



Article Ice Composites Strengthened by Organic and Inorganic Nanoparticles

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Abstract: Extensive development of the Arctic, rich in various natural resources, requires a lot of cheap ecologically safe construction materials preferably using local renewable sources. Ice being easily available in regions with a cold climate meets all the above criteria but has low strength, high fragility and a tendency to creep. Known strengthening techniques using macroscopic and microfiber additives have many drawbacks. This paper describes a new approach to ice strengthening by adding organic or inorganic 50–100 nm nanoparticles (NPs) to the water to be frozen and presents experimental results and possible mechanisms analysis of polycrystalline ice strengthening using NPs. Cellulose and silica NPs have been tested as typical representatives of such additives. Both are hydrophilic, ecologically safe, widespread, cheap and can be produced from local renewable raw materials. It is shown that the addition of 0.01 to 5 wt.% of NPs results in a reduction of ice composite average grain size by a factor of 5.3 ± 0.7 and an increase of its compression strength by a factor of 2.5 ± 0.3 . The highest sensitivity of ice strength to NPs concentration is between 0.1 and 1 wt.%. In this concentration range, the increase in strength is reversely proportional to the square root of the average grain size. Experimental data fit Griffith's relation better than Hall–Petch, so ice strength is limited by cracks with the length proportional to average grain size.

Keywords: ice composites; strengthening by nanoparticles; grain size; Hall–Petch relation; Griffith's relation

1. Introduction

The Arctic, and northern regions of Russia, the USA and Canada in particular, are rich in valuable resources like timber, gas, oil, precious metals, ores and other minerals. However, the development of these hard-to-reach territories demands enormous capital investment. Building roads, runways, crossings, bridges, buildings, etc., requires a large amount of construction materials that have to be delivered from remote industrialized regions. Ideal cheap construction materials could be ice, snow and other local geophysical materials. They are renewable, ecologically safe and easily available in cold regions. They have low density and do not demand special utilization procedures at the end of the life cycle. However, despite all above advantages, the ice as a main component of such composite materials has a number of significant internal drawbacks including low strength, low fracture toughness and high creep rate [1–3] at typical Arctic winter ambient temperatures. During the last century it incites many teams to work on ice strengthening using various approaches [4–6].

Historically, the first approach to ice strengthening was based on its reinforcement by macroscopic additives. Usually, it was cheap waste from the forestry industry (sawdust,



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). shavings and wood chips) [7]. There was a famous project named Habbakuk [8] consisting of the construction of giant aircraft carriers made of ice composites (IC) in the northern Atlantic during World War II to counter the threat posed by German submarines. The addition of the optimal quantity of sawdust to the water to be frozen, which turned out to be 14 wt.% or around one-third of solid material volume, resulted in fourfold ice strengthening. Later, various high-strength microfibers ranging from microcellulose and basalt to Kevlar and carbon nanotubes were tested as reinforcing additives [9–12]. For more than a century, working on ice strengthening using various macro- and microscopic additives resulted in the development of various approaches and technologies for an increase in the strength of constructions made of IC. It allows the building of large-scale dams and dome-shaped buildings with diameters of tens of meters [13,14]. However, the potential of ice strengthening using macro and micro additives is quite limited, and it prevents the wide application of such techniques to the construction of winter roads, river crossings, airfields, etc. Additionally, these techniques are difficult to implement due to stratification or coagulation/sedimentation of additives. Strengthening using long microfibers requires layer-by-layer placement and freezing while employing a fiber matrix for this purpose requires complex techniques of elimination of air bubbles trapped in the matrix. Usually, all the above techniques of IC manufacturing result in ice strengthening by a factor of 3–4, and reaching 5–6 in rare cases. They are not perfect from an ecological point of view and require some special measures for additive utilization after the end of the construction life cycle. Now it is clear that a radical increase in ice strength using only macro- and micro-sized additives is impossible because of the low strength of the ice that is the main component of IC no matter which high-strength reinforcing elements are used.

As can be deduced from the general considerations, the low strength of ice is determined by imperfections of its structure, i.e., by a large number of structural defects in it. In the above context, it is essential to estimate the strength of chemically pure defect-free ice. Though the mechanical characteristics of ice originate from weak hydrogen bonds between H₂O molecules [15], its theoretical strength limit σ_{th} is quite high. It is well-known that the strength of ideal defect-free crystals named ideal or theoretical strength, as well as Young's modulus *E*, is determined by the properties of interatomic bonds and their density at the unit area. Different theories from solid state physics (both classic and quantum ones) give (0.07-0.1)E for σ_{th} [16]. For the ice at temperatures not too close to its melting point, one can accept $\sigma_{th} \approx 0.07E_d \approx 700$ MPa as the lower estimate, where $E_d \approx 10$ GPa is the dynamic value of Young's modulus of pure ice [1,2].

However, the experimental strength of natural ice is 2–3 orders of magnitude lower than σ_{th} and lies between 0.5 and 10 MPa usually [1–3]. It implies the existence of a large and currently unemployed potential for ice and IC strengthening. The origins of so strong discrepancy between theoretical and experimental results are in the presence of a wide variety of structural defects in real ice and IC. The defects with the strongest effect on strength are micro- and macroscopic cracks, air bubbles and other discontinuities of material. It is the reason for the modest results of the efforts on ice strengthening using modifications of hydrogen bonds in ice by macro- and micro-scale additives and chemical doping taken in the last two decades [17–21]. So, the search for new ideas and approaches to ice strengthening still remains.

As far as we know, NPs with 10–100 nm size have not ever been added to the ice intentionally for the purpose of its strengthening. There are scarce and scattered non-systematic data concerning the effect of NPs on ice crystallite nucleation, its growth, strength and recrystallization of polycrystalline ice. For example, refs. [22,23] have described the mechanical properties of ice in wastewater basins, and ref. [24] has presented the data concerning ice on the Yellow River in China, where the water contains up to 0.06 wt.% of suspended particles. Refs. [25,26] report the inhibition of ice grain growth by cellulose NPs during recrystallization.

Summing up this brief review of the current state of ice strengthening problem, one can assert that despite the range of characteristic sizes of additives starting from atomic-

molecular and up to macroscopic that have been tested, radical (more than by a factor of 3–5) well reproducible strengthening of IC has not been achieved yet. However, there are still some white spots in the field of ice strengthening. The most promising and the least studied areas in this field lie in the nano- and sub-micro-scale between atomic–molecular and microscopic levels. This level can be utilized by means of adding natural or synthetic nanoparticles (NP) to the water to be frozen.

As follows from the general principles well known in physical material science, a significant strengthening of polycrystalline material and approaching its theoretical strength limit can be achieved on two different paths. The first one is the reduction of defect concentration so that the material approaches the ideal monocrystalline state. The second one is increasing the defect concentration to a level so high that the material approaches an amorphous state. The second path explored in our recent paper [27] reveals its potential. It renders it possible for strengthening in the uniaxial compression test to reach the factor of 2.5 in some cases. However, this approach requires further systematic research, as long as, unlike microfiber reinforcement, strengthening by NPs can employ many different micro-mechanisms, including grain size reduction, dispersion strengthening of grains, prevention of grain boundary slipping or crack growth and many others.

The aim of this work is experimental proof of the concept of ice strengthening by hydrophilic organic and inorganic NPs. Highly dispersive (10–100 nm) NPs of cellulose and silica have been used as accessible and ecologically safe representatives of the above two types of material

2. Materials and Methods

Organic and inorganic NPs were used to fabricate ice composites. Organic NPs were prepared by wet milling of microcrystalline cellulose (Mingtai Chemical, Taoyuan, China) with an average particle size of 70 μ m. The obtained cellulose NPs will be referred to below as NPs-cellulose. Silica NPs (hereinafter NPs-SiO₂) (Sigma-Aldrich, Saint Louis, MO, USA) with a declared particle size of 10–20 nm were used as inorganic nanoparticles. Cellulose and silica NPs differ significantly in their physical–chemical properties, in particular in water absorption and conditions at their surface in water suspension.

Wet milling of microcrystalline cellulose was carried out in a planetary mill Pulverisette 7 Premium Line (Fritsch, Idar-Oberstein, Germany) for 2 h using 0.6 mm yttria-stabilized zirconia beads (Zhejiang Jinkun Sili Ceramic Beads, Hangzhou, China). The mass ratio of microcrystalline cellulose powder, distilled water and milling media was 1:10:100. The prepared NPs-cellulose slurry was diluted to a mass fraction (*c*) of 2 wt.% by adding distilled water. To homogenize the resulting suspension, it was sonicated at a frequency of 20 kHz using a Vibra-Cell VCX 750 ultrasound processor (Sonics & Materials, Newtown, CT, USA). To prevent heating of the suspension, the ultrasound power was limited to 100 W. Suspensions with a lower mass fraction of NPs-cellulose were prepared from a 2 wt.% suspension by sampling and their successive dilution with distilled water. As a result, suspensions of NPs-cellulose with *c* = 0.003–2 wt.% were obtained.

To prepare suspensions of NPs-SiO₂ with c = 0.003-10 wt.%, a 10 wt.% suspension was first obtained by dispersing an appropriate amount of NPs-SiO₂ in distilled water using ultrasonic treatment similar to that described above. Suspensions with a lower mass fraction of NPs-SiO₂ were prepared in the same way as in the case of suspensions of NPs-Cellulose.

The size (*D*) distribution of NPs-cellulose and NPs-SiO₂ in the prepared suspensions was analyzed by dynamic light scattering method (DLS) using a Zetasizer Nano ZS analyzer (Malvern Instruments, Malvern, UK). Figure 1 shows a monomodal size distribution for NPs-cellulose and NPs-SiO₂ with a maximum at about 80 and 40 nm, respectively. For both NPs-cellulose and NPs-SiO₂, the position of the distribution maximum does not depend on the mass fraction of nanoparticles in the prepared suspensions. The average size of NPs-cellulose and NPs-SiO₂ in the prepared suspensions, calculated from the curves shown in Figure 1, is 97 and 44 nm, respectively. The images of NPs-cellulose and NPs-SiO₂ in a

scanning electron microscope (SEM) Merlin (Carl Zeiss, Oberkochen, Germany) are shown in the insert of Figure 1. The larger size of NPs-SiO₂, determined by DLS measurements, compared to that declared by the manufacturer may be due to the hygroscopicity of NPs-SiO₂, which leads to an increase in the size of NPs-SiO₂ in the aquatic environment.



Figure 1. The size distribution of NPs-cellulose and NPs-SiO₂ in suspensions with different mass content of nanoparticles. The solid curves are plotted using mean values. The inset shows SEM images of (**a**) NPs-cellulose and (**b**) NPs-SiO₂.

The samples of plain ice and IC were fabricated at a temperature of -10 °C in a freezer. The use of fluoroplastic cuvette with individual cells made it possible to prepare 48 samples $10 \times 10 \times 20$ mm³ in size for mechanical tests and microstructural studies in one freezing. The cuvette had a thin bottom wall (~1 mm) and was placed on a massive metal plate. After pouring the samples, the cuvette was thermally insulated from the top and sides with a thick-walled foam box from the freezer atmosphere. Since the coefficient of thermal conductivity of ice is more than an order of magnitude higher than that of fluoroplast at -10 °C, this layout arranged bottom to top uniaxial heat flow in the samples during crystallization.

The microstructure of the obtained samples of ice and ICs was studied in the reflected light mode using an Axio Observer A1m optical microscope (Carl Zeiss, Oberkochen, Germany) equipped with an image capture and analysis system and a detachable thermal chamber with adjustable forced cooling. The grain boundaries were visualized due to thermal etching and segregation of impurities at the boundaries.

The mechanical properties of plain ice and ICs were studied by the uniaxial compression method on an MTS 870 Landmark servo-hydraulic machine (MTS, Eden Prairie, MN, USA) equipped with an environmental chamber. The temperature inside the chamber was maintained at -10 °C by liquid nitrogen vapor entering the chamber from a Dewar vessel. The absolute strain rate in all experiments was 4.8 mm/min, which corresponded to a relative strain rate of $4 \cdot 10^{-3}$ s⁻¹. For each additive concentration, at least eight samples were subjected to mechanical testing.

3. Results

Typical optical images of ice and IC microstructure are shown in Figures 2a–c and 3a–c for samples with different concentrations of cellulose and SiO₂ NPs, respectively. As could be seen, higher NP concentration leads to smaller grain sizes for both NP types. Technical

vision technique was used to obtain grain size distribution. Characteristic grain size d was determined as an average of grain dimensions in two perpendicular axes. The distributions corresponding to images shown in Figures 2a–c and 3a–c are presented in Figures 2d–f and 3d–f accordingly. On processing images of grain structure at various NPs concentrations, we have found that the size distribution d for plain ice is wider than that of ICs and spans the ~100–~1200 µm range with $d_m = 500 \pm 50$ µm as the most probable value. Both cellulose and SiO₂ NPs introduction results in diminishing IC grain size and narrowing size distribution with growing NP concentration. For example, the addition of 1 wt.% of cellulose NPs results in a reduction of d_m to 115 ± 5 µm, which is more than four times lower than that of pure ice, and on adding 5 wt.% of SiO₂ NPs, the d_m drops more than five times down to 95 ± 5 µm. Grains with $d \gtrsim 400$ µm vanish completely in the presence of NPs.



Figure 2. Grain microstructure (**a**–**c**) and size distribution (**d**–**f**) for pure freshwater polycrystalline ice (**a**,**d**) and IC with cellulose NPs concentrations c = 0.3 wt.% (**b**,**e**) and c = 1 wt.% (**c**,**f**). Total number of measured grains N = 100.

Figure 4 presents typical loading diagrams in standard $\sigma - \varepsilon$ coordinates for plain ice and IC containing cellulose or SiO₂ NPs, where σ is engineering uniaxial compression stress, and ε is relative deformation. Plain ice demonstrated linear dependence of strain on stress up to sample brittle fracture without noticeable inelastic deformation except in the initial deformation stage, where the roughness of sample edges was being squashed. This initial stage has been excluded from the loading diagram analysis. The slope at the linear section of the dependence was taken as a conventional value of Young's modulus *E*. However, even a small NP concentration such as c = 0.01-0.03% gives rise to inelastic deformation $\varepsilon_{\rm pl}$ before fracture and reliable strengthening of IC compared to plain ice. At SiO₂ NP concentration c > 3% stress did not drop to zero abruptly on reaching peak value σ_p , but reduced gradually, and the sample kept its integrity. As a result, such ICs demonstrate some peak at the diagram and following quasiplastic flow section up to $\varepsilon > 10\%$. It distinguished such samples from samples with lesser *c* qualitatively, as long as the latter underwent brittle fracture immediately after reaching the peak load. Cellulose NP suspension was unstable at *c* > 3% so we could not obtain the samples with uniform spatial distribution of NPs at higher concentrations and study their mechanical properties. We will characterize IC strengthening induced by NP additive by factor $k = \sigma_p / \sigma_p^*$, where σ_p^* is the peak stress the plain ice can endure.



Figure 3. Grain microstructure (**a**–**c**) and size distribution (**d**–**f**) for IC with silica NPs concentrations c = 0.003 wt.% (**a**,**d**), c = 0.03 wt.% (**b**,**e**), c = 5 wt.% (**c**,**f**). Total number of measured grains N = 100.

Concentration dependences of σ_p , E, ε_{pl} and d_m are shown in Figure 5. Around 150 samples were frozen and tested to reveal them. In general, these dependences demonstrated improving mechanical characteristics (Figure 5a–c), diminishing grain size (Figure 5d) and reducing results dispersion with growing c. However, the sensitivity of the above characteristics to c changes differed. The value of k for IC with cellulose NPs reached 2 at c = 1%, and for IC with SiO₂ NPs, it reached 2.5 at c = 5%, though its growth at c > 1% slowed down substantially, and k(c) dependence tended to saturate. The effect of additive on Young's modulus E was much less pronounced than on σ_p (Figure 5b). Peak E value at c = 1% did not exceed that of plain ice more than by 25%, and at higher c it even dropped slightly (Figure 5b).



Figure 4. Typical loading curves σ - ε : (a) plain ice (1) and IC with cellulose NP concentration c = 0.03% (2), c = 0.3% (3), c = 2% (4); dashed line is (5) linear approximation of elastic section, dashed line is (6) straight line parallel to (5) but drawn through peak stress load point; (b) plain ice (7) and IC with SiO₂ NP concentration c = 0.3% (8), c = 5% (9), c = 10% (10).

As mentioned above, unlike plain ice, IC manifested noticeable inelastic deformation at c > 0.01% for both studied NP types. It showed up as a deviation from linear σ – ε dependence (line 5 in Figure 4) when stress exceeded σ_p^* for the plain ice. The value of inelastic deformation ε_{pl} grew with c both for cellulose and SiO₂ NPs (Figure 5c). It should be noted that at c > 1-3% all three studied mechanical characteristics reach saturation, so NP concentrations above 2–3% are unreasonable.

Grain size and intergrain boundaries strength can affect polycrystal's mechanical properties significantly [28]. As follows from $d_m(c)$ dependence shown in Figure 5d, the introduction of NPs of both types at concentration 1–2% results in diminishing d_m up to sixfold compared to plain ice. In further *c* increasing, $d_m(c)$ saturates just as concentration depends on mechanical properties. It is evidence of a strong connection between mechanical properties and the grain structure of the ice matrix.

Summing up the raw results of the experiments, one can note that IC mechanical characteristics are the most sensitive to NP concentration when the latter is in the range between 0.01 and 1–2%. Redrawing experimental data at the above c range in double logarithmic coordinates reveals linear dependences with high correlation coefficients r for all studied mechanical characteristics (Table 1). For Young's modulus, in which concentration dependence was very weak, the r value was much lower than that for any other property. A good approximation of experimental data for mechanical properties and grain size over-concentration by linear functions in double logarithmic coordinates means power law concentration dependences for these properties with power indices n equal to the approximation line slopes in double logarithmic coordinates. Such data representation is also shown in Figure 5. It allows quantitative characterization and comparison of properties sensitivity to NP concentration by dimensionless n value.



Figure 5. Concentration dependences of peak stress σ_p (**a**), Young's modulus *E* (**b**) and relative inelastic deformation ε_{pl} (**c**) measured in uniaxial compression test and average grain size d_m (**d**) of plain ice (star) and ice composites containing cellulose (blue triangles) and silica (red rhombs) NPs in linear (empty marks) and double logarithmic (filled marks) coordinates. Lines correspond to best fit by power functions.

Table 1. Slope <i>n</i> and correlation coefficient <i>r</i> for dependences between logarithms of various physical-
mechanical properties of IC and logarithm of NP weight fraction in it.

IC Characteristics		Cellulose IC	SiO ₂ IC	Universal
σ _p	п	0.10 ± 0.01	0.12 ± 0.01	0.11 ± 0.01
	r	0.973	0.987	0.983
E	п	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
	r	0.769	0.725	0.718
ε _{pl}	п	0.40 ± 0.17	0.27 ± 0.05	0.30 ± 0.05
	r	0.806	0.923	0.856
d _m	п	-0.17 ± 0.02	-0.20 ± 0.03	-0.18 ± 0.03
	r	-0.982	-0.930	-0.887

4. Discussion

Let us consider plausible mechanisms of revealed IC strengthening caused by cellulose and SiO₂ NPs introduction. As long as significant grain size reduction with growing NP concentration is established, let us discuss the related mechanisms above all. This grain diminishing is obviously due to the increase in heterogeneous crystallization centers number at higher *c*. Grain size, grain boundaries, triple joints and texture are the most important elements of polycrystal ice structure. Grain boundaries are dislocations source and drains, stress concentrators, and places for easy crack nucleation and boundary slipping [28]. It is known that the strengthening effect of grain boundaries, in general, can be described by empiric Hall–Petch relation [1,2,28]

$$\sigma_{\max} = A + K/d_m^n,\tag{1}$$

where *A*, *K* and $n \approx 0.5$ can be treated as material constants at the first approximation. Similar relations govern the inhibition of dislocation multiplication, mobility in basic slip planes due to dispersion strengthening, and breaking of dislocation ensembles through grain boundary. In the latter case, *n* can differ from 0.5 slightly and lie between 0.3 and 0.8.

The low crack resistance of ice which is an order of magnitude lower than that of silicate glasses means easy microcrack nucleation in it. The strength of grain boundaries in ice is usually many times lower than that of grains themselves, so the cracks nucleate mostly at grain boundaries. The crack's initial mean length is determined by grain size so that lower d_m can result in strengthening according to Griffith's relation [3]

$$\sigma_{\rm max} = B/d_{\rm m}^{1/2} \tag{2}$$

where $B = (2E\gamma)^{1/2}$ and γ is effective surface energy.

To choose an actual strengthening mechanism from the above alternatives, which are governed by resembling relations, $\sigma_p(d_m)$ dependence has been plotted and analyzed (Figure 6). As long as concentration dependences of both maximal stress and grain size obey a power law, one should expect the dependence of stress upon grain size obeys it as well. Combining data for $\sigma_p(c)$ and $d_m(c)$ and reducing the *c* variable, one can obtain the power law relation for $\sigma_p(d_m)$ with power index $n = -0.6 \pm 0.1$. Additionally, as discussed in [27], non-linear regression [29] of experimental data on $\sigma_p(d_m)$ in IC containing SiO₂ NPs by power law functions gives a power index close to -0.5, too.



Figure 6. Dependences of peak stress σ_p for IC with cellulose (**a**) and silica (**b**) NPs upon average grain size in linear (filled marks) and linearizing (σ_p — $d_m^{-1/2}$) (empty marks) coordinates.

On this basis, we have used linear regression in $\sigma_p - d_m^{-1/2}$ coordinates in this paper. As a result, the following values of additive term *A* in (1) and correlation coefficient *r* have been found: $A = -1.7 \pm 2.2$ MPa with r = 0.956 for SiO₂ NPs, and $A = 0.7 \pm 2.2$ MPa with r = 0.932 for cellulose NPs. As long as the above two samples turn out to be statistically indiscernible, the datasets have been joined, and the following results have been obtained: $A = 1.8 \pm 3.5$ MPa with r = 0.893 for the generalized sample. Taking high values of correlation coefficients and the range 10–30 MPa of σ_p into account, the value of additive term can be considered as zero within experiment accuracy, and the experimental dependence $\sigma_p(d_m)$ as obeying power law $\sigma_p = B d_m^{-1/2}$ coinciding to (2). This dependence is shown in Figure 6 both in linear σ_p - d_m and linearizing σ_p - $d_m^{-1/2}$ coordinates.

So, the processing of experimental data is evidence that the most preferable mechanism of IC deformation and fracture involves intergrain propagation of the cracks nucleated at the basis of defects with initial size strictly and linearly related to grain size.

In addition to grain diminish and related effects, other mechanisms of NPs' impact on mechanical properties are plausible including dispersion strengthening, grain boundary strengthening, hindering dislocation nucleation and movement within the grain and break-through grain boundaries, crack nucleation and propagation, grain slippage, and others. Emergence and development of irreversible deformation before reaching peak stress and afterward means the transition from brittle fracture typical for plain ice to ductile fracture at larger *c*. The nature of such transition can be very diverse, too. However, the similarity of results for two significantly different types of NPs and high correlation coefficient for σ_p — $d_m^{-1/2}$ dependence for the generalized sample means that in the first approximation, the NPs effect is mainly determined by the induced change of grain size in the studied range of NPs concentration. Obvious restrictions on NP properties include their ability to serve as nucleation centers in ice crystallization and NPs suspension stability relative to aggregation, but otherwise, the physical and chemical properties of utilized NPs are of minimal importance.

Elucidation of detailed mechanisms of NP effect on IC mechanical properties and their potential requires more thorough and systematic experimental research employing NPs of various nature, morphology, size and concentration.

5. Conclusions

The paper presents an experimental study of ice strengthening by adding cellulose and silica nanoparticles to the distilled water to be frozen. It is shown that the highest gain in compressive strength and inelastic deformation before fracture takes place at NP concentration changing from 0.01 to 1 wt.%. Further concentration increase affects mechanical characteristics only slightly, reaching saturation at c = 3-5%, and can even lead to their deterioration at c higher than that. Additionally, NP introduction results in changing fracture mode from brittle to ductile with total deformation before disintegration exceeding 10%. Within the experiment accuracy, the effect of cellulose and silica NPs cannot be discerned despite significant differences in NP composition, morphology and some difference in average size. It is found that inelastic deformation before fracture is the property the most sensitive to NP concentration, while Young's modulus is the least one, and compressive strength lies in between. Emergence and growth of inelastic deformation before reaching peak stress and after that means an increase in fracture energy and transition from brittle fracture typical for plain ice to ductile fracture in growing c.

Introduction of NPs acting as additional nuclei for heterogeneous crystallization results in diminishing grain size of polycrystalline ice with increasing NP concentration. Experimental dependence of strength upon average grain size obeys the law similar to Hall–Petch or Griffith's, but is in much better accordance with the latter. It means that the prevailing factor limiting polycrystalline ice strength is the length of Griffith's cracks at grain boundaries determined by grain size. This result points out the direction for further search and development of techniques for IC strengthening consisting of prevention or impeding crack propagation. In addition to the effect on grain size, NPs could possibly

modify the grain morphology and structure of the grain interior and boundaries in some cases, impeding dislocation multiplication and mobility and microcracks development. Revealing contributions of other micromechanisms of ice strengthening by NPs of various natures, morphology, size, and concentration, the optimal choice of NP properties, methods of NPs preparation and introduction to suspension require additional complex studies.

Obtained results suggest directions for further search and development of IC strengthening techniques by modifying ice microstructure and stimulating the development and employment of novel physical approaches and techniques for ice strengthening on the basis of various possible strengthening mechanisms known in physical material science. These mechanisms are proven reliable for many other structured materials, and there is no reason for them to fail on ice.

Strengthening techniques employing NPs can be developed and applied both as standalone and in conjunction with other ice strengthening techniques, such as chemical modification of ice matrix using soluble polymeric additives, reinforcement by natural or synthetic microfiber, thermal and mechanical processing and others.

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