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Structural Relaxation of the Iron–Copper–Carbon Nanotubes Materials After Mechanochemical Activation

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The processes of the defects' accumulation and relaxation in the nanocomposite materials of Fe (80 wt.%) and Cu (20 wt.%) powders with a small addition of the multiwall carbon nanotubes (from 0.5 to 2 vol.%) are studied. The mechanochemical activation of nanocomposite components is performed in a planetary ball mill. The defects' structures of different types are analysed by the thermopower method. The thermopower and strength values reach higher values for the samples compacted and rolled after mechanochemical activation. The main feature of all obtained thermopower dependences is the absence of saturation for both not pre-treated materials and for samples after mechanochemical activation in a ball mill that is caused by the blocking of dislocation by the interphase boundaries.

В роботі досліджено процеси накопичення дефектів і їх релаксацію в нанокомпозиційному матеріялі з порошків Fe (80 мас.%) і Cu (20 мас.%) з додаванням невеликої кількости багатостінних вуглецевих нанотрубок (від 0,5 до 2 об.%). Механохемічну активацію компонентів нанокомпозиції проводили за допомогою кульового планетарного млина. За допомогою методу термо-е.р.с. було проаналізовано дефектну структуру матеріялу. Значення термо-е.р.с. і міцности матеріялу досягають більших значень для зразків, яких скомпактовано та провальцьовано після їх механохемічної активації. Основна риса всіх одержаних залежностей термо-е.р.с. — відсутність насичення як для попередньо необроблених матеріялів, так і для зразків після механохемічної активації у кульовому млині, що зумовлено блокуванням дислокацій на міжфазних межах.

В работе исследованы процессы накопления дефектов и их релаксация в нанокомпозиционном материале из порошков Fe (80 масс.%) и Cu (20 масс.%) с добавлением небольшого количества многостенных углеродных нанотрубок (от 0,5 до 2 об.%). Механохимическую активацию компонентов нанокомпозиции проводили с помощью шаровой планетарной мель-

ницы. С помощью метода термо-э.д.с. была проанализирована дефектная структура материала. Значения термо-э.д.с. и прочности материала достигают больших значений для образцов, скомпактированных и прокатанных после их механохимической активации. Основная черта всех полученных зависимостей термо-э.д.с. — отсутствие насыщения как для предварительно необработанных материалов, так и для образцов после механохимической активации в шаровой мельнице, что обусловлено блокированием дислокаций на межфазных границах.

Key words: structural relaxation, nanocomposite material, mechanochemical activation, carbon nanotubes, thermopower.

Ключові слова: структурна релаксація, композиційний матеріял, механохемічна активація, вуглецеві нанотрубки, термо-е.р.с.

Ключевые слова: структурная релаксация, нанокомпозитный материал, механохимическая активация, углеродные нанотрубки, термо-э.д.с.

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1. INTRODUCTION

In recent years, heterogeneous systems with highly developed interface are the subjects of an intense interest for researchers. Besides, special attention is given to the developing of novel technologies and nanocomposite materials (NCMs) that meet the growing requirements of modern industry. Both the multilayer metallic nanocomposite materials (MMNCMs), which average layer thickness h is less than 50 nm [1], and the composites obtained by the high-energy mechanochemical treatment of powders' mixture in a planetary ball mill [2] belong to prospective materials. Generally, the insoluble or poorly soluble components are used for the manufacturing of NCMs with the improved physical and mechanical properties. The NCMs' fabrication process includes pressing, sintering, and formation of a subsequent precursor by rolling. Precursors are formed from a pack of the alternating layers of dissimilar metals foils; mixture of powders or pseudoalloys' bars resulting in such final product as a high-strength sheet or a wire. The tensile strength (σ_B) and hardness of these NCMs are usually 1.5–3 times higher than the strength and hardness of the composite's components. In particular, the values of the tensile strength increases into 1.6–1.8 times with h decreasing down to 10 nm compared to the strength of precursors melted from the layered iron-copper composites obtained from the powders non-treated in a planetary mill (method 1). The mutual alloying of iron and copper at room temperature is small and practically does not exceed a level of 0.5 at.%. However, it has changed completely if a planetary ball mill is used for obtaining the

precursors (method 2). As we report in present study, the limitless mutual solubility has been established for iron and copper. Moreover, the analysis of the particle sizes' changes and the phase composition of the components powders' mixture during the high-energy treatment allow us to optimize the structure and practically important features of NCMs obtained.

The aim of our work is to establish the regularities of the NCMs' structure formation with changing the modes of samples' production. The physicochemical activation of powders of raw materials is used for this purpose. The optimization of the regimes of a high-energy treatment is studied and discussed.

2. EXPERIMENTAL PROCEDURE

The nanocomposite samples were prepared from the following components: the iron powder IP-1, the copper powder PMS-1, which were mixed in 2:1, 4:1 and 6:1 weight ratio. Such a concentration ratio of the components has been chosen to determine maximum strength of the samples.

Multiwall carbon nanotubes (MWCNTs) have been added to the iron–copper mixture in an amount of 0.5–2 vol.% (or 0.0125–0.05 wt.%) to determine their effect on the properties of NCMs. Carbon nanotubes were obtained by CVD-technique in a rotating reactor [3, 4]. Average diameter of carbon nanotubes was 10–20 nm, their specific surface area, as determined by desorption of argon, was 200–400 m^2/g, and a bulk density was 20–40 g/dm^3.

The powders of raw materials were mixed in a selected proportion and were cyclically treated in a planetary ball mill (time of a cycle was 5 minutes). Using such technique to obtain a precursor was caused by the fact that treatment of components leads not only to the transformation of the cross-sectional grain powders but also change their phase composition and physical properties. The grains repeatedly collide with each other during treatment of the powders in a ball mill. The surface of the particles is mechanically activated under these collisions resulting in the mutual alloying of the components. It should be noted that the mill, which was used for the treatment of powders' mixture in this study, allows reaching the acceleration up to 50*g* unlike most mills used for obtaining the powders previously [5–7]. Thus, the pressure on the particle substance reaches up to 5 GPa. Fifteen balls from stainless steel were used for each of the 3 isolated from the influence of air milling vials. The powder mixture obtained was compressed under a pressure of 30 GPa. The compacted samples were annealed at 950°C in argon atmosphere during 30 min. The precursor obtained was rolled into sheets of 1.5–2 mm thickness under room temperature. The sam-

ples' total rolling deformation was 80–95%. Rolling was alternated with the annealing under the above conditions.

The tensile strength was measured in the air (by the self-computerized tensile machine of 'Instron' type) at room temperature for samples with a length of the working area $\cong 20$ mm, width of 4–5 mm and thickness of 0.15–0.2 mm, the tensile speed was equal to 5 mm/min. The average value of the tensile strength was found for 10 samples.

The thermopower method was chosen for the analysis of the results obtained because of its uniqueness and informativeness. Considering the fact that the induced deformations of differential thermopower (E_T) adequately reflect the change in the defects' density of the materials' crystal structure at their deformation and annealing [8], this method was used to analyse the structural changes in NCM after treatments. It is effective in controlling the macro- and microstructure of materials, the study of the formation and movement of defects in the crystal structure determination of the energy of dislocations motion, and the activation energy of formation of the thermal motion of vacancies, *etc*. [1].

Micrographs of the metal powders have been obtained with the Carl Zeiss AXIO Observer A1m microscope.

The X-ray diffraction patterns of NCMs were obtained by the automated DRON-4.0 diffractometer with the filtered cobalt radiation $K_\alpha = 1.7909$ Å (discrete mode). The collecting of the diffraction data was performed by a full-profile analysis using the program, which provides the experimental diffraction peaks interpolation by the Lorentz function [9]. X-ray phase analysis was performed using a special set of programs that contains a bank of reference X-ray patterns. Crystal lattice period of each phase component was refined by the least squares method. The relative error in the determination of the lattice periods did not exceed 0.01%.

3. RESULTS AND DISCUSSION

Usually, the structure and characteristics of MMNCMs are analysed after the deformation by the cold rolling of sintered powders' mixture of the precursors. However, considering the effect of the MMNCM's strength increasing with the thickness of layers decreasing, the samples were rolled to the nanoscale h values. In this case, the strength and hardness values' increase describes by the well-known Hall–Petch equation with the supplement contribution caused by the surface tension forces [10]. However, the hardening value is limited by $h \approx 15–10$ nm due to a change of the sample's deformation mechanism from the dislocation one to a slipping of the layers dispersed on each other under rolling. Previously, we

have shown that, for example, for the Fe–Cu composites the boundaries of thin ($h < 500$ nm) layers significantly brake the spread of fatigue cracks and, besides, they block the dislocations effectively at $h < 350$ nm [1]. Moreover, the strength of the material is increased significantly, as it was mentioned above.

The changes in the structure and phase composition of the NCMs obtained by method 2 have been analysed as early as during the stage of the iron–copper powders' mixture treatment in a planetary ball mill due to the fact that under such treatment the grains change significantly their average cross-sectional sizes (s). At that, the phase composition of precursors has been changed either. While the precursors for producing MNCMs contain the iron and copper only, the precursors for the method 2 are absolutely different. In this case the iron (up to 30 at.%) may dissolve completely in copper and form a metastable solid solution depending on the treatment time (τ). The s values of particles used in the producing of powders are follows: the cross section of almost all powder particles is decreased at $\tau = 20$ min.

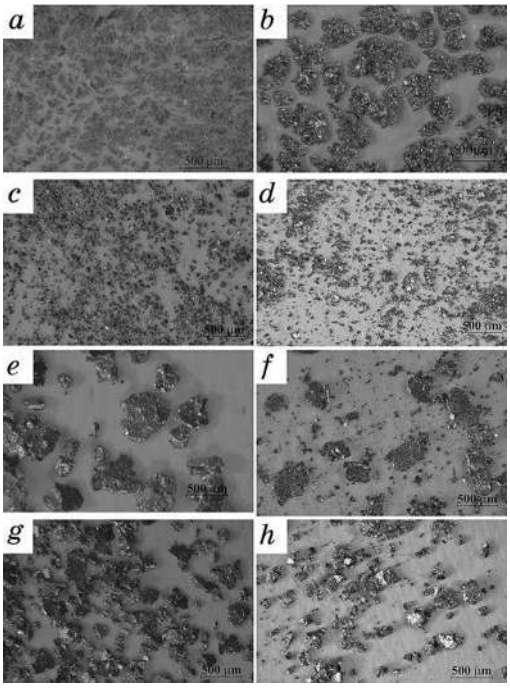

Fig. 1. Optical microscopy of the raw powders of Cu (*a*); Fe (*b*); their microscopy after treatment for 20 minutes (*c*, *d*) and 120 (*e*, *f*) in a planetary ball mill, respectively; Cu (*g*) and Fe (*h*) powder with addition of 1 vol.% of MWCNTs treated in the mill for 120 min.

TABLE 1. Tensile strength for the samples obtained from precursors by rolling with 95% of a total relative deformation

Material	Content of multiwall carbon nanotubes, vol.%										
	0			0.5		1		1.5		2	
	Milling time, min										
	0	20	120	20	60	20	60	20	60	60	120
	Tensile strength for the samples with 95% relative rolling deformation										
Fe–Cu (2:1)	755 ± 41	—	—	—	—	—	—	968 ± 48		850 ± 42	—
Fe–Cu (4:1)	860 ± 18	865 ± 43	860 ± 43	1450 ± 65	1200 ± 54	900 ± 41	1800 ± 81	920 ± 37	1000 ± 45	825 ± 37	820 ± 36
Fe–Cu (6:1)	858 ± 13	795 ± 40	395 ± 20	700 ± 32	1108 ± 50	810 ± 36	849 ± 42	755 ± 34	750 ± 34	—	—
Fe	825 ± 37	900 ± 45	1020 ± 45	975 ± 44	1027 ± 51	525 ± 24	761 ± 38	525 ± 24	758 ± 38	—	—
Cu	382 ± 23	605 ± 33	—	450 ± 22	441 ± 22	—	—	—	—	—	—

TABLE 2. Lattice parameters of nanocomposite materials.

Material	Milling time, min					
	20		60		120	
	Lattice parameter Cu (f.c.c.), Å	Lattice parameter α-Fe (b.c.c.), Å	Lattice parameter Cu (f.c.c.), Å	Lattice parameter α-Fe (b.c.c.), Å	Lattice parameter Cu (f.c.c.), Å	Lattice parameter α-Fe (b.c.c.), Å
Fe–Cu (1:9)	—	—	3.6184	—	3.6214	—
Fe–Cu (1:4)	—	—	3.6187	2.8658	3.6255	—
Fe–Cu (3:7)	3.6143	2.8651	3.6212	2.8657	3.6280	—
Fe–Cu (4:1)	3.6177	2.8669	—	2.8745	—	2.8748

The morphology of a particle has changed either (Fig. 1, *a*–*d*). The individual particles' agglomeration with the formation of small complexes during their sintering takes place under increasing of the treatment time up to 120 minutes due to mechanical activation of the surface (Fig. 1, *d*, *e*). The addition of MWCNTs into powders blocks the formation of such agglomerates and results in an averaging of the particle size (Fig. 1, *g*, *h*). The increase in treatment time up to 120 min may lead again to a reduction of the cross section *s*, *etc*.

After pressing, sintering, and cold rolling, the grains of the precursors obtained demonstrate an elongated structure as in the case of rolling of MMNCMs precursors. Thus, the strength of rolled precursors is also changed (Table 1) in accordance with the increase of the time of mechanochemical activation of powders in a ball mill and the relating change in structure. It is important that not all of the precursors could be rolled due to their embrittlement during that process (for example, we could not roll a precursor from Fe–Cu (2:1)). That is why the data on the value of their σ_B are not listed in Table 1. The most promising material from the viewpoint of obtaining samples with maximum σ_B is the Fe–Cu (4:1) system with an addition of 1 vol.% MWCNTs. For them, σ_B is equal to 1800 ± 81 MPa at $\tau = 60$ min (Table 1). In general, the tensile strength of the samples has been decreased with treatment time increasing up to 120 min (time of the particles' agglomeration formation).

The lattice parameters of powder mixtures are also changed due to mutual mechanical alloying of iron and copper (Table 2). Such changes occur cyclically with increasing activation time. For example, the lat-

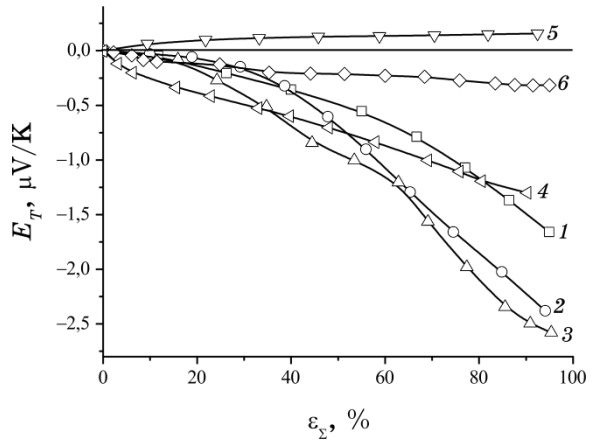

Fig. 2. The dependences of thermopower of the Fe–Cu (4:1) (*1*, *2*); (2:1) (*3*) treated in a planetary ball mill for 20 (*1*) and 120 (*2*, *3*) min; the Cu–Fe (2:1) multilayer composite material (*4*); Cu powder (*5*) and ARMCO Fe (*6*) of the total degree of relative deformation during rolling.

tice parameter of iron for the Fe–Cu (4:1) treated for 20 min is increased from $a \approx 2.8665$ Å to 2.8669 Å, and for copper it increases from $a \approx 3.6150$ Å to 3.6177 Å with τ increasing up to 60 minutes. So, one can speculate about complete dissolving of copper in the iron, which leads to an increase of the iron lattice parameter to 2.8745 Å and it almost does not change with further treatment ($\tau = 120$ min, $a \approx 2.8748$ Å). Dislocation structure of the precursors rolled is changed either along with the change of the lattice parameters of materials.

To clarify the dynamics of the above changes, the method of thermopower was used. The study of thermopower (E_T) dependence on the degree of a relative rolling deformation (ε_Σ) of the MMNCM's and NCM's precursors revealed that E_T is increased. The induced deformation of the samples obtained by the method 2 is higher than for materials obtained by the method 1 for almost all degree of deformation (Fig. 2). This correlates with the increase in the density of crystal defects, and, accordingly, with σ_B increasing. A nonmonotonous character of E_T changes with total relative rolling deformation increasing is the outstanding feature that correlates with defects, in particular, dislocations, and density changing (Fig. 2).

The cross-sectional dimensions and morphology along with the phase structure and composition are modified after the treatment in a planetary mill. All this is reflected in the conditions of the diffusion of current carriers and consequently in the thermoelectric power changes. And, if at the milling time $\tau = 20$ min, the value of E_T varies slightly for the different concentration ratio of the components (Fig. 3, curve *1*), at $\tau = 120$ min maximum change of E_T can reach 20 μV/K (iron concentrations (C) in the precursor is about 60

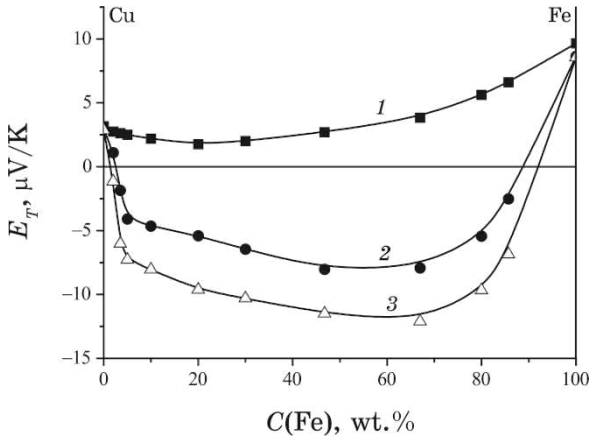

Fig. 3. The thermopower diagrams (relatively Pb) of compacted powders mixtures Fe–Cu after treatment in a planetary ball mill for 20 min (*1*), 60 min (*2*), 120 min (*3*).

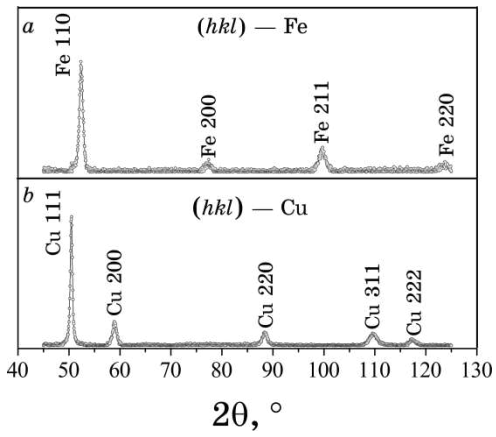

Fig. 4. X-ray patterns of nanocomposite powders of Fe–Cu (1:4) (*a*), Fe–Cu (4:1) (*b*) treated in a planetary mill for 120 min.

wt.%). It is characteristic that the milling of pure source copper and iron powders changes the value of E_T compared to tabulate one (standard Pb) slightly. Therefore, the reference value of E_T for the copper is –3.2 μV/K, and for hardened powder, –3.04 μV/K; for iron, these values are $E_T = 15$ μV/K and 9.18 μV/K, respectively. For the same precursors obtained from powders treated for $\tau = 20$–120 min in a mill, the changes of E_T do not exceed 10%. From our point of view, the changes listed above are caused by both the mutual alloying of components of the powders' mixture and the formation of the related metastable solid solutions. The dynamics of the formation of these solutions can be estimated from the diagram presented at Fig. 3.

We emphasize that according to the X-ray diffraction analysis (Fig. 4) the left part of the diagram on Fig. 3 represents the metastable solid solution of Fe in Cu of f.c.c.-type crystal structure. The right part of the diagram with corresponds to a metastable solid solution of the α-Fe with a b.c.c. lattice (Fig. 4, *b*).

The annealing of the samples causes the process of structural relaxation. The annealing decreases the density of defects in the crystal structure and causes a redistribution of impurities or even a partial recrystallization. All this results in the corresponding changes of E_T during annealing. Figure 5, *a*–*d* demonstrates the thermopower dependences on the annealing temperature of the rolled iron precursors (Fig. 5, *a*) and iron with 1 vol.% of MWCNT (Fig. 5, *b*).

The character of dependencies presented here is almost the same, and the total change of E_T under annealing up to $T = 700$°C does not exceed $\Delta E_T = 0.7$ μV/K. At the same time, the presence of nanotubes in the samples did not significantly influences on the character of

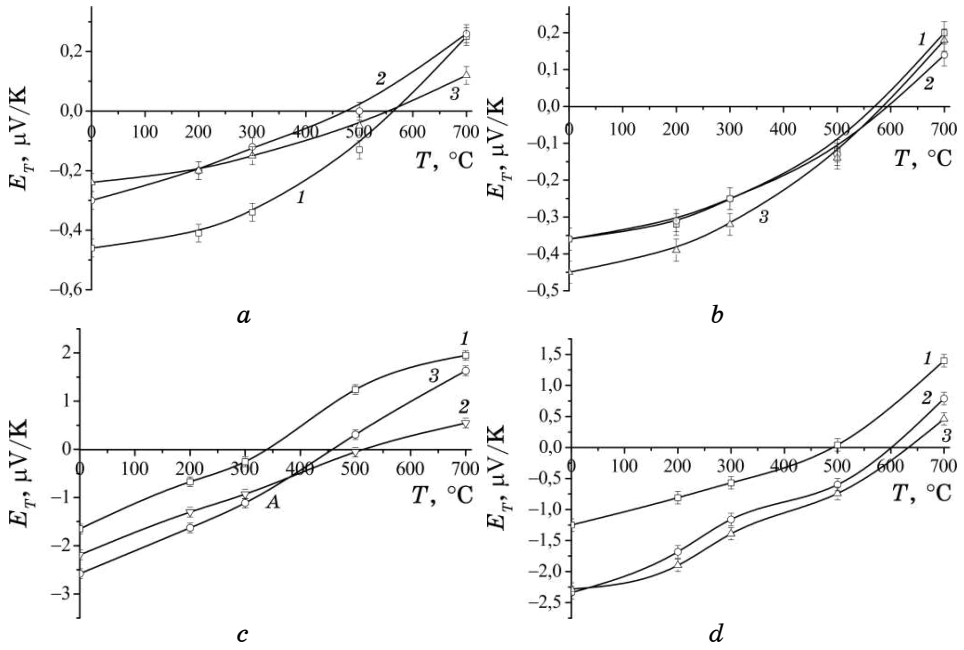

Fig. 5. The dependences of thermopower of the samples with 95% of total degree of relative deformation during rolling: of Fe (*a*); Fe–MWCNT (1 vol.% (*b*); Fe–Cu 4:1 nanocomposite materials (*c*); Fe–Cu (4:1)–MWCNT (1 vol.%) nanocomposite materials (*d*), treated in a planetary mill for 20 (*1*); 60 (*2*); 120 min (*3*) of the temperature of multiple isochronous ($t = 100$ min) annealing.

the dependences (Fig. 5, *b*) and general changes in the value of E_T for both cases.

General changes of E_T after annealing are significantly higher for NCMs than for iron and can reach $\Delta E_T \approx 4$ μV/K (Fig. 5, *d*). However, the presence of nanotubes affects ΔE_T as for the iron. Since the general changes of the thermopower are higher than these ones generated by the increasing of defects' density during rolling, one may assume that the redistribution of impurities and formation of a new configuration of the grain structure of the samples are responsible for it.

4. CONCLUSIONS

1. The morphology of the NCMs studied is changed under the mechanochemical activation of the metal powders in a planetary ball mill depending on the mode of activation used.
2. The condition for the mutual alloying of the even not soluble component has been achieved. The mechanochemical activation of

the metal powders' mixture, which are substantially insoluble in the molten state like iron and copper do not form an equilibrium solid solution. It allows to synthesize a composition, which contains their metastable solid solutions and to increase the physical and mechanical properties of nanocomposites obtained.

3. The optimization of the high-energy treatment time of the powders in a planetary ball mill enables to improve the mechanical characteristics up to 2–3 times as compared with the additive characteristics formed on the base of fabricated nanocomposite materials. For the Fe–Cu (4:1)–MWCNT (1 vol.%) nanocomposite, the obtained tensile strength is equal to 1800 ± 81 MPa.

4. The using of thermopower method for the analysis of the processes of accumulation of defects in the crystal structure during rolling of samples and relaxation under annealing allows determine the boundary parameters of NCMs using. The relative level of the total rolling deformation for maximum tensile strength should be at least $\varepsilon_\Sigma \geq 95\%$, and the annealing temperature for the structural relaxation has to vary in a temperature range from 300°C to 600°C depending on the type of material.

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