფანტვის არეების ზემოქმედების მოცულობა, ნანოსტრუქტურირებული ელემენტების რაოდენობა და ტექნიკურად სუფთა რკინისა და ფოლადის ფიზიკურ და მექანიკურ თვისებებზე ქვენაწილაკების არასწორი მიმართულების კუთხე. ნაჩვენებია 62% პოლიგონიზაციის ნანოსკალის სტრუქტურის თერმული სტაბილიზაციის შესაძლებლობა 500°C-ზე წინასწარი რეკრისტალიზაციის სითბური დამუშავებისას, კომბინირებული პლასტმასის დეფორმაციის შემდეგ.

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